Supporting Information

# Low-spin 1,1′-diphosphametallocenates of Chromium and Iron

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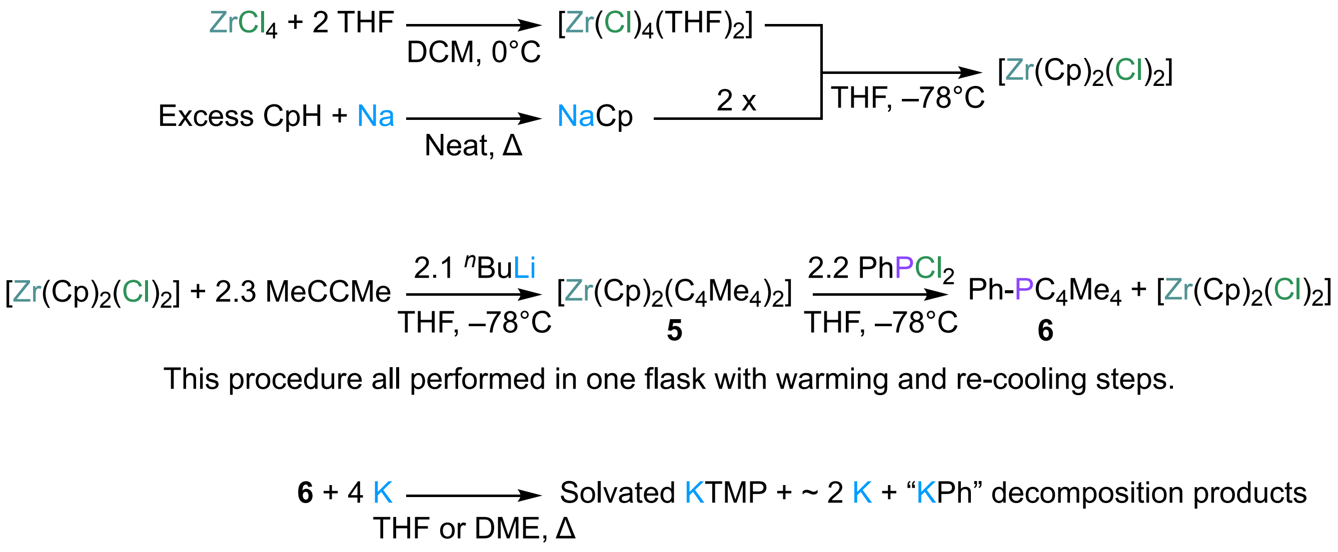
# S1. Experimental Details

## *General considerations*

All syntheses and manipulations were conducted under UHP argon (AirGas) with rigorous exclusion of oxygen and water using Schlenk line and glove box techniques. Molecular sieves (4 Å, Sigma Aldrich, 8-12 mesh) were activated at 200 °C for 12 hours, at $5\text{x}10^{-4}$ mbar. All solvents were degassed (by bubbling Ar through them, or under dynamic vacuum) prior to drying procedures. Anhydrous THF (Sigma Aldrich) was degassed, refluxed over K/$Ph_2CO$ until a persistent purple color was obtained, then distilled and stored over 4 Å molecular sieves. Anhydrous hexane and toluene (Sigma Aldrich) were degassed, refluxed over NaK/$Ph_2CO$ for several days until dark coloration (purple solutions or purple/green solids) were observed, then distilled and stored over 4 Å molecular sieves. All solvents were tested with a dilute THF solution of $Na_2Ph_2CO$ (150 mg $Ph_2CO$ in 20 mL of THF with an excess of Na metal) such that ethereal solvents required 1 drop / mL to retain purple coloration and hydrocarbon solvents required 1 drop / 2 mL. Anhydrous $C_6D_6$ and $C_4D_8O$ (both Sigma Aldrich) for NMR spectroscopy were degassed, stirred with NaK for 72 hours and filtered through a glass-fiber filter disc prior to use. $KC_8$ was prepared by heating graphite flakes (200 mesh, Sigma Aldrich) and 1/8th of a molar equivalent of freshly cleaned K metal together in a glass scintillation vial inside an argon glovebox with vigorous stirring using a metal spatula. 2-butyne was vacuum transferred and stored over 4 Å sieves for 4 days prior to use. 2.2.2-cryptand (Alfa Aesar) was dried under vacuum ($5\text{x}10^{-4}$ mbar) for 48 hours and stored in a glovebox. $PhPCl_2$, anhydrous $CrCl_2$ (Alfa Aesar), anhydrous $FeCl_2$ (Alfa Aesar) and anhydrous $CoCl_2$ (Fisher Scientific) were used as received. [M(TMP)$_2$] (**1-M**, M = Cr or Fe) were prepared using a procedure slightly modified from those previously described;[1,2] anhydrous $FeCl_2$ and $CrCl_2$ were combined with base free KTMP in THF at room temperature, and the complexes were crystallized from hexane. The glovebox atmosphere was periodically checked using a dilute toluene solution of $[Ti(Cp)_2(\mu\text{-}Cl)]_2$ (200 mg of commercial $[Ti(Cp)_2(Cl)_2]$ reduced over an excess of Zn powder in 20 mL of toluene, and filtered. A drop of the green solution was allowed to dry on a vial lid (Urea, VWR) prior to any manipulations, such that the residue dried to a dark green color each time (a color change to yellow or orange indicates decomposition of the Ti test compound and atmospheric $O_2$/$H_2O$ removal is required). All glassware, and glass-fiber filter discs, were stored in an oven (>150 °C) for 24 hours prior to being brought into the glovebox, and FEP (fluorinated ethylene propylene) NMR liners were brought into the box *via* overnight vacuum cycles. The NMR solutions were loaded into a fresh FEP NMR liner, stoppered with a PTFE plug, and then placed in J. Young tap appended NMR tubes. This was done as it facilitates the easy handling of material in facilities primarily concerned with Th/dU work and is a local requirement for the area this work had to be performed in. Crystals for single-crystal X-ray diffraction were mounted on nylon loops in Paratone-N oil. Solution phase electronic absorption spectra were collected at ambient temperature using a Varian Cary 6000i UV-vis-nIR spectrometer. Solutions were contained in low volume (1 mL) screw-capped quartz cuvettes (1 cm path length). ATR-FTIR spectra were obtained using a Thermo Scientific Nicolet iS5 FTIR spectrometer using a Golden Gate Diamond ATR (ZnSe lenses) with a reaction anvil. Experimental details for other techniques ($^{57}$Fe Mössbauer and EPR spectroscopies, and SQUID magnetometry) are described separately in their corresponding sections.

## S1.1. Preparation of KTMP

Base-free KTMP was prepared by a multi-step procedure adapted from several literature procedures and beginning with cheap, commercially available starting materials (Scheme 1). Here we have structurally characterized two of the intermediates, [Zr(Cp)$_2$(C$_4$Me$_4$) (**5**) and Ph-PC$_4$Me$_4$ (Ph-TMP, **6**) for the first time.



**Scheme S1.** Synthesis of KTMP, beginning from dicyclopentadiene / Na and anhydrous ZrCl$_4$.

[Zr(Cp)$_2$(Cl)$_2$] was prepared from [Zr(Cl)$_4$(THF)$_2$] (prepared from ZrCl$_4$ and stoichiometric THF in DCM, and recrystallized from DCM)[3] and two equivalents of NaCp (prepared from dicyclopentadiene and Na metal) in THF,[4] followed by solvent removal and extraction of the bright yellow residue with DCM. [Zr(Cp)$_2$(C$_4$Me$_4$)] (**5**) was prepared from [Zr(Cp)$_2$(Cl)$_2$], $^n$BuLi, and 2-butyne, and crystallized from hexane or used *in situ*.[5,6] Ph-TMP (**6**) was prepared from **5** and PhPCl$_2$, then purified by distillation which afforded colorless crystals, rather than a colorless oil.[5] During the course of this study we have structurally characterized **5** and **6** for the first time (*vide infra*). Base-free KTMP was prepared from **6** and a four-fold excess of K metal in boiling DME or THF, followed by filtration of the bright orange solution and exhaustive extraction of the gray/brown residue. Multiple crops of colorless crystals were collected by repeated concentration and cooling of the orange solution. This material was then fully desolvated *in vacuo* to afford a white powder, which was confirmed to be base-free by elemental analysis. $(TMP)_2$ was prepared as previously described, and purified by crystallization from hexane.[5]

## S1.2. Synthesis of 2-M (M = Cr, Fe)

**Synthesis of [K(2.2.2-crypt)][Cr(TMP)₂] 2-Cr:** A solution of **1-Cr** (55 mg, 0.17 mmol) and 2.2.2-crypt (62 mg, 0.17 mmol) in THF (1 mL) was prepared in a 20 mL glass scintillation vial equipped with a Teflon stir bar, then cooled to –35°C for 1 hour. Separately, a vial of $KC_8$ was also chilled to –35°C along with an aluminum vial block. Cold $KC_8$ (25 mg, 0.18 mmol, 1.1 eq.) was added rapidly to the vigorously stirred THF solution which was maintained close to –35°C by the vial block. The solution immediately turned from dark red to dark brown/black. The brown/black solution was filtered from black solids (presumably graphite) through a glass pipette loaded with a glass-fiber disc padded with a 2 mm layer of $KC_8$ into a 4 mL glass vial. Hexane (3 mL) was carefully layered on top of the THF solution, and the vial was then stored at –35°C for 18 hours. The pale brown/colorless supernatant was decanted and the brown/black crystals were washed with room temperature hexane (3 x 2 mL) followed by drying *in vacuo* to afford **2-Cr** (yield 102 mg, 82%). $CrKP_2N_2O_6C_{34}H_{60}$; calcd. C 54.75, H 8.11, N 3.76; found C 54.32, H 8.18, N 3.49. $^1H$ NMR ($C_4D_8O$, 400 MHz, 298 K): 2.63, 3.62, 3.65, only peaks attributable to free 2.2.2-cryptand, and to the solvent residual signals were observed. $^{31}P\{^1H\}$ NMR ($C_4D_8O$, 162 MHz, 298 K): 74.55, diamagnetic impurity, corresponds to free $\{TMP\}^-$ anion. ATR-IR ($\bar{\nu}$, $cm^{-1}$): 2958 (m), 2935 (w), 2922 (w), 2866 (m), 2825 (s), 2727 (w), 2698 (w), 2360 (m), 2343 (m), 1477 (m), 1454 (w), 1442 (m), 1412 (w), 1398 (w), 1369 (m), 1358 (m), 1350 (s), 1300 (m), 1292 (m), 1257 (m), 1240 (w), 1169 (w), 1132 (s), 1101 (vs), 1080 (vs), 1057 (m), 1018 (m), 947 (s), 931 (s), 831 (m), 820 (m), 752 (m), 681 (w), 669 (w), 658 (vw), 571 (m). UV-vis-nIR (THF) $\lambda_{max}$ ($cm^{-1}$, ε): 502 (19904, 4180, vbr).

**Synthesis of [K(2.2.2-crypt)][Fe(TMP)₂] 2-Fe:** A solution of **1-Fe** (150 mg, 0.45 mmol) and 2.2.2-crypt (170 mg, 0.45 mmol) in THF (1 mL) was prepared in a 20 mL glass scintillation vial equipped with a Teflon stir bar, then cooled to –35°C for 1 hour. Separately, a vial of $KC_8$ was also chilled to –35°C along with an aluminum vial block. Cold $KC_8$ (67 mg, 0.50 mmol, 1.1 eq.) was added rapidly to the vigorously stirred THF solution which was maintained close to –35°C by the vial block. The solution immediately turned from dark red to dark green/black. The green/black solution was filtered from black solids (presumably graphite) through a glass pipette loaded with a glass-fiber disc padded with a 2 mm layer of $KC_8$ into a 4 mL glass vial. Hexane (3 mL) was carefully layered on top of the THF solution, and the vial was then stored at –35°C for 18 hours. The pale brown/colorless supernatant was decanted and the green/black crystals were washed with room temperature hexane

(3 x 2 mL) followed by drying in vacuo to afford **2-Fe** (yield 243 mg, 72%). $FeKP_2N_2O_6C_{34}H_{60}$; calcd. C 54.47, H 8.07, N 3.74; found C 54.96, H 8.35, N 3.61. $^1H$ NMR ($C_4D_8O$, 400 MHz, 298 K): 1.94 (s, 12H, TMP-3,4-Me$_2$), 2.19 (d, $^3J_{HP}$ = 10.29 Hz, 12H, TMP-2,5-Me$_2$), 2.28 (s, 12H, 2.2.2-crypt), 3.30 (s, 12H, 2.2.2-crypt), 3.37 (s, 24H, 2.2.2-crypt). $^{31}P\{^1H\}$ NMR ($C_4D_8O$, 162 MHz, 298 K): 74.46, diamagnetic impurity, corresponds to free $\{TMP\}^-$ anion. ATR-IR ($\bar{\nu}$, cm$^{-1}$): 2954 (w), 2873 (m), 2835 (m), 2729 (w), 2698 (w), 2360 (w), 2343 (w), 2324 (w), 1475 (m), 1442 (m), 1414 (w), 1390 (w), 1358 (m), 1350 (m), 1296 (m), 1257 (m), 1240 (w), 1173 (w), 1132 (s), 1099 (vs), 1078 (vs), 1020 (m), 947 (s), 931 (s), 829 (m), 820 (m), 796 (w), 752 (m), 679 (w), 667 (w), 638 (vw), 625 (vw), 588 (w), 569 (w), 553 (w), 536 (w). UV-vis-nIR (THF) $\lambda_{max}$ (cm$^{-1}$, ε): 428 (23375, 2220, vbr), 533 (18754, 1830, vbr), 616 (16239, 1720, vbr), 885 (11297, 1760), 924 (10818, 1730).

## S1.3. Attempted extension to Mn and Co

The synthesis of a redox series, such as that for **3-M** and **4-M** (M = Mn, Fe, Co) was desirable. Attempts to synthesize the required **1-Mn** from commercial $MnCl_2$, $MnCl_2(THF)_n$ prepared *in-situ*, $MnCl_2(DME)_n$ prepared *in-situ*, or $MnCl_2(PMe_3)$ with two equivalents of KTMP in THF, DME or toluene resulted in intractable mixtures of dark powder that were insoluble in all common solvents that are compatible with this ligand set. The synthesis of **1-Co** was attempted using anhydrous $CoCl_2$ and two equivalents of K-TMP in THF (see below).

