Supporting Information

Reduced Thione Ligation is Preferred over Neutral Phosphine Ligation in Diiron Biomimics Regarding Electronic Functionality: a Spectroscopic and Computational Investigations

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Experimental section

General methods. All reactions were carried out using standard Schlenk and vacuum line techniques under an atmosphere of purified nitrogen. All commercially available chemicals were of ACS grade and used without further purification. Solvents were of HPLC grade and purified as follows: diethyl ether and THF were distilled from sodium/benzophenone under N_2. Hexane was distilled from sodium under N_2. Dichloromethane was distilled from CaH_2 under N_2. Acetonitrile was distilled first over CaH_2 and then from P_2O_5 under N_2. Deuterated solvents obtained from Merck were distilled from 4 Å molecular sieves under N_2 prior to use. [(μ-pdt)$Fe_2(CO)_5(PPh_2H)$] (**1A**) and [(μ-edt)$Fe_2(CO)_5(PPh_2H)$] (**1B**) were prepared according to related literature procedures.[1] Infrared spectra were recorded with a Perkin Elmer Spectrum One using a 0.05 mm CaF_2 cell. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker AV-500 or DRX-500 spectrometer operating at 500, 125.7, and 202.49 MHz. Spectra are referenced to tetramethylsilane (TMS) for ^1H and $^{13}C\{^1H\}$ and 85% H_3PO_4 for $^{31}P\{^1H\}$ NMR spectroscopy. Mass spectral analyses were performed with a Waters LCT Premier XE at the Mass Spectrometry Center in the Institute of Chemistry, Academia Sinica. Elemental analyses were performed with an Elementar vario EL III elemental analyzer. Continuous wave EPR measurements were performed at X band using a Bruker ESP300 spectrometer equipped with a Bruker ER4102ST cavity. EPR spectra of [(μ-pdt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4]^-$ (**3A**$^-$) in frozen THF solution were obtained in a 4 mm JY-type EPR tube at 77 K. The following experimental conditions were used: A microwave power of 0.1917 mW, microwave frequency of 9.409 GHz, conversion time of 20.48 ms, receiver gain of 3990 and modulation amplitude of 10 G/100 kHz. EPR were simulated by the WINEPR SimFonia program.

Electrochemistry. Electrochemical measurements were recorded on a CH Instruments 630C electrochemical potentiostat using a gastight three-electrode cell under N_2 at 298 K unless otherwise stated. A vitreous carbon electrode (1 or 3 mm in diameter) and a platinum wire were used as the working and auxiliary electrodes, respectively. A Ag metal wire was used as the pseudo-reference electrode. All potentials were measured in THF solution containing 0.1 M [$^n Bu_4N$][PF_6]. The potentials are reported against the ferrocenium/ferrocene (Fc^+/Fc) couple.

Molecular Structure Determinations. The X-ray single crystal crystallographic data collections for **2A** (CCDC1503132), **3A** (CCDC1503134), **2B** (CCDC1505630), **3B** (CCDC1505631) and **4** (CCDC1503135) were performed at 150 K on a Bruker

SMART APEX CCD four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and outfitted with a low-temperature nitrogen-stream aperture. The structures were solved using direct methods in conjunction with standard difference Fourier techniques and refined by full-matrix least-squares procedures. A summary of the crystallographic data for all complexes is shown in Table S1. Selected metric data of each structure are listed in the figure captions. The experimental data and the computed results are summarized in Table S3 for comparison. An empirical absorption correction (multi-scan) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically calculated positions using the riding model. All software used for diffraction data processing and crystal structure solution and refinement are contained in the SHELXTL97 program suite.[2] The co-solvated hexane molecule in the unit cell of **2A** was disordered. The C6 atom of the pdt dithiolate linker in **3A** was disordered.

Computational Studies. All Kohn-Sham DFT calculations were performed using the Gaussian09 suite of the *ab initio* program[3] with a hybrid functional B3LYP[4] and a basis set 6-311G* to obtain the geometry optimization and free energy. Complexes **5**, **6** and their corresponding one-electron redox species were re-computed based on the same basis functional and basis set. The computational solvent effect was applied using the polarizable continuum model (PCM)[5] for THF (ε = 7.4257) in all calculated results. All geometries were fully optimized and applied for harmonic vibrational frequency calculations at 298 K. For **3A**$^{-}$, open shell unrestricted formalisms were performed with the same functional/basis set to determine the lowest-energy solution. Since several solutions to the spin-unrestricted approaches may be achieved, we have used the following two notations for the calculation: [Fe_2(*m*),L(*n*)] and [Fe^S(*m1*),Fe^P(*m2*),L(*n*)] in which *m*, *m1*, *m2*, *n* denote the spin multiplicity of each fragment in addition to the spin-unrestricted calculation without spin assignment. For the class in which the Fe_2 moiety was treated to one unit, the calculations were performed for [Fe_2(*2*),L(*1*)] and [Fe_2(*1*),L(*2*)]. When two Fe centers were individually treated, [Fe^S(*3*),Fe^P(*-2*),L(*1*)], [Fe^S(*2*),Fe^P(*-3*),L(*1*)] and [Fe^S(*2*),Fe^P(*-2*),L(*2*)] were calculated. All calculations with spin assignments converged to the same results with the calculation without any spin assignment. Convergence was not achieved for the calculation of [Fe^S(*2*),Fe^P(*-3*),L(*1*)], suggesting that population of unpaired spin on the Fe^P was less likely. The orbital contributions of atoms were analyzed by the QMForge program.[6] The natural bond orbital (NBO) analysis[7] was performed using the NBO program in Gaussian09 program package.

Synthesis of [(μ-pdt)$Fe_2(CO)_5(PPh_2C(S)SMe)$] (2A). To a 10 mL THF solution of [(μ-pdt)$Fe_2(CO)_5(PPh_2H)$] (200 mg, 0.37 mmole) was added ^{n}BuLi (230 μL, 0.37 mmole) at 198 K. The color of solution changed from orange red to dark purple. The solution was stirred at 198 K for 10 minutes and CS_2 (22 μL, 0.37 mmole) was added. The color changed to dark red within 30 minutes. Then the solution was added MeI (23 μL, 0.37 mmole). The resulted solution was evaporated under reduced pressure. The residue was purified by chromatography on silica gel with dichloromethane/hexane (v/v 1:3) as eluent to give [(μ-pdt)$Fe_2(CO)_5(PPh_2C(S)SMe)$] (200.5 mg, 86 % yield) as a red solid. Crystals of [(μ-pdt)$Fe_2(CO)_5(PPh_2C(S)SMe)$]·0.5hexane (**2A**·0.5hexane) suitable for X-ray crystallographic analysis were grown from CH_2Cl_2-hexane solution at 253 K. IR (THF, cm^{-1}): ν_{CO} 2045 (vs), 1989 (vs), 1981 (sh), 1964 (m), 1944 (w). ^1H NMR (500.13 MHz, $CDCl_3$, 253 K): 0.94 (br, 1H, S(CH_2)$_3$S), 1.26 (br, 2H, S(CH_2)$_3$S), 1.39 (br, 1H, S(CH_2)$_3$S), 1.67 (m, 2H, S(CH_2)$_3$S), 2.73 (s, 3H, SCH_3), 7.40-8.00 (m, 10 H, P(C_6H_5)$_2$) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$, 253 K): 21.55 (s, 1C, SCH$_3$), 21.61 (s, 2C, S(CH$_2$)$_3$S), 29.87 (s, 1C, S(CH$_2$)$_3$S), 128.49 (d, J_{PC} = 9.31 Hz, 4C, P(C_6H$_5$)$_2$), 131.229 (s, 2C, P(C_6H$_5$)$_2$), 133.52 (d, J_{PC} = 35.09 Hz, 2C, *ipso*- P(C_6H$_5$)$_2$), 134.58 (d, J_{PC} = 11.32 Hz, 4C, P(C_6H$_5$)$_2$), 209.27 (br, 3C, *C*O), 212.64 (d, J_{PC} = 6.54 Hz, 2C, *C*O), 241.72 (d, J_{PC} = 11.07 Hz, 1C, PCS$_2$) ppm. $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$, 253 K): 100.19 (s, 1P, C*P*Ph$_2$) ppm. FAB-MS: m/z 635.9 $\{M + H\}^+$. Anal. Calc. for $C_{22}H_{19}Fe_2O_5PS_4$: C, 41.66; H, 3.02. Found: C, 41.67; H, 3.01 %.

Synthesis of [(μ-edt)$Fe_2(CO)_5(PPh_2C(S)SMe)$] (2B). To a 10 mL THF solution of [(μ-edt)$Fe_2(CO)_5(PPh_2H)$] (300 mg, 0.57 mmole) was added ^{n}BuLi (353 μL, 0.36 mmole) at 198 K. The color of solution changed from orange red to dark purple. The solution was stirred at 198 K for 10 minutes and CS_2 (34 μL, 0.57 mmole) was added. The color changed to dark red within 30 minutes. Then the solution was added MeI (35 μL, 0.57 mmole). The resulted solution was evaporated under reduced pressure. The residue was purified by chromatography on silica gel with dichloromethane/hexane (v/v 1:3) as eluent to give [(μ-edt)$Fe_2(CO)_5(PPh_2C(S)SMe)$] (273 mg, 78 % yield) as a red solid. Crystals of [(μ-edt)$Fe_2(CO)_5(PPh_2C(S)SMe)$] (**2B**) suitable for X-ray crystallographic analysis were grown from CH_2Cl_2-hexane solution at 253 K. IR (THF, cm^{-1}): ν_{CO} 2048 (vs), 1991 (vs), 1981 (sh), 1967 (sh), 1945 (w). ^1H NMR (500.13 MHz, $CDCl_3$, 253 K): 1.16 (m, 2H, S(CH_2)$_2$S), 1.85 (m, 2H, S(CH_2)$_2$S), 2.71 (s, 3H, SCH_3), 7.40-7.8 (m, 10

H, $P(C_6\mathit{H}_5)_2$) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$, 253 K): 21.5 (s, 1C, $S\mathit{C}H_3$), 34.96 (s, 2C, $S(\mathit{C}H_2)_2S$), 128.53 (d, J_{PC} = 9.18 Hz, 4C, $P(\mathit{C}_6H_5)_2$), 131.19 (s, 2C, $P(\mathit{C}_6H_5)_2$), 133.69 (2C, *ipso*-$P(\mathit{C}_6H_5)_2$), 134.00 (d, J_{PC} = 10.94 Hz, 4C, $P(\mathit{C}_6H_5)_2$), 211.63 (br, 3C, *C*O), 214.24 (d, J_{PC} = 6.41 Hz, 2C, *C*O), 240.82 (d, J_{PC} = 9.68 Hz, 1C, $P\mathit{C}S_2$) ppm. $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$, 253 K): 97.75 (s, 1P, $C\mathit{P}Ph_2$) ppm. FAB-MS: m/z 620.9 $\{M + H\}^+$, 591.9 $\{M - CO\}^+$, 563.9 $\{M - 2CO\}^+$, 535.9 $\{M - 3CO\}^+$, 479.9 $\{M - 5CO\}^+$. Anal. Calc. for $C_{21}H_{17}Fe_2O_5PS_4$: C, 40.66; H, 2.76. Found: C, 40.55; H, 2.78 %.

