Electronic Supplementary Information

Reductive cleavage of P_4 by iron(I) centres: synthesis and structural characterisation of $Fe_2(P_2)_2$ complexes with two bridging P_2^{2-} ligands

Shenglai Yao, ^a Tibor Szilvási, ^b Nils Lindenmaier, ^a Yun Xiong, ^a Shigeyoshi Inoue, ^a Mario Adelhardt, ^c Jörg Sutter, ^c Karsten Meyer, ^c and Matthias Driess * ^a

^a Technische Universität Berlin, Institute of Chemistry: Metalorganics and Inorganic Materials, Sekr. C2, Strasse des 17. Juni 135, D-10623 Berlin, Germany. Fax: +49(0)30-314-29732 Tel:+49(0)30-314-29731; E-mail: <u>matthias.driess@tuberlin.de</u>^b Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szent Gellért tér 4, 1111 Budapest (Hungary) ^c Inorganic Chemistry, Department of Chemistry andPharmacy,Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Egerlandstrasse 1, 91058 Erlangen (Germany)

A. Experimental Section

General Considerations: All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material $[L^{Dipp}H]$ (1) ^[1] (L = CH{(CH)(2,6-^{*i*}Pr₂C₆H₃N}₂) and FeCl₂(thf)_{1.5} ^[2] were prepared according to literature procedures. The NMR spectra were recorded on Bruker Spectrometers ARX 200 and AV 400 with residual solvent signals as internal reference (¹H). High-resolution ESI-MS were measured on a Thermo Scientific LTQ *orbitrap* XL. Solution magnetic susceptibilities were determined by the Evans method. ^[3]

Single-Crystal X-ray Structure Determinations: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N₂ flow. The data were collected on an Oxford Diffraction SuperNova, Single source at offset, Atlas at 150 K (Cu-K α radiation, $\lambda = 1.54184$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97^[4] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC 1042230-1042232 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Crystal data for **2**: $C_{34}H_{45}FeN_2$, M = 537.57, triclinic, space group P-1, Z = 2, a = 10.1306(4), b = 11.1529(5), c = 13.6025(5) Å, $\alpha = 93.475(3)^{\circ}$, $\beta = 92.686(3)^{\circ}$, $\gamma = 101.503(4)^{\circ}$. V = 1500.5(1) Å³, T = 150 K, 10686 reflections collected, 5264 independent ($R_{int} = 0.0218$) which were used in all calculations. The final wR(F₂) was 0.0720 (all data). *Crystal data* for **3**: $C_{54}H_{74}Fe_2N_4P_4$, M = 1014.75, monoclinic, space group $P2_1/c$, Z = 2, a = 14.4521(8), b = 12.9461(6), c= 14.8567(8) Å, β = 105.421(6)°. V = 2679.6(2) Å³, T = 150 K, 10249 reflections collected, 4737 independent (R_{int} = 0.0474) which were used in all calculations. The final wR(F₂) was 0.1851 (all data). Crystal data for 4: $C_{86}H_{138}Fe_2KN_4O_4P_4$, M = 1630.68, monoclinic, space group $P2_1/c$, Z = 2, a = 13.2205(1), b = 18.4486(1), c = 18.4434(1)Å, $\beta = 90.303(1)^{\circ}$. V = 4498.28(5) Å³, T = 150 K, 31580 reflections collected, 8037 independent (R_{int} = 0.0265) which were used in all calculations. The final $wR(F_2)$ was 0.1013 (all data).

Cyclic Voltammetry Measurement:

Cyclic voltammetry (CV) measurements were carried out at 295 K by using a Biologic SP-150 potentiostat and a three electrode set-up. Pt-wire was used as an auxiliary electrode, as a working electrode a freshly polished glassy carbon disc (3 mm diameter) and as a pseudo reference electrode Ag/Ag^+ was used. All cyclic voltammograms were referenced against the Cp₂Fe/Cp₂Fe⁺ redox couple which was used as an internal standard. As an electrolyte, 0.3 M solutions of TBAPF₆ in THF were used. The iR-drop was determined and compensated by using the impedance measurement technique implemented in the EC-Lab Software V10.37.

Magnetic Susceptibility Measurement:

Magnetism data of crystalline, finely powdered samples (16 - 18 mg), contained within a polycarbonate gel capsule, were recorded with a Quantum Design MPMS–XL SQUID magnetometer. DC magnetization data were collected in the temperature range of 2 - 300 K with an applied DC field of 1 T.

⁵⁷Fe Mößbauer Measurement:

⁵⁷Fe Mößbauer spectra were recorded on a WissEl Mößbauer spectrometer (MRG-500) at 77 K in constant acceleration mode. ⁵⁷Co/Rh was used as the radiation source. WinNormos for Igor Pro software has been used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.20 mm s⁻¹. The temperature of the samples was controlled by an MBBC-HE0106 MÖSSBAUER He/N₂ cryostat within an accuracy of ±0.3 K. Isomer shifts were determined relative to α-iron at 298 K.

