Intramolecular electron transfer between molybdenum and iron mimicking bacterial sulphite dehydrogenase

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Electronic Supporting Information

Fig. S1. DFT (B3LYP; LANL2DZ+polarisation functions for N, O; PCM THF) optimised geometry of $\mathbf{2}^{Fc}$ including natural atomic charges on Fe in red; distances in Å.

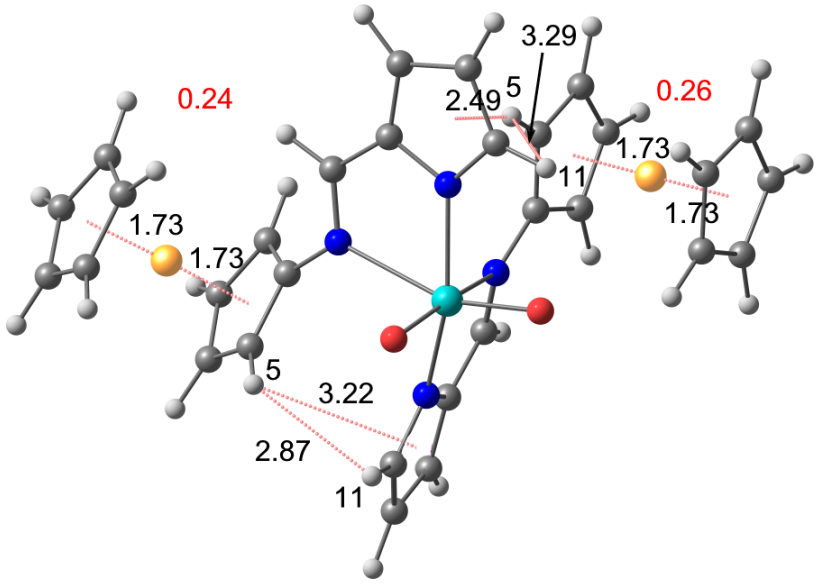


Fig. S2. UV/Vis spectra of $\mathbf{2^{Fc}}$ (and Gaussian deconvolution) and $\mathbf{2^{tBu}}$ in THF.

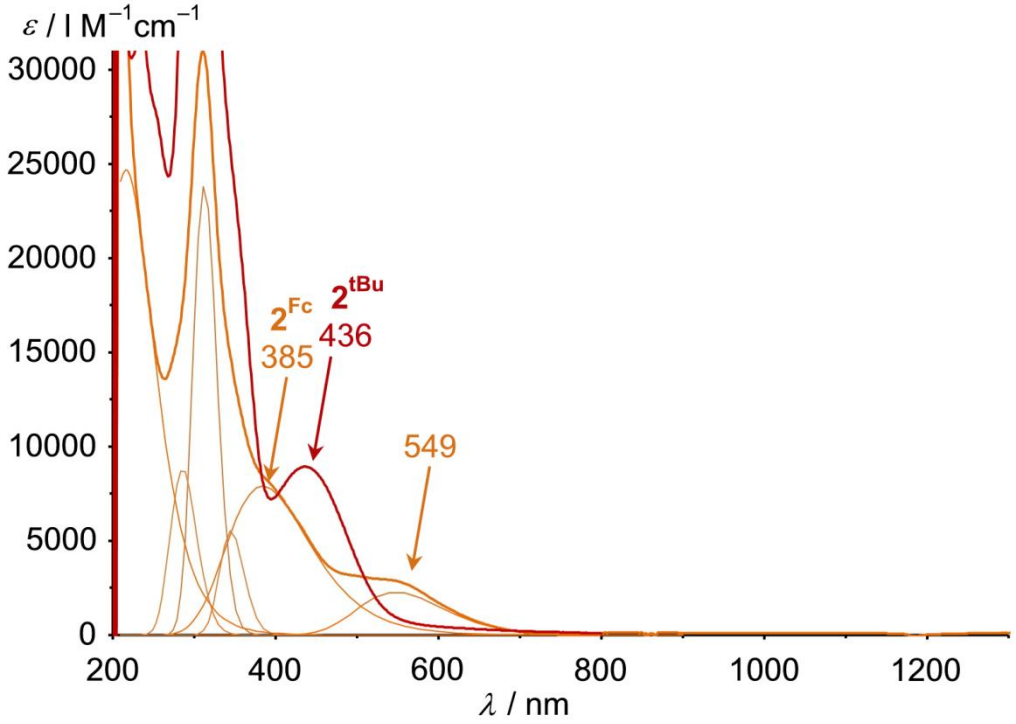
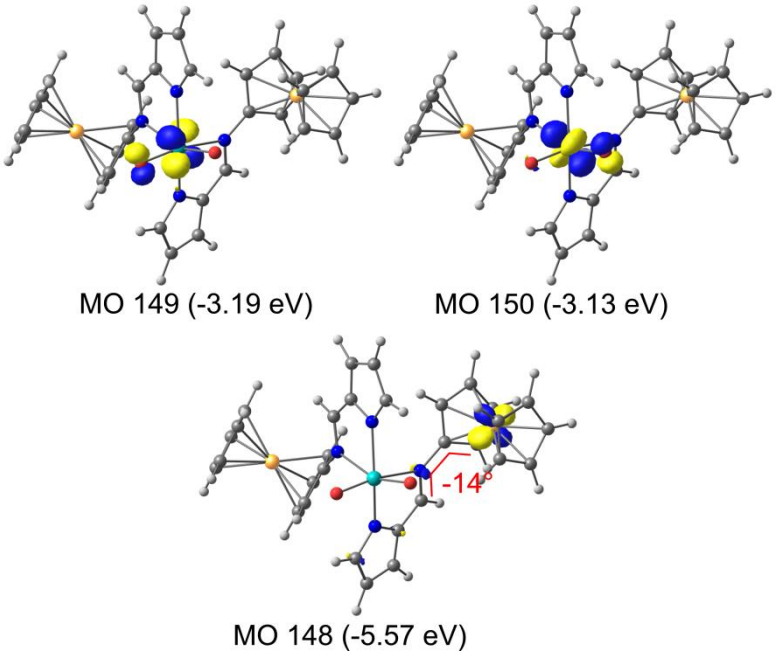


Fig. S3. Pictorial description of MO 148 (HOMO) and MOs 149 – 150 (LUMOs) of $\mathbf{2}^{\mathbf{Fc}}$



Results of the TD-DFT calculation for **2**

```
Excited State   1:      Singlet-A      1.6788 eV  738.52 nm  f=0.0081
<S**2>=0.000
     144 ->157         0.12452
     146 ->155        -0.24498
     148 ->149         0.42505
     148 ->150        -0.34776
     148 ->153         0.11149
     148 ->156        -0.10660
     148 ->157         0.21958
```

Energy and intensity of the transition are governed by the relative orientation of the iron d orbital and Mo=O units. Hence, a perfect match between TD-DFT calculation and experiment is not expected.

Fig. S4. $^{31}P\{^{1}H\}$ NMR spectrum of **3a**^{Fc} and **3b**^{Fc} in d_8-THF.

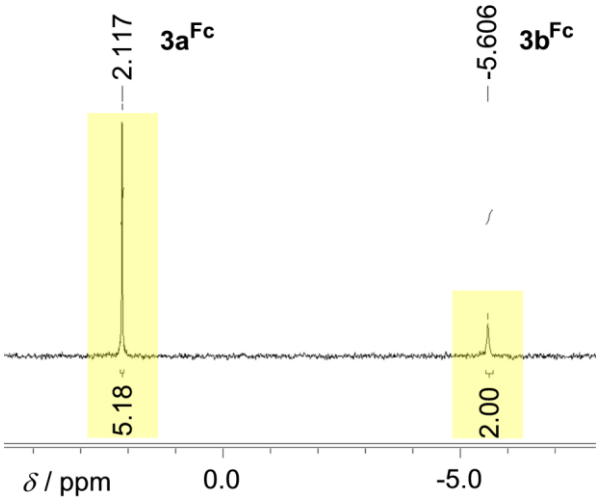


Fig. S5. NOE contacts in **3a**^{Fc} (red arrows, s = strong, m = medium, w = weak)

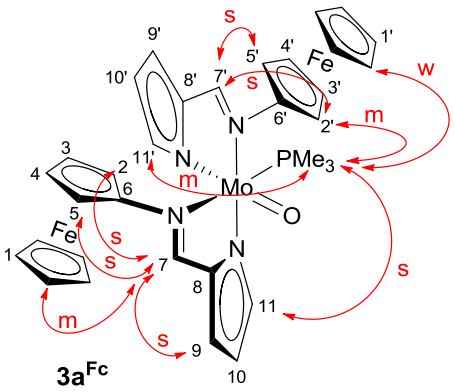


Fig. S6. DFT (B3LYP; LANL2DZ+polarisation functions for N, O; PCM THF) optimised geometry of **3a**^{Fc} including natural atomic charges on Fe in red; distances in Å; hydrogen atoms omitted.