Synthesis of [(μ-pdt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4$] (3A). To a 10 mL THF solution of [(μ-pdt)$Fe_2(CO)_5(PPh_2H)$] (200 mg, 0.37 mmole) was added ^{n}BuLi (230 μL, 0.37 mmole) at 198 K. The color of solution changed from orange red to dark purple. The solution was stirred at 198 K for 10 minutes and CS_2 (22 μL, 0.37 mmole) was added. The color changed to dark red within 30 minutes. Then the solution was added MeI (23 μL, 0.37 mmole) and stirred at ambient temperature for 5 days. The resulted solution was evaporated under reduced pressure. The residue was purified by chromatography on silica gel with dichloromethane/hexane (v/v 1:3) as eluent to give [(μ-pdt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4$] (138 mg, 62 % yield) as a purple solid. Crystals of [(μ-pdt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4$] (**3A**) suitable for X-ray crystallographic analysis were grown from THF-hexane solution at 253 K. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1999 (s), 1969 (vs), 1935 (s), 1924 (sh). ^1H NMR (600.18 MHz, $CDCl_3$, 298 K): 1.70 (m, 2H, $S(C\mathit{H}_2)_3S$), 1.94 (m, 1H, $S(C\mathit{H}_2)_3S$), 2.09 (br, 1H, $S(C\mathit{H}_2)_3S$), 2.21 (br, 1H, $S(C\mathit{H}_2)_3S$), 2.27 (br, 1H, $S(C\mathit{H}_2)_3S$), 2.69 (s, 3H, $SC\mathit{H}_3$), 7.30-8.00 (br, 10H, $P(C_6\mathit{H}_5)_2$) ppm. $^{13}C\{^1H\}$ NMR (125.78 MHz, $CDCl_3$, 298 K): 22.4 (s, 1C, $S\mathit{C}H_3$), 25.72 (s, 1C, $S(\mathit{C}H_2)_3S$), 26.4 (s, 1C, $S(\mathit{C}H_2)_3S$), 30.47 (s, 1C, $S(\mathit{C}H_2)_3S$), 128.43 (s, 2C, $P(\mathit{C}_6H_5)_2$), 128.85 (s, 2C, $P(\mathit{C}_6H_5)_2$), 130.35 (s, 1C, $P(\mathit{C}_6H_5)_2$), 130.65 (d, J_{PC} = 6.04 Hz, 2C, $P(\mathit{C}_6H_5)_2$), 131.49 (s, 1C, $P(\mathit{C}_6H_5)_2$), 132.03 (d, J_{PC} = 28.2 Hz, 1C, *ipso*-$P(\mathit{C}_6H_5)_2$), 135.14 (s, 2C, $P(\mathit{C}_6H_5)_2$), 135.46 (1C, *ipso*-$P(\mathit{C}_6H_5)_2$), 211.27 (s, 1C, *C*O), 213.34 (s, 1C, *C*O), 214.04 (d, J_{PC} = 26.41 Hz, 1C, *C*O), 214.53 (s, 1C, *C*O), 235.79 (s, 1C, $P\mathit{C}S_2$) ppm. $^{31}P\{^1H\}$ NMR (242.96 MHz, $CDCl_3$, 298 K): 80.75 (s, 1P, $C\mathit{P}Ph_2$) ppm. FAB-MS: m/z 606.9 $\{M + H\}^+$, 549.9 $\{M - 2CO\}^+$, 493.9 $\{M - 4CO\}^+$. Anal. Calc. for $C_{21}H_{19}Fe_2O_4PS_4$: C, 41.60; H, 3.16. Found: C, 41.48; H, 3.06 %.

Synthesis of [(μ-edt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4$] (3B). To a 50 mL THF solution of [(μ-edt)$Fe_2(CO)_5(PPh_2H)$] (1 g, 1.89 mmole) was added ^{n}BuLi (786 μL, 1.89 mmole) at 198 K. The color of solution changed from orange red to dark green. The solution was stirred at 198 K for 10 minutes and CS_2 (113.8 μL, 1.89 mmole) was added. The color changed to dark red within 30 minutes. Then the solution was added MeI (117.44 μL, 1.89 mmole) and stirred at ambient temperature for 5 days. The resulted solution was evaporated under reduced pressure. The residue was purified by chromatography on silica gel with dichloromethane/hexane (v/v 1:3) as eluent to give [(μ-edt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4$] (469.5 mg, 42 % yield) as a purple solid. Crystals of [(μ-edt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4$] (**3B**) suitable for X-ray crystallographic analysis were grown from CH_2Cl_2-hexane solution at 253 K. IR (THF, cm^{-1}): ν_{CO} 2000 (s), 1970 (vs), 1938 (s), 1926 (m). ^1H NMR (500.13 MHz, $CDCl_3$, 298 K): 2.22 (br, 2H, $S(CH_2)_2S$), 2.35 (br, 1H, $S(CH_2)_2S$), 2.5 (br, 1H, $S(CH_2)_2S$), 2.71 (s, 3H, SCH_3), 7.3-8.00 (br, 10H, $P(C_6H_5)_2$) ppm. $^{13}C\{^1H\}$ NMR (125.78 MHz, $CDCl_3$, 298 K): 22.44 (s, 1C, SCH_3), 36.75 (s, 1C, $S(CH_2)_2S$), 36.69 (s, 1C, $S(CH_2)_2S$), 128.51 (s, 2C, $P(C_6H_5)_2$), 128.94 (s, 2C, $P(C_6H_5)_2$), 130.38 (s, 1C, $P(C_6H_5)_2$), 130.69 (s, 2C, $P(C_6H_5)_2$), 131.51 (s, 1C, $P(C_6H_5)_2$), 132.43 (d, J_{PC} = 29.7 Hz, 1C, *ipso*-$P(C_6H_5)_2$), 135.08 (br, 3C, $P(C_6H_5)_2$, *ipso*-$P(C_6H_5)_2$), 210.72 (s, 1C, *C*O), 212.08 (s, 1C, *C*O), 215.33 (br, 1C, *C*O), 215.73 (s, 1C, *C*O), 235.43 (s, 1C, PCS_2) ppm. $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$, 298 K): 82.91 (s, 1P, $CPPh_2$) ppm. FAB-MS: m/z 591.9 $\{M\}^+$, 563.9 $\{M – CO\}^+$, 536.0 $\{M – 2CO\}^+$, 479.9 $\{M – 4CO\}^+$. Anal. Calc. for $C_{20}H_{17}Fe_2O_4PS_4$: C, 40.56; H, 2.89. Found: C, 40.47; H, 2.84 %.

Synthesis of $H_3BPPh_2CS(S)Me$ (4). To a 0.5 mL CS_2 solution was added 0.5 M $KPPh_2$ (4.42 mL, 2.21 mmole) at 198 K. The solution was stirred for 30 minutes and was added MeI (165 μL, 2.65 mmole). The resulted solution was added 1M $BH_3·THF$ (2.21 mL, 2.21 mmole). The solution was evaporated under reduced pressure. The residue was purified by chromatography on silica gel with dichloromethane/hexane (v/v 1:1) as eluent to give $H_3BPPh_2C(S)SMe$ as a white solid. Crystals of $H_3BPPh_2CS(S)Me$ (**4**) suitable for X-ray crystallographic analysis were grown from CH_2Cl_2-hexane solution at 253 K. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 0.86-1.85 (br, 3H, BH_3), 2.72 (s, 3H, SCH_3), 7.38-7.55 (m, 10H, $P(C_6H_5)_2$) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 44.42 (br, 1P, H_3BPPh_2) ppm. FAB-MS: m/z 289.1 $\{M – H\}^+$. Anal. Calc. for $C_{14}H_{16}BPS_2$: C, 57.95; H, 5.56. Found: C, 57.90; H, 5.40 %.

Reduction of [(μ-pdt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4$] (3A). To a 10 mL THF solution of complex **3A** was added 1 equiv. of decamethylcobaltocene. The solution was stirred at 231 K and monitored by FTIR spectroscopy. The reaction was complete within 30 minutes. The FTIR signals of **3A** disappeared, accompanying the generation of a new set of signals (1970 s, 1934 vs, 1895 s, and 1881 m cm^{-1}, **3A**$^{-}$), which was of the same pattern with **3A** but lower in energy by ave. 37 cm^{-1}.

Reduction of [(μ-edt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4$] (3B). To a 10 mL THF solution of complex **3B** was added 1 equiv. of decamethylcobaltocene. The solution was stirred at 230 K and monitored by FTIR spectroscopy. The reaction was complete within 30 minutes. The FTIR signals of **3B** disappeared, accompanying the generation of a new set of signals (1972 s, 1935 vs, 1897 s, and 1883 m cm^{-1}, **3B**$^{-}$), which was of the same pattern with **3B** but lower in energy by ave. 37 cm^{-1}.

Figures

Figure S1. The FTIR spectra of (A) **2A**, (B) **3A**, (C) **2B**, and (D) **3B** in THF solution.

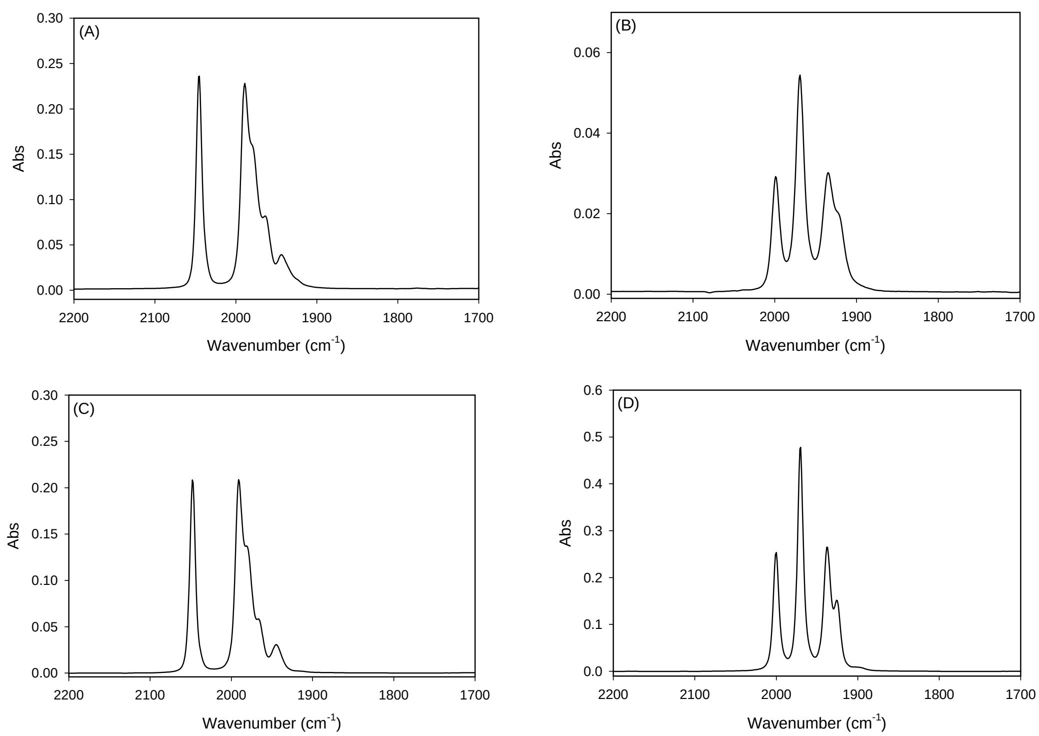


Figure S2. Molecular structures of (A) **2A**, (B) **2B**, (C) **3B** and (D) **4**, thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

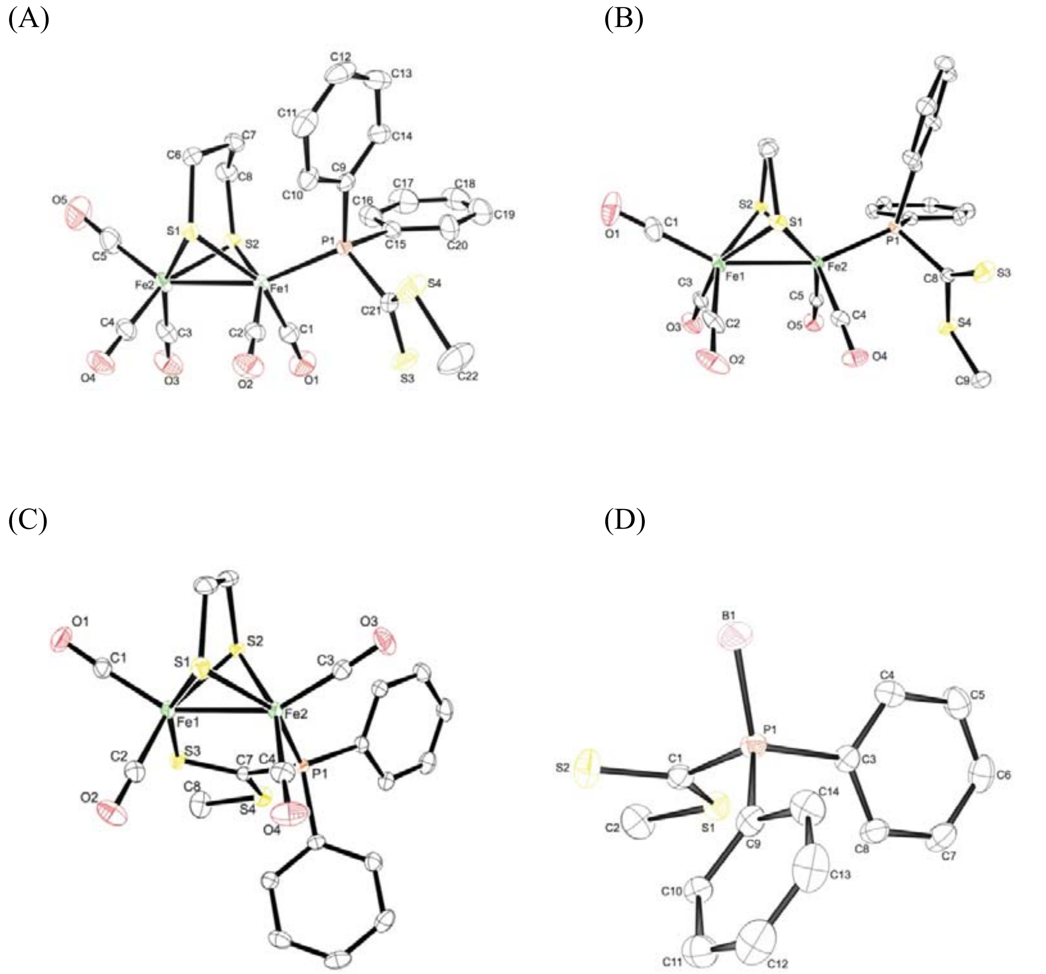


Figure S3. Cyclic voltammograms of (A) **2A**, (B) **3B**, and (C) **4** in THF solution under N_2 atmosphere at 275 K ([complex] = 1mM, υ = 100 mV s^{-1}, 0.1 M $^{n}Bu_4NPF_6$). The asterisk in (C) is the signal from impurity.