Synthesis of 2

To a cooled (-30 °C) solution of **1** (1.80 g, 4.61 mmol) in THF (40 ml) was added ^{*n*}BuLi (1.84 ml, 2.5 M in hexane, 4.61 mmol) with stirring. The reaction mixture was allowed to warm to room temperature and stirred further for 3h. FeCl₂.(THF)_{1.5} (1.08g, 4.61 mmol) was added and the mixture was stirred overnight. Volatiles were removed in vacuum and 50 ml toluene and 0.74g KC₈ (5.53 mmol) was added. The reaction mixture was stirred for 17h and the colour of the resulted mixture turned to green. Volatiles were removed in vacuum, and the residue was extracted with a solvent mixture of n-hexane (50 ml) and toluene (2 ml). After filtration and concentration, the saturated solution was cooled to -20°C for 72 h, compound **2** crystallized from the solution as dark green crystals (1.86 g, 3.46 mmol, 75 %). M.p. 152 °C (decomp.). Elemental analysis (%): calcd for C₃₄H₄₅N₂Fe: C, 75.96; H, 8.44; N, 5.21. Found: C, 72.32; H, 8.24; N, 5.08 (consistently low C analysis may due to the high reactivity towards oxygen). μ_{eff} (Evans, C₆D₆, RT) 1.83 μ_B



Figure S1. Molecular structure of 2. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Fe1-N1 1.954(1), Fe1-N2 1.955(1), N1-C1 1.326(2), C1-C2 1.378(3), N2-C3 1.326(2), C2-C3 1.383(3), Fe...C_{ring} 2.117(2) - 2.146(2), N1-Fe1-N2 91.78(6).

Synthesis of 3

To a solution of **2** (1.48 g, 2.75 mmol) in toluene (60 ml) was added white phosphorus (P₄) (0.17 g, 1.38 mmol). After stirred for 3h, the colour of the solution changed from green to dark green and a dark green precipitate of LFeP4FeLh formed. After filtration, the precipitate was washed with 5 ml toluene and dried under reduced pressure to give the product as a dark green solid (1.23 g, 1.21 mmol, 88 %). M.p. 221 °C (decomp.). μ_{eff} (Evans, THF-D₈, RT) 1.12 μ_{B} . HR ESI-MS (Ion spray voltage 5kV, flow rate 5 μ L/*min*, in THF): m/z: calcd for [M+H]⁺ (C₅₄H₇₅N₄Fe₂P₄): 1015.36356, found: 1020.36258. Elemental analysis (%): calcd for $C_{54}H_{74}N_4Fe_2P_4$: C, 63.91; H, 7.35; N, 5.52. Found: C, 63.89; H, 7.52; N, 5.49. IR (KBr, cm⁻¹): $\nu = 515$ (w), 525 (w), 741 (m), 754 (w), 777 (w), 800 (w), 970 (w), 1057 (w), 1094 (w), 1106 (w), 1142 (w), 1177 (w), 1199 (w), 1241 (w), 1254 (w), 1301 (s), 1344 (m), 1361 (w), 1383 (w), 1436 (s), 1501 (m), 1569 (m), 1590 (w), 2865 (w), 2926 (w), 2960 (m), 3059 (w).

Synthesis of 4

To a Schlenk tube with potassium mirror (0.053g, 1.35 mmol) was added a suspension of LFeP4FeL (0.27 g, 0.27 mmol) in THF (80 ml). After stirred for 30 min, the color of the solution turned from green to brown red and the reaction mixture was filtrated. The filtrate was concentrated and cooled to -20°C for 3 days to yield **4** as dark brown crystals (0.35 g, 0.23 mmol, 88 %). M.p. 198 °C (decomp.). μ_{eff} (Evans, THF-D₈, RT) 4.50 μ_{B} . Elemental analysis (%): calcd for C₈₆H₁₃₈N₄Fe₂P₄KO₈: C, 63.34; H, 8.53; N, 3.44. Found: C, 62.95; H, 8.38; N, 3.53. IR (KBr, cm⁻¹): ν = 514 (w), 607 (w), 723(w), 754(m), 775 (w), 800 (w), 897 (w), 972 (w), 1053 (m), 1192 (w), 1106 (w), 1141 (w), 1203 (w), 1242 (m), 1253 (w), 1312(s), 1347 (m), 1359 (w), 1380 (m), 1434 (s), 1456 (s), 1505 (s), 1572 (s), 2862 (m), 2925 (m), 2958 (s), 3055 (w).