**Synthesis of [Co(η$^5$-TMP)(μ$^2$:η$^1$:η$^1$-TMP)]$_2$ 7:** $CoCl_2$ (65 mg, 0.5 mmol) was slurried in THF (4 mL) in a 20 mL glass scintillation vial at room temperature. K-TMP (178 mg, 1 mmol) was added to the blue suspension, which immediately turned dark brown. The brown mixture was stirred for 16 hours at room temperature. Volatiles were removed *in vacuo* and the black tacky residue was extracted with hot (60 °C) hexane (6 mL) which afforded a dark brown/black solution which was concentrated to 1.5 mL and stored at room temperature for 16 hours to afford black crystals of **7** along with sticky brown residues (mass 14 mg). We were unable to optimize the yield of this complex. A $^{31}P\{^1H\}$ NMR taken of the crystalline material indicated several products (Figure S21).

**Attempted reduction of crude 7:** The reaction above was repeated on the same scale. We then attempted reduction of the crude mixture, assuming an arbitrary 80% conversion of the reactants to **7**, presuming any reduced product might form a salt-like complex as **2-M**, and be separable from **7** based on solubility. After stirring for 16 hours at room temperature, the crude mixture was reduced to dryness in vacuo, and extracted with warm (45 °C) toluene (5 mL), filtered through a glass pipette loaded with a glass-fiber disc into a 20 mL glass scintillation vial, and the brown/black solution was reduced to dryness in vacuo. Solid 2.2.2-crypt (151 mg, 0.4 mmol, 0.8 eq. assuming 80% conversion) was added along with a Teflon stir bar, and then the tacky black residue was dissolved in THF (2 mL), and cooled to –35 °C. Pre-cooled (–35 °C) solid $KC_8$ (54 mg, 0.40 mmol, 0.8 eq. assuming 80% conversion) was added to the rapidly stirred solution which was maintained at –35°C using a chilled vial block. No perceptible color change was observed. After stirring for 1 minute the black solution was filtered underneath pre-cooled hexane (10 mL) in a 20 mL glass scintillation vial, and stored overnight at –35°C which afforded several low quality crystals of [K(2.2.2-crypt)][TMP] (**8**), 2.2.2-crypt, and no other crystalline products. The brown solution was decanted from the crystals and reduced to a thin oil in vacuo, which formed biphasic mixtures in hydrocarbon solvents (pentane, hexane, toluene), and pale brown solutions in ethereal solvents (THF, DME, $Et_2O$), but no further crystalline products could be isolated. When the reaction was repeated at room temperature, the observed colors and biphasic mixtures etc. were all identical, and likewise no crystalline products that contained Co could be isolated in our hands.

## S2. Crystallography

### *General considerations*

The crystal data for complexes **1-Cr, 1-Fe, 2-Cr, 2-Fe, 5 – 8** are compiled in Tables **S1-3**. Crystals of **1-Fe**, **2-Cr**, **2-Fe**, **7**, and **8** were examined with a Bruker D8 Quest diffractometer equipped with a CMOS detector and using mirror-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) operating in shutterless mode; crystals of **1-Cr** was examined with a Bruker APEX II diffractometer equipped with a CCD detector and using mirror-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å); crystals of **5** were examined using an Oxford Diffraction Supernova diffractometer, equipped with CCD area detector and a mirror-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å); and crystals of 4 were examined with a Rigaku XtalLAB AFC11 diffractometer, equipped with CCD detector and mirror-monochromated Cu Kα radiation ($\lambda$ = 1.54184 Å). APEX II (APEX II), or APEX III (D8 Quest), or CrysAlisPro (Rigaku XtalLAB AFC11) software was used for control and solving the unit cells prior to data collection. Intensities were integrated from data recorded on 0.5° frames by ω rotation with 10s frame exposure (**1-Cr**), 13s frame exposure (**1-Fe**), 25s frame exposure (**2-Fe**), 30s frame exposure (**2-Cr**), or 90s frame exposure; or by 0.7° frames by ω rotation with 1s or 2s frame exposure (**6**); or finally by 0.8° frames by ω rotation with 30s frame exposure (**5**). CrysAlisPro was used for final unit cell determination and parameters were refined from the observed positions of all strong reflections in each data set and an analytical absorption correction was applied.[7] The Olex2[8] GUI was used for structure solution and refinement utilizing the ShelX software packages.[9,10] The structures were solved using ShelXT;[10] the datasets were refined by ShelXL[9] using full-matrix least-squares on all unique $F^2$ values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; $U_{\mathrm{iso}}$(H) was set at 1.2 (1.5 for methyl groups) times $U$eq of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. Olex2 combined with Inkscape was employed for molecular graphics.[8,11] CCDC 2003385 (**1-Cr**), 2003386 (**1-Fe**), 2003387 (**2-Cr**), 2003388 (**2-Fe**), 2003389 (**5**), 2003390 (**6**), 2017380 (**7**), and 2017381 (**8**) contain the supplementary crystal data for this article.[§] These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[§] LA-UR-20-20981

**Table S1. Crystallographic data for 1-Cr, 1-Fe, 2-Cr, and 2-Fe.**

| | **1-Cr** | **1-Fe** | **2-Cr** | **2-Fe** |
|---|---|---|---|---|
| Internal identifier | Apx2920 | Dq0894 | Dq1027 | Dq0907 |
| CCDC ref code | 2003385 | 2003386 | 2003387 | 2003389 |
| Formula | $CrP_2C_{16}H_{24}$ | $FeP_2C_{16}H_{24}$ | $KCrP_2N_2O_6C_{34}H_{60}$ | $KFeP_2N_2O_6C_{34}H_{60}$ |
| Fw | 330.29 | 334.14 | 745.88 | 749.73 |
| Crystal syst | Monoclinic | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/n$ | $C2/c$ | $P–1$ | $P–1$ |
| $a$, Å | 7.8420(3) | 14.2948(7) | 10.1994(4) | 10.1947(2) |
| $b$, Å | 12.5620(4) | 12.8549(6) | 14.2193(7) | 14.2373(4) |
| $c$, Å | 8.8611(3) | 8.8448(4) | 15.0882(6) | 15.0677(3) |
| α, ° | 90 | 90 | 62.328(4) | 62.275(2) |
| β, ° | 109.444(4) | 104.364(5) | 86.597(3) | 85.840(2) |
| γ, ° | 90 | 90 | 87.156(3) | 87.045(2) |
| $V$, Å$^3$ | 823.13(5) | 1574.50(13) | 1933.91(16 | 1930.42(8) |
| Z | 2 | 4 | 2 | 2 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.333 | 1.410 | 1.281 | 1.290 |
| $\mu$, mm$^{-1}$ | 0.874 | 1.146 | 0.529 | 0.624 |
| $F$(000) | 348 | 704 | 798 | 802 |
| Cryst size, mm | 0.30 x 0.35 x 0.42 | 0.16 x 0.19 x 0.29 | 0.30 x 0.30 x 0.30 | 0.05 x 0.22 x 0.25 |
| Temperature, K | 100(2) | 100(2) | 100(2) | 100(2) |
| no. reflections (unique) | 6774 (1508) | 6215 (1605) | 23292 (7060) | 25573 (7807) |
| $R_{int}$ | 0.017 | 0.032 | 0.033 | 0.036 |
| $R_1(wR_2)$ ($F^2 > 2\sigma(F^2)$) | 0.0252 (0.0667) | 0.0312 (0.0789) | 0.0338 (0.0872) | 0.0400 (0.1035) |
| $S^a$ | 1.09 | 1.12 | 1.10 | 1.09 |
| min./max. diff map, Å$^{-3}$ | –0.26, 0.33 | –0.24, 0.56 | –0.25, 0.49 | –0.26, 0.62 |

[a] $R = \sum||F_O| - |F_C||/\sum|F_O|$; $R_W = [\sum w(F_O^2 - F_C^2)^2/\sum w(F_O^2)^2]^{0.5}$; $S = [\sum w(F_O^2 - F_C^2)^2/(\text{no. data} - \text{no. params})]^{0.5}$ for all data.

**Table S2. Crystallographic data for 5 – 8.**

| | **5** | **6** | **7** | **8** |
|---|---|---|---|---|
| Internal identifier | Adpm457 | Ldpm35 | Dq1025 | Dq0919 |
| Formula | $ZrC_{18}H_{22}$ | $PC_{14}H_{17}$ | $Co_2P_4C_{32}H_{48}$ | $K_2P_2O_{12}N_4C_{52}H_{96}\cdot C_4H_8O$ |
| Fw | 329.57 | 216.24 | 674.44 | 1181.57 |
| Crystal syst | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | *I*2/a | *P*–1 | *C*2/c | *P*–1 |
| $a$, Å | 14.1554(8) | 8.0727(2) | 20.161(3) | 12.7189(8) |
| $b$, Å | 9.6976(4) | 8.74422(19) | 9.0620(4) | 15.9437(10) |
| $c$, Å | 12.0182(6) | 18.4065(4) | 20.214(3) | 17.8937(12) |
| α, ° | 90 | 103.1739(17) | 90 | 64.066(6) |
| β, ° | 112.336(6) | 92.6248(19) | 119.71(2) | 85.655(5) |
| γ, ° | 90 | 100.705(2) | 90 | 86.321(5) |
| $V$, Å$^3$ | 1526.00(15) | 1237.81(5) | 3207.6(9) | 3251.9(4) |
| Z | 4 | 4 | 4 | 2 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.434 | 1.160 | 1.397 | 1.207 |
| $\mu$, mm$^{-1}$ | 0.705 | 1.664 | 1.254 | 0.254 |
| $F$(000) | 680 | 464 | 1416 | 1280 |
| Cryst size, mm | 0.04 x 0.12 x 0.17 | 0.09 x 0.18 x 0.19 | 0.10 x 0.12 x 0.40 | 0.05 x 0.14 x 0.37 |
| Temperature, K | 150(2) | 150(2) | 100(2) | 100(2) |
| no. reflections (unique) | 2872 (1558) | 13067 (4482) | 17531 (2935) | 31744 (13040) |
| $R_{int}$ | 0.028 | 0.019 | 0.065 | 0.065 |
| $R_1$(w$R_2$) ($F^2 > 2\sigma(F^2)$) | 0.0330 (0.0805) | 0.0329 (0.0899) | 0.0333 (0.0834) | 0.0673 (0.1979) |
| $S$[a] | 1.07 | 1.04 | 1.01 | 1.06 |
| min./max. diff map, Å$^{-3}$ | –0.54, 0.46 | –0.26, 0.32 | –0.34, 0.50 | –0.54, 0.73 |

[a] $R = \sum||F_O| - |F_C||/\sum|F_O|$; $R_W = [\sum w(F_O^2 - F_C^2)^2/\sum w(F_O^2)^2]^{0.5}$; $S = [\sum w(F_O^2 - F_C^2)^2/(\text{no. data} - \text{no. params})]^{0.5}$ for all data.

## S3. Molecular structures

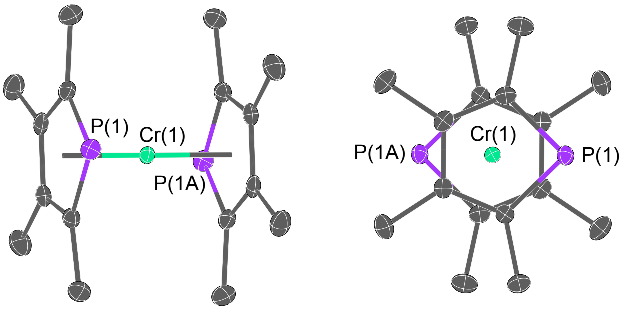


**Figure S1.** Side view (left) and top view (right) of the molecular structure of **1-Cr** with ellipsoids set at 50%, and hydrogen atoms removed for clarity. Cr(1) sits on a site of symmetry, and thus the inter-ring angle is necessarily 180°. (operations: x, y, z; 1–x, 1–y, 1–z).

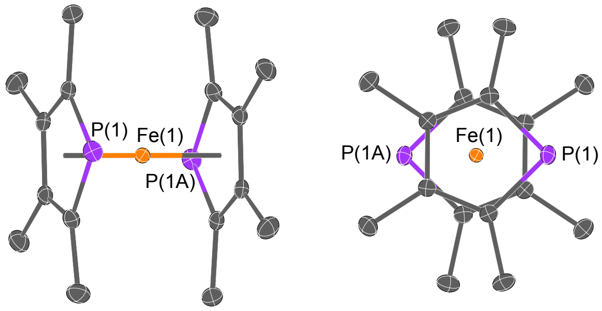


**Figure S2.** Side view (left) and top view (right) of the molecular structure of **1-Fe** with ellipsoids set at 50%, and hydrogen atoms removed for clarity. Fe(1) sits on a site of symmetry, and thus the inter-ring angle is necessarily 180°. (operations: x, y, z; ½–x, ½–y, 1–z).

### Table S3. Structural parameters for 1-Cr and 1-Fe.

| **M = Cr or Fe**[a] | **1-Cr** | **1-Fe** |
|---|---|---|
| P–M / Å | 2.3812(4) | 2.2932(4) |
| $\text{TMP}_{\text{cent}}\cdots\text{M}$ / Å | 1.795(1) | 1.660(1) |
| $\text{PC}_{2\text{plane}}\cdots\text{C}_{4\text{plane}}$[b] / ° | 4.45(12) | 1.27(13) |

[a] Prior-reported CCDC codes for **1-Cr**: NORRAN; **1-Fe**: ABIGAU.

[b] A plane is defined by the three atoms, P and the two adjoining C atoms; a second plane is defined by all four C atoms of the TMP ring. The “hinge angle”, HA, between these two planes is reported.