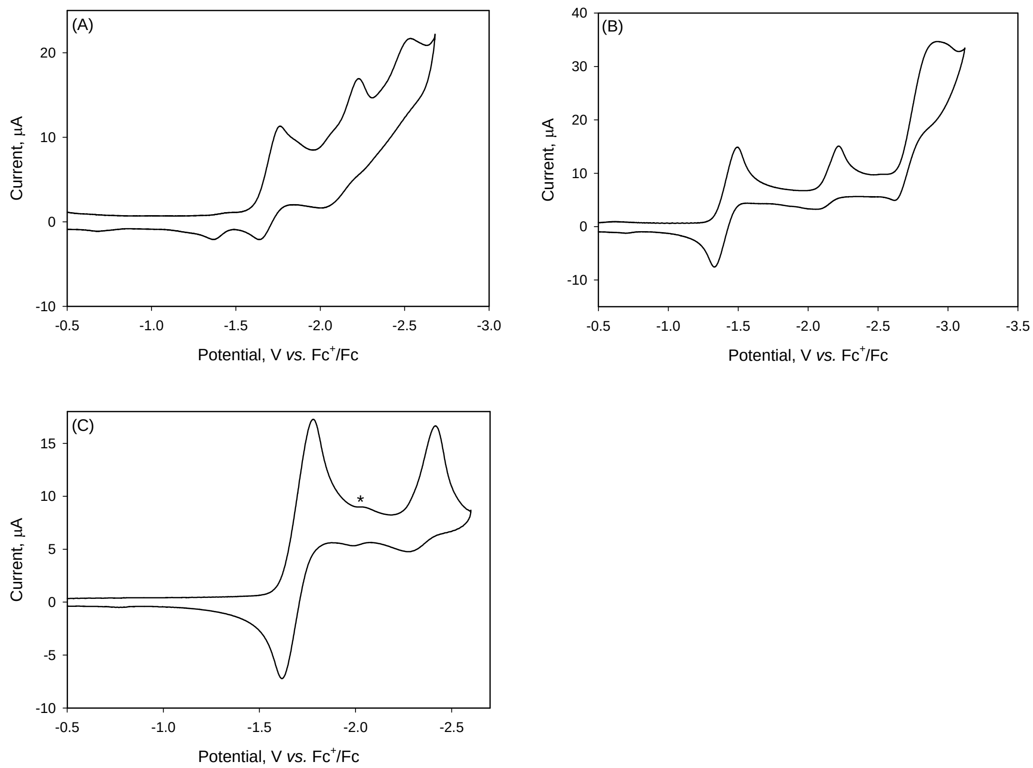


Figure S4. FTIR spectra of (A) **3A**⁻ (red) and (B) **3B**⁻ (blue) recorded in THF solution at 231 K. The FTIR bands of **3A** or **3B** are displayed as a black trace.

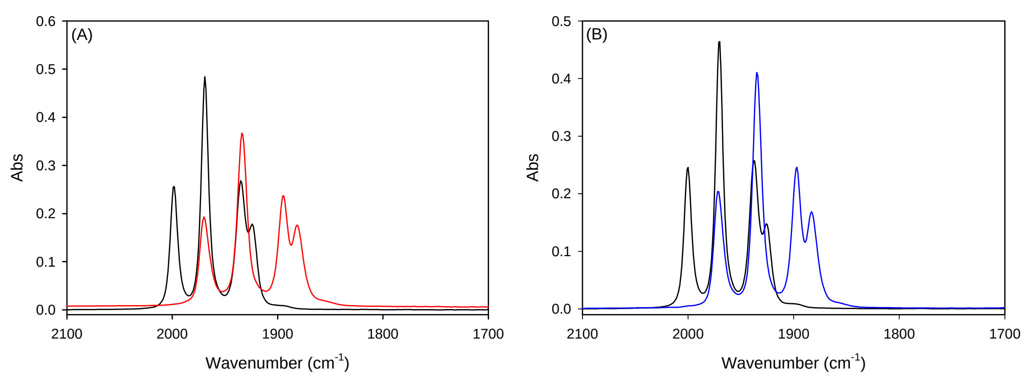
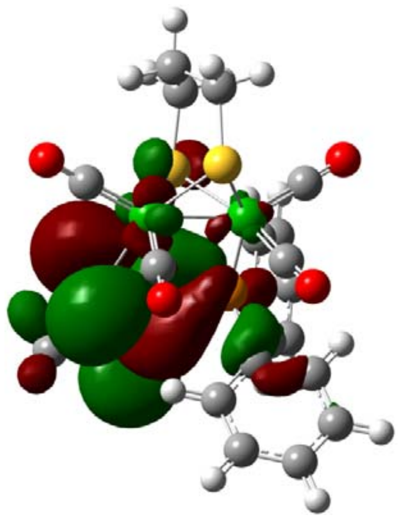
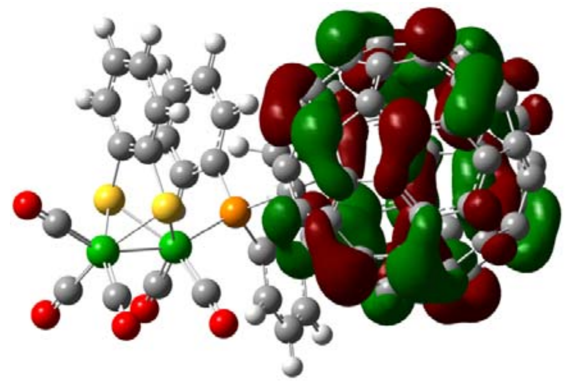


Figure S5. The lowest unoccupied molecular orbitals of (A) **3A** and (B) **5**, and (C) the highest occupied molecular orbital of **6**.

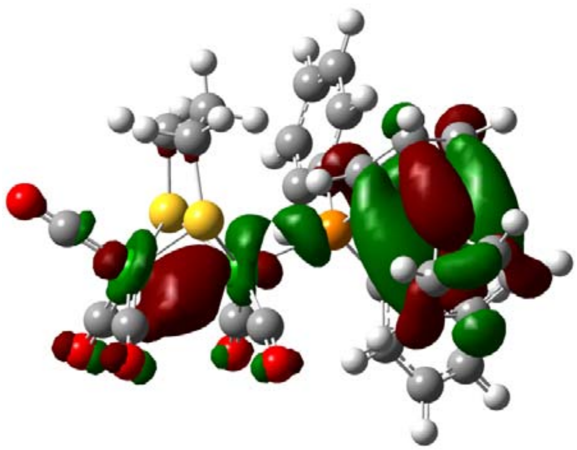
(A)



(B)



(C)



Tables

Table S1. X-ray crystallographic data.

	2A·0.5hexane	**3A**	**2B**
Empirical formula	$C_{25}H_{26}Fe_2O_5PS_4$	$C_{21}H_{19}Fe_2O_4PS_4$	$C_{21}H_{17}Fe_2O_5PS_4$
Formula weight	677.37	606.27	620.26
T, K	150(2)	150(2)	150(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/n$	$P2_1/n$
a, Å	9.2411(3)	11.7609(3)	9.4733(3)
b, Å	11.5601(4)	13.8406(3)	25.2126(8)
c, Å	15.5168(6)	15.6381(4)	10.1241(3)
α, °	92.0833(13)	90	90
β, °	103.4051(11)	104.0906(12)	93.1920(10)
γ, °	113.4163(11)	90	90
V, Å^3	1464.26(9)	2468.95(10)	2414.35(13)
Z	2	4	4
ρ_{calcd}, Mg m^{-3}	1.536	1.631	1.706
μ, mm^{-1}	1.364	1.604	1.646
F (000)	694	1232	1256
Reflections collected	12322	16697	16614
Independent reflections	6703	5663	5505
R_{int}	0.0161	0.0321	0.0269
Goodness-of-fit on F^2	1.047	1.027	1.032
R1 [$I > 2\sigma(I)$] (all data)[a]	0.0278 (0.0362)	0.0259 (0.036)	0.0260 (0.0353)
wR2 [$I > 2\sigma(I)$] (all data)[b]	0.0654 (0.0689)	0.0572 (0.0603)	0.0539 (0.0565)

[a] $R1 = (\Sigma||F_o|-|F_c||)/(\Sigma|F_o|)$. [b] $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S1. X-ray crystallographic data (cont.).

	3B	**4**
Empirical formula	$C_{20}H_{17}Fe_2O_4PS_4$	$C_{14}H_{16}BPS_2$
Formula weight	592.24	290.17
T, K	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	9.6554(4)	11.3924(7)
b, Å	16.4735(8)	9.7151(6)
c, Å	14.8482(8)	13.2754(7)
α, °	90	90
β, °	103.6630(14)	92.909(3)
γ, °	90	90
V, Å^3	2294.90(19)	1467.40(15)
Z	4	4
ρ_{calcd}, Mg m^{-3}	1.714	1.313
μ, mm^{-1}	1.724	0.45
F (000)	1200	608
Reflections collected	15756	8163
Independent reflections	5273	3281
R_{int}	0.0252	0.0423
Goodness-of-fit on F^2	1.026	1.036
R1 [$I > 2\sigma(I)$] (all data)[a]	0.0244 (0.0341)	0.0461 (0.081)
wR2 [$I > 2\sigma(I)$] (all data)[b]	0.0516 (0.0551)	0.1066 (0.1217)

[a] $R1 = (\Sigma||F_o|-|F_c||)/(\Sigma|F_o|)$. [b] $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Experimental and computed vibrational frequencies in the carbonyl region for complexes **2A**, **2B**, **3A**, **3A⁻**, **3B**, **3B⁻**, **5**, **5⁻**, **6**, and **6⁺**.

Complex	ν_{CO}, cm^{-1}	solvent
2A	2045 vs, 1989 vs, 1981 sh, 1964 m, 1944 w	THF
3A	1999 s, 1969 vs, 1935 s, 1924 sh	THF
	(2065 m, 2022 vs, 2001 s, 1992 sh)[a]	
3A⁻	1970 s, 1934 vs, 1895 s, 1881 m	THF
	(2038 m, 1990 vs, 1966 s, 1958 m)[a]	
2B	2048 vs, 1991 vs, 1981 sh, 1967 sh, 1945 w	THF
3B	2000 s, 1970 vs, 1938 s, 1926 m	THF
3B⁻	1972 s, 1935 vs, 1897 s, 1883 m	THF
5	2053 vs, 1995 vs, 1985 sh, 1941 w	THF[b]
5⁻	2047 vs, 1990 vs, 1978 s, 1938 w	THF[b]
6	2044 s, 1981 vs, 1960 sh, 1930 w	CH_2Cl_2[c]
6⁺	2050 s, 1985 vs, 1963 sh, 1931 w	CH_2Cl_2[c]

[a] The data were obtained from DFT calculations. [b] The data were taken from *Inorg. Chem.* **2012**, *51*, 5997-5999. [c] The data were taken from *Eur. J. Inorg. Chem.* **2011**, 1155-1162.

Table S3. Selected bond distances (Å) of the experimental and computed data of **3A** and **3A⁻**.

Selected bond	**3A**		**3A⁻**
	Exp.	Cal.	Cal.
Fe1-Fe2	2.4896(3)	2.464	2.463
Fe1-S1	2.2599(5)	2.321	2.329
Fe1-S2	2.2628(5)	2.291	2.306
Fe2-S1	2.2720(5)	2.332	2.326
Fe2-S2	2.2410(5)	2.274	2.289
Fe1-P1	2.2052(5)	2.237	2.269
Fe2-S3	2.2184(5)	2.299	2.34
C20-S3	1.6529(18)	1.666	1.733
C20-S4	1.7160(18)	1.722	1.778

Table S4. Electrochemical data of **2A**, **3A**, **2B**, **3B**, and **4**.

Complex	E_{pc}^{red}, V[a]
2A	–1.76, –2.24, –2.54
3A	–1.43[b], –2.24, –2.75
2B	–1.68[b], –2.32
3B	–1.42[b], –2.22, –2.94
4	–1.70[b], –2.42

[a] All data were collected in THF solution at 275 K. Potentials are against the Fc^+/Fc pair. Conditions: 1 mM, υ = 100 mV s^{-1}, 0.1 M $^nBu_4PF_6$. [b] $E_{1/2}$ values.

Table S5. NPA charges of **3A**, **3A**⁻, **5**, **5**⁻, **6**, and **6**⁺, and the differences between the parent complex and the species after redox reactions.