CV studies on 3

A cyclic voltammogram (CV) of a 3mM solution of **3** in THF/ 0.3M TBAPF₆ recorded at a scan rate v = 100 mV·s⁻¹ showed one reversible redox event at $E^{1/2} = -1.5$ V (vs Fc/Fc⁺) and a quasi-reversible electrode process at $E^{1/2} = -2.8$ V (vs Fc/Fc⁺). After scanning to cathodic potentials, species possibly generated upon the quasi-reversible process were observed in the reverse scan at $E^{1/2} = -2.0$ V and -1.3 to -0.9 V(vs Fc/Fc⁺). A separate scan indicated furthermore two irreversible oxidation processes at $E^{ox} = -0.2$ and 0.6 V (vs Fc/Fc) which, in the reverse scan, led to the formation of a new species ($E^{red} = -0.8$ V (vs Fc/Fc⁺)) as well as a not fully reversible redox process at $E^{1/2} = -1.5$ V (vs Fc/Fc⁺) which was probably caused by proceeding oxidative degradation (*see* Fig. S2).



Figure S2: The CV of **3** (3mM in THF/ 0.3M TBAPF₆) recorded at a scan rate $v = 100 \text{ mV} \cdot \text{s}^{-1}$ showed one reversible redox event (*see below*) at $E^{1/2} = -1.5 \text{ V}$ (*vs* Fc/Fc⁺) and a quasi-reversible electrode process (*see below*) at $E^{1/2} = -2.7 \text{ V}$ (*vs* Fc/Fc⁺) (*left*). Moreover, at a scan rate $v = 100 \text{ mV} \cdot \text{s}^{-1}$ as well two irreversible oxidative processes at $E_{pa} = -0.2$ (*see below*) and 0.6 V (*vs* Fc/Fc⁺) were observed (*right*).

Quasireversible ET at $E^{1/2} = -2.7 V$ (vs Fc/Fc⁺)

The redox event at $E^{1/2} = -2.8 \text{ V} (vs \text{ Fc/Fc}^+)$ was determined to be quasi-reversible since only for scan rates v higher than 100 mV·s⁻¹ reverse peak currents i_{pa} were observed (see Fig. S3).



Figure S3: Quasireversible redox event at $E^{1/2} = -2.8 \text{ V} (vs \text{ Fc/Fc}^+)$ measured with scan rates $v = 100 - 800 \text{ mV} \cdot \text{s}^{-1}$.

$v [mV \cdot s^{-1}]$	E_{pc} [V]	E_{pa} [V]	$\Delta E_p [mV]$	<i>i_{pc}</i> [µА]	<i>i_{pa}</i> [μA]	i _{pa} /i _{pc}	$i_{pc}/(v^{1/2})$
50	-2.793			9			1.3
100	-2.786			9			0.9
200	-2.799	-2.718	81	11	7	0.7	0.8
400	-2.815	-2.718	97	13	10	0.8	0.6
800	-2.827	-2.714	113	16	13	0.8	0.6

Table S1: Data for the quasireversible electron transfer at $E^{1/2} = -2.8 \text{ V} (vs \text{ Fc/Fc}^+)$

Furthermore, a linear dependence of the forward peak current i_{pc} on the square-root of the scan rate v implied diffusion control for the redox processes at $E^{1/2} = -2.8$ V (vs Fc/Fc⁺).



Figure S4: Linear dependence of the forward peak current i_{pa} on the square-root of the scan rate v indicates diffusion control for the redox process at $E^{1/2} = -2.8$ V (vs Fc/Fc⁺). The linear fit (*red*) was calculated by the least square approach using the model function y = a + bx.

Furthermore, the electrochemical data for the redox process at $E^{1/2} = -2.8 \text{ V}$ (*vs* Fc/Fc⁺) suggest that this electron transfer is succeeded by a chemical reaction. Diagnostic criteria like the increase of i_{pa}/i_{pc} , the shift of the forward peak potential E_{pc} towards more cathodic potentials as well as the decrease of the current function $i_{pc}/(v^{1/2})$ by a factor of 2 with increasing scan rates *v* indicate a second order irreversible chemical reaction following the electron transfer. However, the exact nature of this chemical reaction was not fully revealed (*see* Tab. S1 and *Fig. S5*).



Figure S5: Diagnostic criteria indicating a second order irreversible chemical reaction following the electron transfer at $E^{1/2} = -2.8 \text{ V}$ (vs Fc/Fc⁺): a) shift of the forward peak potential E_{pc} towards more cathodic potentials with increasing v (*left*) b) decreasing current function $i_{pc}/(v^{1/2})$ with increasing v.

Reversible ET at $E^{1/2} = -1.5 V$ (vs Fc/Fc⁺)

The redox event at $E^{1/2} = -1.5$ V (vs Fc/Fc⁺) was determined to be reversible since the ratio of the peak current equals 1 for scan rates v from 50 – 400 mV·s⁻¹ (0.9 for 800 mV·s⁻¹, see Fig. S6). Slight deviations for other diagnostic criteria (e.g. ΔE_p or $i_{pc}/(v^{1/2})$ vs. v) from perfect reversible behavior are attributed to not fully compensated iR-drop (see Tab. S2).