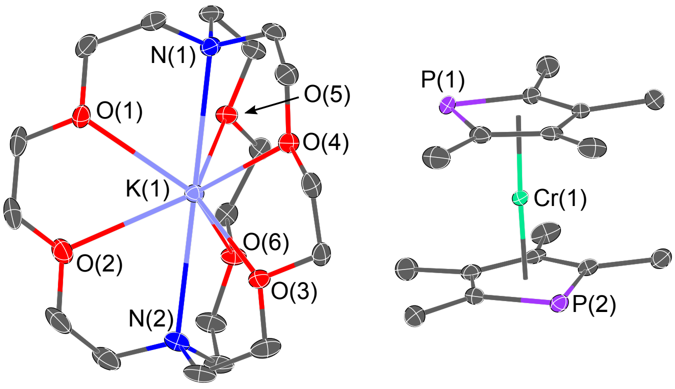


**Figure S3.** Molecular structure of **2-Cr** with ellipsoids set at 50%, and hydrogen atoms removed for clarity. The structure has been inverted for this image to show the similarity to **2-Fe** (below).

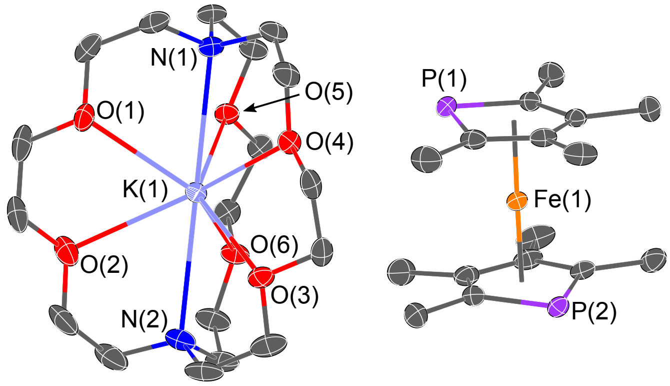


**Figure S4.** Molecular structure of **2-Fe** with ellipsoids set at 50%, and hydrogen atoms removed for clarity.

**Table S4. Structural parameters for 2-Cr and 2-Fe.**

| **M = Cr or Fe** | **2-Cr** | **2-Fe** |
|---|---|---|
| P–M / Å | 2.3596(8) / 2.3595(7) | 2.3842(8) / 2.4078(7) |
| $\text{TMP}_{\text{cent}}\cdots\text{M}$ / Å | 1.739(1) / 1.737(1) | 1.714(1) / 1.711(1) |
| $\text{TMP}_{\text{cent}}\cdots\text{M}\cdots\text{TMP}_{\text{cent}}$ / ° | 177.60(4) | 178.78(2) |
| $\text{PC}_{2\text{plane}}\cdots\text{C}_{4\text{plane}}$[a] / ° | 3.57(2) / 4.64(2) | 6.58(2) / 8.73(2) |
| P–M–P ring twist / ° | 139.82(5) | 146.35(5) |

[a] A plane is defined by the three atoms, P and the two adjoining C atoms; a second plane is defined by all four C atoms of the TMP ring. The "hinge angle", HA, between these two planes is reported.

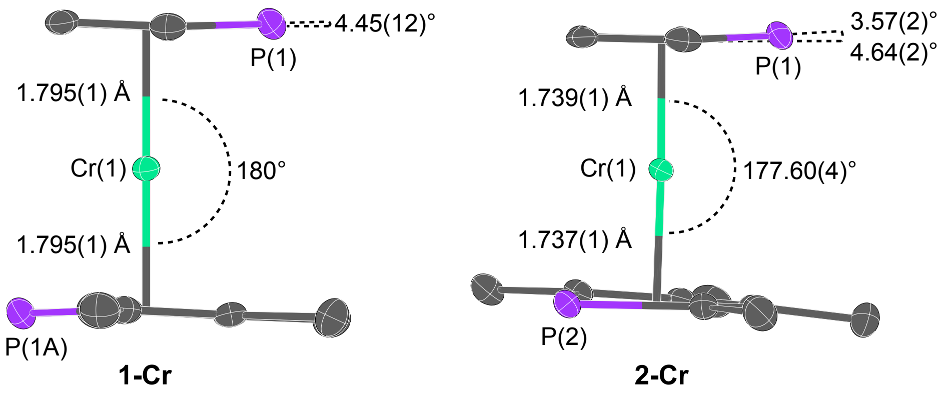


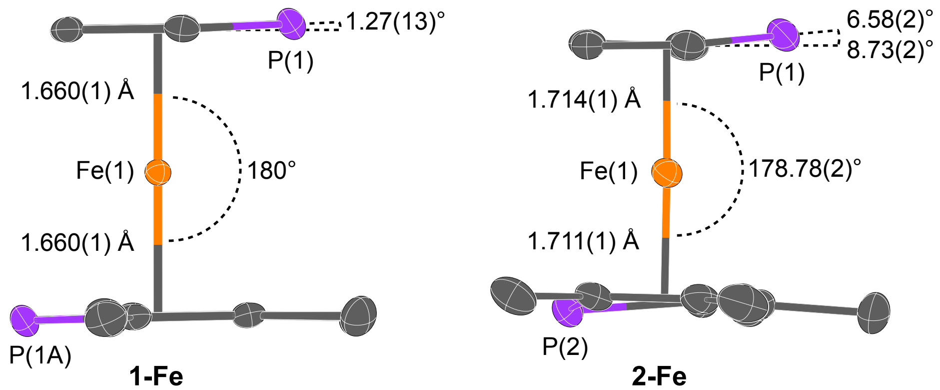
**Figure S5.** Molecular structure of **1-Cr** (left), and the anion of **2-Cr** (right) with ellipsoids set at 50%. Hydrogen atoms, methyl groups on P(1) ring, and the cation of **2-Cr** removed for clarity. Intended to show structural comparisons of the 1,1′-diphosphametallocene fragment. The pair of numbers for the hinge angle corresponds to the P(1) ring / P(2) ring respectively.

**Table S5. Structural comparisons between the 1-Cr and 2-Cr pair.**

| **M = Cr** | **1-Cr** | **2-Cr** | **Δ** |
|---|---|---|---|
| P–M / Å | 2.3812(4) | 2.3596(8) / 2.3595(7) | –0.022(1) |
| TMP$_{\text{cent}}$···M / Å | 1.795(1) | 1.739(1) / 1.737(1) | Avg. –0.057(1) |
| TMP$_{\text{cent}}$···M···TMP$_{\text{cent}}$[b] / ° | 180 | 177.60(4) | –2.40° |
| PC$_{2\text{plane}}$···C$_{4\text{plane}}$[a] / ° | 4.45(12) | 3.57(2) / 4.64(2) | *c* |

[a] A plane is defined by the three atoms, P and the two adjoining C atoms; a second plane is defined by all four C atoms of the TMP ring. The "hinge angle", HA, between these two planes is reported.

[b] The propagated error is too large and precludes meaningful analysis beyond that **2-Cr** has approximately the same deviation of the P atoms from the TMP plane a **1-Cr**.



**1-Fe** **2-Fe**

**Figure S6.** Molecular structure of **1-Fe** (left) and the anion of **2-Fe** (right) with ellipsoids set at 50%. Hydrogen atoms, methyl groups on P(1) ring, and the cation of **2-Fe** removed for clarity. Intended to show structural comparisons of the 1,1′-diphosphametallocene fragment. The pair of numbers for the hinge angle corresponds to the P(1) ring / P(2) ring respectively.

**Table S6. Structural comparisons between the 1-Fe and 2-Fe pair.**

| **M = Fe** | **1-Fe** | **2-Fe** | **Δ** |
|---|---|---|---|
| P–M / Å | 2.2932(4) | 2.3842(8) / 2.4078(7) | +0.103(1) |
| $\mathrm{TMP_{cent}}\cdots\mathrm{M}$ / Å | 1.660(1) | 1.714(1) / 1.711(1) | Avg. +0.053(1) |
| $\mathrm{TMP_{cent}}\cdots\mathrm{M}\cdots\mathrm{TMP_{cent}}^{b}$ / ° | 180 | 178.78(2) | –1.12 |
| $\mathrm{PC_{2plane}}\cdots\mathrm{C_{4plane}}^{a}$ / ° | 1.27(13) | 6.58(2) / 8.73(2) | *c* |

[a] A plane is defined by the three atoms, P and the two adjoining C atoms; a second plane is defined by all four C atoms of the TMP ring. The “hinge angle”, HA, between these two planes is reported.

[b] The propagated error is too large and precludes meaningful analysis beyond that **2-Fe** has a much larger deviation of the P atoms from the TMP plane than **1-Fe**.

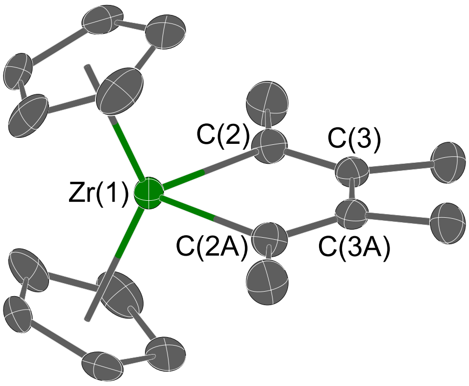


**Figure S7.** Molecular structure of **5** with ellipsoids set at 50%. A disordered component for both Cp rings, and hydrogen atoms removed for clarity. Zr(1) sits on a site of symmetry, thus half the molecule is symmetry generated (operations: x, y, z; ½–x, y, 1–z).

Zr(1)···$Cp_{cent}$ = 2.210(5) Å; Zr(1)–C(2) = 2.232(3) Å; C(2)–C(3) = 1.355(4) Å; C(3)–C(3A) = 1.505(6) Å.

$Cp_{cent}$···Zr(1) ···$Cp_{cent}$ = 133.6(2)°; C(2)–Zr(1)–C(2A) = 81.22(15)°; $Cp_{cent}$···Zr(1) ···$Cp_{cent}$ dihedral C(2)–Zr(1)–C(2A) = 91.66°.

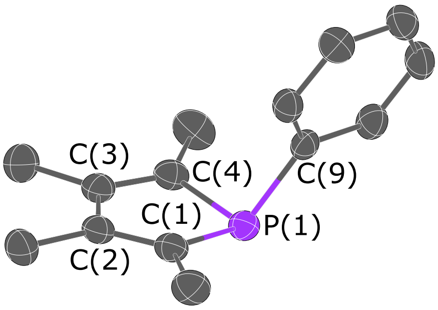


**Figure S8.** Molecular structure of **6** with ellipsoids set at 50%. A second molecule in the asymmetric unit, and hydrogen atoms removed for clarity.

P(1)–C(1) = 1.7987(13) Å; P(1)–C(4) = 1.8057(17) Å; P(1)–C(9) = 1.8313(16) Å; C(1)–C(2) = 1.353(2) Å; C(2)–C(3) = 1.477(2) Å; C(3)–C(4) = 1.347(2) Å.

C(1)–P(1)–C(4) = 1.7979(13)°; C(1)–P(1)–C(9) = 106.06(6)°; C(4)–P(1)–C(9) = 103.36(7)°.

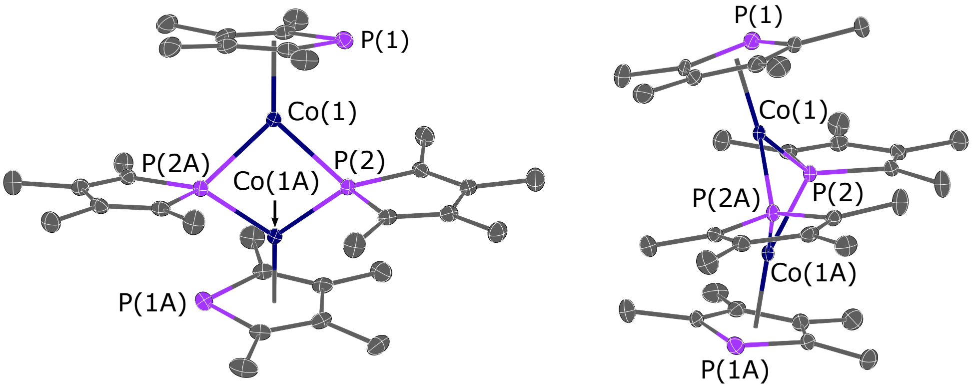


**Figure S9.** Front view (left) and side view (right) of the molecular structure of **7** with ellipsoids set at 50%, and hydrogen atoms removed for clarity.

Co(1)···Co(1A) = 2.685(1) Å; Co(1)–P(1) = 2.2963(10) Å; Co(1)–P(2) = 2.1697(10) Å; P(1)TMP$_{\text{cent}}$···Co(1) = 1.705(1) Å.

TPM$_{\text{cent}}$···Co(1···Co(1A) = 166.57(4)°; Co(1)–P(2)–Co(1A) = 76.38(4)°; P(2)–Co(1)–P(2A) = 94.06(4)°; $\sum_{\text{Co(1)–P(2A)–Co(1A)–P(2)}}$ = 340.88°.

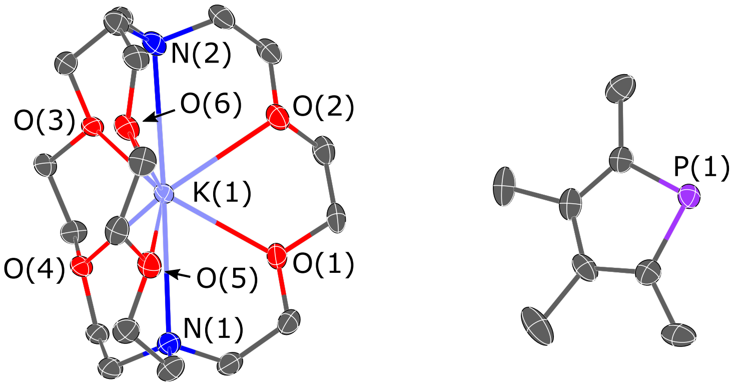


**Figure S10.** Molecular structure of **8** with ellipsoids set at 50%. Hydrogen atoms, a second set of [K(2.2.2-crypt)] and TMP, and a THF molecule removed for clarity. The extensive disorder components were also removed, and preclude meaningful discussion of the metrical parameters for this compound.