Complex	{(μ-xdt)$Fe_2(CO)_n$}[a,b]	Ligand[a]
3A	–0.30	+0.30
3A⁻	–0.54	–0.46
5	–0.12	+0.12
5⁻	–0.16	–0.84
6	–0.20	+0.20
6⁺	–0.14	+1.14
Δ**3A**/**3A**⁻	–0.24	–0.76
Δ**5**/**5**⁻	–0.04	–0.96
Δ**6**/**6**⁺	+0.06	+0.94

[a] Given values represent the sum over the respective atoms or groups. [b] n = 4 for **3A** and **3A**⁻, n = 5 for **5**, **5**⁻, **6**, and **6**⁺.

Natural population analysis (NPA)

Natural population analysis (NPA) charge represents the electron density distribution within a molecule.[8] NPA is based on the natural bond orbital (NBO) scheme in which the occupancies of the natural atomic orbitals are summed up to give the atomic population for a specific atom, i.e. NPA charge of a specific atom.[7] NPA charge is a better alternative to Mulliken charge because atomic partial charge by the NPA method is converged to a stable value in different basis sets while charges from the Mulliken population analysis method are dependent on the basis set employed. Similar to Mulliken charges, NPA charges are commonly used for the comparison of atomic charge differences.

Natural bond orbital (NBO) analysis

NBO analysis provides a way to quantify the interaction between a filled Lewis type NBO (donor) and an empty non-Lewis NBO (acceptor).[7] The donor-acceptor interaction is estimated by second-order perturbation theory. For each donor NBO (i) and acceptor NBO (j), the stabilization energy E^2 is associated with delocalization $i \rightarrow j$, given by

$$E^2 = \Delta E_{ij} = [q_i F(i,j)^2]/(\varepsilon_i - \varepsilon_j)$$

where q_i is the donor orbital occupancy, $F(i,j)$ is the Fock matrix elements between the NBO i and j, and ε_i and ε_j are diagonal elements orbitals energies. Since these interactions lead to loss of electron density from the localized NBOs of the idealized Lewis structure into empty non-Lewis orbitals, they are referred to as 'delocalization' corrections to the natural Lewis structure. In general, the larger E^2 value, the more enhanced is the interaction between electron donors and electron acceptors, in other words, the more donation tendency from electron donors to election acceptors.

Tables S7-S15 show the donor/acceptor interactions between selected NBOs of complexes **3A**, **5**, **6** and their corresponding reduced/oxidized species. The stabilization energies for the interactions are included. When the antibonding orbital of Fe2-S3 acted as an acceptor in **3A**$^-$, several S3-related donor orbitals that had strong interactions with it were observed. The stabilization energies for the following major interactions were 73.05 (α-BD*$1_{Fe1\text{-}Fe2}$ → α-BD*$1_{Fe2\text{-}S3}$), 30.05 (α-LP2_{S2} → α-BD*$1_{Fe2\text{-}S3}$), 16.79 (α-LP1_{C4} → α-BD*$1_{Fe2\text{-}S3}$), 7.6 (α-BD$1_{Fe1\text{-}Fe2}$ → α-BD*$1_{Fe2\text{-}S3}$), 5.06 (α-BD$1_{Fe1\text{-}S2}$ → α-BD*$1_{Fe2\text{-}S3}$), and 3.17 kcal/mol (LP2_{S1} → BD*$1_{Fe2\text{-}S3}$). These large E^2 values indicated that the diiron core was capable of sharing the electron density to the sulfur atom of the

PS ligand. In contrast to the orbitals related to S3, the acceptor orbitals related to phosphorous (α-BD*$1_{P1\text{-}C14}$, α-BD*$2_{P1\text{-}C14}$, α-BD*$1_{P1\text{-}C8}$, and α-BD*$1_{P1\text{-}C20}$) had weaker interactions with their donor orbitals. It was found that the total stabilization energy related to sulfur (S3) acceptor orbitals was much larger than the energy related to the phosphorous (P1) acceptor orbitals, 302.00 and 39.58 kcal mol^{-1}, respectively. It indicated that sulfur provided a better route than phosphorous for accepting electron density from the diiron core. The same analysis was employed to donor orbitals concerning α-BD*$1_{Fe2\text{-}S3}$, α-BD*$1_{P1\text{-}C14}$, α-BD*$2_{P1\text{-}C14}$, α-BD*$1_{P1\text{-}C8}$, and α-BD*$1_{P1\text{-}C20}$. The energy stabilized by S3-related donor orbital was larger than the energy by P1-related donor orbitals, 252.64 and 171.29 kcal mol^{-1}, respectively. The results suggested that the electron density propagation between the ligand and the [2Fe2S] core was much more effective via the sulfur atom than the phosphorous.

Table S6. The stabilization energy (E^2) concerning the $S^{dithioformate}$ and P involvement in the Fe-X bonding of **3A**, **5**, **6** and their corresponding one-electron redox species according to NBO analysis.

Selected NBOs		Donors, E^2, kcal mol^{-1}					
		[2Fe2S][a]					
		3A	**3A**$^{-}$	**5**	**5**$^{-}$	**6**	**6**$^{+}$
$S^{dithioformate}$ related NBOs	alpha		151.65				
	beta	11.76	149.35	NA	NA	NA	NA
	total		301.00				
P related NBOs	alpha		23.29		14.14		12.16
	beta	36.06	16.29	29.85	14.08	21.44	12.50
	total		39.58		28.22		24.66

Selected NBOs		Acceptors, E^2, kcal mol^{-1}					
		[2Fe2S][b]					
		3A	**3A**$^{-}$	**5**	**5**$^{-}$	**6**	**6**$^{+}$
$S^{dithioformate}$ related NBOs	alpha		128.93				
	beta	123.24	123.71	NA	NA	NA	NA
	total		252.64				
P related NBOs	alpha		81.17		58.12		63.21
	beta	153.61	90.12	119.91	58.92	125.97	63.63
	total		171.29		117.04		126.84

[a] The [2Fe2S] related orbitals act as NBO donor orbitals. [b] The [2Fe2S] related orbitals act as NBO acceptor orbitals. The [2Fe2S] fragment includes the Fe_2 core, CO groups and the dithiolate bridge.

Table S7. The stabilization energies between donors and acceptors of NBOs in [(μ-pdt)(μ-$PPh_2C(S)SMe)Fe_2(CO)_4$] (**3A**).

Donor (*i*)	Acceptor (*j*)	E^2, kcal/mol
$LP1_{S3}$	BD^*1_{Fe2-S2}	9.53
$LP1_{S3}$	BD^*1_{P1-C20}	9.37
$LP1_{S3}$	BD^*1_{Fe2-C3}	3.85
$LP1_{S3}$	$BD^*1_{Fe1-Fe2}$	1.19
$LP1_{S3}$	LP^*4_{Fe2}	1.07
$LP1_{S3}$	BD^*1_{S4-C20}	0.63
$LP1_{S3}$	LP^*6_{Fe2}	0.52
$LP1_{S3}$	BD^*1_{S1-C5}	0.18
$LP1_{S3}$	BD^*1_{C3-O3}	0.27
$LP1_{S3}$	BD^*2_{C3-O3}	0.19
$LP1_{S3}$	BD^*1_{C4-O4}	0.45
$LP1_{S3}$	BD^*2_{C4-O54}	0.18
$LP2_{S3}$	BD^*1_{Fe2-S2}	64.99
$LP2_{S3}$	BD^*1_{S4-C20}	14.4
$LP2_{S3}$	BD^*1_{Fe2-C3}	8.73
$LP2_{S3}$	LP^*6_{Fe2}	8.43
$LP2_{S3}$	BD^*1_{C3-O3}	4.73
$LP2_{S3}$	$BD^*1_{Fe1-Fe2}$	4.58
$LP2_{S3}$	LP^*4_{Fe2}	3.03
$LP2_{S3}$	BD^*1_{C4-O4}	1.73
$LP2_{S3}$	BD^*1_{S1-C5}	1.31
$LP2_{S3}$	BD^*1_{P1-C8}	1.02
$LP2_{S3}$	BD^*1_{P1-C20}	0.85
$LP2_{S3}$	$BD^*1_{C21-H21A}$	0.65
$LP2_{S3}$	BD^*2_{C4-O4}	0.44
$LP2_{S3}$	BD^*2_{C3-O3}	0.32
$LP2_{S3}$	BD^*3_{C3-O3}	0.46
$LP2_{S3}$	BD^*3_{C4-O4}	0.27
$LP2_{S3}$	BD^*1_{Fe1-C1}	0.16
$LP2_{S3}$	LP^*5_{Fe1}	0.07

$LP2_{S3}$	$BD^{*}1_{Fe1-S2}$	0.05
$LP1_{P1}$	$BD^{*}1_{Fe1-S2}$	88.51
$LP1_{P1}$	$BD^{*}1_{Fe1-C1}$	14.54
$LP1_{P1}$	$LP^{*}6_{Fe1}$	12.2
$LP1_{P1}$	$LP^{*}4_{Fe1}$	9.55
$LP1_{P1}$	$BD^{*}1_{Fe1-Fe2}$	4.99
$LP1_{P1}$	$BD^{*}1_{S4-C20}$	4.3
$LP1_{P1}$	$BD^{*}2_{C14-C19}$	4.21
$LP1_{P1}$	$BD^{*}1_{C8-C13}$	3.53
$LP1_{P1}$	$BD^{*}3_{C1-O1}$	0.84
$LP1_{P1}$	$BD^{*}1_{C1-O1}$	2.51
$LP1_{P1}$	$BD^{*}2_{C1-O1}$	2.4
$LP1_{P1}$	$BD^{*}2_{C2-O2}$	2.18
$LP1_{P1}$	$BD^{*}1_{S1-C5}$	1.86
$LP1_{P1}$	$BD^{*}1_{C14-C19}$	1.32
$LP1_{P1}$	$BD^{*}2_{C8-C9}$	1.01
$LP1_{P1}$	$BD^{*}2_{S3-C20}$	0.62
$LP1_{P1}$	$BD^{*}1_{Fe2-C3}$	0.16
$LP1_{P1}$	$LP^{*}5_{Fe2}$	0.07
$LP1_{P1}$	$BD^{*}1_{C5-H5B}$	0.05
$LP1_{P1}$	$LP^{*}5_{Fe1}$	0.05
$LP1_{P1}$	$BD^{*}3_{C2-O2}$	0.54
$BD1_{S3-C20}$	$BD^{*}1_{P1-C20}$	2.07
$BD1_{S3-C20}$	$LP^{*}6_{Fe1}$	0.37
$BD1_{S3-C20}$	$LP^{*}6_{Fe2}$	0.16
$BD1_{S3-C20}$	$BD^{*}1_{Fe1-S2}$	0.14
$BD1_{S3-C20}$	$BD^{*}1_{Fe1-C1}$	0.13
$BD1_{S3-C20}$	$BD^{*}1_{Fe2-S2}$	0.55
$BD1_{S3-C20}$	$BD^{*}1_{Fe2-C3}$	0.39
$BD1_{S3-C20}$	$BD^{*}1_{S1-C5}$	0.4
$BD2_{S3-C20}$	$BD^{*}1_{P1-C14}$	1.91
$BD2_{S3-C20}$	$LP^{*}4_{Fe2}$	0.1
$BD2_{S3-C20}$	$LP^{*}6_{Fe2}$	0.14
$BD2_{S3-C20}$	$BD^{*}2_{S3-C20}$	0.55

$BD2_{S3-C20}$	$BD^{*}1_{P1-C8}$	0.67
$BD2_{S3-C20}$	$BD^{*}1_{Fe2-S2}$	0.42
$BD2_{S3-C20}$	$BD^{*}1_{Fe2-C3}$	0.3
$BD2_{S3-C20}$	$BD^{*}1_{S1-C5}$	0.98
$BD2_{S3-C20}$	$BD^{*}1_{C3-O3}$	0.44
$BD2_{S3-C20}$	$BD^{*}1_{C4-O4}$	0.21
$BD2_{S3-C20}$	$BD^{*}2_{C3-O3}$	0.06
$BD^{*}2_{S3-C20}$	$BD^{*}1_{S3-C20}$	1.99
$BD^{*}2_{S3-C20}$	$BD^{*}1_{P1-C14}$	1.23
$BD^{*}2_{S3-C20}$	$BD^{*}1_{C4-O4}$	0.5
$BD^{*}2_{S3-C20}$	$BD^{*}1_{Fe2-S2}$	0.44
$BD^{*}2_{S3-C20}$	$BD^{*}1_{Fe2-C3}$	0.25
$BD^{*}2_{S3-C20}$	$BD^{*}1_{C3-O3}$	0.47
$BD^{*}2_{S3-C20}$	$BD^{*}2_{C3-O3}$	0.06
$BD1_{P1-C8}$	$BD^{*}1_{C9-C10}$	3.8
$BD1_{P1-C8}$	$BD^{*}1_{C12-C13}$	3.42
$BD1_{P1-C8}$	$BD^{*}1_{S3-C20}$	2.34
$BD1_{P1-C8}$	$BD^{*}1_{C8-C13}$	1.58
$BD1_{P1-C8}$	$BD^{*}1_{C14-C19}$	1.57
$BD1_{P1-C8}$	$BD^{*}1_{C8-C9}$	1.23
$BD1_{P1-C8}$	$BD^{*}2_{S3-C20}$	0.79
$BD1_{P1-C8}$	$BD^{*}2_{C14-C19}$	0.79
$BD1_{P1-C8}$	$BD^{*}1_{P1-C14}$	0.68
$BD1_{P1-C8}$	$BD^{*}1_{Fe1-C1}$	0.3
$BD1_{P1-C8}$	$BD^{*}1_{Fe1-S2}$	0.27
$BD1_{P1-C8}$	$BD^{*}1_{Fe2-C3}$	0.07
$BD1_{P1-C8}$	$LP^{*}6_{Fe1}$	0.06
$BD1_{P1-C14}$	$BD^{*}1_{C15-C16}$	3.8
$BD1_{P1-C14}$	$BD^{*}1_{C18-C19}$	3.35
$BD1_{P1-C14}$	$BD^{*}1_{C8-C9}$	1.98
$BD1_{P1-C14}$	$BD^{*}1_{C14-C19}$	1.63
$BD1_{P1-C14}$	$BD^{*}2_{S3-C20}$	1.49
$BD1_{P1-C14}$	$BD^{*}1_{S3-C20}$	1.2
$BD1_{P1-C14}$	$BD^{*}1_{C14-C15}$	1.14