Figure S6: Reversible redox event at $E^{1/2} = -1.5 \text{ V} (vs \text{ Fc/Fc}^+)$ measured with scan rates $v = 50 - 800 \text{ mV} \cdot \text{s}^{-1}$.

v [mV·s ⁻¹]	E_{pc} [V]	E_{pa} [V]	$\Delta E_p [\mathrm{mV}]$	<i>i_{pc}</i> [μA]	<i>i_{pa}</i> [μA]	i _{pa} /i _{pc}	$i_{pc}/(v^{1/2})$
50	-1.533	-1.458	75	11	10	1.0	1.5
100	-1.541	-1.449	92	15	14	1.0	1.5
200	-1.545	-1.443	103	20	20	1.0	1.4
400	-1.555	-1.434	121	28	26	1.0	1.4
800	-1.565	-1.426	139	37	35	0.9	1.3

Table S2: Data for the reversible ET at $E^{1/2} = -1.5 \text{ V} (vs \text{ Fc/Fc}^+)$

Furthermore, a linear dependence of the forward peak current i_{pc} on the square-root of the scan rate v implied diffusion control for the redox processes at $E^{1/2} = -1.5$ V (vs Fc/Fc⁺).



Figure S7: Linear dependence of the forward peak current i_{pc} on the square-root of the scan rate v indicates diffusion control for the redox process at $E^{1/2} = -1.5$ V. The linear fit (*red*) was calculated by the least square approach using the model function y = a + bx.

Irreversible ET at $E^{1/2} = -0.2 V$ (vs Fc/Fc⁺)

The redox event at $E^{1/2} = -0.2 \text{ V}$ (vs Fc/Fc⁺) was determined to be irreversible since no reverse peak current i_{pc} was observed for scan rates v from 50 – 800 mV·s⁻¹ (see Fig. S8 and Tab. S3).



Figure S8: Irreversible redox event at $E^{1/2} = -0.2 \text{ V}$ (vs Fc/Fc⁺) measured with scan rates $v = 50 - 800 \text{ mV} \cdot \text{s}^{-1}$.

v [mV·s⁻¹]	E_{pc} [V]	E_{pa} [V]	<i>i_{pa}</i> [μA]	$i_{pa}/(v^{1/2})$
50		-0.256	12	1.67
100		-0.220	11	1.12
200		-0.205	11	0.81
400		-0.180	12	0.58
800		-0.373	11	0.40

Table S3: Data for the irreversible ET at $E^{1/2} = -0.2 \text{ V} (vs \text{ Fc/Fc}^+)$





Figure S9: Temperature dependence of effective magnetic moment per dinuclear molecule of solid **3** obtained with an applied magnetic field B of 1 T.

Temperature dependent magnetization measurements of 4



Figure S10: Temperature dependence of effective magnetic moment per dinuclear molecule of solid **4** obtained with an applied magnetic field B of 1 T.

B. Quantum-chemical Calculations

Broken-symmetry DFT calculations were carried out by using the GAUSSIAN 09 program.⁵ Geometry optimization was performed with the BP86 functional⁶ and subsequent single point calculations were done with the B3LYP functional⁷. For all calculations, aug-cc-pVTZ basis set was used for P and Fe atoms while 6-31G(d) basis set for all other atoms.¹⁸

Table S4. Results of the NBO analysis. Overall charge, spin density and oxidation state of the Fe centers and P atoms in minimum energy spin state in **3**, **4**, and $[\{(C_3Me_5)Fe(\mu_2;\eta^2,\eta^2-P_2)\}_2](V)$. Note that there are two Fe centers and four P atoms in every compound that is why we separated these results with slash mark. Negative and positive values in the spin density only mean that these are opposite signs in spin density.

	charge		spin		oxidation state	
	Fe	Р	Fe	Р	Fe	Р
3	0.36/0.36	-0.16/-0.16/-0.16/-0.16	-2.26/2.26	0.02/0.02/0.02/0.02	+3	-1
4	0.39/0.16	-0.19/-0.19/-0.19/-0.19	-2.34/1.62	-0.01/0.00/-0.01/0.00	+3, +2	-1
V	0.36/0.36	-0.17/-0.17/-0.17/-0.17	-0.96/0.96	0.00/0.00/0.00/0.00	+3	-1