## S4. NMR Spectroscopy

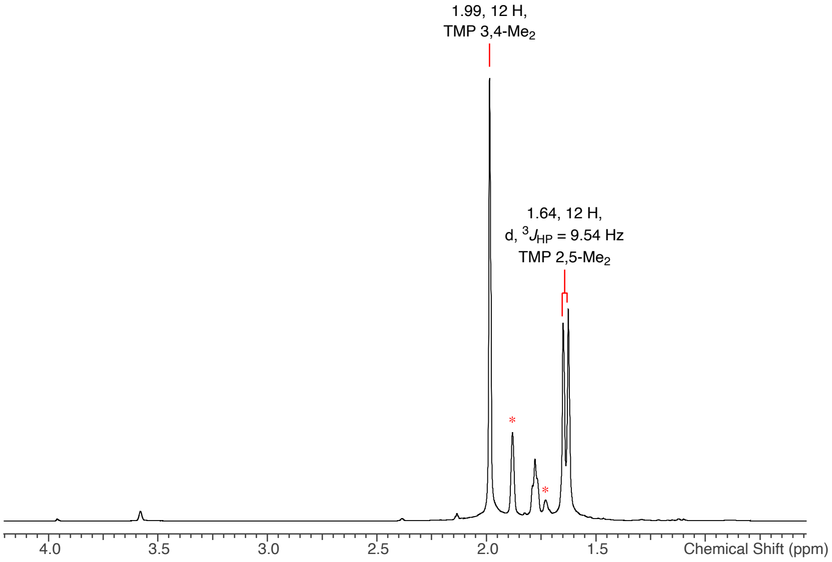


**Figure S11.** $^1$H NMR spectrum of **1-Fe** in $C_6D_6$ at room temperature, spectrum cropped to show all observed peaks. * denotes a small amount of $(TMP)_2$, presumably formed *via* oxidative coupling of K-TMP from traces of $FeCl_3$ in commercial samples of $FeCl_2$. An authentic sample of $(TMP)_2$ was prepared and the $^1$H NMR spectra were compared (*vide infra*, Figure S17) which agreed well with literature values.[2]

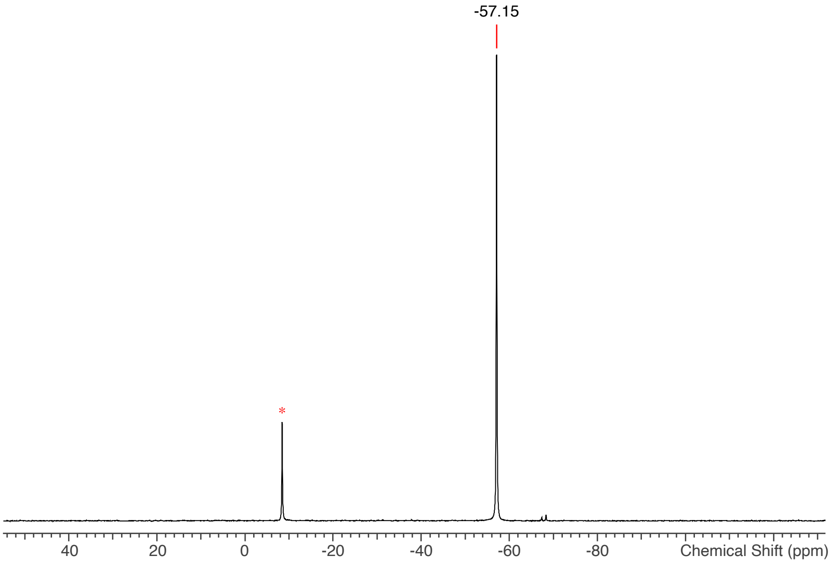


**Figure S12.** $^{31}P\{^1H\}$ NMR spectrum of **1-Fe** in $C_6D_6$ at room temperature, spectrum cropped to show all observed peaks. *denotes a small amount of $(TMP)_2$.

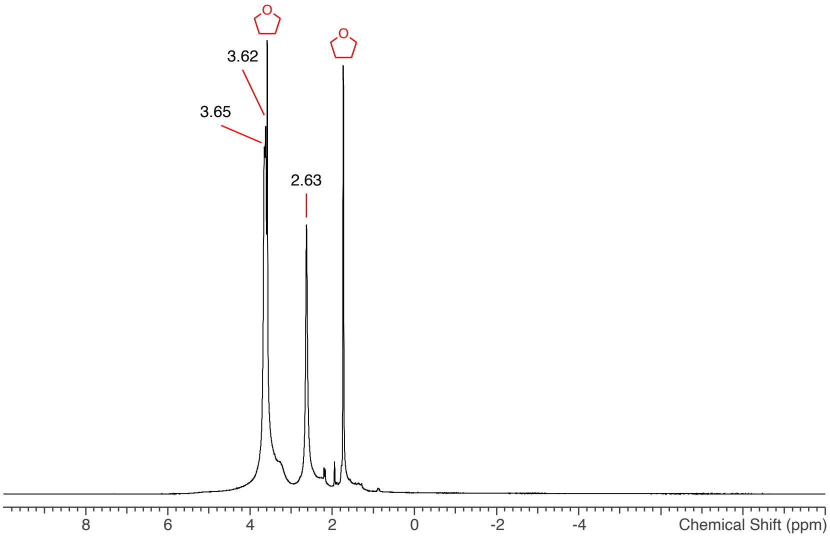


**Figure S13.** $^1$H NMR spectrum of **2-Cr** in $C_4D_8O$ at room temperature, spectrum cropped to show all observed peaks.

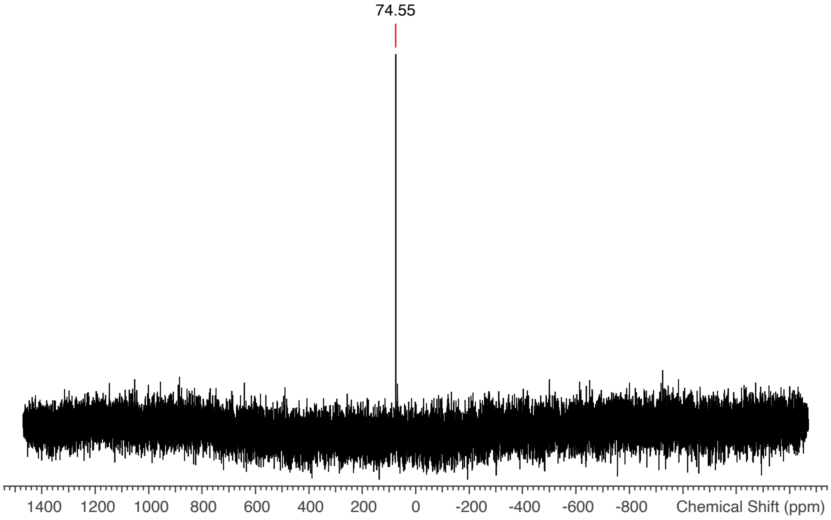


**Figure S14.** $^{31}P\{^1H\}$ NMR spectrum of **2-Cr** in $C_4D_8O$ at room temperature. The sole observed peak at 74.55 ppm corresponds well to the reported $^{31}P$ resonance for [K(18-crown-6)(TMP)], and is likely a diamagnetic impurity due to decomposition.

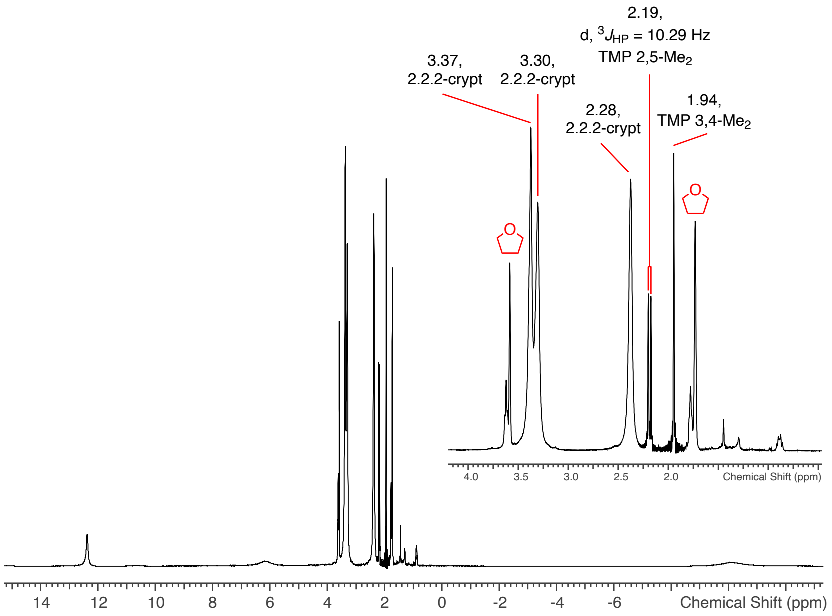


**Figure S15.** $^{1}$H NMR spectrum of **2-Fe** in $C_4D_8O$ at room temperature, spectrum cropped to show all observed peaks. Broad features around –10 ppm, 6 ppm and 12.5 ppm could not be identified by integration or by comparison with known complexes. The spectrum can be compared with that of **1-Fe** (Figure S11).

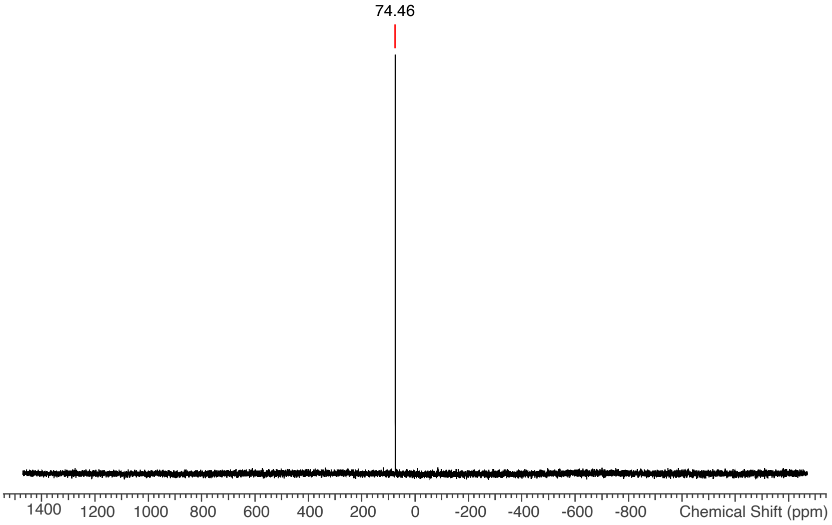


**Figure S16.** $^{31}P\{^{1}H\}$ NMR spectrum of **2-Fe** in $C_4D_8O$ at room temperature. The sole observed peak at 74.46 ppm corresponds well to the reported $^{31}$P resonance for [K(18-crown-6)(TMP)], and is likely a diamagnetic impurity due to decomposition.

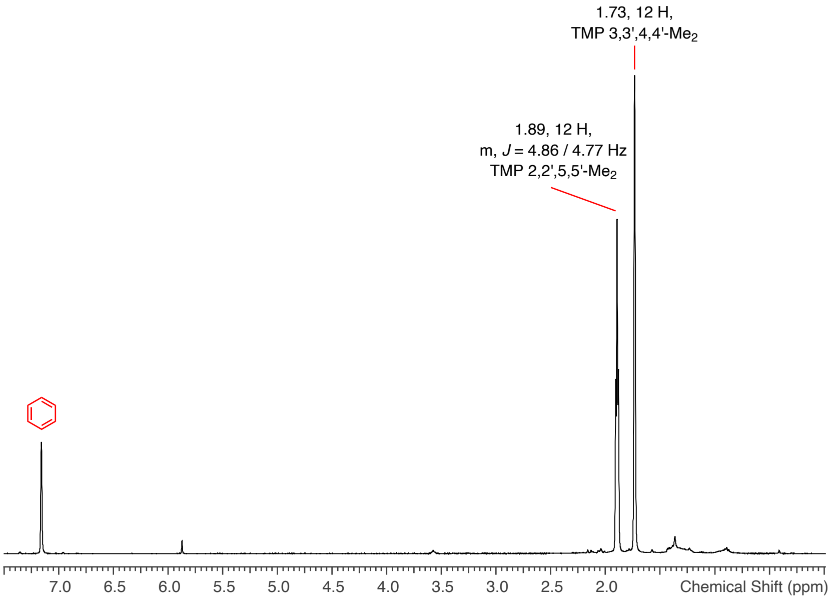


**Figure S17.** $^1$H NMR spectrum of (TMP)$_2$, in $C_6D_6$ at room temperature, spectrum cropped to show all observed peaks. The peak at 1.89 ppm presents as a triplet but could plausibly be a doublet of doublets due to ABB′ coupling of the $CH_3$ group with the 1,3-P and the 1,4-P.

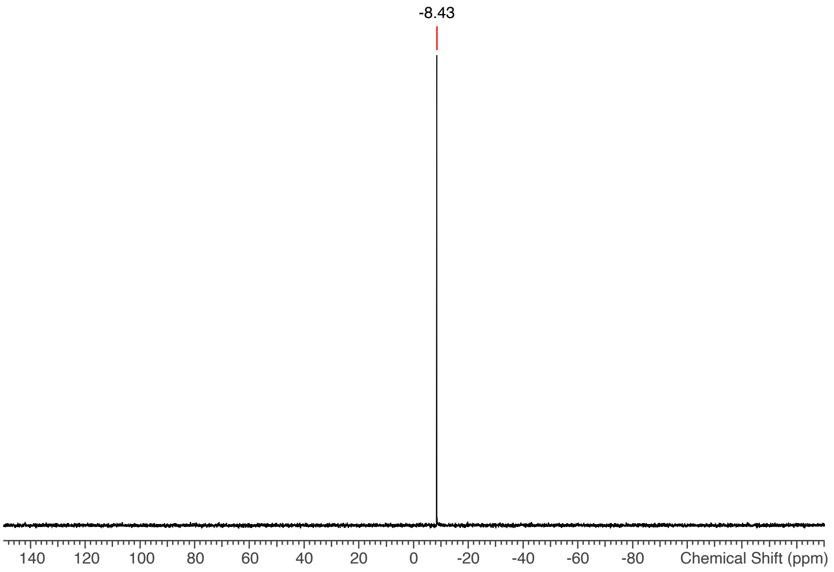


**Figure S18.** $^{31}$P{$^1$H} NMR spectrum of (TMP)$_2$, in $C_6D_6$ at room temperature.

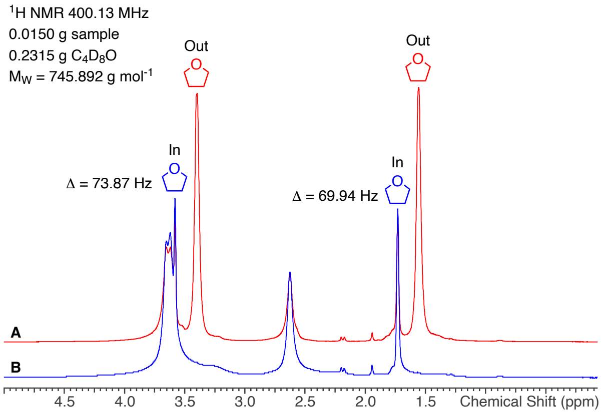


**Figure S19.** $^1$H NMR spectrum of **2-Cr** in $C_4D_8O$, with an external drop of $C_4H_8O$ outside the FEP liner to act as a reference. Collected at room temperature.