BD1$_{P1-C14}$	BD*1$_{P1-C8}$	0.61
BD1$_{P1-C14}$	BD*1$_{P1-C20}$	0.58
BD1$_{P1-C14}$	BD*1$_{C15-H15}$	0.53
BD1$_{P1-C14}$	BD*1$_{Fe1-S2}$	0.37
BD1$_{P1-C14}$	BD*2$_{C1-O1}$	0.19
BD1$_{P1-C14}$	BD*1$_{C1-O1}$	0.17
BD1$_{P1-C14}$	BD*1$_{Fe1-C8}$	0.15
BD1$_{P1-C14}$	BD*1$_{Fe1-Fe2}$	0.11
BD1$_{P1-C20}$	BD*1$_{C14-C15}$	1.79
BD1$_{P1-C20}$	BD*1$_{C8-C9}$	1.4
BD1$_{P1-C20}$	BD*1$_{S4-C21}$	1.34
BD1$_{P1-C20}$	BD*1$_{Fe1-C1}$	0.55
BD1$_{P1-C20}$	BD*1$_{S1-C5}$	0.39
BD1$_{P1-C20}$	BD*1$_{P1-C14}$	0.53
BD1$_{P1-C20}$	BD*1$_{Fe1-S2}$	0.31
BD1$_{P1-C20}$	LP*6$_{Fe1}$	0.16
BD1$_{P1-C20}$	BD*1$_{Fe1-Fe2}$	0.12
BD*1$_{P1-C8}$	BD*1$_{Fe1-S2}$	3.55
BD*1$_{P1-C8}$	BD*1$_{S3-C20}$	1.88
BD*1$_{P1-C8}$	BD*1$_{C9-H9}$	1.03
BD*1$_{P1-C8}$	BD*1$_{C13-H13}$	0.97
BD*1$_{P1-C8}$	BD*1$_{C12-C13}$	0.61
BD*1$_{P1-C8}$	LP*6$_{Fe1}$	0.33
BD*1$_{P1-C8}$	BD*1$_{Fe1-C1}$	0.06
BD*1$_{P1-C20}$	BD*1$_{S4-C20}$	2.43
BD*1$_{P1-C20}$	BD*1$_{Fe2-S2}$	2.39
BD*1$_{P1-C20}$	BD*1$_{Fe1-S2}$	2.05
BD*1$_{P1-C20}$	BD*1$_{S3-C20}$	1.59
BD*1$_{P1-C20}$	BD*1$_{P1-C8}$	1.28
BD*1$_{P1-C20}$	BD*1$_{S1-C5}$	0.89
BD*1$_{P1-C20}$	BD*1$_{P1-C14}$	0.88
BD*1$_{P1-C20}$	LP*4$_{Fe1}$	0.27
BD*1$_{P1-C20}$	LP*6$_{Fe1}$	0.23
BD*1$_{P1-C20}$	BD*1$_{Fe2-C3}$	0.17

$BD1_{P1-C8}$	$BD^{*}1_{S3-C20}$	2.34
$BD^{*}1_{P1-C8}$	$BD^{*}1_{S3-C20}$	1.88
$BD1_{P1-C20}$	$BD^{*}1_{S3-C20}$	1.59
$BD1_{P1-C14}$	$BD^{*}1_{S3-C20}$	1.2
$BD^{*}2_{C3-O3}$	$BD^{*}1_{S3-C20}$	0.18
$LP1_{C4}$	$BD^{*}1_{S3-C20}$	0.88
$BD1_{Fe2-C3}$	$BD^{*}1_{S3-C20}$	0.33
$LP1_{Fe2}$	$BD^{*}1_{S3-C20}$	0.49
$LP2_{Fe2}$	$BD^{*}1_{S3-C20}$	0.42
$LP1_{S1}$	$BD^{*}1_{S3-C20}$	0.08
$LP3_{S1}$	$BD^{*}1_{S3-C20}$	0.13
$BD^{*}1_{Fe1-Fe2}$	$BD^{*}1_{S3-C20}$	0.07
$BD^{*}1_{Fe1-S2}$	$BD^{*}1_{S3-C20}$	0.14
$BD^{*}1_{Fe2-S2}$	$BD^{*}1_{S3-C20}$	0.55
$BD^{*}1_{Fe1-C1}$	$BD^{*}1_{S3-C20}$	0.09
$BD^{*}1_{C4-O4}$	$BD^{*}1_{S3-C20}$	0.21
$BD^{*}2_{C4-O4}$	$BD^{*}1_{S3-C20}$	0.2
$BD1_{Fe1-S2}$	$BD^{*}1_{S3-C20}$	0.08
$LP1_{S4}$	$BD^{*}1_{S3-C20}$	7.44
$BD^{*}2_{S3-C20}$	$BD^{*}1_{S3-C20}$	1.99
$BD2_{C4-O4}$	$BD^{*}1_{S3-C20}$	0.05
$LP2_{S4}$	$BD^{*}2_{S3-C20}$	54.69
$LP1_{Fe2}$	$BD^{*}2_{S3-C20}$	2.18
$LP2_{Fe2}$	$BD^{*}2_{S3-C20}$	2.06
$BD1_{P1-C14}$	$BD^{*}2_{S3-C20}$	1.49
$BD2_{C8-C9}$	$BD^{*}2_{S3-C20}$	0.66
$LP2_{S1}$	$BD^{*}2_{S3-C20}$	1.95
$BD2_{C14-C19}$	$BD^{*}2_{S3-C20}$	0.53
$LP1_{C2}$	$BD^{*}2_{S3-C20}$	0.21
$LP1_{C4}$	$BD^{*}2_{S3-C20}$	0.79
$BD1_{P1-C8}$	$BD^{*}2_{S3-C20}$	0.79
$LP1_{S1}$	$BD^{*}2_{S3-C20}$	0.08
$LP1_{P1}$	$BD^{*}2_{S3-C20}$	0.62
$BD2_{S3-C20}$	$BD^{*}2_{S3-C20}$	0.55

$BD1_{Fe2-C3}$	$BD^{*}2_{S3-C20}$	0.15
$BD1_{C3-O3}$	$BD^{*}2_{S3-C20}$	0.06
$LP2_{Fe1}$	$BD^{*}2_{S3-C20}$	0.06
$BD1_{Fe2-S2}$	$BD^{*}2_{S3-C20}$	0.1
$BD1_{Fe1-Fe2}$	$BD^{*}2_{S3-C20}$	0.22
$BD1_{C12-C13}$	$BD^{*}1_{P1-C8}$	5.22
$BD1_{Fe1-Fe2}$	$BD^{*}1_{P1-C8}$	4.04
$BD1_{C9-C10}$	$BD^{*}1_{P1-C8}$	4.68
$BD1_{Fe1-C1}$	$BD^{*}1_{P1-C8}$	3.27
$BD2_{C14-C19}$	$BD^{*}1_{P1-C8}$	2.49
$BD1_{C8-C9}$	$BD^{*}1_{P1-C8}$	1.8
$LP2_{Fe1}$	$BD^{*}1_{P1-C8}$	1.79
$BD1_{C8-C13}$	$BD^{*}1_{P1-C8}$	1.75
$BD^{*}1_{P1-C20}$	$BD^{*}1_{P1-C8}$	1.28
$BD^{*}2_{C14-C19}$	$BD^{*}1_{P1-C8}$	1.24
$LP1_{S3}$	$BD^{*}1_{P1-C8}$	1.02
$BD^{*}2_{C3-O3}$	$BD^{*}1_{P1-C8}$	0.13
$BD2_{S3-C20}$	$BD^{*}1_{P1-C8}$	0.67
$BD1_{P1-C14}$	$BD^{*}1_{P1-C8}$	0.61
$LP2_{S1}$	$BD^{*}1_{P1-C8}$	0.26
$BD1_{C3-O3}$	$BD^{*}1_{P1-C8}$	0.05
$LP3_{S1}$	$BD^{*}1_{P1-C8}$	0.1
$BD1_{Fe2-S2}$	$BD^{*}1_{P1-C8}$	0.11
$LP1_{Fe1}$	$BD^{*}1_{P1-C8}$	0.43
$BD3_{C1-O1}$	$BD^{*}1_{P1-C8}$	0.2
$BD1_{Fe2-C3}$	$BD^{*}1_{P1-C8}$	0.47
$BD1_{Fe1-S2}$	$BD^{*}1_{P1-C8}$	0.44
$BD^{*}1_{Fe1-Fe2}$	$BD^{*}1_{P1-C8}$	0.15
$BD^{*}1_{Fe2-S2}$	$BD^{*}1_{P1-C8}$	0.48
$BD^{*}1_{C1-O1}$	$BD^{*}1_{P1-C8}$	0.83
$BD^{*}1_{C3-O3}$	$BD^{*}1_{P1-C8}$	0.22
$LP1_{C2}$	$BD^{*}1_{P1-C8}$	0.47
$BD^{*}2_{C2-O2}$	$BD^{*}1_{P1-C8}$	0.1
$LP1_{C4}$	$BD^{*}1_{P1-C8}$	0.08

$LP3_{Fe1}$	$BD^{*}1_{P1-C8}$	0.11
$LP2_{Fe2}$	$BD^{*}1_{P1-C8}$	0.1
$BD1_{C18-C19}$	$BD^{*}1_{P1-C14}$	5.34
$BD1_{C15-C16}$	$BD^{*}1_{P1-C14}$	4.77
$LP1_{S1}$	$BD^{*}1_{P1-C14}$	3.4
$LP3_{S1}$	$BD^{*}1_{P1-C14}$	3.05
$BD1_{C14-C19}$	$BD^{*}1_{P1-C14}$	2.03
$BD2_{S3-C20}$	$BD^{*}1_{P1-C14}$	1.91
$LP1_{Fe1}$	$BD^{*}1_{P1-C14}$	1.88
$BD1_{C14-C15}$	$BD^{*}1_{P1-C14}$	1.87
$BD^{*}2_{S3-C20}$	$BD^{*}1_{P1-C14}$	1.23
$BD^{*}2_{C1-O1}$	$BD^{*}1_{P1-C14}$	0.05
$LP2_{S1}$	$BD^{*}1_{P1-C14}$	0.15
$BD1_{P1-C8}$	$BD^{*}1_{P1-C14}$	0.68
$BD1_{P1-C20}$	$BD^{*}1_{P1-C14}$	0.53
$BD2_{C8-C9}$	$BD^{*}1_{P1-C14}$	0.51
$BD^{*}1_{C2-O2}$	$BD^{*}1_{P1-C14}$	0.09
$BD^{*}2_{C2-O2}$	$BD^{*}1_{P1-C14}$	0.1
$BD^{*}1_{P1-C20}$	$BD^{*}1_{P1-C14}$	0.88
$LP1_{C2}$	$BD^{*}1_{P1-C14}$	0.72
$BD1_{Fe1-Fe2}$	$BD^{*}1_{P1-C14}$	0.05
$BD1_{Fe1-S2}$	$BD^{*}1_{P1-C14}$	0.19
$BD1_{Fe1-C1}$	$BD^{*}1_{P1-C14}$	0.09
$BD3_{C1-O1}$	$BD^{*}1_{P1-C14}$	0.09
$LP1_{S3}$	$BD^{*}1_{P1-C20}$	9.37
$BD2_{C8-C9}$	$BD^{*}1_{P1-C20}$	5.12
$BD1_{S4-C21}$	$BD^{*}1_{P1-C20}$	4.3
$BD^{*}2_{C8-C9}$	$BD^{*}1_{P1-C20}$	4.04
$BD1_{Fe1-C1}$	$BD^{*}1_{P1-C20}$	2.42
$LP1_{C2}$	$BD^{*}1_{P1-C20}$	2.13
$BD1_{S3-C20}$	$BD^{*}1_{P1-C20}$	2.07
$LP2_{Fe1}$	$BD^{*}1_{P1-C20}$	1.75
$BD^{*}1_{Fe1-Fe2}$	$BD^{*}1_{P1-C20}$	1.15
$LP1_{S4}$	$BD^{*}1_{P1-C20}$	1.29