Since broken-symmetry DFT were applied, NBO analyses were evaluated separately on alpha and beta spin orbitals. Therefore, in the upper two pictures (Figure S11-12) bonds represent the one-electron bonds with alpha and beta spin orbitals suggested by NBO. Then, we paired these one electron bonds together to regular two electron bonds, if it offered itself, that is, there are one electron bonding orbitals with alpha and beta spin between the same two atoms which may suggest a usual two electron bond picture similarly to regular NBO analysis on closed shell molecules. If this pairing was not possible, dashed line indicated the one electron interaction (we used this methodology for the possible η^2 interaction of P₂ moiety with Fe center). The bottom right pictures of Figure S11-12 show a fully partitioned picture of the bonding motifs when we have tried to assign the two electron orbitals to atoms, based on electronegativity, which may provide further help to elucidate the bonding nature of the P-system. The calculations predict S = 0 for the electronic ground state of **3** (Fig. S11) with three unpaired spins on each Fe centre but antiferromagnetically coupled ($J = -68 \text{ cm}^{-1}$). In contrast to this electronic structure of **3**, complex **4** adopts S = $\frac{1}{2}$ ground state, 3 and 2 unpaired spins with antiferromagnetic coupling ($J = -64 \text{ cm}^{-1}$, Fig. S12) according to the calculations.

alpha spin one electron orbitals

beta spin one electron orbitals







fully partitioned two electron orbitals



Figure S11. Graphical representation of the result of the NBO analysis on **3**. See details in the previous paragraph. It shows that the P_2 moiety has two extra electrons that characterized as dianionic $P_2^{2^2}$ moiety.



beta spin one electron orbitals







Figure S12. Graphical representation of the result of the NBO analysis on **4**. See details in the previous paragraph. It shows that the P_2 moiety has two extra electrons that characterized as dianionic $P_2^{2^2}$ moiety.



Figure S13. Spin density distribution in **3**.



Figure S14. Spin density distribution in **4**.



Figure S15. Spin density distribution in V.

Table S5.	Cartesian	geometry o	of 3 in	Angstrom	[Å]	١.
-----------	-----------	------------	----------------	----------	-----	----

Atomtype	X coordinates	Y coordinates	Z coordinates
С	-3.164279	3.142563	-0.630112
С	-2.928777	2.450259	0.580346
С	-3.976355	1.800621	1.285043
С	-5.273862	1.857455	0.733428
С	-5.527412	2.537771	-0.468256
С	-4.476616	3.179555	-1.142284
Ν	-1.585564	2.477090	1.117492
С	-1.402947	3.308681	2.149093
С	-0.170170	3.650147	2.744708
С	1.095543	3.381452	2.185817
Ν	1.349663	2.579447	1.146188
С	2.674818	2.679270	0.584713
С	2.808172	3.414271	-0.623770
С	4.086015	3.543913	-1.196667
С	5.213172	2.980660	-0.569300
С	5.061060	2.281604	0.635447
С	3.794517	2.114542	1.240313
С	1.608080	4.154543	-1.207869
С	1.513498	5.564180	-0.562301
С	3.699065	1.392924	2.577463
С	4.378234	0.000565	2.521566
С	-3.773185	1.112073	2.630140
С	-4.407139	1.956186	3.768503
С	-2.044723	3.905120	-1.330282
С	-2.079487	3.757294	-2.871936

Fe	-0.069252	1.281747	0.525300
Р	-1.007581	-0.685290	1.485098
Р	1.033673	-0.585247	1.497861
Fe	0.069261	-1.281760	-0.525303
Р	1.007588	0.685339	-1.485355
Р	-1.033614	0.585386	-1.498037
Ν	-1.349664	-2.579467	-1.146158
С	-1.095547	-3.381512	-2.185757
С	0.170163	-3.650238	-2.744637
С	1.402941	-3.308760	-2.149034
Ν	1.585563	-2.477134	-1.117463
С	2.928777	-2.450293	-0.580320
С	3.164273	-3.142559	0.630160
С	4.476610	-3.179546	1.142334
С	5.527411	-2.537793	0.468284
С	5.273867	-1.857515	-0.733423
С	3.976360	-1.800688	-1.285040
С	2.044711	-3.905082	1.330355
С	2.079475	-3.757205	2.872004
С	3.773196	-1.112182	-2.630158
С	4.407143	-1.956337	-3.768495
С	-2.674824	-2.679255	-0.584690
С	-3.794511	-2.114537	-1.240319
С	-5.061061	-2.281566	-0.635460
С	-5.213192	-2.980580	0.569310
С	-4.086046	-3.543824	1.196706
С	-2.808197	-3.414215	0.623816
С	-3.699038	-1.392964	-2.577491
С	-4.329820	-2.260497	-3.703699
С	-1.608117	-4.154480	1.207951
С	-1.622426	-4.246083	2.747996
С	2.075542	-5.401452	0.923261
С	4.357610	0.323173	-2.633166
С	-1.513546	-5.564140	0.562430
С	-4.378193	-0.000596	-2.521647
С	1.622372	4.246197	-2.747912
С	4.329848	2.260427	3.703693
С	-4.357587	-0.323287	2.633100
С	-2.075568	5.401476	-0.923137
Н	0.709000	3.603508	-0.918037
Н	0.616459	6.078145	-0.933273
Н	0.678775	4.687775	-3.093804
Н	2.457611	4.875194	-3.084101
н	-4 676154	3 715102	-2 077337
11	-4.070134	2.565769	-2.077337
Н	-0.543826	2.565/68	-0.880244
Н	-6.098508	1.360078	1.257371
Н	-5.449791	-0.283143	2.528665
Н	-4.102234	-0.816551	3.580772
Н	-3.939397	-0.901520	1.801380
Н	-5.481406	2.083889	3.579782
Н	-1.094263	3.492198	-0.981490
Н	-3.078538	5.812543	-1.101412
н	-1 342658	5 960631	-1 520645
11	1.000000	5.500051	-1.520045
п	-1.828086	5.502439	0.141849