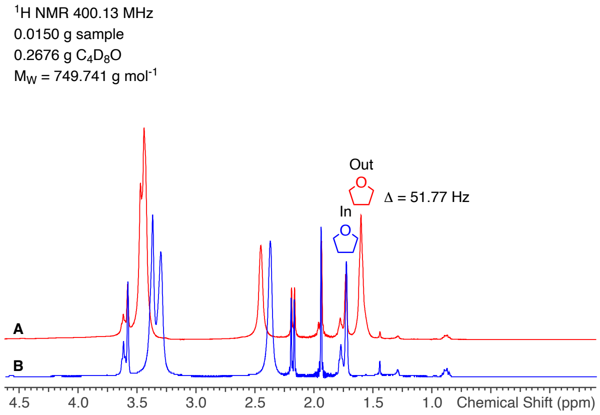


**Figure S20.** $^1$H NMR spectrum of **2-Fe** in $C_4D_8O$, with an external drop of $C_4H_8O$ outside the FEP liner to act as a reference. Collected at room temperature. The second external THF resonance could not be distinguished from overlapping sample peaks.

**Table S7. Solution magnetic susceptibility data for 2-Cr and 2-Fe via Evans NMR method.**[a]

| [b] Sample / peak | $\mu_{eff}$ / B.M mol$^{-1}$ | $\chi'_m$T (S.I.)/ m$^3$ mol$^{-1}$ | $\chi'_m$T (c.g.s. e.m.u.)/ cm$^3$ mol$^{-1}$ K | $\chi'_m$T (S.I.)/ m$^3$ mol$^{-1}$ K | mass of sample / g | mass of solvent + sample / g | *$M_r$ / g mol$^{-1}$* | Δ peak / Hz |
|---|---|---|---|---|---|---|---|---|
| [K(2.2.2-crypt)][Cr(TMP)$_2$] peak 1 | **1.455** | 1.12E-08 | **0.265** | 3.33E-06 | 0.0150 | 0.2465 | 745.892 | 73.87 |
| [K(2.2.2-crypt)][Cr(TMP)$_2$] peak 2 | **1.433** | 1.12E-08 | **0.257** | 3.33E-06 | 0.0150 | 0.2465 | 745.892 | 69.94 |
| [K(2.2.2-crypt)][Fe(TMP)$_2$] | **1.376** | 1.12E-08 | **0.237** | 3.33E-06 | 0.0150 | 0.2826 | 749.741 | 51.77 |

[a] The small masses engender large errors in this methodology, the results should be cautiously interpreted along with other data. [b] Spectrometer frequency 400.130 MHz. Simple diamagnetic correction of $M_r$ / -2,000,000 applied. $\rho_{D8THF}$ = 0.985 g mL$^{-1}$.

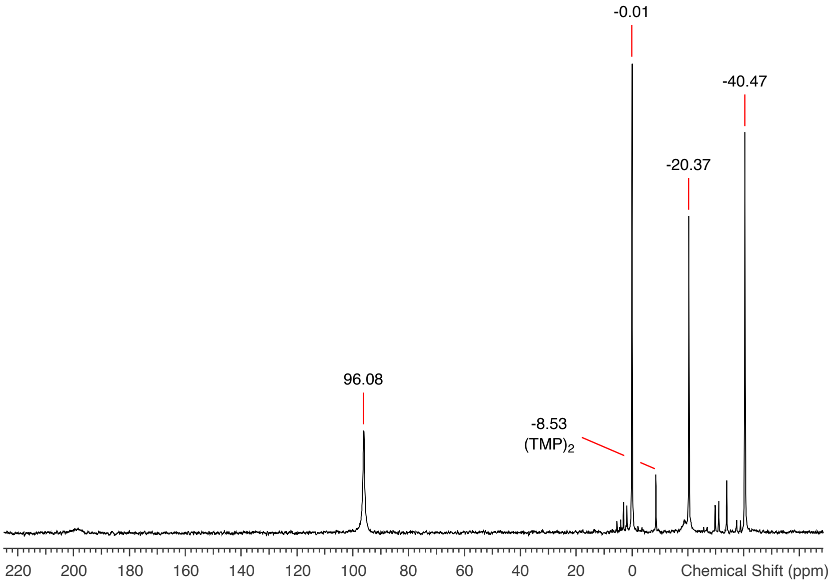


**Figure S21.** $^{31}P\{^1H\}$ NMR spectrum of crystals of **7** in $C_6D_6$ at room temperature.

## S5. UV-vis-nIR Spectroscopy

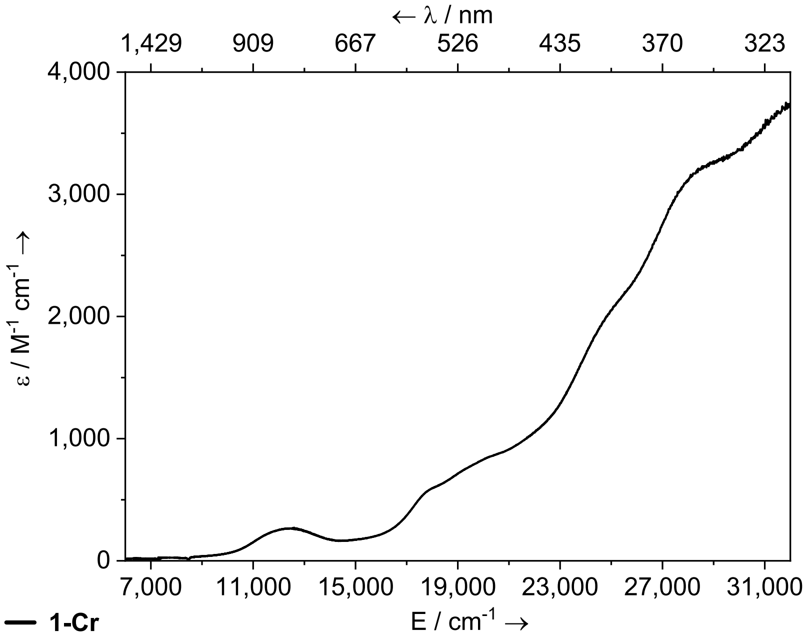


**Figure S22.** UV-vis-nIR spectrum of **1-Cr** in THF (0.63 mM) at room temperature recorded between 5,556–36,364 cm$^{-1}$ (1,800–275 nm), window shown between 6,000–32,000 cm$^{-1}$ (1,667–313 nm).

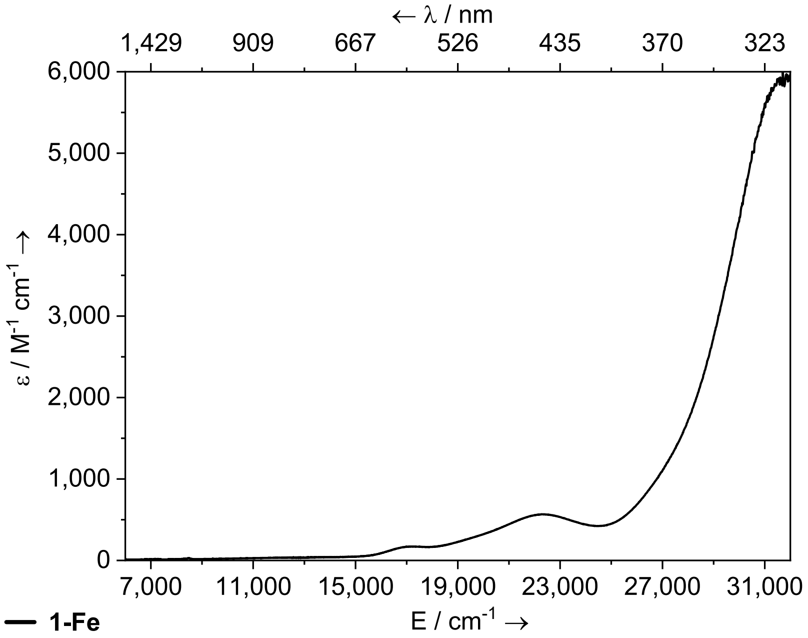


**Figure S23.** UV-vis-nIR spectrum of **1-Fe** in THF (0.50 mM) at room temperature recorded between 5,556–36,364 cm$^{-1}$ (1,800–275 nm), window shown between 6,000–32,000 cm$^{-1}$ (1,667–313 nm).

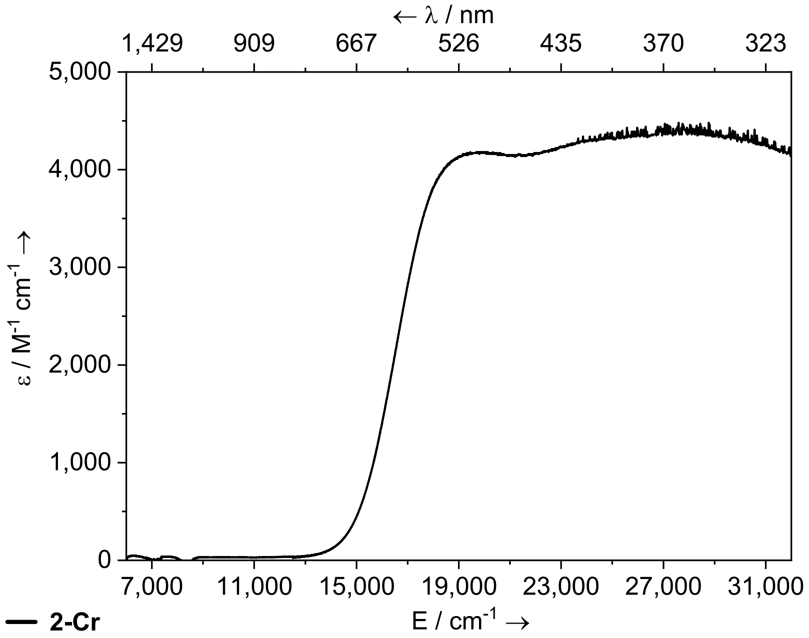


**Figure S24.** UV-vis-nIR spectrum of **2-Cr** in THF (0.40 mM) at room temperature recorded between 5,556–36,364 cm$^{-1}$ (1,800–275 nm), window shown between 6,000–32,000 cm$^{-1}$ (1,667–313 nm). Features either side of 7,000 cm$^{-1}$ are due to imperfect background subtraction.

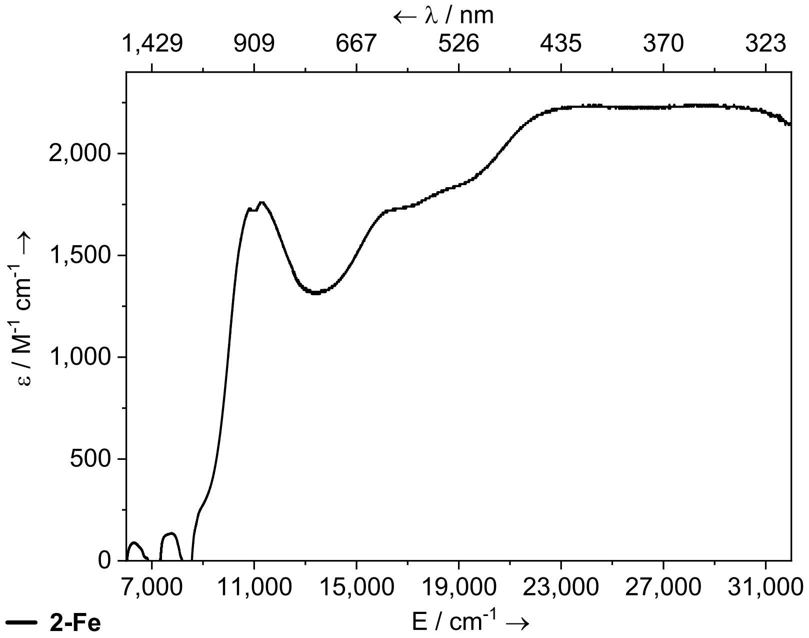


**Figure S25.** UV-vis-nIR spectrum of **2-Fe** in THF (0.40 mM) at room temperature recorded between 5,556–36,364 cm$^{-1}$ (1,800–275 nm), window shown between 6,000–32,000 cm$^{-1}$ (1,667–313 nm). Features either side of 7,000 cm$^{-1}$ are due to imperfect background subtraction.

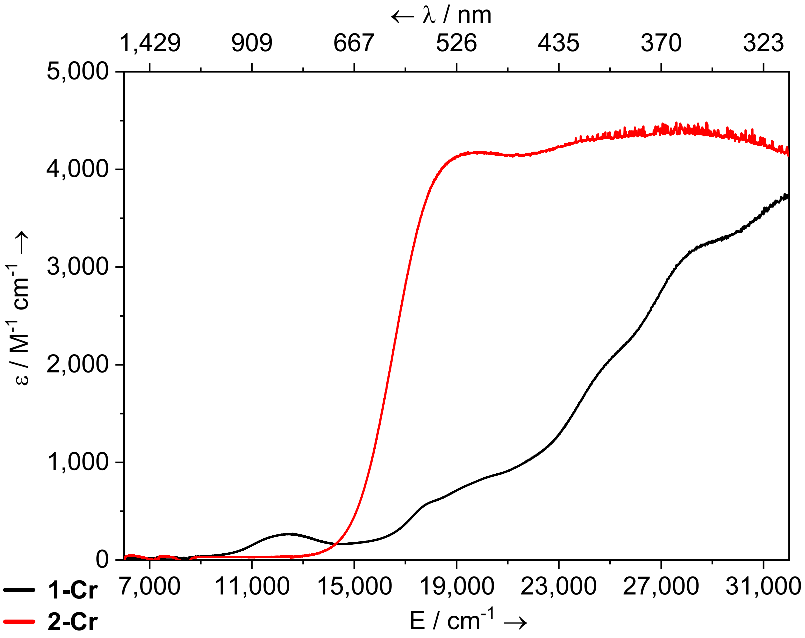


**Figure S26.** UV-vis-nIR spectrum of both **1-Cr** (black, bottom line) and **2-Cr** (red, top line) in THF at room temperature recorded between 5,556–36,364 cm$^{-1}$ (1,800–275 nm), window shown between 6,000–32,000 cm$^{-1}$ (1,667–313 nm). Intended to highlight the spectral differences upon reduction.