LP_{S1}	BD^*1_{P1-C20}	0.32
$LP1_{S1}$	BD^*1_{P1-C20}	0.49
BD^*2_{C1-O1}	BD^*1_{P1-C20}	0.81
$LP1_{Fe1}$	BD^*1_{P1-C20}	0.65
BD^*1_{C3-O3}	BD^*1_{P1-C20}	0.13
$BD1_{Fe1-S2}$	BD^*1_{P1-C20}	0.21
$BD1_{Fe2-C3}$	BD^*1_{P1-C20}	0.31
$BD1_{Fe2-S2}$	BD^*1_{P1-C20}	0.27
$BD2_{C1-O1}$	BD^*1_{P1-C20}	0.08
$BD3_{C1-O1}$	BD^*1_{P1-C20}	0.18
$BD^*2_{C14-C19}$	BD^*1_{P1-C20}	0.86
$LP2_{S3}$	BD^*1_{P1-C20}	0.85
$BD1_{C15-H15}$	BD^*1_{P1-C20}	0.61
$BD1_{P1-C14}$	BD^*1_{P1-C20}	0.58
$BD1_{S4-C20}$	BD^*1_{P1-C20}	0.59
$BD2_{C2-O2}$	BD^*1_{P1-C20}	0.07
$BD1_{C2-O2}$	BD^*1_{P1-C20}	0.07
BD^*1_{C2-O2}	BD^*1_{P1-C20}	0.36
BD^*2_{C2-O2}	BD^*1_{P1-C20}	0.55
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C20}	0.42

Table S8. The stabilization energies between donors and acceptors of alpha NBOs in $[(\mu\text{-pdt})(\mu\text{-PPh}_2\text{C(S)SMe})\text{Fe}_2(\text{CO})_4]^-$ (**3A**$^-$).

Donor (*i*)	Acceptor (*j*)	E^2, kcal/mol
BD^*1_{Fe2-S3}	BD^*1_{Fe2-C3}	67.49
BD^*1_{Fe2-S3}	BD^*1_{Fe1-S2}	26.46
BD^*1_{Fe2-S3}	BD^*1_{Fe1-C1}	7.22
BD^*1_{Fe2-S3}	BD^*1_{P1-C20}	4.6
BD^*1_{Fe2-S3}	LP^*5_{Fe2}	4.29
BD^*1_{Fe2-S3}	LP^*6_{Fe2}	2.96
BD^*1_{Fe2-S3}	BD^*1_{S3-C20}	1.58

BD^*1_{Fe2-S3}	BD^*3_{C2-O2}	0.07
BD^*1_{Fe2-S3}	BD^*3_{C4-O4}	0.18
BD^*2_{P1-C14}	$BD^*2_{C15-C16}$	27.62
BD^*2_{P1-C14}	BD^*1_{Fe1-S2}	6.03
BD^*2_{P1-C14}	BD^*1_{P1-C8}	3.63
BD^*2_{P1-C14}	BD^*1_{P1-C14}	3.16
BD^*2_{P1-C14}	BD^*1_{P1-C20}	2.14
BD^*2_{P1-C14}	$BD^*1_{C14-C19}$	1.04
BD^*2_{P1-C14}	BD^*1_{S4-C20}	0.65
BD^*2_{P1-C14}	BD^*1_{Fe1-C1}	0.7
BD^*2_{P1-C14}	BD^*2_{C2-C2}	0.52
BD^*2_{P1-C14}	BD^*2_{C8-C9}	0.33
BD^*2_{P1-C14}	$BD^*1_{Fe1-Fe2}$	0.33
BD^*2_{P1-C14}	LP^*4_{Fe1}	0.27
BD^*2_{P1-C14}	LP^*6_{Fe1}	0.28
BD^*2_{P1-C14}	$BD^*1_{C14-C15}$	0.3
BD^*2_{P1-C14}	BD^*1_{S1-C5}	0.28
BD^*2_{P1-C14}	BD^*3_{C2-O2}	0.05
BD^*1_{P1-C8}	BD^*1_{S3-C20}	2.42
BD^*1_{P1-C8}	BD^*1_{Fe1-S2}	1.57
BD^*1_{P1-C8}	$BD^*1_{C12-C13}$	0.37
BD^*1_{P1-C8}	$BD^*1_{C13-H13}$	0.62
BD^*1_{P1-C8}	BD^*1_{C8-C13}	0.38
BD^*1_{P1-C8}	BD^*1_{C9-H9}	0.62
BD^*1_{P1-C8}	BD^*1_{C9-C10}	0.29
BD^*1_{P1-C14}	BD^*1_{Fe1-S2}	3.68
BD^*1_{P1-C14}	BD^*1_{S3-C20}	1.26
BD^*1_{P1-C14}	$BD^*1_{C18-C19}$	0.33
BD^*1_{P1-C14}	$BD^*1_{C19-H19}$	0.55
BD^*1_{P1-C14}	$BD^*1_{C15-H15}$	0.63
BD^*1_{P1-C14}	$BD^*1_{C15-C16}$	0.3
BD^*1_{P1-C20}	BD^*1_{S3-C20}	7.09
$BD1_{Fe2-S3}$	BD^*1_{S4-C20}	4.14
$BD1_{Fe2-S3}$	BD^*1_{Fe2-C3}	3.25

$BD1_{Fe2\text{-}S3}$	$BD^*1_{C3\text{-}O3}$	2.56
$BD1_{Fe2\text{-}S3}$	LP^*_{Fe2}	1.74
$BD1_{Fe2\text{-}S3}$	$BD^*1_{Fe1\text{-}Fe2}$	1.49
$BD1_{Fe2\text{-}S3}$	$BD^*1_{Fe2\text{-}S3}$	1.1
$BD1_{Fe2\text{-}S3}$	$BD^*1_{S1\text{-}C5}$	1.09
$BD1_{Fe2\text{-}S3}$	$BD^*1_{Fe1\text{-}C1}$	0.98
$BD1_{Fe2\text{-}S3}$	$BD^*1_{S3\text{-}C20}$	0.88
$BD1_{Fe2\text{-}S3}$	$BD^*1_{C4\text{-}O4}$	0.78
$BD1_{Fe2\text{-}S3}$	$BD^*2_{C4\text{-}O4}$	0.13
$BD1_{Fe2\text{-}S3}$	$BD^*3_{C4\text{-}O4}$	0.62
$BD1_{Fe2\text{-}S3}$	$BD^*1_{Fe1\text{-}S2}$	0.67
$BD1_{Fe2\text{-}S3}$	$BD^*3_{C3\text{-}O3}$	0.68
$BD1_{Fe2\text{-}S3}$	$BD^*1_{P1\text{-}C8}$	0.45
$BD1_{S3\text{-}C20}$	$BD^*1_{P1\text{-}C8}$	0.34
$BD1_{S3\text{-}C20}$	$BD^*1_{P1\text{-}C20}$	0.9
$LP1_{S3}$	$BD^*1_{P1\text{-}C20}$	4.35
$LP1_{S3}$	$BD^*1_{Fe2\text{-}C3}$	1.91
$LP1_{S3}$	$BD^*1_{Fe1\text{-}Fe2}$	0.54
$LP1_{S3}$	LP^*4_{Fe2}	0.35
$LP1_{S3}$	$BD^*1_{C4\text{-}O4}$	0.23
$LP1_{S3}$	$BD^*2_{C4\text{-}O4}$	0.08
$LP2_{S3}$	$BD^*1_{C3\text{-}O3}$	1.43
$LP2_{S3}$	$BD^*1_{S1\text{-}C5}$	0.44
$LP2_{S3}$	$BD^*1_{C4\text{-}O4}$	0.16
$LP2_{S3}$	$BD^*1_{C4\text{-}O4}$	0.03
$BD1_{P1\text{-}C8}$	$BD^*2_{P1\text{-}C14}$	2.42
$BD1_{P1\text{-}C8}$	$BD^*1_{C9\text{-}C10}$	2
$BD1_{P1\text{-}C8}$	$BD^*1_{C12\text{-}C13}$	1.72
$BD1_{P1\text{-}C8}$	$BD^*1_{P1\text{-}C14}$	1.35
$BD1_{P1\text{-}C8}$	$BD^*1_{S3\text{-}C20}$	1.21
$BD1_{P1\text{-}C8}$	$BD^*1_{C14\text{-}C19}$	1.01
$BD1_{P1\text{-}C8}$	$BD^*1_{C8\text{-}C13}$	0.8
$BD1_{P1\text{-}C8}$	$BD^*1_{P1\text{-}C20}$	0.5
$BD1_{P1\text{-}C8}$	$BD^*1_{C8\text{-}C9}$	0.61

$BD1_{P1-C8}$	BD^*1_{Fe1-S2}	0.69
$BD1_{P1-C8}$	BD^*1_{Fe1-C1}	0.35
$BD1_{P1-C8}$	BD^*1_{P1-C8}	0.5
$BD1_{P1-C8}$	$BD^*1_{C13-H13}$	0.25
$BD1_{P1-C14}$	BD^*2_{P1-C14}	7.95
$BD1_{P1-C14}$	$BD^*1_{C15-C16}$	1.75
$BD1_{P1-C14}$	$BD^*1_{C18-C19}$	1.73
$BD1_{P1-C14}$	BD^*1_{P1-C8}	0.99
$BD1_{P1-C14}$	BD^*1_{P1-C14}	0.83
$BD1_{P1-C14}$	BD^*1_{Fe1-S2}	0.86
$BD1_{P1-C14}$	$BD^*1_{C14-C15}$	0.78
$BD1_{P1-C14}$	BD^*1_{C8-C9}	0.78
$BD1_{P1-C14}$	$BD^*1_{C14-C19}$	0.73
$BD1_{P1-C14}$	BD^*1_{S3-C20}	0.66
$BD1_{P1-C14}$	$BD^*1_{C15-H15}$	0.25
$BD1_{P1-C14}$	BD^*2_{C1-O1}	0.3
$BD1_{P1-C14}$	$BD^*2_{C15-C16}$	0.36
$BD1_{P1-C14}$	BD^*1_{P1-C20}	0.66
$BD1_{P1-C14}$	$LP1_{C19}$	0.54
$BD2_{P1-C14}$	BD^*1_{Fe1-S2}	39.5
$BD2_{P1-C14}$	LP^*6_{Fe1}	6.18
$BD2_{P1-C14}$	BD^*1_{Fe1-C1}	5.67
$BD2_{P1-C14}$	LP^*4_{Fe1}	4.32
$BD2_{P1-C14}$	BD^*1_{P1-C8}	2.93
$BD2_{P1-C14}$	BD^*1_{S4-C20}	2.75
$BD2_{P1-C14}$	BD^*1_{P1-C14}	2.48
$BD2_{P1-C14}$	$BD^*1_{Fe1-Fe2}$	2.46
$BD2_{P1-C14}$	BD^*1_{P1-C20}	2.26
$BD2_{P1-C14}$	BD^*1_{C1-O1}	1.94
$BD2_{P1-C14}$	$BD^*2_{C15-C16}$	1.67
$BD2_{P1-C14}$	BD^*2_{C1-O1}	1.63
$BD2_{P1-C14}$	BD^*1_{C8-C13}	1.27
$BD2_{P1-C14}$	BD^*2_{C2-O2}	1.18
$BD2_{P1-C14}$	$LP1_{C19}$	3.85