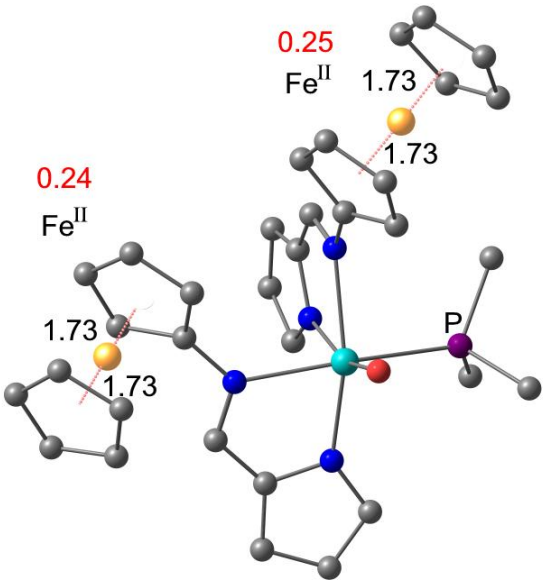


Fig. S7. UV/Vis spectra of $\mathbf{1}^{Fc}$ (orange) and $[\mathbf{1}^{Fc}]^{+}$ (blue) in THF including Gaussian band shape analyses.

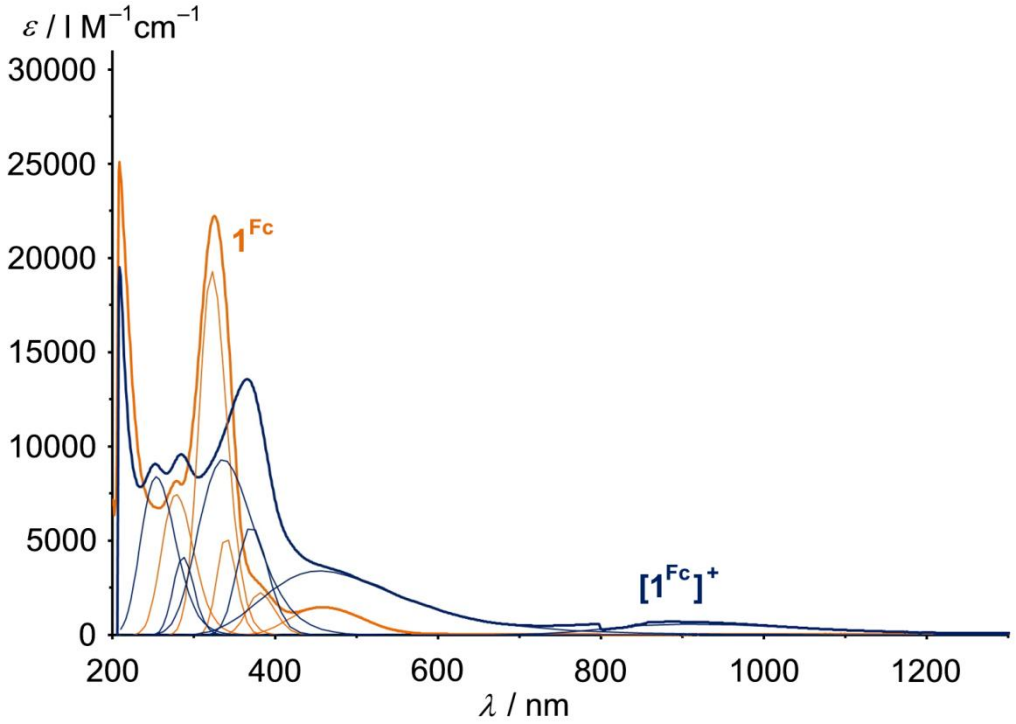


Fig. S8. UV/Vis spectra of $\mathbf{2}^{Fc}$ (orange) in THF and $[\mathbf{2}^{Fc}]^{2+}$ (blue) in CH_3CN including Gaussian band shape analyses.

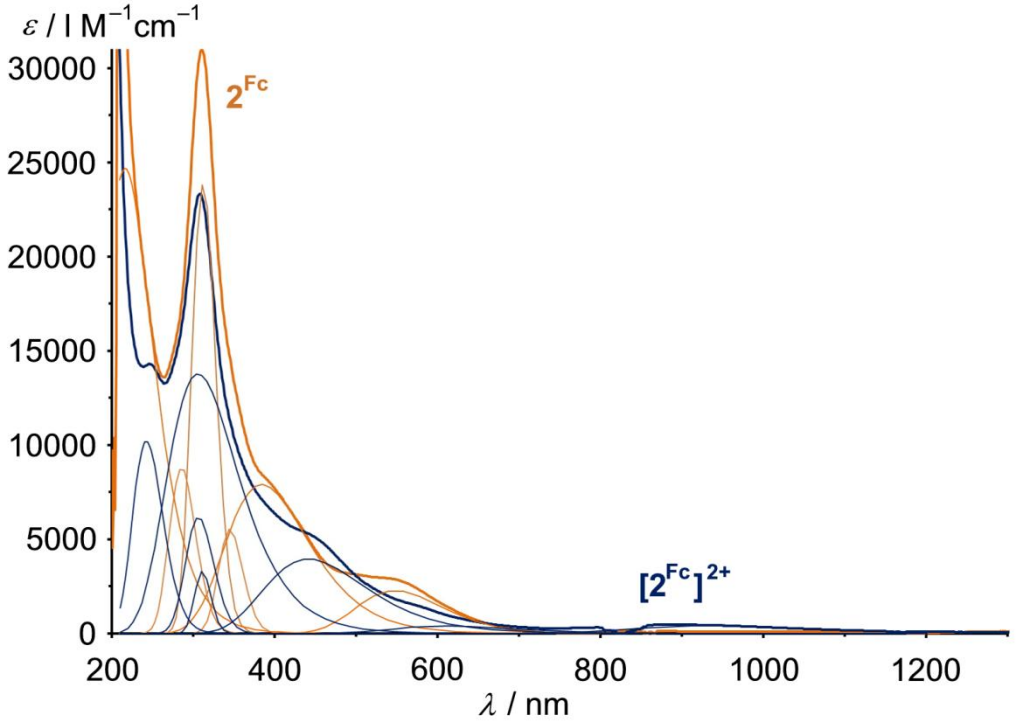


Fig. S9. Spectroelectrochemical oxidation of $\mathbf{2}^{\mathbf{Fc}}$ in THF/[^{n}Bu$_4$N][B(C$_6$F$_5$)$_4$]; Pt electrodes; detector switch at 800 nm

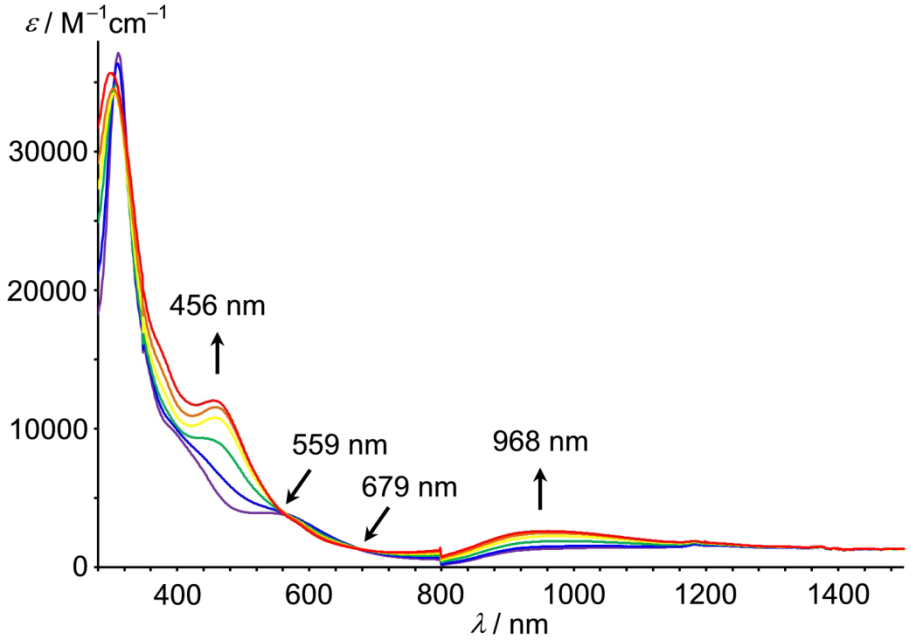


Fig. S10. Paramagnetic ^{1}H NMR spectra of $[\mathbf{2}^{Fc}]^{2+}$ in CD_3CN, including zoom in pyrrolate region; sharp resonances in the diamagnetic region are due to residual solvent.