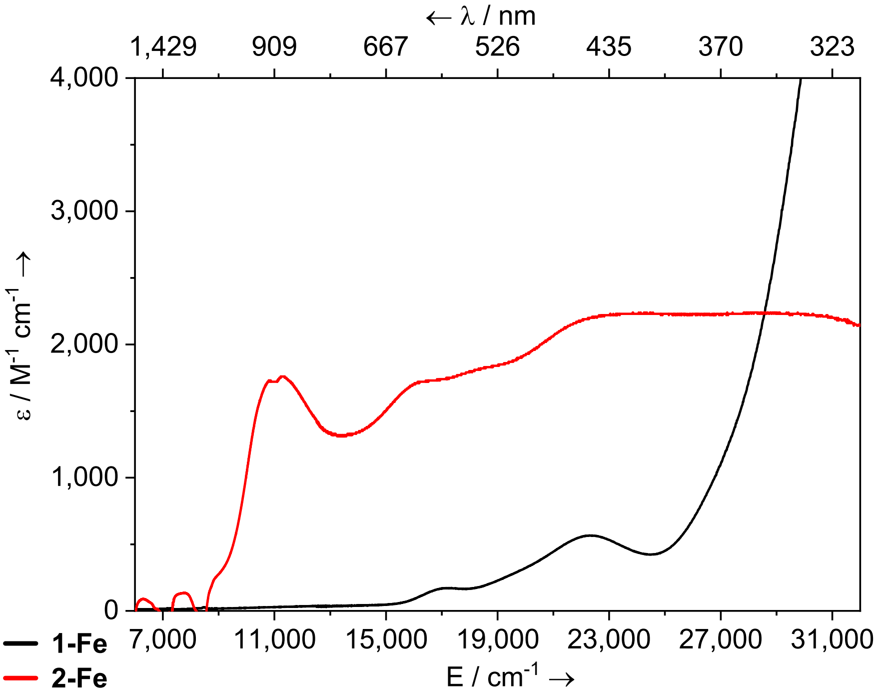


**Figure S27.** UV-vis-nIR spectrum of both **1-Fe** (black, bottom line) and **2-Fe** (red, top line) in THF at room temperature recorded between 5,556–36,364 cm$^{-1}$ (1,800–275 nm), window shown between 6,000–32,000 cm$^{-1}$ (1,667–313 nm). Intended to highlight the spectral differences upon reduction.

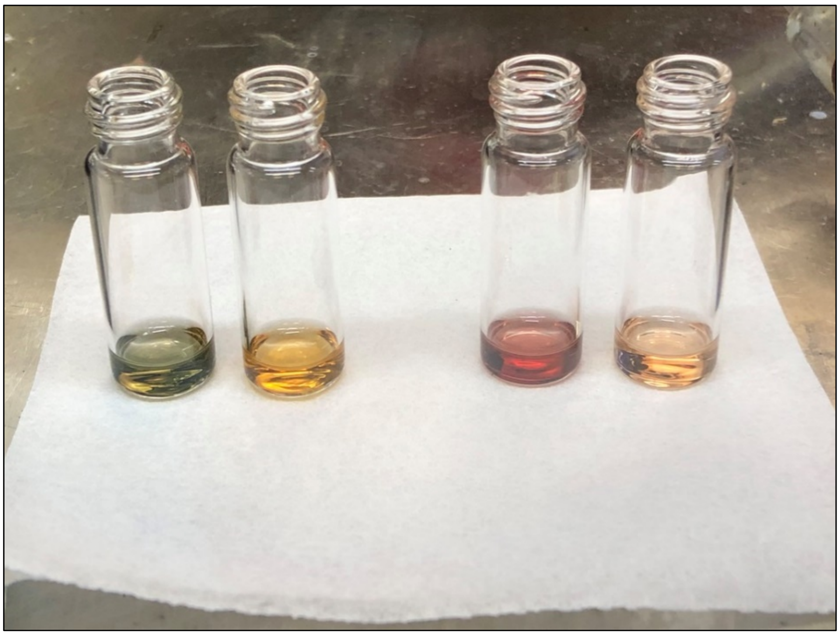


**Figure S28.** A photograph of the solutions used for the UV-vis-nIR measurements. From left to right, **2-Fe**, **1-Fe**, **2-Cr**, and **1-Cr**.

# S6. ATR-FTIR Spectroscopy

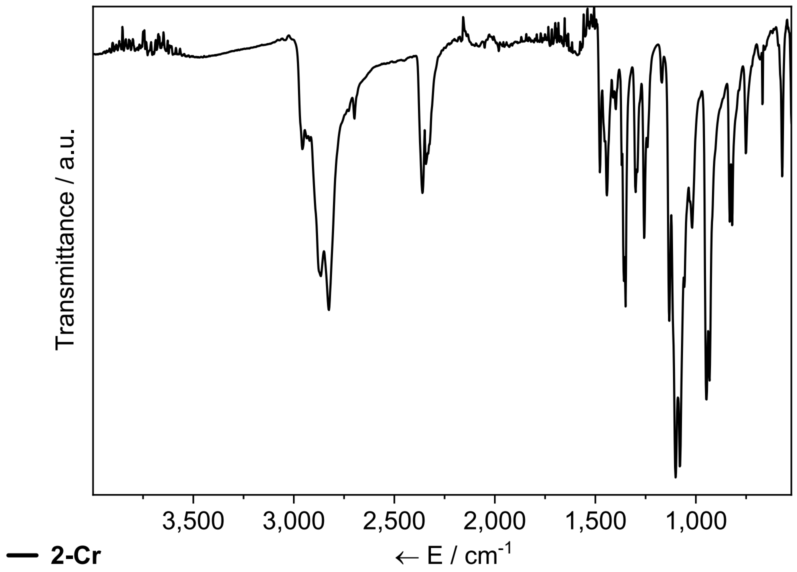


**Figure S29.** FT-IR spectrum of both **2-Cr** a microcrystalline powder, between 4,000-525 cm$^{-1}$.

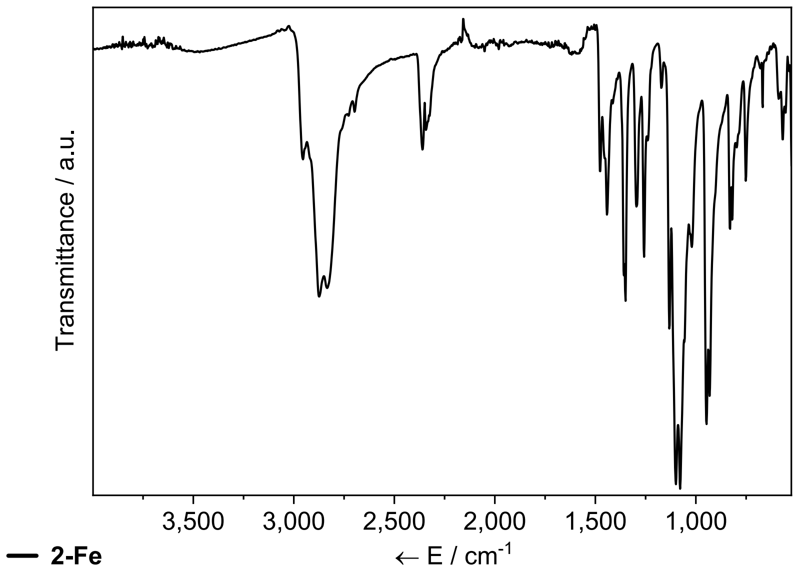


**Figure S30.** FT-IR spectrum of both **2-Fe** a microcrystalline powder, recorded between 4,000-525 cm$^{-1}$.

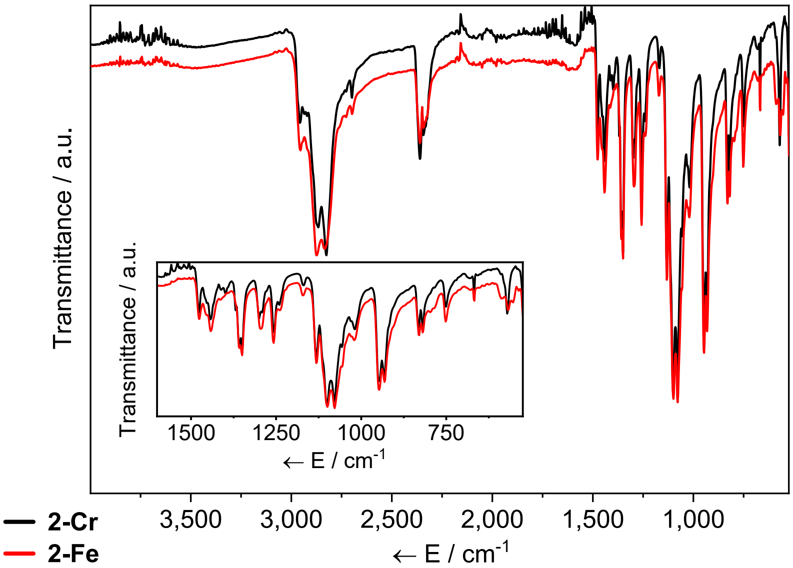


**Figure S31.** FT-IR spectrum of both **2-Cr** (black, top line) and **2-Fe** (red, bottom line) as a microcrystalline powder, recorded between 4,000-525 cm$^{-1}$. Inset shown between 1,600-500 cm$^{-1}$, to show that the two complexes are essentially identical in the fingerprint region.

## S7. EPR Spectroscopy

*General considerations:* High-Field/Frequency Electron Paramagnetic Resonance spectra were recorded on powder samples of **2-Cr** and **2-Fe**. Samples were loaded into polyethylene cups and immobilized with a PTFE stopper. All sample manipulations were performed in an inert atmosphere glovebox. The transmission-type spectrometer used in this study combined a 17 T superconducting magnet with a phase-locked source (Virginia Diodes Inc., Charlottesville, VA, USA) with a series of frequency multipliers. The field modulated signal was detected by an InSb hot-electron bolometer (QMC Ltd., Cardiff, U.K.). Temperature control was achieved using an Oxford Instruments (Oxford, U.K.) continuous-flow cryostat. Spectral simulations were generated using EasySpin.[12]

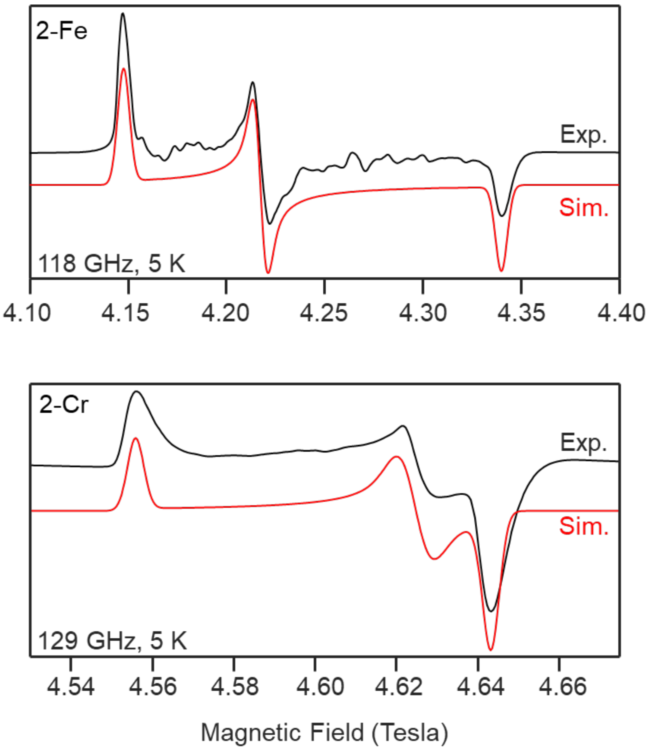


**Figure S32.** Experimental (black) and simulated (red) EPR spectra of **2-Fe** (top), **2-Cr** (bottom), note the x-axis scale for **2-Cr**. Spectra were recorded at the temperatures and frequencies denoted on the respective figures. Note: the baseline features in the **2-Fe** spectrum results from micro-crystallites in the imperfectly ground powder. Multi-frequency studies of **2-Cr** and **2-Fe** reveal no additional features arising from higher spin states. However, **2-Fe** exhibits a minor impurity at lower field which is omitted here for clarity and is shown below in Figure S33. The *g*-values used in the simulations are reported the main text as well as in Table S8.

**Table S8. Experimental and CASSCF/NEVPT2 Calculated Spin Hamiltonian Parameters.**

| | | $S$ | $g_1, g_2, g_3$ |
|---|---|---|---|
| **2-Fe** | Exp. | 1/2 | 2.033(5), 1.999(5), 1.943(5) |
| | *NEVPT2* | 1/2 | *2.116, 2.029,1.919* |
| **2-Cr** | Exp. | 1/2 | 2.023(5), 1.993(5), 1.985(5) |
| | *NEVPT2* | 1/2 | *2.007, 1.984, 1.978* |

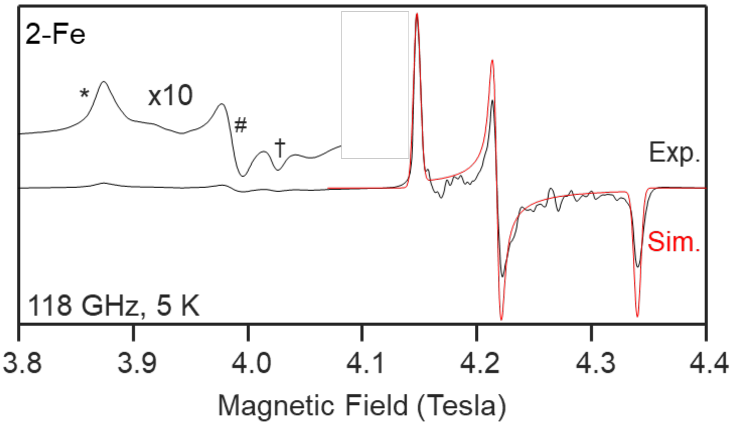


**Figure S33.** Spectrum of **2-Fe** (same as Figure S32) with an extended axis to show the unknown minor species. The g-values of these features are: ~ 2.09 (*), 2.12 (#), and ~2.18 (†). No evidence of this species was present in **2-Cr**.