Н	-2.135557	2.695318	-3.143183
Н	-1.165645	4.193045	-3.296139
н	-2.954126	4 280399	-3 281776
н	-4 203462	-4 087592	2 140367
н	-6 205454	-3 087418	1 024133
н	-5 942827	-1 852277	-1 126109
н	-3 965791	0 584906	-1 692395
н	-4 196519	0.530881	-3 465676
н	-5 459876	-0.116585	-2 373679
н	1 733123	3 242069	-3 178462
н	-1 959616	-3 887210	-2 642910
н	0 199772	-4 176197	-3 704377
н н	2 303/81	-3.780518	-2 570085
н н	-2.505481	-1 248456	-2.814260
н ц	-2.041177	2 517668	-2.814200
н ц	-3.303133	-2.317008	-3.430243
п u	-4.327807	-1.094200	-4.043332
п	-3.730000	-5.1640/1	-3.634103
п	-2.404823	-0.149404	0.827001
н	-1.431824	-3.409039	-0.528980
н	2.098812	-1.041303	-2.820015
H	3.930312	-2.944433	-3.814/00
H	4.264045	-1.441868	-4./28808
H	1.959608	3.88/143	2.642985
H	-0.199783	4.1/60/1	3./0446/
H	-2.303489	3.780420	2.5/0160
Н	2.641207	1.248397	2.814237
Н	5.363182	2.51/61/	3.436234
Н	4.32/851	1.694187	4.645327
Н	3.750026	3.183990	3.834192
Н	2.404767	6.149463	-0.826921
Н	1.451788	5.469663	0.529112
Н	-2.698801	1.041197	2.820593
H	-3.930318	2.944285	3.814741
H	-4.264038	1.441688	4.728800
H	-1.733169	-3.241939	3.178511
H	4.203416	4.087/14	-2.140311
H	6.205428	3.087524	-1.024129
Н	5.942834	1.852308	1.126074
Н	3.965832	-0.584914	1.692299
Н	4.196575	-0.530945	3.465580
Н	5.459915	0.116571	2.373592
Н	-0.709030	-3.603464	0.918107
Н	-0.616515	-6.078102	0.933427
Н	-0.678835	-4.687658	3.093911
Н	-2.457674	-4.875059	3.084198
Н	4.676144	-3.715063	2.077404
Н	6.543825	-2.565785	0.880273
Η	6.098517	-1.360161	-1.257383
Н	5.449814	0.283023	-2.528730
Н	4.102262	0.816409	-3.580853
Н	3.939425	0.901438	-1.801465
Н	5.481408	-2.084044	-3.579769
Н	1.094254	-3.492163	0.981550
Н	3.078508	-5.812522	1.101549
Н	1.342626	-5.960581	1.520787

Н	1.828060	-5.502450	-0.141722
Н	2.135554	-2.695220	3.143215
Н	1.165628	-4.192934	3.296222
Н	2.954109	-4.280305	3.281862

Table S6. Cartesian geometry of **4** in Angstrom [Å].