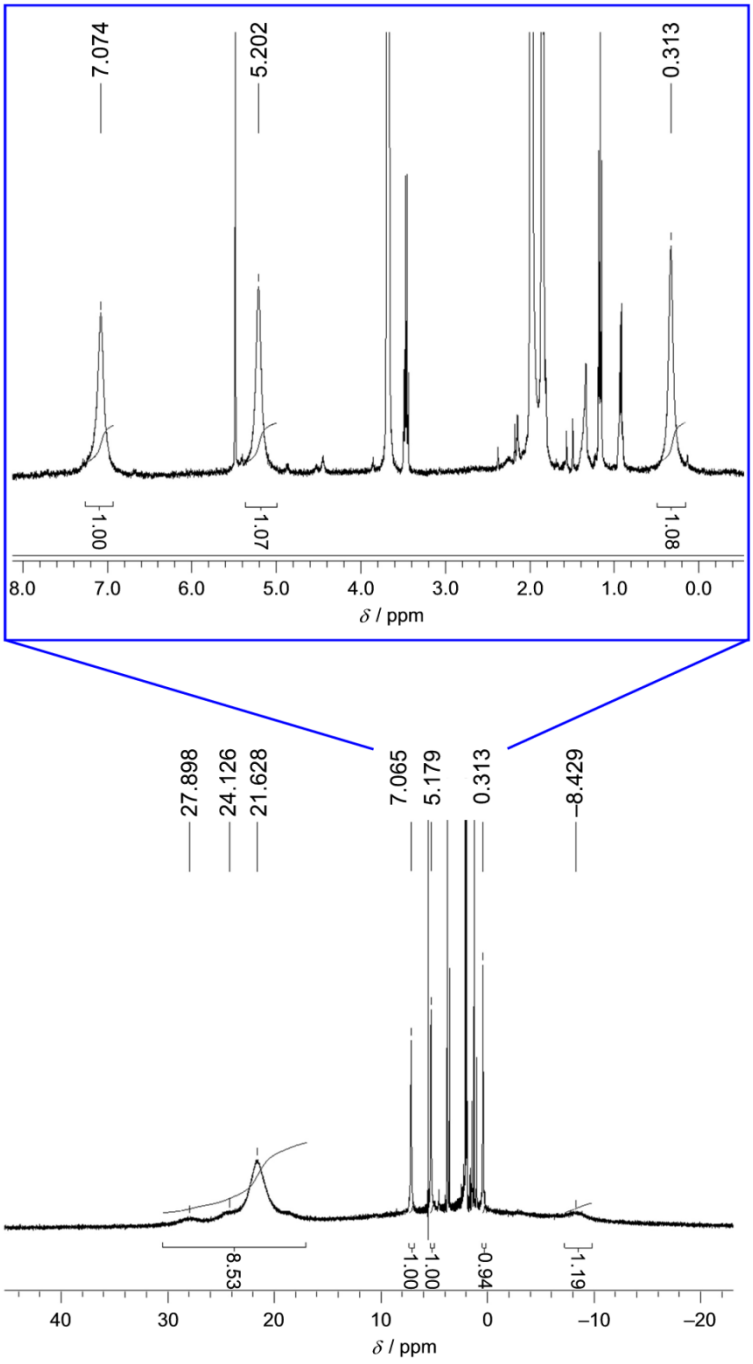


Fig. S11. DFT optimized geometry (B3LYP; LANL2DZ+polarisation functions for N, O, P; PCM THF) of a) $[\mathbf{2}^{\mathbf{Fc}}]^{2+}$ and b) $[\mathbf{4}^{\mathbf{Fc}}]^{2+}$ in the singlet states (distances in Å; angles in deg; natural atomic charges at iron in red; hydrogen atoms omitted).

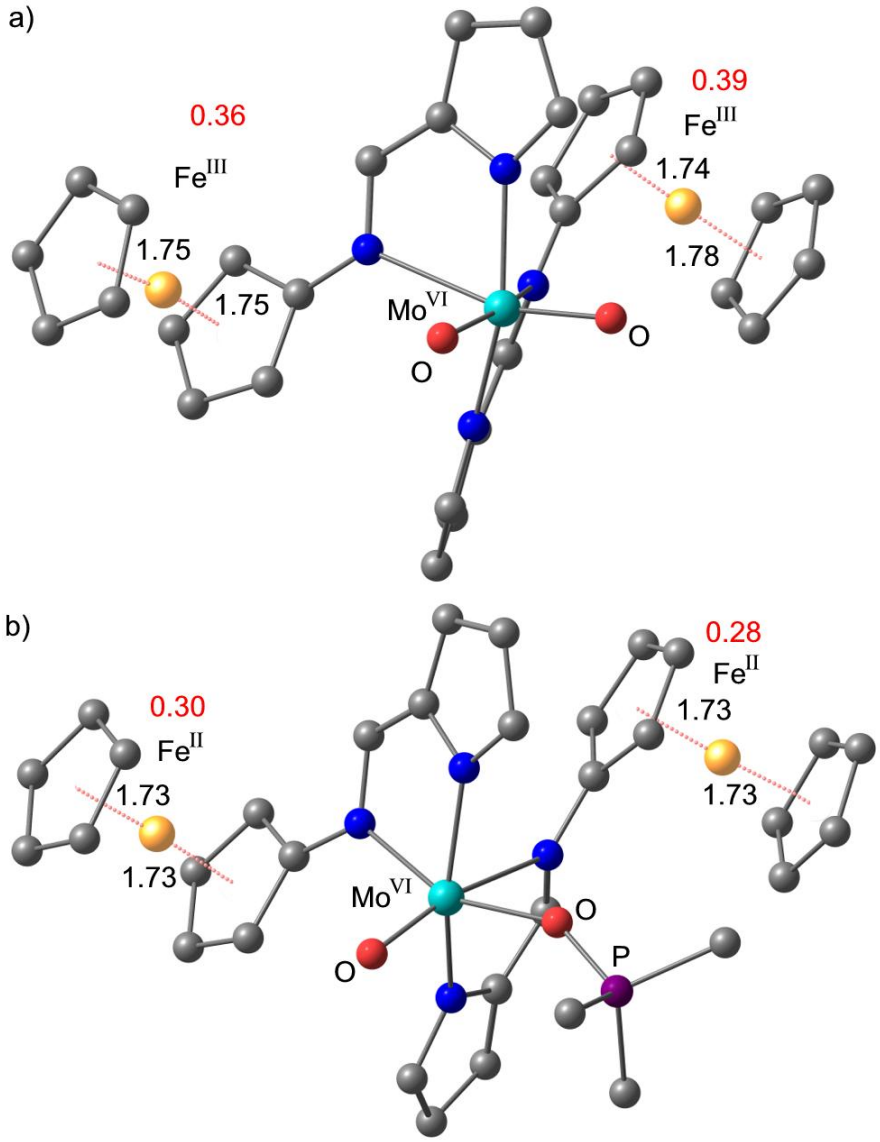


Fig. S12. $^{31}P\{^{1}H\}$ NMR spectrum of **2^{Fc}** and PMe_3 (exc.) in d_8-THF after removing volatiles (PMe_3).

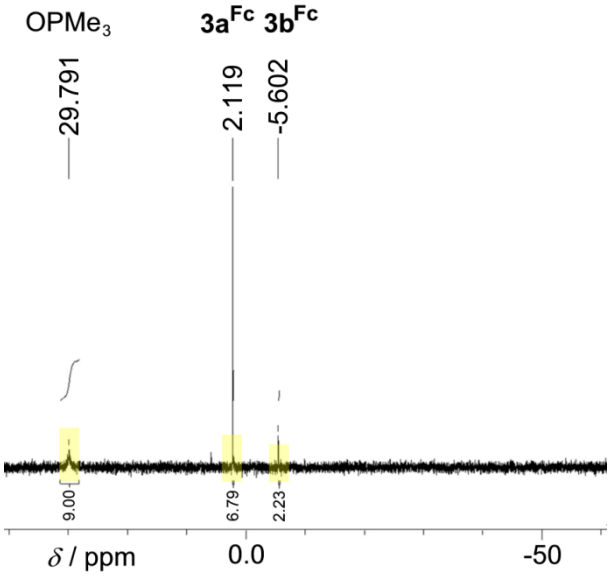
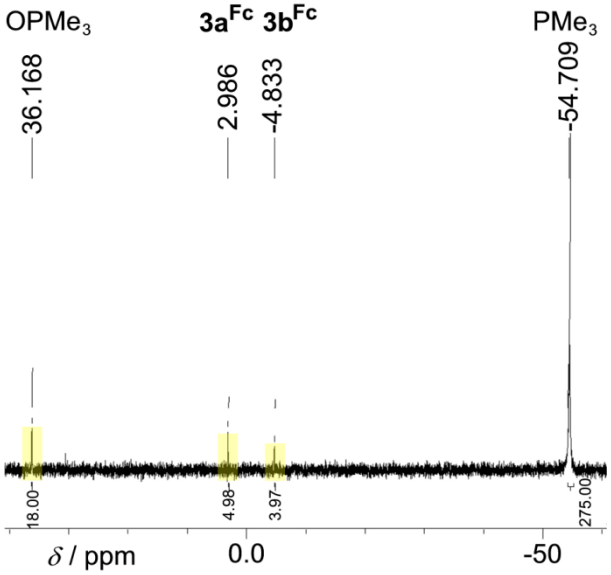