BD2$_{P1-C14}$	BD*1$_{S1-C5}$	0.73
BD2$_{P1-C14}$	BD*2$_{C8-C9}$	0.48
BD2$_{P1-C14}$	BD*3$_{C1-O1}$	0.3
BD2$_{P1-C14}$	BD*1$_{C8-C9}$	0.38
BD2$_{P1-C14}$	BD*1$_{C2-O2}$	0.03
BD2$_{P1-C14}$	BD*3$_{C2-O2}$	0.25
BD1$_{P1-C20}$	BD*1$_{P1-C14}$	1.84
BD1$_{P1-C20}$	BD*1$_{C14-C15}$	0.97
BD1$_{P1-C20}$	BD*1$_{Fe1-S2}$	0.63
BD1$_{P1-C20}$	BD*1$_{P1-C14}$	0.87
BD1$_{P1-C20}$	BD*1$_{C8-C9}$	0.58
BD1$_{P1-C20}$	BD*1$_{Fe1-C1}$	0.44
BD1$_{P1-C20}$	BD*1$_{P1-C8}$	0.68
BD*1$_{Fe1-Fe2}$	BD*1$_{Fe2-S3}$	73.05
LP2$_{S2}$	BD*1$_{Fe2-S3}$	30.05
LP1$_{C4}$	BD*1$_{Fe2-S3}$	16.79
BD1$_{Fe1-Fe2}$	BD*1$_{Fe2-S3}$	7.6
BD1$_{Fe1-S2}$	BD*1$_{Fe2-S3}$	5.06
LP2$_{S1}$	BD*1$_{Fe2-S3}$	3.17
LP1$_{S2}$	BD*1$_{Fe2-S3}$	2.99
BD1$_{Fe2-C3}$	BD*1$_{Fe2-S3}$	2.66
LP1$_{C2}$	BD*1$_{Fe2-S3}$	1.46
BD1$_{Fe2-S3}$	BD*1$_{Fe2-S3}$	1.1
LP3$_{S1}$	BD*1$_{Fe2-S3}$	0.92
BD1$_{Fe1-C1}$	BD*1$_{Fe2-S3}$	0.95
BD1$_{S4-C20}$	BD*1$_{Fe2-S3}$	0.34
BD3$_{C3-O3}$	BD*1$_{Fe2-S3}$	0.6
LP1$_{S1}$	BD*1$_{Fe2-S3}$	0.64
BD*2$_{C2-O2}$	BD*1$_{Fe2-S3}$	0.04
BD1$_{C4-O4}$	BD*1$_{Fe2-S3}$	0.1
BD3$_{C4-O4}$	BD*1$_{Fe2-S3}$	0.33
BD*1$_{C4-O4}$	BD*1$_{Fe2-S3}$	0.23
BD*2$_{C4-O4}$	BD*1$_{Fe2-S3}$	0.1
LP1$_{O4}$	BD*1$_{Fe2-S3}$	0.07

$BD^{*}1_{P1-C20}$	$BD^{*}1_{S3-C20}$	7.09
$LP2_{S4}$	$BD^{*}1_{S3-C20}$	3.38
$BD^{*}1_{P1-C8}$	$BD^{*}1_{S3-C20}$	2.42
$LP1_{S4}$	$BD^{*}1_{S3-C20}$	1.71
$BD^{*}1_{Fe2-S3}$	$BD^{*}1_{S3-C20}$	1.58
$BD^{*}1_{P1-C14}$	$BD^{*}1_{S3-C20}$	1.26
$BD1_{P1-C8}$	$BD^{*}1_{S3-C20}$	1.21
$BD^{*}2_{C4-O4}$	$BD^{*}1_{S3-C20}$	0.03
$LP1_{C4}$	$BD^{*}1_{S3-C20}$	0.55
$BD^{*}1_{C4-O4}$	$BD^{*}1_{S3-C20}$	0.14
$BD^{*}2_{C4-O4}$	$BD^{*}1_{S3-C20}$	0.1
$BD1_{Fe2-S3}$	$BD^{*}1_{S3-C20}$	0.88
$BD1_{P1-C14}$	$BD^{*}1_{S3-C20}$	0.66
$LP2_{Fe2}$	$BD^{*}1_{S3-C20}$	0.43
$BD1_{C4-O4}$	$BD^{*}1_{S3-C20}$	0.03
$BD1_{P1-C14}$	$BD^{*}2_{P1-C14}$	7.95
$BD1_{Fe1-Fe2}$	$BD^{*}2_{P1-C14}$	4.24
$BD1_{P1-C8}$	$BD^{*}2_{P1-C14}$	2.42
$BD1_{P1-C20}$	$BD^{*}2_{P1-C14}$	1.84
$BD1_{C14-C19}$	$BD^{*}2_{P1-C14}$	1.32
$LP2_{Fe1}$	$BD^{*}2_{P1-C14}$	1.17
$BD2_{C15-C16}$	$BD^{*}2_{P1-C14}$	20
$BD1_{Fe1-S2}$	$BD^{*}2_{P1-C14}$	0.94
$BD1_{Fe1-C1}$	$BD^{*}2_{P1-C14}$	0.42
$BD1_{C14-C15}$	$BD^{*}2_{P1-C14}$	0.76
$LP3_{S1}$	$BD^{*}2_{P1-C14}$	0.8
$LP1_{C2}$	$BD^{*}2_{P1-C14}$	0.18
$BD^{*}2_{P1-C14}$	$BD^{*}1_{P1-C8}$	3.63
$BD2_{P1-C14}$	$BD^{*}1_{P1-C8}$	2.93
$BD1_{C12-C13}$	$BD^{*}1_{P1-C8}$	2.49
$LP1_{C20}$	$BD^{*}1_{P1-C8}$	2.39
$BD1_{C9-C10}$	$BD^{*}1_{P1-C8}$	2.2
$BD1_{Fe1-Fe2}$	$BD^{*}1_{P1-C8}$	1.06
$LP1_{C2}$	$BD^{*}1_{P1-C8}$	0.28

$BD1_{P1-C14}$	BD^*1_{P1-C8}	0.99
$BD1_{C8-C13}$	BD^*1_{P1-C8}	0.86
$BD1_{Fe1-C1}$	BD^*1_{P1-C8}	0.82
$BD1_{P1-C20}$	BD^*1_{P1-C8}	0.68
$BD1_{C8-C9}$	BD^*1_{P1-C8}	0.84
$LP2_{Fe1}$	BD^*1_{P1-C8}	0.52
$BD1_{Fe2-S3}$	BD^*1_{P1-C8}	0.45
$BD1_{S3-C20}$	BD^*1_{P1-C8}	0.34
$BD1_{P1-C8}$	BD^*1_{P1-C8}	0.5
BD^*1_{C1-O1}	BD^*1_{P1-C8}	0.32
BD^*2_{C2-O2}	BD^*1_{P1-C8}	0.12
$LP1_{C4}$	BD^*1_{P1-C8}	0.04
$LP1_{C20}$	BD^*1_{P1-C14}	4.5
BD^*2_{P1-C14}	BD^*1_{P1-C14}	3.16
$BD2_{P1-C14}$	BD^*1_{P1-C14}	2.48
$BD1_{C18-C19}$	BD^*1_{P1-C14}	2.32
$BD1_{C15-C16}$	BD^*1_{P1-C14}	2.24
$LP1_{S1}$	BD^*1_{P1-C14}	1.41
$LP3_{S1}$	BD^*1_{P1-C14}	1.15
$BD1_{C14-C19}$	BD^*1_{P1-C14}	1.08
$BD1_{C14-C15}$	BD^*1_{P1-C14}	0.95
$BD1_{P1-C20}$	BD^*1_{P1-C14}	0.87
$BD1_{P1-C14}$	BD^*1_{P1-C14}	0.83
$LP1_{Fe1}$	BD^*1_{P1-C14}	0.82
$BD2_{C8-C9}$	BD^*1_{P1-C14}	0.54
$BD1_{Fe1-C1}$	BD^*1_{P1-C14}	0.32
$BD1_{P1-C8}$	BD^*1_{P1-C14}	1.35
$BD2_{C15-C16}$	BD^*1_{P1-C14}	0.27
BD^*2_{C8-C9}	BD^*1_{P1-C14}	0.26
$LP1_{C2}$	BD^*1_{P1-C14}	0.11
BD^*1_{C2-O2}	BD^*1_{P1-C14}	0.08
$LP1_{C19}$	BD^*1_{P1-C14}	0.52
BD^*1_{Fe2-S3}	BD^*1_{P1-C20}	4.6
$LP1_{S3}$	BD^*1_{P1-C20}	4.35

$BD2_{P1-C14}$	BD^*1_{P1-C20}	2.26
BD^*2_{P1-C14}	BD^*1_{P1-C20}	2.14
$BD2_{C8-C9}$	BD^*1_{P1-C20}	1.72
$LP1_{S4}$	BD^*1_{P1-C20}	1.67
$LP2_{S4}$	BD^*1_{P1-C20}	1.32
$BD1_{S4-C21}$	BD^*1_{P1-C20}	1.2
BD^*2_{C8-C9}	BD^*1_{P1-C20}	1.01
$LP1_{C2}$	BD^*1_{P1-C20}	0.95
$BD1_{S3-C20}$	BD^*1_{P1-C20}	0.9
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C20}	0.36
$BD1_{Fe1-C1}$	BD^*1_{P1-C20}	0.44
$BD1_{P1-C8}$	BD^*1_{P1-C20}	0.5
$LP2_{Fe1}$	BD^*1_{P1-C20}	0.85
$BD1_{P1-C14}$	BD^*1_{P1-C20}	0.66
$BD1_{S4-C20}$	BD^*1_{P1-C20}	0.3
BD^*1_{C2-O2}	BD^*1_{P1-C20}	0.1
BD^*2_{C2-O2}	BD^*1_{P1-C20}	0.13
$BD1_{C2-O2}$	BD^*1_{P1-C20}	0.03
$BD2_{C2-O2}$	BD^*1_{P1-C20}	0.03
$BD3_{C2-O2}$	BD^*1_{P1-C20}	0.03

Table S9. The stabilization energies between donors and acceptors of beta NBOs in $[(\mu\text{-pdt})(\mu\text{-PPh}_2\text{C(S)SMe})\text{Fe}_2(\text{CO})_4]^-$ (**3A**$^-$).

Donor (*i*)	Acceptor (*j*)	E^2, kcal/mol
$BD1_{Fe2-S3}$	BD^*1_{S4-C20}	4.25
$BD1_{Fe2-S3}$	BD^*1_{Fe2-C3}	3.53
$BD1_{Fe2-S3}$	BD^*1_{C3-O3}	2.81
$BD1_{Fe2-S3}$	LP^*5_{Fe2}	1.83
$BD1_{Fe2-S3}$	$BD^*1_{Fe1-Fe2}$	1.57
$BD1_{Fe2-S3}$	BD^*1_{Fe2-S3}	1.2
$BD1_{Fe2-S3}$	BD^*1_{S1-C5}	1.07

$BD1_{Fe2-S3}$	$BD^{*}1_{Fe1-C1}$	1.02
$BD1_{Fe2-S3}$	$BD^{*}1_{S3-C20}$	0.87
$BD1_{Fe2-S3}$	$BD^{*}1_{C4-O4}$	0.77
$BD1_{Fe2-S3}$	$BD^{*}3_{C3-O3}$	0.68
$BD1_{Fe2-S3}$	$BD^{*}3_{C4-O4}$	0.63
$BD1_{Fe2-S3}$	$BD^{*}1_{Fe1-S2}$	0.62
$BD1_{Fe2-S3}$	$BD^{*}1_{P1-C8}$	0.44
$BD1_{Fe2-S3}$	$BD^{*}2_{C4-O4}$	0.13
$BD1_{S3-C20}$	$BD^{*}1_{P1-C20}$	1.02
$BD1_{S3-C20}$	$BD^{*}1_{P1-C8}$	0.38
$BD2_{S3-C20}$	$BD^{*}1_{P1-C14}$	1.37
$BD2_{S3-C20}$	$BD^{*}1_{P1-C8}$	0.78
$BD2_{S3-C20}$	$BD^{*}1_{C3-O3}$	0.69
$BD2_{S3-C20}$	$BD^{*}1_{S1-C5}$	0.64
$BD2_{S3-C20}$	$BD^{*}1_{S4-C21}$	0.5
$BD2_{S3-C20}$	$BD^{*}1_{C4-O4}$	0.07
$BD^{*}1_{Fe2-S3}$	$BD^{*}1_{Fe2-C3}$	67.41
$BD^{*}1_{Fe2-S3}$	$BD^{*}1_{Fe1-S2}$	22.11
$BD^{*}1_{Fe2-S3}$	$BD^{*}1_{S4-C20}$	8.19
$BD^{*}1_{Fe2-S3}$	$BD^{*}1_{Fe1-C1}$	7.22
$BD^{*}1_{Fe2-S3}$	$BD^{*}1_{P1-C20}$	5.4
$BD^{*}1_{Fe2-S3}$	$LP^{*}5_{Fe2}$	4.17
$BD^{*}1_{Fe2-S3}$	$LP^{*}6_{Fe2}$	1.57
$BD^{*}1_{Fe2-S3}$	$BD^{*}1_{S3-C20}$	1.2
$BD^{*}1_{Fe2-S3}$	$BD^{*}3_{C4-O4}$	0.18
$BD^{*}1_{Fe2-S3}$	$BD^{*}3_{C2-O2}$	0.07
$BD^{*}2_{S3-C20}$	$BD^{*}1_{P1-C14}$	0.62
$BD^{*}2_{S3-C20}$	$BD^{*}1_{C3-O3}$	0.4
$BD^{*}2_{S3-C20}$	$BD^{*}1_{P1-C8}$	0.37
$BD^{*}2_{S3-C20}$	$BD^{*}1_{S4-C21}$	0.35
$BD^{*}2_{S3-C20}$	$BD^{*}1_{C4-O4}$	0.12
$BD1_{P1-C8}$	$BD^{*}1_{C9-C10}$	1.99
$BD1_{P1-C8}$	$BD^{*}1_{C12-C13}$	1.62
$BD1_{P1-C8}$	$BD^{*}1_{P1-C14}$	1.49