The sign of $\Delta g_\mu$ ($g_\mu - g_e$), i.e., whether the $g$ – value is less than or greater than the free election value, $g_e$, is determined by the competition of the low-energy α- and β- electron transitions. If the excited states contributing to $\Delta g$ are predominately accessed by transitions involving α-electrons, then $\Delta g < 0$ while those involving low-lying β-electrons will result in $\Delta g > 0$. The $g$-values are reasonably well reproduced by the CASSCF + NEVPT2 calculations (see Table S8) and some qualitative insight may be gleaned from examining the AILFT orbital diagrams in Figure 3. In the case of **2-Cr** the lowest energy state (transitions: $\{d_{xy}/d_{y2\text{-}y2}\} \rightarrow \{d_{z2}\}$) do not mix by spin-orbit coupling and the sign and magnitude of $\Delta g$ are determined by the mixing of numerous higher energy excited states. This explains the relatively small $\Delta g$ values (**2-Cr**, $|\Delta g_{avg}| = 0.0158$). For **2-Fe** the first excited state can be described as an α- electron transition from $\{d_{xz}\} \rightarrow \{d_{yz}\}$ which will mix with the ground state and negative $\Delta g$ along $z$. As in the case of **2-Cr**, several higher energy excited states make up the remaining contributions. However, the comparatively large mixing induced by the first excited state is likely a key contributor to the larger observed $|\Delta g_{avg}| = 0.0311$ in **2-Fe**.

## S8. $^{57}$Fe Mössbauer Spectroscopy

*General considerations:* Spectra were recorded at 120 K in zero applied field using a constant acceleration spectrometer and a $^{57}$Co/Rh source. The samples used for these measurements consisted of ground powders of **1-Fe** and **2-Fe** that were contained in polyethylene sample cups with tightly fitted lids. The isomer shift is reported relative to that of α-Fe at room temperature. Spectral simulations were generated using the WMOSS software package (SEE Co. Minneapolis, MN).[13]

**Table S9. Experimental and DFT Calculated $^{57}$Fe Mössbauer Parameters.**

| | | $\delta$ (mm/sec) | $\Delta E_Q$ (mm/sec) | $\Gamma$ (mm/sec)[a] |
|---|---|---|---|---|
| **2-Fe** | Exp. | 0.65 | 1.28 | -0.602 |
| | *DFT* | *0.66* | *1.46* | - |
| **1-Fe** | Exp. | 0.48 | 2.02 | 0.318 |
| | *DFT* | *0.50* | *1.91* | - |

[a] Positive and negative linewidths indicate Lorentzian and Gaussian lineshapes, respectively.

# S9. Quantum Chemical Calculations

*DFT Calculations:* Calculations for **1-Cr**, **2-Cr**, **1-Fe**, and **2-Fe** were performed using the atomic coordinates determined by X-ray crystallography (with hydrogen positions optimized). These calculations were performed using ORCA V4.1 with the BP86 functional along with the def2-tzvp basis sets.[14-18] The functional was chosen from our previous success in reproducing $^{57}$Fe Mössbauer parameters using the BP86 functional.[19] The resolution of the identity approximation was used along with auxiliary basis sets generated using the 'autoaux' command.[20] The quadrupole splitting and isomer shifts were then calculated using the BP86 functional with CP(PPP) (Fe)/def2-tzvp(C)/def2-svp(H). The RI approximation was not used for calculation of $^{57}$Fe Mössbauer Parameters. The computed density at the Fe nucleus was converted to experimental values of the isomer shift using the calibration curve described by Römelt, *et al.*[21] Example input files are shown below.

*Complete Active Space Self-Consistent Field/AILFT Calculations:* State-averaged complete active space self- consistent field (SA-CASSCF) followed by second-order N-electron valence perturbation theory (NEVPT2) calculations were performed on the same structures used in the DFT calculations (*vide supra*). Scalar relativistic effects were accounted for by the Douglas−Kroll−Hess (DKH) procedure. SOC was accounted for by quasi-degenerate perturbation theory. This methodology of accounting for SOC has proven successful in numerous other studies.[22-30] The dkh-def2-tzvp (Fe,C)/dkh-def2-svp (H) basis set combination was used. The active space consisted of the five 3d – orbitals and all of the 3d – electrons (six for $Fe^{2+}$, seven for $Fe^{+}$, four for $Cr^{2+}$, five for $Cr^{+}$). All roots for all multiplicities were included. This means that for $Cr^{2+}$/$Fe^{2+}$ 5 quintet, 45 triplet, and 50 singlet states were included. For $Cr^{+}$ 1 sextet, 24 quartet, and 75 singlet states were included. For $Fe^{+}$ 10 quartet states and 40 doublet states were included. The *ab-initio* ligand field analysis was performed as implemented in ORCA V4.1 and the energies presented in the text are those associated with the mapping of the CASSCF+NEVPT2 energies. Example input files are shown below.[27]

## S9.1. Example ORCA input files

Optimize Hydrogen Positions:

```
! BP86 def2-tzvp autoaux opt
%geom
optimizehydrogens true
end
*xyz charge multiplicity
xyz coordinates of structure
*
```

$^{57}$Fe Mössbauer Parameters:

```
! BP86 def2-tzvp NoFinalGrid
%method
SpecialGridAtoms 26
SpecialGridIntAcc 7
end
%basis
NewGTO H “def2-svp”
NewGTO Fe “CP(PPP)”
end
*xyz charge multiplicity
xyz coordinates of structure
*
%eprnmr
nuclei = all Fe {rho, fgrad}
end
```

CASSCF + NEVPT2:

```
!DKH dkh-def2-tzvp autoaux normalprint moread
%moinp “guess.gbw” # Here the guess orbitals were from a single point DFT calculation
%casscf # Here the Fe+/d7 settings are used as an example
nel 7
norb 5
mult 4,2
nroots 10,40
actorbs dorbs
trafostep RI
nevpt2 true
rel
dosoc true
gtensor true
end
end
%basis
NewGTO H “def2-svp”
NewGTO Fe “CP(PPP)”
end
*xyz -1 2
xyz coordinates of structure
*
```

**Table S10. Summary of CASSCF+NEVPT2 and AILFT results for 1-Fe, 2-Fe, 1-Cr, and 2-Cr.**

|  | Method | Spin Ground State | AILFT Energies (cm$^{-1}$) |
|---|---|---|---|
| **1-Fe** | CASSCF | 2 | 0.0, 1018.7, 3671.5, 18514.2, 21138.6 |
|  | CASSCF+NEVPT2 | 0 | 0.0, 899.0, 2984.5, 23425.8, 25707.1 |
| **2-Fe** | CASSCF | 3/2 | 0.0, 389.9, 4677.5, 14412.4, 19698.6 |
|  | CASSCF+NEVPT2 | 1/2 | 0.0, 354.7, 4364.2, 19153.3, 25100.0 |
| **1-Cr** | CASSCF | 2 | 0.0, 2226.9, 5170.3, 18790.0, 22484.6 |
|  | CASSCF+NEVPT2 | 1 | 0.0, 2518.0, 4620.0, 21382.7, 24956.9 |
| **2-Cr** | CASSCF | 1/2 | 0.0, 461.3, 7483.5, 21077.6, 25943.8 |
|  | CASSCF+NEVPT2 | 1/2 | 0.0, 343.7, 6144.3, 24766.6, 29492.1 |

## S10. SQUID Magnetometry

*General considerations:* Samples of **1-Cr, 2-Cr,** and **2-Fe** used for measurements consisted of crushed microcrystalline powders weighed (28.0 mg, **1-Cr**; 23.6 mg, **2-Cr**; 29.0 mg, **2-Fe**) into thin-walled precision borosilicate NMR tubes, which were flame sealed under vacuum. A diamagnetic correction was performed using two further NMR tubes from the same batch also sealed under vacuum.

Magnetic measurements were performed with a Quantum Design SQUID magnetometer MPMS-XL. The temperature dependence of magnetic susceptibility was measured in a direct current (DC) applied magnetic field of 0.1 T in the range from 1.8 to 300 K.

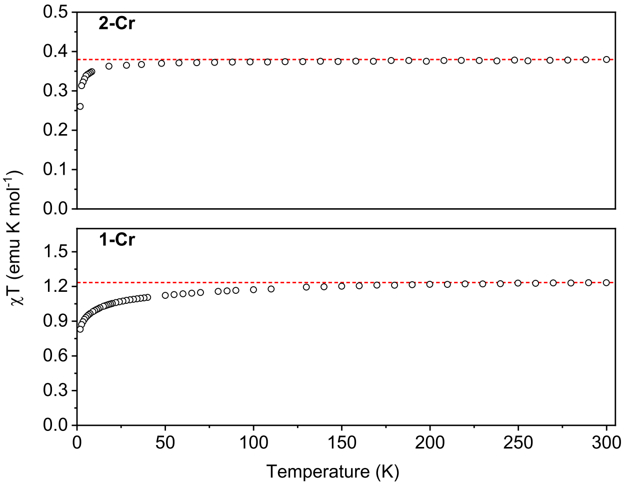


**Figure S34.** Temperature dependence of $\chi$T for **1-Cr** and **2-Cr** between 1.8 and 300 K. The red lines are to guide the eye for values at 298 K (**1-Cr**, 1.24 emu·K/mol; **2-Cr**, 0.38 emu·K/mol).

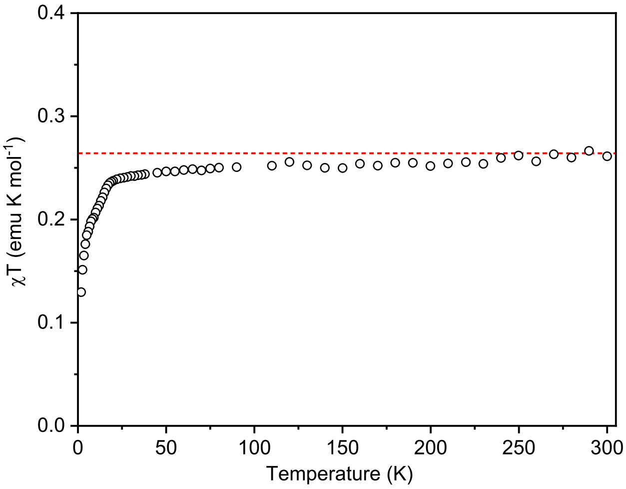


**Figure S35.** Temperature dependence of $\chi$T for **2-Fe** between 1.8 and 300 K. The red line is to guide the eye for the value at 298 K (0.26 emu·K/mol).

## S11. Qualitative ligand HOMOs in $Cp^-$ vs $\{PC_4H_4\}^-$

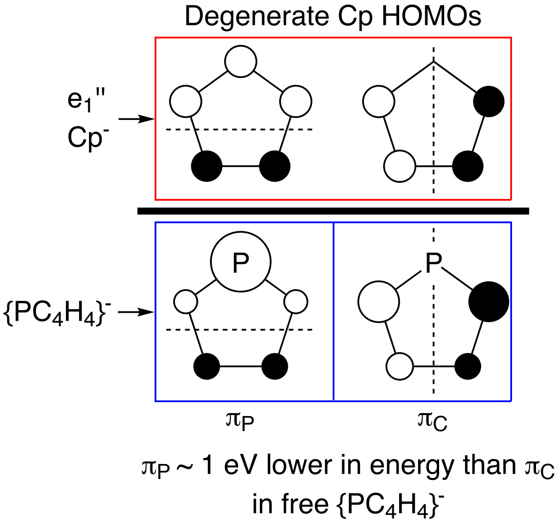


**Figure S36.** Illustrative pictures of the ligand HOMOs relevant to the LUMO in FcH, and $[Fe(PC_4H_4)_2]$.

The ligand HOMO in $Cp^-$ in $D_{5h}$ symmetry is comprised of two degenerate orbitals. However, for $\{PC_4H_4\}^-$, the P atom breaks the 5-fold symmetry, and thus the analogous orbitals are not degenerate. While both the $\pi_P$ and $\pi_C$ orbitals shown above are of appropriate symmetry to interact with the metal $d_{xz}$, $d_{yz}$ orbitals, they differ in energy by ~ 1 eV, and thus the $[Fe(PC_4H_4)_2]$ complex LUMO is mostly comprised of the $\pi_P$ orbital and a metal $d_{yz}$ orbital. Please see Fenske *et al* for a much more in depth analysis,[31] as the above discussion does not fully account for the lower symmetry of **2-Fe**.

## Author Contributions

CAPG performed all synthesis, UV-vis-nIR and NMR characterization and sample preparation, and X-ray diffraction data collection and interpretation with supervision by BLS. SMG performed EPR and Mössbauer spectroscopies and interpreted the data, and also performed all theoretical work, with supervision by BWS. OU performed SQUID magnetometry measurements and interpretation. RJB sealed samples for analysis and was supervised by JLK. CAPG lead the project with project scope and design helped by SMG. The manuscript was prepared by CAPG with input from all authors.