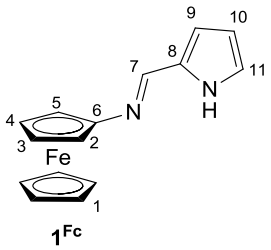
Fig. S13. $^{31}P\{^{1}H\}$ NMR spectrum of **[2^{Fc}]$^{2+}$** and PMe_3 (exc.) in CD_3CN.



General Procedures

All reactions were performed under argon atmosphere unless otherwise noted. THF was distilled from potassium. Aminoferrocene[1,2] and $MoCl_2O_2(dme)$[3] were prepared according to literature procedures. Filtrations from precipitated silver after oxidation were performed with syringe filters (Rotilabo-Spritzenfilter, Ø = 25 mm, pore size = 0.20 µm; Carl Roth GmbH + Co. KG, Germany). NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400.31 MHz (^{1}H), 100.66 MHz (^{13}C{^{1}H}), 162.05 MHz (^{31}P{^{1}H}) and 40.56 MHz (^{15}N). All resonances are reported in ppm versus the solvent signal as internal standard [d_8-THF (^{1}H: δ = 1.73, 3.57; ^{13}C: δ = 25.5, 67.7 ppm); CD_3CN (^{1}H: δ = 1.94)], versus external H_3PO_4 (85%) (^{31}P: δ = 0 ppm) or versus external CH_3NO_2 (90% in $CDCl_3$) (^{15}N: δ = 380.23 ppm). ^{15}N data are reported vs. liquid NH_3 as reference (δ = 0 ppm). IR spectra were recorded with a BioRad Excalibur FTS 3100 spectrometer as KBr disks. Electrochemical experiments were carried out on a BioLogic SP-50 voltammetric analyzer using platinum wires as counter and working electrodes and a 0.01 M $Ag/AgNO_3$ electrode as reference electrode. The cyclic voltammetry measurements were carried out at scan rate of 50–100 mV s^{-1} using 0.1 M (nBu$_4$N)(B(C_6F_5)$_4$) as supporting electrolytes in THF. Potentials are referenced to the ferrocene/ferrocenium couple ($E_{½}$ = 270 ± 5 mV under the experimental conditions). Spectroelectrochemical experiments were performed using a thin layer quartz glass (path length 1 mm) cell kit (GAMEC Analysentechnik, Illingen, Germany) equipped with a Pt gauze working electrode, a Pt counter electrode and a $Ag/AgNO_3$ reference electrode in THF/0.1 M (nBu$_4$N)(B(C_6F_5)$_4$). UV/Vis/NIR spectra were recorded on a Varian Cary 5000 spectrometer using 1.0 cm cells (Hellma, suprasil). FD mass spectra were recorded on a FD Finnigan MAT90 spectrometer. ESI mass spectra were recorded on a Micromass Q-TOF-Ultima spectrometer. X-band CW EPR spectra were recorded on a magnettech MS 300 spectrometer with a frequency counter Hewlett Packard 5340A at a microwave frequency of 9.39 GHz in frozen THF solution (77 K). Mn^{2+} in ZnS was used as external standard. Simulations were performed with the program package EasySpin.[4]

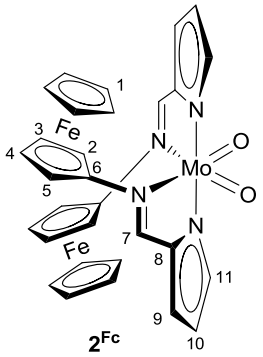
Synthesis of 1^{Fc}



1^{Fc}

1H-Pyrrole-2-carbaldehyde (310 mg, 3.26 mmol), aminoferrocene[1,2] (650 mg, 3.23 mmol), molecular sieves (6 g) and toluene (80 ml) were heated to 90°C for 4 h. The suspension was filtered while hot and the solvent was removed under reduced pressure. The resulting red powder was purified by chromatography (Alox 15×3.5 cm, CH_2Cl_2) giving red crystals in 90% yield (926 mg, 2.88 mmol). M.p. 133°C. $R_f(CH_2Cl_2)$ = 0.7. ^{1}H NMR (d_8-THF): δ = 10.93 (br.s, 1H, NH), 8.38 (s, 1H, H^7), 6.90 (s, 1H, H^{11}), 6.46 (dd, 1H, H^9), 6.13 (dd, 1H, H^{10}), 4.45 (s, 2H, $H^{2,5}$), 4.12 (s, 2H, $H^{3,4}$), 4.09 (s, 5H, H^1) ppm. $^{13}C\{^1H\}$ NMR (d_8-THF): δ = 149.2 (s, C^7), 132.9 (s, C^8), 123.1 (s, C^{11}), 115.1 (s, C^9), 110.3 (s, C^{10}), 107.9 (s, C^6), 70.1 (s, C^1), 67.5 (s, $C^{3,4}$), 63.0 (s, $C^{2,5}$) ppm. NH-HMBC (d_8-THF): δ = 345.6 (s, N^p), 392.9 (s, N^i) ppm. IR (KBr): $\tilde{\nu}$ = 3447, 3158 (w, NH), 3095, 2956, 2850 (m, CH), 1602 (m, C=N), 1413 (m), 1129 (m), 1035 (m) cm^{-1}. UV/Vis (THF): λ = 457 (1470), 382 (sh, 2670), 323 (22060), 279 (8170 M^{-1} cm^{-1}) nm. MS (FD): *m*/*z* (%) = 278.3 (100, M^+). CV (THF): $E_{½}$ = –40 mV (rev.). Elemental analysis calcd. (%) for $C_{15}H_{14}N_2Fe$ (278.14): C 64.78, H 5.07, N 10.07; found C 64.39, H 5.31, N 9.87.

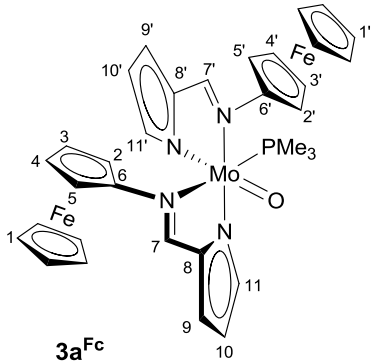
Synthesis of 2^{Fc}



2^{Fc}

Ligand $\mathbf{1}^{Fc}$ (200 mg, 0.72 mmol) was dissolved in THF (10 ml) and deprotonated with triethyl amine (0.4 ml, 290 mg, 2.9 mmol). In a separate flask $MoCl_2O_2(dme)$[3] (104 mg, 0.36 mmol) was dissolved in THF (5 ml) and the deprotonated ligand was added. After stirring for 2 h the suspension was filtered and the red filtrate was dried under reduced pressure giving the raw product in nearly quantitative yield. The raw product was recrystallised from toluene/petroleum ether 40-60°C (1:1) at 8°C giving a dark red crystalline solid in 26% yield (65 mg, 0.095 mmol). Single crystals were obtained by recrystallisation from toluene/ petroleum ether 40-60°C (1:1). M.p. >250°C (decomp.). ^{1}H NMR (d_8-THF): δ = 8.58 (s, 1H, H^7), 7.33 (s, 1H, H^{11}), 6.67 (d, 1H, H^9), 6.31 (dd, 1H, H^{10}), 4.12 (s, 5H, H^1), 3.97 (m, 1H, H^2), 3.88 (m, 1H, H^3), 3.87 (m, H, H^4), 3.74 (m, 1H, H^5) ppm. ^{13}C{^{1}H} NMR (d_8-THF): δ = 159.0 (s, C^7), 143.9 (s, C^{11}), 140.2 (s, C^8), 119.4 (s, C^9), 115.4 (s, C^{10}), 106.7 (s, C^6), 70.5 (s, C^1), 66.2, 65.2 (2×s, $C^{3,4}$), 63.5 (s, C^5), 63.0 (s, C^2) ppm. IR (KBr): $\tilde{\nu}$ = 3094 (w, CH), 1579 (vs, C=N), 1421 (m), 1406 (m), 1292 (m), 1039 (s), 929 (m, Mo=O), 905 (m, Mo=O) cm^{-1}. UV/Vis (THF): λ = 549 (2865), 385 (8420), 312 (30875 M^{-1} cm^{-1}) nm. MS (FD): *m*/*z* (%) = 684.1 (62, M^+, correct isotopic distribution). CV (THF): E_p = –1540 (qrev), –30 (rev.), +80 (rev.) mV. Elemental analysis calcd. (%) for $C_{30}H_{26}N_4O_2Fe_2Mo$ (682.20)×0.2toluene: C 53.83, H 3.97, N 8.00; found C 54.48, H 4.23, N 8.85.