Atomtype	X coordinates	Y coordinates	Z coordinates
С	3.095087	3.159094	-0.780812
С	2.829015	2.620328	0.509583
С	3.864774	2.031272	1.280200
С	5.154704	1.954691	0.718756
С	5.426268	2.458901	-0.557140
С	4.399596	3.067848	-1.293171
Ν	1.489681	2.699995	1.014509
С	1.262435	3.676209	1.891186
С	0.011704	4.086848	2.389494
С	-1.241198	3.683649	1.890564
Ν	-1.474538	2.707700	1.015038
С	-2.815631	2.635387	0.513424
С	-3.852101	2.050906	1.286425
С	-5.144630	1.984053	0.729741
С	-5.417595	2.492882	-0.544027
С	-4.389506	3.095861	-1.283001
С	-3.082500	3.177376	-0.775342
С	-3.621550	1.564573	2.715386
С	-4.157511	2.605229	3.729245
С	-1.984762	3.910770	-1.541830
С	-2.101960	3.799885	-3.074167
С	3.637132	1.551761	2.712020
С	4.273823	0.173799	2.993170
С	2.000444	3.899746	-1.544586
С	2.113678	3.788205	-3.077207
Fe	0.004342	1.383715	0.473384
Р	-1.006486	-0.543239	1.576740
Р	1.026653	-0.541230	1.556840
Fe	-0.004674	-1.383578	-0.473435
Р	1.005976	0.543363	-1.576817
Р	-1.027157	0.541362	-1.556855
Ν	1.474695	-2.706979	-1.014840
С	1.241959	-3.683024	-1.890412
С	-0.010698	-4.086798	-2.389471
С	-1.261674	-3.676685	-1.891337
Ν	-1.489539	-2.700478	-1.014809
С	-2.829033	-2.621731	-0.510162
С	-3.094716	-3.159462	0.780745
С	-4.399593	-3.069883	1.292450
С	-5.427020	-2.463638	0.555246
С	-5.155827	-1.960599	-0.721189
С	-3.865529	-2.035604	-1.282004
С	-1.999151	-3.897437	1.545781
С	-1.962822	-5.383234	1.114585
С	-3.638343	-1.558491	-2.714693
С	-4.179318	-2.604655	-3.720320
С	2.815607	-2.633857	-0.512844
С	3.851575	-2.046750	-1.284555
С	5.143704	-1.978593	-0.727100

С	5.416798	-2.488596	0.546173
С	4.389239	-3.094014	1.283887
С	3.082621	-3.176888	0.775448
С	3.620916	-1.558141	-2.712723
С	4.159508	-2.595769	-3.728292
С	1.985562	-3.912748	1.540541
C	2 101848	-3 803479	3 073065
C	-2 113170	-3 784325	3 078230
C	-4 277870	-0 182489	-2 998947
C	1 943122	-5 397239	1 105412
C C	4 259070	-0 179373	-2 985772
C C	-4 262180	0.187582	2 991521
C C	-1 939957	5 395712	-1 108477
C C	4 180757	2 594696	3 719572
C C	1 966712	5 385126	-1 111734
с u	2 13/210	1 255000	-1.111/34
н ц	0.013051	4.233909	2.227320
н ц	2 100425	4.908030	2 225601
п u	-2.109423	4.209379	2.223001
п	2.334330	1.430198	2.8/1945
п	3.208/01	2.724291	3.364231
п	3.99/40/	2.236413	4.733220
п	5./01841	3.377232	3.362732
п	1.041333	5.449455	-1.230008
п	1.764209	5.474333	-0.030202
п	1.101955	5.921145	-1.045500
п	2.928092	3.8/381/	-1.34/008
п	-3.943045	1.322904	1.511045
п	-0.424810	2.419078	-0.902343
п	-4.604/92	3.502001	-2.2/280/
п	-1.028100	5.453822	-1.2301/0
п	-2.898870	5.891200	-1.341800
п	-1.152557	5.920303	-1.041148
п	-1./5500/	3.483108	-0.02/143
п	-2.104524	2.744922	-3.382288
п	-1.208943	4.246458	-3.542043
H	-2.986817	4.338505	-3.456401
H	-2.538643	1.4640//	2.8/1206
п	-3.304330	0.250291	2.986246
H	-3.948914	-0.1/3208	3.986495
H	-3.954208	-0.551/85	2.241157
п	-3.074938	3.380333	5.594008
H	-3.9/1/30	2.263856	4.762780
Н	-5.245468	2./398/1	3.598542
Н	-4.61354/	-3.4/2/69	2.283984
Н	-6.432365	-2.3836//	0.977000
Н	-5.956582	-1.497865	-1.301550
Н	-3.968271	0.561670	-2.253986
H	-3.965623	0.171087	-3.996826
H	-5.380115	-0.244286	-2.992037
H	-2.999411	-4.319433	3.462355
H	-1.220903	-4.233481	3.545058
H	-2.171423	-2.728851	3.385391
H	4.613841	3.471547	-2.284311
H	6.431284	2.377655	-0.979432
H	5.954829	1.489609	1.298109
Н	3.962244	-0.568163	2.246831