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# S13. CIF Reports

## checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1-Cr

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.  CIF dictionary  Interpreting this report

## Datablock: 1-Cr

---

```
Bond precision:   C-C = 0.0021 A          Wavelength=0.71073

Cell:             a=7.8420(3)     b=12.5620(4)        c=8.8611(3)
                  alpha=90        beta=109.444(4)     gamma=90
Temperature:      100 K

                 Calculated                   Reported
Volume           823.13(5)                    823.13(5)
Space group      P 21/n                       P 1 21/n 1
Hall group       -P 2yn                       -P 2yn
Moiety formula   C16 H24 Cr P2                C16 H24 Cr P2
Sum formula      C16 H24 Cr P2                C16 H24 Cr P2
Mr               330.29                       330.29
Dx,g cm-3        1.333                        1.333
Z                2                            2
Mu (mm-1)        0.874                        0.874
F000             348.0                        348.0
F000'            349.12
h,k,lmax         9,15,10                      9,15,10
Nref             1507                         1508
Tmin,Tmax        0.700,0.769                  0.804,1.000
Tmin'            0.686

Correction method= # Reported T Limits: Tmin=0.804 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.001          Theta(max)= 25.349

R(reflections)= 0.0252( 1441)     wR2(reflections)= 0.0667( 1508)

S = 1.091                 Npar= 92
```

---

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

```
Alert level G
PLAT328_ALERT_4_G Possible Missing H on sp3? Phosphorus .........         P1 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....        C6 Check
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........        4.5 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         6 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   5 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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**PLATON version of 16/07/2020; check.def file version of 12/07/2020**

## checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1-Fe

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No syntax errors found.   CIF dictionary   Interpreting this report

## Datablock: 1-Fe

---

```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71073

Cell:            a=14.2948(7)     b=12.8549(6)        c=8.8448(4)
                 alpha=90         beta=104.364(5)     gamma=90
Temperature:     100 K

                Calculated                  Reported
Volume          1574.50(13)                 1574.50(13)
Space group     C 2/c                       C 1 2/c 1
Hall group      -C 2yc                      -C 2yc
Moiety formula  C16 H24 Fe P2               C16 H24 Fe P2
Sum formula     C16 H24 Fe P2               C16 H24 Fe P2
Mr              334.14                      334.14
Dx,g cm-3       1.410                       1.410
Z               4                           4
Mu (mm-1)       1.146                       1.146
F000            704.0                       704.0
F000'           706.33
h,k,lmax        17,16,11                    17,16,11
Nref            1608                        1605
Tmin,Tmax       0.770,0.832                 0.850,1.000
Tmin'           0.717

Correction method= # Reported T Limits: Tmin=0.850 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 26.370

R(reflections)= 0.0312( 1407)     wR2(reflections)= 0.0798( 1605)

S = 1.117                  Npar= 92
```

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

```
● Alert level C
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.29 Report
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          4 Report
```

```
● Alert level G
PLAT328_ALERT_4_G Possible Missing H on sp3? Phosphorus ..........         P1 Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.9 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          6 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   3 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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**PLATON version of 16/07/2020; check.def file version of 12/07/2020**

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 2-Cr

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No syntax errors found.      CIF dictionary      Interpreting this report

## Datablock: 2-Cr

---

```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71073

Cell:           a=10.1994(4)      b=14.2193(7)     c=15.0882(6)
                alpha=62.328(4)   beta=86.597(3)   gamma=87.156(3)
Temperature:    100 K

                 Calculated                  Reported
Volume           1933.91(16)                 1933.91(16)
Space group      P -1                        P -1
Hall group       -P 1                        -P 1
                 C18 H36 K N2 O6, C16 H24    C16 H24 Cr P2, C18 H36 K
Moiety formula   Cr P2                       N2 O6
Sum formula      C34 H60 Cr K N2 O6 P2       C34 H60 Cr K N2 O6 P2
Mr               745.88                      745.88
Dx,g cm-3        1.281                       1.281
Z                2                           2
Mu (mm-1)        0.529                       0.529
F000             798.0                       798.0
F000'            799.73
h,k,lmax         12,17,18                    12,17,18
Nref             7083                        7060
Tmin,Tmax        0.853,0.853                 0.902,1.000
Tmin'            0.853

Correction method= # Reported T Limits: Tmin=0.902 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.350

R(reflections)= 0.0338( 5848)     wR2(reflections)= 0.0872( 7060)

S = 1.100                  Npar= 423
```

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

---

### ● Alert level C

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         13 Report
```

---

### ● Alert level G

```
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT328_ALERT_4_G Possible Missing H on sp3? Phosphorus ..........         P1 Check
PLAT328_ALERT_4_G Possible Missing H on sp3? Phosphorus ..........         P2 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....         C7 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....        C16 Check
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         10 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          1 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.3 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          8 Info
```

---

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

---

---

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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---

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No syntax errors found.     CIF dictionary     Interpreting this report

## Datablock: 2-Fe

---

```
Bond precision:  C-C = 0.0034 A          Wavelength=0.71073

Cell:          a=10.1947(2)      b=14.2373(4)     c=15.0677(3)
               alpha=62.275(2)   beta=85.840(2)   gamma=87.045(2)
Temperature:   100 K

                Calculated                  Reported
Volume          1930.42(8)                  1930.42(8)
Space group     P -1                        P -1
Hall group      -P 1                        -P 1
Moiety formula  C18 H36 K N2 O6, C16 H24    C16 H24 Fe P2, C18 H36 K
                Fe P2                       N2 O6
Sum formula     C34 H60 Fe K N2 O6 P2       C34 H60 Fe K N2 O6 P2
Mr              749.73                      749.73
Dx,g cm-3       1.290                       1.290
Z               2                           2
Mu (mm-1)       0.624                       0.624
F000            802.0                       802.0
F000'           803.77
h,k,lmax        12,17,18                    12,17,18
Nref            7890                        7807
Tmin,Tmax       0.856,0.969                 0.872,1.000
Tmin'           0.856

Correction method= # Reported T Limits: Tmin=0.872 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.989          Theta(max)= 26.370

R(reflections)= 0.0400( 6351)     wR2(reflections)= 0.1035( 7807)

S = 1.090                  Npar= 423
```

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

---

### Alert level C

```
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.41 Report
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.110 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         60 Report
```

---

### Alert level G

```
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.002 Degree
PLAT328_ALERT_4_G Possible Missing H on sp3? Phosphorus ..........         P1 Check
PLAT328_ALERT_4_G Possible Missing H on sp3? Phosphorus ..........         P2 Check
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         22 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          1 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.3 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          6 Info
```

---

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

---

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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---

**PLATON version of 16/07/2020; check.def file version of 12/07/2020**

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 5

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.      CIF dictionary      Interpreting this report

## Datablock: 5

---

```
Bond precision:  C-C = 0.0040 A          Wavelength=0.71073

Cell:            a=14.1554(8)    b=9.6976(4)        c=12.0182(6)
                 alpha=90        beta=112.336(6)     gamma=90
Temperature:     150 K

                Calculated                 Reported
Volume          1526.00(15)                1525.99(14)
Space group     I 2/a                      I 1 2/a 1
Hall group      -I 2ya                     -I 2ya
Moiety formula  C18 H22 Zr                 C18 H22 Zr
Sum formula     C18 H22 Zr                 C18 H22 Zr
Mr              329.58                     329.57
Dx,g cm-3       1.434                      1.435
Z               4                          4
Mu (mm-1)       0.705                      0.705
F000            680.0                      680.0
F000'           668.18
h,k,lmax        17,12,15                   17,12,15
Nref            1559                       1558
Tmin,Tmax       0.905,0.974                0.775,1.000
Tmin'           0.889

Correction method= # Reported T Limits: Tmin=0.775 Tmax=1.000
AbsCorr = GAUSSIAN

Data completeness= 0.999          Theta(max)= 26.386

R(reflections)= 0.0330( 1401)     wR2(reflections)= 0.0805( 1558)

S = 1.068                  Npar= 117
```

---

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

**Alert level G**

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         15 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records          1 Report
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )        53% Note
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....          ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............         144 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          1 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........         1.8 Low
PLAT955_ALERT_1_G Reported (CIF) and Actual (FCF) Lmax Differ by .          1 Units
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          8 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  11 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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**Publication of your CIF in other journals**

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**PLATON version of 16/07/2020; check.def file version of 12/07/2020**

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 6

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No syntax errors found.  CIF dictionary  Interpreting this report

## Datablock: 6

---

```
Bond precision:  C-C = 0.0020 A          Wavelength=1.54184

Cell:          a=8.0727(2)         b=8.74422(19)     c=18.4065(4)
               alpha=103.1739(17)  beta=92.6248(19)  gamma=100.705(2)
Temperature:   150 K

                Calculated                  Reported
Volume          1237.81(5)                  1237.81(5)
Space group     P -1                        P -1
Hall group      -P 1                        -P 1
Moiety formula  C14 H17 P                   C14 H17 P
Sum formula     C14 H17 P                   C14 H17 P
Mr              216.25                      216.24
Dx,g cm-3       1.160                       1.160
Z               4                           4
Mu (mm-1)       1.664                       1.664
F000            464.0                       464.0
F000'           466.15
h,k,lmax        9,10,22                     9,10,22
Nref            4541                        4482
Tmin,Tmax       0.760,0.862                 0.703,1.000
Tmin'           0.690

Correction method= # Reported T Limits: Tmin=0.703 Tmax=1.000
AbsCorr = GAUSSIAN

Data completeness= 0.987           Theta(max)= 68.247

R(reflections)= 0.0329( 4211)      wR2(reflections)= 0.0899( 4482)

S = 1.036                  Npar= 279
```

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

**Alert level C**

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         55 Report
```

**Alert level G**

```
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H6A      ..H5D      .       2.02 Ang.
                                                     x,y,z  =     1_555 Check
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          5 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........        2.9 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          8 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          2 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   5 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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**PLATON version of 16/07/2020; check.def file version of 12/07/2020**

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 7

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No syntax errors found.      CIF dictionary      Interpreting this report

## Datablock: 7

---

```
Bond precision:  C-C = 0.0040 A          Wavelength=0.71073

Cell:            a=20.161(3)     b=9.0620(4)        c=20.214(3)
                 alpha=90        beta=119.71(2)     gamma=90
Temperature:     100 K

                Calculated                  Reported
Volume          3207.6(9)                   3207.7(9)
Space group     C 2/c                       C 1 2/c 1
Hall group      -C 2yc                      -C 2yc
Moiety formula  C32 H48 Co2 P4              C32 H48 Co2 P4
Sum formula     C32 H48 Co2 P4              C32 H48 Co2 P4
Mr              674.44                      674.44
Dx,g cm-3       1.397                       1.397
Z               4                           4
Mu (mm-1)       1.254                       1.254
F000            1416.0                      1416.0
F000'           1420.68
h,k,lmax        24,10,24                    24,10,24
Nref            2938                        2935
Tmin,Tmax       0.835,0.882                 0.861,1.000
Tmin'           0.606

Correction method= # Reported T Limits: Tmin=0.861 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 25.342

R(reflections)= 0.0333( 2325)     wR2(reflections)= 0.0834( 2935)

S = 1.009                 Npar= 180
```

---

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

```
Alert level G
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Co1      --P1       .        5.5 s.u.
PLAT328_ALERT_4_G Possible Missing H on sp3? Phosphorus .........          P1 Check
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          4 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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---

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## checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 8

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No syntax errors found.  CIF dictionary  Interpreting this report

## Datablock: 8

---

```
Bond precision:  C-C = 0.0050 A          Wavelength=0.71073

Cell:           a=12.7189(8)      b=15.9437(10)    c=17.8937(12)
                alpha=64.066(6)   beta=85.655(5)   gamma=86.321(5)
Temperature:    100 K

                 Calculated                  Reported
Volume           3251.9(4)                   3251.9(4)
Space group      P -1                        P -1
Hall group       -P 1                        -P 1
                 2(C18 H36 K N2 O6), 2(C8    2(C8 H12 P), C4 H8 O,
Moiety formula   H12 P), C4 H8 O             2(C18 H36 K N2 O6)
Sum formula      C56 H104 K2 N4 O13 P2       C56 H104 K2 N4 O13 P2
Mr               1181.57                     1181.57
Dx,g cm-3        1.207                       1.207
Z                2                           2
Mu (mm-1)        0.254                       0.254
F000             1280.0                      1280.0
F000'            1281.74
h,k,lmax         15,19,22                    15,19,22
Nref             13295                       13040
Tmin,Tmax        0.958,0.987                 0.826,1.000
Tmin'            0.910

Correction method= # Reported T Limits: Tmin=0.826 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.981          Theta(max)= 26.372

R(reflections)= 0.0673( 8417)     wR2(reflections)= 0.1979( 13040)

S = 1.063                  Npar= 1310
```

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

---

### Alert level C

```
PLAT088_ALERT_3_C Poor Data / Parameter Ratio ....................       9.95 Note
PLAT329_ALERT_4_C Carbon Atom Hybridisation Unclear for ..........       C35B Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............      0.005 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      3.712 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        168 Report
PLAT977_ALERT_2_C Check Negative Difference Density on H6B              -0.35 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H6C              -0.40 eA-3
```

---

### Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         10 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...        136 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          3 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          5 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )       100% Note
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  3  )       100% Note
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  4  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  6  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  7  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  8  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  9  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  1  )      57.33 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  2  )      55.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  3  )       5.67 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  4  )       7.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  6  )      17.14 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  7  )       3.86 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  8  )      10.85 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  9  )       2.14 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....         C5 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....         C6 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....         C7 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....         C8 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C31A Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C32A Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C33A Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C34A Check
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O13A            100.9 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O13B             87.6 Degree
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H5A       ..H53C     .       2.09 Ang.
                                                1-x,1-y,1-z  =      2_666 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H6C       ..H42A     .       2.09 Ang.
                                                 1-x,-y,1-z  =      2_656 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H6C       ..H42C     .       2.09 Ang.
                                                 1-x,-y,1-z  =      2_656 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          4 Note
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C35B     --C36B             1.78 Ang.
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C45B     --C46B             1.86 Ang.
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          2 Note
              C18 H36 K N2 O6
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          4 Note
              C18 H36 K N2 O6
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....          ! Info
```

```
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............       2121 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         4 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        84 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         4 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........        2.4 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         5 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by         1 Check
```

---

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  7 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 47 ALERT level G = General information/check it is not something unexpected

  1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 13 ALERT type 2 Indicator that the structure model may be wrong or deficient
 10 ALERT type 3 Indicator that the structure quality may be low
 28 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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**PLATON version of 16/07/2020; check.def file version of 12/07/2020**