Synthesis of 3a^{Fc}



3a^{Fc}

Dioxido complex **2^{Fc}** (19 mg, 0.028 mmol) was dissolved in THF (3 ml) and trimethylphosphane (1M in THF, 0.11 ml, 0.11 mmol) was added. After stirring for 2 d at room temperature volatiles were removed under reduced pressure and the residue was washed with petroleum ether 40-60°C to give a green powder in 68% yield (14 mg, 0.019 mmol). ^{1}H NMR (d_8-THF): δ = 8.60 (d, $^{4}J_{PH}$ = 2.7 Hz, 1H, H^{7}), 8.22 (s, 1H, H$^{7'}$), 7.51 (bs, 1H, H^{11}), 6.99 (d, $^{3}J_{HH}$ = 3.4 Hz, 2H, H^{9}), 6.45 (m, 1H, H^{10}), 6.31 (m, 1H, H$^{10'}$), 5.78 (bs, 1H, H$^{11'}$), 5.75 (dd, 1H, H$^{9'}$), 4.87 (pt, 1H, H$^{2'}$), 4.70 (pt, 1H, H$^{5'}$), 4.41 4.37 (2×pt, 2×1H, pt, 1H, H^{2,5}), 4.23 (1, 5H, H$^{1'}$), 4.15 (m, 2H, H$^{3',4'}$), 4.02 (m, 2H, H^{3,4}), 3.97 (s, 5H, H^{1}), 1.27 (d, $^{2}J_{PH}$ = 8.64 Hz, 9H, P(CH$_3$)$_3$) ppm (major isomer **3a^{Fc}**). ^{31}P{^{1}H} NMR (d_8-THF): δ = 2.1 (s, major), –5.6 (s, minor) ppm (ratio 5:2).

Oxidation of $\mathbf{1^{Fc}}$ to $\mathbf{[1^{Fc}](SbF_6)}$

Ligand $\mathbf{1^{Fc}}$ (14 mg, 0.05 mmol) was dissolved in THF (3 ml) and $AgSbF_6$ (17.3 mg, 0.05 mmol) dissolved in THF (2 ml) was added ($E_{½}(Ag/Ag^+)$ = 410 mV vs. Fc/Fc^+ [16]). After stirring for 30 min the solution was filtered via syringe filters to remove precipitated silver. An aliquot of this solution was transferred into an EPR tube, frozen to 77 K and an EPR spectrum was recorded. A further aliquot of the solution was subjected to UV/Vis spectroscopic analysis. EPR (THF, 77 K): g = 3.37, 1.989, 1.815. UV/Vis (THF): λ_{max} = 917 (610), 456 (3690), 366 (13580), 284 (9580 M^{-1} cm^{-1}) nm. ESI-MS: *m*/*z* (%) = 278.0 (24, $\mathbf{[1^{Fc}]^+}$).

Oxidation of $\mathbf{2^{Fc}}$ to $\mathbf{[2^{Fc}](SbF_6)_2}$

Complex $\mathbf{2^{Fc}}$ (14.16 mg, 0.021 mmol) was dissolved in THF (3 ml) and $AgSbF_6$ (14.34 mg, 0.042 mmol) dissolved in THF (1 ml) was added. After stirring for 10 min the solution was allowed to stand for 12 h at room temperature. A precipitate including elemental silver had formed and was collected by filtration, washed three times with THF and dried to give a brown powder (12 mg). The solid material was dissolved in CH_3CN (3 ml) and filtered via syringe filters to remove undissolved silver. A part of the resulting solution was transferred into an EPR tube, frozen to 77 K and an EPR spectrum was recorded. A further part of the solution was subjected to UV/Vis spectroscopic analysis, mass spectrometry and NMR spectroscopy (after drying and redissolving in CD_3CN). EPR (CH_3CN, 77 K): silent. ^1H NMR (CD_3CN): δ = 27.9, 24.2, 21.6 (br. m, 9H, CpH), 7.1 (br., 1H, pyrrol-H), 5.2 (br., 1H, pyrrol-H), 0.3 (br., 1H, pyrrol-H), –8.4 (br., 1H, imine-H) ppm. UV/Vis (CH_3CN): λ_{max} = 934 (445), 442 (sh, 5295), 308 (23340), 247 (14305) nm. ESI-MS: *m*/*z* (%) = 684.0 (62%, $\mathbf{[2^{Fc}]^+}$), 918.9 (11%, $\mathbf{[2^{Fc}](SbF_6)}$).

Reaction of $\mathbf{[2^{Fc}](SbF_6)_2}$ with exc. $\mathbf{PMe_3}$

To a solution of $\mathbf{[2^{Fc}](SbF_6)_2}$ (7.7 mg, 0.0066 mmol) dissolved in CD_3CN (ca. 0.3 ml) and filtered via a syringe filter in an NMR tube was added an excess PMe_3 (1 M in THF, 20 µl, 0.02 mmol). ^1H and ^{31}P NMR spectra were recorded after a few minutes. All resonances appear in the diamagnetic region. In some instances traces of a pale, fluffy precipitate formed during this time. The (filtered and redissolved) precipitate is identified as $OPMe_3$ by ^1H NMR (δ = 1.34 ppm, d, $^2J_{PH}$ = 13.2 Hz) and ^{31}P NMR (δ = 36.2 ppm) in [D_6]-DMSO. ^1H NMR (CD_3CN): δ = 1.41 (d, $^2J_{PH}$ = 13.1 Hz, $OPMe_3$), 1.29 (d, $^2J_{PH}$ = 8.8 Hz, $\mathbf{3a^{Fc}}$), 0.85 (d, $^2J_{PH}$ = 8.5 Hz, $\mathbf{3b^{Fc}}$) ppm. $^{31}P\{^1H\}$ NMR (CD_3CN): δ = 36.2 (s, $OPMe_3$), 3.0 (s, $\mathbf{3a^{Fc}}$), –4.8 ($\mathbf{3b^{Fc}}$), –54.7 (PMe_3) ppm.

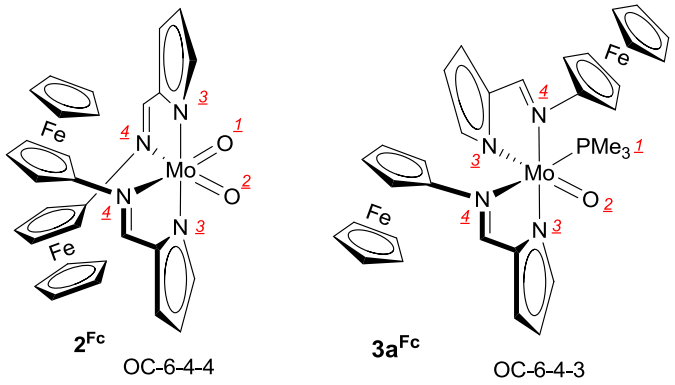
X-ray structure determinations

Intensity data were collected with a Bruker AXS Smart 1000 CCD diffractometer with an APEX II detector and an Oxford cooling system and corrected for absorption and other effects using Mo K_α radiation (λ = 0.71073 Å) at 173(2) K. The diffraction frames were integrated using the SAINT package, and most were corrected for absorption with MULABS.[5,6] The structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package.[7,8] All non-hydrogen atoms were refined anisotropically, while the positions of all hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent atoms with fixed isotropic thermal parameters. The asymmetric unit of a crystal of $\mathbf{1}^{\mathbf{Fc}}$ contains two independent molecules. The asymmetric unit of a crystal of $\mathbf{2}^{\mathbf{Fc}}$ contains two independent complex molecules and a toluene molecule (s.o.f. 0.5) disordered over an inversion centre. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-956709 ($\mathbf{1}^{\mathbf{Fc}}$) and CCDC-956710 ($\mathbf{2}^{\mathbf{Fc}}$). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (0.44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk].