Н	3.961290	-0.181136	3.990477
Н	5.376197	0.233226	2.985859
Н	3.000593	4.322386	-3.461069
Н	1.221921	4.239276	-3.543162
Н	2.170181	2.733001	-3.385615
Н	-2.133146	-4.256806	-2.227559
Н	-0.012493	-4.908027	-3.107041
Н	2.110484	-4.268411	-2.225268
Н	-2.555679	-1.460994	-2.874386
Н	-5.267098	-2.736305	-3.585174
Н	-3.996327	-2.270108	-4.756589
Н	-3.698348	-3.585897	-3.581283
Н	-1.040666	-3.445884	1.257733
Н	-1.779758	-5.473528	0.033216
Н	-1.157378	-5.917362	1.647046
Н	-2.924096	-5.873241	1.350072
Н	5.944274	-1.515343	-1.307343
Н	6.423682	-2.414336	0.965315
Н	4.604620	-3.501063	2.273385
Н	1.028384	-3.456854	1.254950
Н	2.902650	-5.891664	1.338654
Н	1.136056	-5.929703	1.637084
Н	1.758859	-5.483611	0.023889
Н	2.162696	-2.748785	3.382447
Н	1.209266	-4.251921	3.539985
Н	2.987316	-4.341232	3.455103
Н	2.537912	-1.459392	-2.868988
Н	5.361361	-0.239993	-2.980010
Н	3.945671	0.182790	-3.980204
Н	3.949271	0.557924	-2.234111
Н	3.678782	-3.578099	-3.595870
Н	3.973684	-2.252738	-4.761269
Н	5.247649	-2.728540	-3.597202

Table S7. Cartesian geometry of $[{(C_5Me_5)Fe(\mu_2;\eta^2,\eta^2-P_2)}_2](V)$ in Angstrom [Å].

Atomtype	X coordinates	Y coordinates	Z coordinates
С	-3.041609	0.464103	-1.095127
С	-3.091514	-0.915562	-0.711245
С	-3.047949	-0.985828	0.726400
С	-2.963891	0.348957	1.245980
С	-2.978068	1.251257	0.112650
Fe	-1.275385	0.015989	-0.000725
Р	0.010564	1.534697	-1.113858
Р	0.029127	1.578973	1.008364
Fe	1.276549	-0.018638	-0.026075
Р	-0.031450	-1.507166	-1.151472
Р	-0.011590	-1.605299	0.964469
С	-3.293420	-2.101045	-1.617861
С	-3.220924	-2.238781	1.545554
С	-2.982119	0.719400	2.704797
С	-3.064598	2.752257	0.174303
С	-3.170589	0.997786	-2.498824
С	3.061359	0.748646	0.945781
С	3.041686	1.105382	-0.450182
С	2.989452	-0.110812	-1.225477
С	3.004392	-1.213362	-0.290253

С	3.033463	-0.669295	1.050808
С	3.222664	1.719563	2.088738
С	3.188211	2.504341	-0.984877
С	3.035329	-0.212960	-2.728509
С	3.118185	-2.671651	-0.648347
С	3.165128	-1.473985	2.317996
Н	4.072833	-0.126412	-3.098444
Н	2.499163	-2.920297	-1.521838
Н	2.627916	-1.180556	-3.055485
Н	2.434128	0.585346	-3.188084
Н	2.935376	2.540594	-2.053602
Н	4.230323	2.847181	-0.857382
Н	2.529893	3.204725	-0.448497
Н	-2.881426	-3.123796	0.987880
Н	-2.671010	3.127330	1.129069
Н	-4.118454	3.067064	0.079963
Н	-2.489585	3.214013	-0.641681
Н	-2.648450	1.959818	-2.595630
Н	-4.233824	1.145770	-2.758781
Н	-2.730207	0.293949	-3.219825
Н	-2.972776	-1.871238	-2.643703
Н	-4.362485	-2.378546	-1.638697
Н	-2.719891	-2.970269	-1.263594
Н	2.715781	2.669669	1.868204
Н	4.294471	1.926688	2.258434
Н	2.797214	1.306965	3.014231
Н	2.698019	-0.948589	3.163673
Н	4.231754	-1.634729	2.555427
Н	2.679100	-2.453905	2.212727
Н	2.799873	-3.305496	0.191317
Н	4.167833	-2.914743	-0.889723
Н	-4.288395	-2.376011	1.795318
Н	-2.652579	-2.181364	2.484420
Н	-2.603388	1.740593	2.850951
Н	-2.344627	0.033434	3.282389
Н	-4.007735	0.663161	3.111367

C. References

- D. J. E. Spencer, A. M. Reynolds, P. L. Holland, B. A. Jazdzewski, C. Duboc-Toia, L. L. Pape, S. Yokota, Y. Tachi, S. Itoh, W. B. Tolman, *Inorg. Chem.* 2002, 47, 6307.
- [2] R. J. Kern, J. Inorg. Nucl. Chem. 1962, 24, 1105.
- [3] a) D. F. Evans, J. Chem. Soc. 1959, 2003; b) T. Ayers, R. Turk, C. Lane, J. Goins, D. Jameson, S. J. Slattery, Inorg. Chim. Acta 2004, 357, 202.
- [4] G. M. Sheldrick, SHELX-97 Program for Crystal Structure Determination, Universität Göttingen (Germany) 1997.
- [5] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

- [6] a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; b) J. D. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
- [7] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [8] a) M. J. Frisch, J. A. Pople, J. S. Binkley. J. Chem. Phys. 1984, 80, 3265; b) T. H. Dunning. J. Chem. Phys. 1989, 90, 1007.