	1^{Fc}	**2**^{Fc}
empirical formula	$C_{15}H_{14}N_2Fe$	$C_{31.75}H_{28}Fe_2MoN_4O_2$
Fw	278.13	705.22
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a / Å	11.5135(4)	10.5484(3)
b / Å	9.2502(3)	15.3410(4)
c / Å	23.8167(9)	34.5525(10)
β / deg	100.173(1)	96.912(2)
volume / Å^3	2496.65(15)	5550.8(3)
Z	8	8
density (calcd), Mg m^3	1.480	1.688
absorp coeff, mm^{-1}	1.189	1.514
F(000)	1152.0	2852.0
cryst size, mm^3	0.62×0.21×0.02	0.41 × 0.12 × 0.06
θ range for data collection	2.37 to 35.05	2.35 to 29.19
index ranges	$-18 \le h \le 18$	$-14 \le h \le 14$
	$-14 \le k \le 14$	$-21 \le k \le 21$
	$-37 \le l \le 38$	$-47 \le l \le 47$
no. of reflns collected	133696	136381
no. of indep reflns	11016	15018
R_{int}	0.0661	0.00937
completeness to θ_{max}	99.9	99.9
max. / min transmn	0.9766 / 0.5260	0.9146 / 0.5757
goodness-of-fit on F^2	0.898	0.931
final R indices [$I > 2\sigma(I)$]]	R_1 = 0.0336	R_1 = 0.0336
	wR_2 = 0.0695	wR_2 = 0.0737
R indices (all data)	R_1 = 0.0665	R_1 = 0.0556
	wR_2 = 0.0756	wR_2 = 0.0787
Largest diff peak and hole, e / Å^3	0.550 / –0.391	0.700 / –0.733

DFT calculations were carried out with the *Gaussian09*/DFT[9] series of programs. The B3LYP formulation of DFT was used employing the LANL2DZ basis set set supplemented by d-type polarisation functions[10] on N (ζ = 0.864), O (ζ = 1.154) and P (ζ = 0.340).[9] No symmetry constraints were imposed on the molecules. The presence of energy minima was checked by analytical frequency calculations. The integral-equation-formalism polarisable continuum model (IEFPCM, THF) was employed for solvent modeling. All calculations were performed without explicit counterions and solvent molecules. For NBO calculations NBO Version 3.1 as implemented in Gaussian 03 was used.

Description of the stereochemistry of 2^{Fc} and $3a^{Fc}$



The stereochemistry of the complexes under study will be described by the configuration index according to the Cahn-Ingold-Prelog system[11-14] in an octahedral complex OC-6-x-y with the priority sequence used as follows: PMe_3 > O > $N^{pyrrolato}$ > N^{imine}. The first index x refers to the ligand priority of the ligand *trans* to the ligand of the highest priority (axial ligands) and the second index y refers to the ligand priority *trans* to that ligand of the equatorial plane which has the highest priority of these four equatorial ligands. Thus, molybdenum(VI) complex $\mathbf{2^{Fc}}$ possess OC-6-4-4 stereochemistry, while molybdenum(IV) complex $\mathbf{3a^{Fc}}$ is the OC-6-4-3 stereoisomer as depicted in the above scheme. For the sake of better comparison with previously reported oxido/imido complexes[15] we have enumerated both oxido ligands in $\mathbf{2^{Fc}}$. Correctly, the preferred isomer of $\mathbf{2^{Fc}}$ should be described by OC-6-3-3 as there is no distinguished fourth donor atom present.

Cartesian coordinates of DFT optimized 2^{Fc}

42	-0.308923000	0.550043000	1.708070000
26	4.432140000	-0.351412000	-0.795539000
26	-4.213709000	-0.321558000	-1.075872000
8	-1.888247000	0.853990000	2.311455000
8	0.734370000	0.709120000	3.059966000
7	0.327994000	2.384107000	0.953837000
7	-1.246742000	0.816074000	-0.605394000
7	-0.658767000	-1.519068000	1.662555000
7	1.404146000	-0.470500000	0.337226000
6	1.101114000	3.370790000	1.528677000
1	1.511664000	3.249288000	2.522143000
6	1.217729000	4.454465000	0.644001000
1	1.755270000	5.373745000	0.831956000
6	0.492075000	4.109082000	-0.536391000
1	0.368259000	4.708073000	-1.429021000
6	-0.042580000	2.827697000	-0.314924000
6	-0.869449000	1.968480000	-1.101369000
1	-1.165510000	2.301214000	-2.095194000
6	-2.124790000	0.018539000	-1.377859000
6	-2.899559000	0.432599000	-2.541015000
1	-2.955712000	1.426068000	-2.961279000
6	-3.585077000	-0.723767000	-3.055186000
1	-4.237789000	-0.738847000	-3.916924000
6	-3.269517000	-1.846084000	-2.206032000
1	-3.638932000	-2.855463000	-2.320168000
6	-2.383224000	-1.389624000	-1.168024000
1	-1.967335000	-1.997064000	-0.382779000
6	-5.159766000	-0.698917000	0.781788000
1	-4.778735000	-1.362521000	1.544884000
6	-4.866672000	0.709774000	0.660411000
1	-4.208344000	1.271906000	1.307316000
6	-5.564359000	1.210503000	-0.499190000
1	-5.543560000	2.228410000	-0.863579000
6	-6.290721000	0.111881000	-1.093757000
1	-6.907972000	0.162677000	-1.980275000
6	-6.042038000	-1.068129000	-0.299602000
1	-6.436646000	-2.056877000	-0.489474000
6	-1.605162000	-2.290709000	2.295810000
1	-2.398493000	-1.840064000	2.876404000
6	-1.344530000	-3.652237000	2.054362000
1	-1.922557000	-4.485780000	2.428743000
6	-0.182616000	-3.714266000	1.228986000
1	0.301559000	-4.601748000	0.843631000
6	0.217038000	-2.382733000	1.007693000
6	1.287612000	-1.774145000	0.285955000
1	1.986934000	-2.389197000	-0.279170000
6	2.379132000	0.161913000	-0.475968000
6	2.623729000	-0.111909000	-1.879702000
1	2.112043000	-0.857140000	-2.473116000
6	3.611589000	0.826288000	-2.346480000

1	3.998098000	0.889491000	-3.353939000
6	3.989231000	1.667302000	-1.235199000
1	4.717687000	2.465379000	-1.260103000
6	3.237403000	1.250692000	-0.079757000
1	3.288704000	1.682422000	0.907705000
6	4.993513000	-2.003036000	0.414179000
1	4.352909000	-2.507001000	1.124750000
6	5.843802000	-0.872453000	0.700023000
1	5.945260000	-0.380576000	1.657487000
6	6.527669000	-0.509229000	-0.518590000
1	7.226311000	0.307769000	-0.635281000
6	6.099868000	-1.415646000	-1.558165000
1	6.425894000	-1.399793000	-2.588993000
6	5.151731000	-2.339578000	-0.981688000
1	4.652115000	-3.143352000	-1.504841000

Cartesian coordinates of DFT optimized 3a^{Fc}

8	-0.153429000	0.850971000	-2.117095000
7	2.033291000	0.528730000	0.123675000
7	-0.095681000	1.943479000	1.675231000
7	1.530408000	3.045413000	-0.724072000
7	-1.207958000	-0.159633000	0.394622000
6	3.035656000	1.387359000	0.156278000
6	2.820986000	2.718152000	-0.293612000
6	3.691229000	3.819419000	-0.479854000
6	2.903632000	4.845974000	-1.058554000
6	1.590075000	4.327995000	-1.185813000
6	-1.375794000	-0.090370000	1.700942000
6	-0.809301000	1.003245000	2.414338000
6	-0.806923000	1.356497000	3.790346000
6	-0.059100000	2.556550000	3.880227000
6	0.356200000	2.874667000	2.556868000
1	4.026436000	1.084601000	0.494198000
1	4.743526000	3.857851000	-0.229119000
1	3.229178000	5.835232000	-1.351507000
1	0.725427000	4.826593000	-1.603942000
1	-1.958615000	-0.841160000	2.233227000
1	-1.276024000	0.807509000	4.597282000
1	0.162428000	3.126310000	4.773746000
1	0.949490000	3.720143000	2.230090000
42	0.105140000	1.463248000	-0.542562000
26	3.740844000	-2.206570000	0.102853000
26	-3.719562000	-2.129344000	-0.299156000
6	-1.723529000	-1.297541000	-0.280834000
6	-2.253001000	-1.315306000	-1.622636000
1	-2.352260000	-0.454479000	-2.264824000
6	-2.556673000	-2.680364000	-1.970623000
1	-2.956965000	-3.018005000	-2.916291000
6	-2.233722000	-3.513926000	-0.836598000
1	-2.343611000	-4.587994000	-0.781573000
6	-1.736651000	-2.661712000	0.213315000

1	-1.373468000	-2.983695000	1.178827000
6	-4.964332000	-2.370029000	1.403030000
1	-4.629452000	-2.687076000	2.381161000
6	-5.040589000	-1.007715000	0.931926000
1	-4.774063000	-0.125543000	1.496993000
6	-5.534534000	-1.032107000	-0.424879000
1	-5.709108000	-0.171990000	-1.056077000
6	-5.764437000	-2.409327000	-0.791416000
1	-6.127202000	-2.760457000	-1.747694000
6	-5.412161000	-3.236508000	0.338276000
1	-5.462394000	-4.316073000	0.375897000
6	2.237904000	-0.774831000	0.640060000
6	3.035417000	-1.139727000	1.795347000
1	3.592924000	-0.455241000	2.419304000
6	2.891974000	-2.558417000	2.002796000
1	3.350492000	-3.131121000	2.796802000
6	2.024825000	-3.075203000	0.970190000
1	1.725833000	-4.106504000	0.846409000
6	1.631122000	-1.976794000	0.124796000
1	0.980459000	-2.029869000	-0.734426000
6	4.962336000	-1.423316000	-1.441780000
1	4.828946000	-0.455201000	-1.904782000
6	4.353469000	-2.658374000	-1.875128000
1	3.686035000	-2.774950000	-2.717688000
6	4.781339000	-3.705922000	-0.977892000
1	4.488586000	-4.745613000	-1.029830000
6	5.654497000	-3.118261000	0.010869000
1	6.134705000	-3.641609000	0.826288000
6	5.767031000	-1.707109000	-0.276346000
1	6.350781000	-0.990429000	0.284912000
15	-1.903770000	3.026773000	-0.680979000
6	-3.530359000	2.360213000	-0.073380000
6	-2.307348000	3.552889000	-2.420432000
6	-1.796300000	4.633964000	0.246936000
1	-1.696116000	4.420538000	1.316103000
1	-0.920411000	5.206088000	-0.072705000
1	-2.701199000	5.229849000	0.076434000
1	-4.329922000	3.095089000	-0.229860000
1	-3.448259000	2.136931000	0.995999000
1	-3.772842000	1.434230000	-0.603902000
1	-1.450216000	4.074102000	-2.861559000
1	-2.515101000	2.664019000	-3.026689000
1	-3.181276000	4.215613000	-2.435021000

Cartesian coordinates of DFT optimized $[2^{Fc}]^{2+}$ (singlet)

42	-0.035849000	0.015101000	1.990608000
26	4.329945000	0.017148000	-0.983148000
26	-4.303495000	-0.020034000	-1.002461000
8	-1.456465000	0.066882000	2.936731000
8	1.259944000	0.025841000	3.101363000
7	0.274731000	2.024592000	1.429513000

7	-1.333311000	0.482165000	-0.073618000
7	-0.287106000	-2.006214000	1.481346000
7	1.365570000	-0.471260000	0.042691000
6	0.932907000	3.034246000	2.043869000
1	1.419603000	2.899182000	3.001287000
6	0.870704000	4.225514000	1.248451000
1	1.306751000	5.177316000	1.514012000
6	0.144066000	3.909978000	0.096919000
1	-0.106586000	4.562785000	-0.727513000
6	-0.233955000	2.532701000	0.218193000
6	-1.051781000	1.704607000	-0.553273000
1	-1.485482000	2.080351000	-1.476454000
6	-2.153330000	-0.349313000	-0.799960000
6	-2.566466000	-0.212480000	-2.205683000
1	-2.176762000	0.492726000	-2.924321000
6	-3.458088000	-1.290416000	-2.500089000
1	-3.900937000	-1.492953000	-3.464617000
6	-3.689398000	-2.044747000	-1.289058000
1	-4.345849000	-2.897004000	-1.192281000
6	-2.930466000	-1.451618000	-0.234661000
1	-2.898131000	-1.781888000	0.790036000
6	-5.773766000	0.491642000	0.464994000
1	-5.764931000	0.186001000	1.501145000
6	-5.214257000	1.709076000	-0.066247000
1	-4.670383000	2.453138000	0.500710000
6	-5.433735000	1.728853000	-1.489974000
1	-5.132033000	2.510571000	-2.171914000
6	-6.170825000	0.535354000	-1.836868000
1	-6.493587000	0.252246000	-2.828787000
6	-6.382539000	-0.225903000	-0.630245000
1	-6.886336000	-1.179885000	-0.564307000
6	-0.956815000	-3.018073000	2.095082000
1	-1.486319000	-2.868824000	3.027209000
6	-0.837676000	-4.217857000	1.332623000
1	-1.266530000	-5.173328000	1.597102000
6	-0.062567000	-3.912319000	0.202371000
1	0.236066000	-4.580189000	-0.593600000
6	0.282981000	-2.532161000	0.308619000
6	1.132822000	-1.697109000	-0.432096000
1	1.629956000	-2.075700000	-1.322095000
6	2.213245000	0.378335000	-0.653641000
6	2.549413000	0.338757000	-2.081282000
1	2.103196000	-0.303848000	-2.826136000
6	3.463131000	1.412331000	-2.339659000
1	3.864745000	1.675402000	-3.307549000
6	3.769209000	2.067474000	-1.090118000
1	4.453647000	2.892895000	-0.959842000
6	3.036100000	1.415563000	-0.046613000
1	3.061434000	1.663746000	1.002215000
6	5.144148000	-1.816445000	-0.192647000
1	4.566733000	-2.566345000	0.331441000
6	5.789887000	-0.677944000	0.410474000

1	5.813030000	-0.443720000	1.464959000
6	6.422413000	0.079865000	-0.644020000
1	6.984836000	0.994500000	-0.520130000
6	6.147606000	-0.580471000	-1.895961000
1	6.472323000	-0.248462000	-2.872051000
6	5.344912000	-1.749691000	-1.618590000
1	4.985170000	-2.461174000	-2.347954000

Cartesian coordinates of DFT optimized $[2^{Fc}]^{2+}$ (triplet)

42	0.311760000	0.385907000	-1.599281000
26	-4.698837000	-0.260874000	0.658840000
26	4.469495000	-0.231159000	0.910856000
8	1.879145000	0.621254000	-2.248075000
8	-0.748385000	0.447938000	-2.937382000
7	-0.293402000	2.266919000	-0.930747000
7	1.322217000	0.797879000	0.685083000
7	0.626472000	-1.661650000	-1.309903000
7	-1.450357000	-0.470352000	-0.113947000
6	-1.053038000	3.227340000	-1.546917000
1	-1.460600000	3.071692000	-2.537185000
6	-1.168655000	4.359968000	-0.711297000
1	-1.699946000	5.270000000	-0.950419000
6	-0.450496000	4.074218000	0.475139000
1	-0.317906000	4.717641000	1.334575000
6	0.086474000	2.773376000	0.318644000
6	0.938176000	1.989339000	1.124453000
1	1.257703000	2.386721000	2.086603000
6	2.275029000	0.115902000	1.436991000
6	3.203600000	0.676058000	2.412356000
1	3.276189000	1.711858000	2.711269000
6	3.985066000	-0.397963000	2.965707000
1	4.718313000	-0.303758000	3.753944000
6	3.612379000	-1.613574000	2.281818000
1	4.010194000	-2.600713000	2.468179000
6	2.593607000	-1.288744000	1.319579000
1	2.110355000	-1.992912000	0.664308000
6	5.435747000	-0.856992000	-0.974441000
1	5.091502000	-1.657175000	-1.614893000
6	5.062752000	0.527460000	-1.080097000
1	4.359357000	0.937170000	-1.792103000
6	5.728546000	1.250484000	-0.028216000
1	5.657493000	2.313112000	0.156578000
6	6.528149000	0.308040000	0.725384000
1	7.164916000	0.542434000	1.566596000
6	6.346050000	-0.997144000	0.133629000
1	6.809703000	-1.916244000	0.463329000
6	1.550389000	-2.511592000	-1.860696000
1	2.313883000	-2.151829000	-2.536847000
6	1.315379000	-3.830147000	-1.413189000
1	1.884587000	-4.704612000	-1.694172000
6	0.194907000	-3.781278000	-0.544850000

1	-0.266385000	-4.607595000	-0.021406000
6	-0.216732000	-2.429173000	-0.497960000
6	-1.285004000	-1.757638000	0.138357000
1	-1.967175000	-2.313678000	0.780814000
6	-2.467694000	0.223841000	0.544278000
6	-2.927860000	0.032039000	1.905956000
1	-2.514823000	-0.666156000	2.620631000
6	-3.950337000	1.008787000	2.177508000
1	-4.442766000	1.161417000	3.127142000
6	-4.171710000	1.768474000	0.967044000
1	-4.869084000	2.584389000	0.843573000
6	-3.283261000	1.259225000	-0.044395000
1	-3.215517000	1.604700000	-1.064061000
6	-5.373238000	-2.095714000	-0.422176000
1	-4.726141000	-2.752488000	-0.987661000
6	-6.051344000	-0.938749000	-0.936183000
1	-6.021676000	-0.587423000	-1.958218000
6	-6.780641000	-0.326752000	0.149710000
1	-7.405579000	0.552311000	0.080002000
6	-6.537476000	-1.107543000	1.342057000
1	-6.953520000	-0.921181000	2.321990000
6	-5.657652000	-2.197122000	0.983796000
1	-5.291378000	-2.962589000	1.653450000

Cartesian coordinates of DFT optimized $[4^{Fc}]^{2+}$ (singlet)

42	-0.383153000	1.267016000	-0.356756000
26	-4.731792000	-0.914112000	0.293564000
26	4.010015000	-1.955656000	0.261543000
8	1.270948000	2.316153000	-0.837757000
8	-1.577854000	2.458063000	-0.461819000
7	-0.345319000	1.491376000	1.678339000
7	1.242112000	-0.345583000	0.545347000
7	-0.037949000	0.273936000	-2.196430000
7	-1.627566000	-0.446769000	-0.249976000
6	-0.997836000	2.375060000	2.512588000
1	-1.621754000	3.164206000	2.117286000
6	-0.701855000	2.072826000	3.847429000
1	-1.067134000	2.605572000	4.714378000
6	0.180030000	0.935672000	3.848242000
1	0.605062000	0.441345000	4.710715000
6	0.388323000	0.598593000	2.512316000
6	1.202339000	-0.367663000	1.854726000
1	1.794974000	-1.066890000	2.442530000
6	2.005605000	-1.322050000	-0.134787000
6	2.049833000	-2.745749000	0.163894000
1	1.503272000	-3.242623000	0.953266000
6	2.878630000	-3.375162000	-0.828888000
1	3.096661000	-4.431694000	-0.890722000
6	3.375362000	-2.352290000	-1.716819000
1	4.039275000	-2.507831000	-2.554871000
6	2.848120000	-1.084647000	-1.285077000

1	3.040749000	-0.123920000	-1.738153000
6	5.673372000	-0.702211000	0.686832000
1	5.883309000	0.241858000	0.203750000
6	4.890228000	-0.889690000	1.883529000
1	4.410806000	-0.108070000	2.456956000
6	4.855984000	-2.302353000	2.179623000
1	4.352086000	-2.766906000	3.015624000
6	5.625570000	-2.986902000	1.167969000
1	5.784675000	-4.054254000	1.104565000
6	6.129301000	-1.999102000	0.245300000
1	6.731641000	-2.197196000	-0.630168000
6	0.721363000	0.450992000	-3.300805000
1	1.280704000	1.363188000	-3.463720000
6	0.642499000	-0.700079000	-4.149391000
1	1.124836000	-0.805730000	-5.110164000
6	-0.181964000	-1.629774000	-3.504367000
1	-0.465398000	-2.613690000	-3.851074000
6	-0.595970000	-1.013610000	-2.279130000
6	-1.434429000	-1.368901000	-1.228061000
1	-1.971076000	-2.311821000	-1.218147000
6	-2.642182000	-0.690991000	0.697886000
6	-3.130983000	-2.001371000	1.122832000
1	-2.745958000	-2.962718000	0.815940000
6	-4.123028000	-1.779934000	2.137379000
1	-4.650271000	-2.553933000	2.676097000
6	-4.303490000	-0.358543000	2.298592000
1	-5.000859000	0.120697000	2.969865000
6	-3.403129000	0.316272000	1.405663000
1	-3.309755000	1.383245000	1.285377000
6	-5.195051000	-0.702257000	-1.777291000
1	-4.471579000	-0.525636000	-2.561656000
6	-5.876562000	0.312591000	-1.012757000
1	-5.760768000	1.381039000	-1.127539000
6	-6.743388000	-0.350800000	-0.067452000
1	-7.383883000	0.133304000	0.656270000
6	-6.592023000	-1.774092000	-0.245183000
1	-7.098641000	-2.541887000	0.322715000
6	-5.628920000	-1.993458000	-1.298896000
1	-5.302755000	-2.954305000	-1.671212000
1	2.650412000	3.379131000	1.660549000
6	2.195908000	4.174103000	1.060319000
1	1.187561000	4.379892000	1.432931000
1	2.803346000	5.082515000	1.145859000
1	4.256246000	2.533255000	-0.677426000
6	3.797523000	3.307995000	-1.300677000
1	4.406951000	4.217438000	-1.256334000
1	3.745674000	2.957530000	-2.336692000
1	1.946857000	5.890341000	-1.618622000
6	1.344353000	4.977196000	-1.682015000
1	1.279384000	4.661529000	-2.728102000
1	0.338259000	5.181938000	-1.301857000
15	2.117388000	3.657863000	-0.688183000

Cartesian coordinates of DFT optimized $[4^{Fc}]^{2+}$ (triplet)

42	0.183631000	1.410221000	0.644308000
26	4.682863000	-0.807851000	-0.393403000
26	-3.595489000	-2.348908000	-0.449694000
8	-1.713575000	2.146497000	0.831964000
8	1.145179000	2.718243000	1.098676000
7	0.296124000	1.926453000	-1.407126000
7	-0.961323000	-0.392826000	-0.723530000
7	-0.206776000	0.312476000	2.375914000
7	1.706075000	-0.136452000	0.599249000
6	0.836079000	3.013745000	-2.031450000
1	1.327779000	3.798206000	-1.470879000
6	0.650615000	2.917965000	-3.433441000
1	0.982324000	3.639216000	-4.166784000
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1	-0.340494000	1.299586000	-4.628218000
6	-0.245998000	1.106945000	-2.402813000
6	-0.870045000	-0.094993000	-2.014782000
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6	-1.485838000	-1.633313000	-0.375678000
6	-1.644411000	-2.817216000	-1.216780000
1	-1.363736000	-2.908092000	-2.255953000
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6	-2.369889000	-3.379265000	0.929714000
1	-2.749559000	-3.937164000	1.773096000
6	-1.997268000	-1.986257000	0.935982000
1	-2.057699000	-1.324442000	1.785080000
6	-5.369145000	-1.330795000	0.184268000
1	-5.457072000	-0.766087000	1.101552000
6	-4.947908000	-0.809465000	-1.097243000
1	-4.667490000	0.212588000	-1.304411000
6	-4.960258000	-1.898864000	-2.043140000
1	-4.686142000	-1.839158000	-3.086880000
6	-5.400824000	-3.092568000	-1.350568000
1	-5.510485000	-4.075101000	-1.786528000
6	-5.658394000	-2.739192000	0.024636000
1	-5.988214000	-3.411776000	0.803404000
6	-1.059063000	0.395477000	3.443969000
1	-1.834302000	1.148328000	3.490867000
6	-0.741334000	-0.607429000	4.388008000
1	-1.243993000	-0.772397000	5.330565000
6	0.360766000	-1.338543000	3.869249000
1	0.868331000	-2.174447000	4.331157000
6	0.674443000	-0.749923000	2.624376000
6	1.670715000	-0.960967000	1.639697000
1	2.399491000	-1.762700000	1.733940000
6	2.605319000	-0.391498000	-0.472494000
6	2.875570000	-1.688675000	-1.063684000
1	2.455083000	-2.630942000	-0.741359000

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1	4.146370000	-2.254064000	-2.829854000
6	4.044122000	-0.070007000	-2.274513000
1	4.686857000	0.400838000	-3.004276000
6	3.337212000	0.605447000	-1.218642000
1	3.345729000	1.666457000	-1.019808000
6	5.411241000	-0.677118000	1.596039000
1	4.832356000	-0.389641000	2.463197000
6	6.150555000	0.219379000	0.740677000
1	6.214546000	1.293018000	0.849543000
6	6.784622000	-0.568959000	-0.289284000
1	7.400334000	-0.188198000	-1.092221000
6	6.436289000	-1.952526000	-0.071110000
1	6.747804000	-2.789603000	-0.680314000
6	5.587121000	-2.020212000	1.094812000
1	5.164017000	-2.920321000	1.519431000
1	-3.500099000	2.514166000	-1.608786000
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15	-2.643016000	3.387871000	0.482647000

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