$BD1_{P1-C8}$	BD^*1_{Fe1-S2}	1.4
$BD1_{P1-C8}$	BD^*1_{S3-C20}	1.14
$BD1_{P1-C8}$	BD^*1_{P1-C20}	1.06
$BD1_{P1-C8}$	$BD^*1_{C14-C19}$	1
$BD1_{P1-C8}$	BD^*1_{C8-C13}	0.9
$BD1_{P1-C8}$	BD^*2_{S3-C20}	0.67
$BD1_{P1-C8}$	BD^*1_{Fe1-C1}	0.53
$BD1_{P1-C8}$	BD^*1_{P1-C8}	0.53
$BD1_{P1-C8}$	BD^*1_{C8-C9}	0.52
$BD1_{P1-C8}$	BD^*2_{C2-O2}	0.03
$BD1_{P1-C14}$	$BD^*1_{C18-C19}$	1.83
$BD1_{P1-C14}$	$BD^*1_{C15-C16}$	1.75
$BD1_{P1-C14}$	BD^*1_{P1-C8}	1.61
$BD1_{P1-C14}$	BD^*1_{Fe1-S2}	1.2
$BD1_{P1-C14}$	BD^*1_{P1-C20}	1.02
$BD1_{P1-C14}$	BD^*1_{C8-C9}	0.84
$BD1_{P1-C14}$	BD^*2_{S3-C20}	0.83
$BD1_{P1-C14}$	$BD^*1_{C14-C19}$	0.75
$BD1_{P1-C14}$	BD^*1_{S3-C20}	0.67
$BD1_{P1-C14}$	$BD^*1_{C14-C15}$	0.66
$BD1_{P1-C14}$	BD^*1_{P1-C14}	0.54
$BD1_{P1-C14}$	BD^*1_{S4-C20}	0.28
$BD1_{P1-C14}$	BD^*2_{C1-O1}	0.26
$BD1_{P1-C14}$	BD^*1_{Fe1-C1}	0.26
$BD1_{P1-C14}$	$BD^*1_{C15-H15}$	0.25
$BD1_{P1-C20}$	BD^*1_{Fe1-S2}	1.35
$BD1_{P1-C20}$	BD^*1_{P1-C14}	1.21
$BD1_{P1-C20}$	BD^*1_{P1-C8}	1.08
$BD1_{P1-C20}$	$BD^*1_{C14-C15}$	0.94
$BD1_{P1-C20}$	BD^*1_{Fe1-C1}	0.69
$BD1_{P1-C20}$	BD^*2_{C8-C9}	0.55
BD^*1_{P1-C8}	BD^*1_{Fe1-S2}	4.14
BD^*1_{P1-C8}	BD^*1_{S3-C20}	0.95
BD^*1_{P1-C8}	BD^*1_{C8-C13}	0.45

$BD^{*}1_{P1-C8}$	$BD^{*}1_{C13-H13}$	0.63
$BD^{*}1_{P1-C8}$	$BD^{*}1_{C9-H9}$	0.62
$BD^{*}1_{P1-C8}$	$BD^{*}1_{C12-C13}$	0.41
$BD^{*}1_{P1-C8}$	$BD^{*}1_{C9-C10}$	0.3
$BD^{*}1_{P1-C14}$	$BD^{*}1_{Fe1-S2}$	5.36
$BD^{*}1_{P1-C14}$	$BD^{*}1_{C15-H15}$	0.52
$BD^{*}1_{P1-C14}$	$BD^{*}1_{S3-C20}$	0.48
$BD^{*}1_{P1-C14}$	$BD^{*}1_{C19-H19}$	0.46
$BD^{*}1_{P1-C14}$	$BD^{*}1_{C18-C19}$	0.3
$BD^{*}1_{P1-C14}$	$BD^{*}1_{C15-C16}$	0.27
$BD^{*}1_{P1-C20}$	$BD^{*}1_{S3-C20}$	2.96
$BD^{*}1_{P1-C20}$	$BD^{*}1_{Fe1-S2}$	2.45
$LP1_{S3}$	$BD^{*}1_{P1-C20}$	4.26
$LP1_{S3}$	$BD^{*}1_{Fe2-C3}$	1.95
$LP1_{S3}$	$BD^{*}1_{Fe1-Fe2}$	0.57
$LP1_{S3}$	$LP^{*}4_{Fe2}$	0.35
$LP1_{S3}$	$BD^{*}1_{C4-O4}$	0.24
$LP1_{S3}$	$BD^{*}2_{C4-O4}$	0.09
$LP1_{P1}$	$BD^{*}1_{Fe1-S2}$	44.7
$LP1_{P1}$	$BD^{*}1_{P1-C8}$	12.91
$LP1_{P1}$	$BD^{*}1_{P1-C20}$	10.68
$LP1_{P1}$	$BD^{*}1_{P1-C14}$	7.75
$LP1_{P1}$	$LP^{*}6_{Fe1}$	6.96
$LP1_{P1}$	$BD^{*}1_{Fe1-C1}$	6.04
$LP1_{P1}$	$BD^{*}1_{C14-C15}$	5.39
$LP1_{P1}$	$LP^{*}4_{Fe1}$	4.51
$LP1_{P1}$	$BD^{*}1_{Fe1-Fe2}$	3.14
$LP1_{P1}$	$BD^{*}1_{S4-C20}$	3.04
$LP1_{P1}$	$BD^{*}1_{C1-O1}$	2.09
$LP1_{P1}$	$BD^{*}2_{C2-O2}$	1.74
$LP1_{P1}$	$BD^{*}2_{C1-O1}$	1.63
$LP1_{P1}$	$BD^{*}2_{C8-C9}$	1.15
$LP1_{P1}$	$BD^{*}1_{C8-C9}$	1.07
$LP1_{P1}$	$BD^{*}1_{S1-C5}$	0.85

$LP1_{P1}$	$BD^{*}1_{S3-C20}$	0.75
$LP1_{P1}$	$BD^{*}1_{C8-C29}$	0.62
$LP1_{P1}$	$BD^{*}3_{C1-O1}$	0.45
$LP1_{P1}$	$BD^{*}2_{S3-C20}$	0.31
$LP1_{P1}$	$BD^{*}3_{C2-O2}$	0.29
$LP1_{P1}$	$BD^{*}1_{C2-O2}$	0.05
$BD^{*}1_{Fe1-Fe2}$	$BD^{*}1_{Fe2-S3}$	68.11
$LP2_{S2}$	$BD^{*}1_{Fe2-S3}$	29.33
$LP1_{C4}$	$BD^{*}1_{Fe2-S3}$	16.57
$BD1_{Fe1-Fe2}$	$BD^{*}1_{Fe2-S3}$	6.92
$BD1_{Fe1-S2}$	$BD^{*}1_{Fe2-S3}$	6.75
$LP2_{S1}$	$BD^{*}1_{Fe2-S3}$	3.35
$LP1_{S2}$	$BD^{*}1_{Fe2-S3}$	2.99
$BD1_{Fe2-C3}$	$BD^{*}1_{Fe2-S3}$	2.7
$LP1_{C2}$	$BD^{*}1_{Fe2-S3}$	1.44
$BD1_{Fe2-S3}$	$BD^{*}1_{Fe2-S3}$	1.2
$BD1_{Fe1-C1}$	$BD^{*}1_{Fe2-S3}$	0.96
$LP3_{S1}$	$BD^{*}1_{Fe2-S3}$	0.78
$BD^{*}1_{S2-C7}$	$BD^{*}1_{Fe2-S3}$	0.65
$LP1_{S1}$	$BD^{*}1_{Fe2-S3}$	0.65
$BD3_{C3-O3}$	$BD^{*}1_{Fe2-S3}$	0.59
$BD1_{S4-C20}$	$BD^{*}1_{Fe2-S3}$	0.35
$BD3_{C4-O4}$	$BD^{*}1_{Fe2-S3}$	0.33
$BD^{*}2_{C3-O3}$	$BD^{*}1_{Fe2-S3}$	0.27
$BD^{*}1_{C4-O4}$	$BD^{*}1_{Fe2-S3}$	0.25
$BD^{*}2_{C4-O4}$	$BD^{*}1_{Fe2-S3}$	0.11
$BD1_{C4-O4}$	$BD^{*}1_{Fe2-S3}$	0.11
$LP1_{O4}$	$BD^{*}1_{Fe2-S3}$	0.07
$BD^{*}2_{C2-O2}$	$BD^{*}1_{Fe2-S3}$	0.04
$BD^{*}1_{P1-C20}$	$BD^{*}1_{S3-C20}$	2.96
$LP1_{S4}$	$BD^{*}1_{S3-C20}$	2.85
$LP2_{S4}$	$BD^{*}1_{S3-C20}$	1.26
$BD^{*}1_{Fe2-S3}$	$BD^{*}1_{S3-C20}$	1.2
$BD1_{P1-C8}$	$BD^{*}1_{S3-C20}$	1.14

$BD^{*}1_{S4\text{-}C20}$	$BD^{*}1_{S3\text{-}C20}$	1.12
$BD^{*}1_{P1\text{-}C8}$	$BD^{*}1_{S3\text{-}C20}$	0.95
$BD1_{Fe2\text{-}S3}$	$BD^{*}1_{S3\text{-}C20}$	0.87
$LP1_{P1}$	$BD^{*}1_{S3\text{-}C20}$	0.75
$BD1_{P1\text{-}C14}$	$BD^{*}1_{S3\text{-}C20}$	0.67
$LP1_{C4}$	$BD^{*}1_{S3\text{-}C20}$	0.54
$BD^{*}1_{P1\text{-}C14}$	$BD^{*}1_{S3\text{-}C20}$	0.48
$LP2_{Fe2}$	$BD^{*}1_{S3\text{-}C20}$	0.31
$BD^{*}1_{C4\text{-}O4}$	$BD^{*}1_{S3\text{-}C20}$	0.13
$BD^{*}2_{C4\text{-}O4}$	$BD^{*}1_{S3\text{-}C20}$	0.09
$BD1_{C4\text{-}O4}$	$BD^{*}1_{S3\text{-}C20}$	0.03
$LP2_{S4}$	$BD^{*}2_{S3\text{-}C20}$	7.41
$BD1_{S4\text{-}C21}$	$BD^{*}2_{S3\text{-}C20}$	1.06
$BD1_{P1\text{-}C14}$	$BD^{*}2_{S3\text{-}C20}$	0.83
$LP1_{Fe2}$	$BD^{*}2_{S3\text{-}C20}$	0.79
$BD1_{P1\text{-}C8}$	$BD^{*}2_{S3\text{-}C20}$	0.67
$LP2_{S1}$	$BD^{*}2_{S3\text{-}C20}$	0.53
$LP1_{S4}$	$BD^{*}2_{S3\text{-}C20}$	0.41
$LP2_{Fe2}$	$BD^{*}2_{S3\text{-}C20}$	0.31
$LP1_{P1}$	$BD^{*}2_{S3\text{-}C20}$	0.31
$BD2_{C8\text{-}C9}$	$BD^{*}2_{S3\text{-}C20}$	0.29
$BD1_{Fe2\text{-}C3}$	$BD^{*}2_{S3\text{-}C20}$	0.26
$LP1_{C4}$	$BD^{*}2_{S3\text{-}C20}$	0.07
$LP1_{C2}$	$BD^{*}2_{S3\text{-}C20}$	0.05
$LP1_{P1}$	$BD^{*}1_{P1\text{-}C8}$	12.91
$BD1_{C12\text{-}C13}$	$BD^{*}1_{P1\text{-}C8}$	2.56
$BD1_{C9\text{-}C10}$	$BD^{*}1_{P1\text{-}C8}$	2.22
$BD1_{P1\text{-}C14}$	$BD^{*}1_{P1\text{-}C8}$	1.61
$BD1_{P1\text{-}C20}$	$BD^{*}1_{P1\text{-}C8}$	1.08
$BD1_{Fe1\text{-}Fe2}$	$BD^{*}1_{P1\text{-}C8}$	0.8
$BD2_{S3\text{-}C20}$	$BD^{*}1_{P1\text{-}C8}$	0.78
$BD1_{C8\text{-}C9}$	$BD^{*}1_{P1\text{-}C8}$	0.74
$BD1_{C8\text{-}C13}$	$BD^{*}1_{P1\text{-}C8}$	0.7
$BD1_{P1\text{-}C8}$	$BD^{*}1_{P1\text{-}C8}$	0.53

$BD1_{Fe1\text{-}C1}$	$BD^{*}1_{P1\text{-}C8}$	0.45
$BD1_{Fe2\text{-}S3}$	$BD^{*}1_{P1\text{-}C8}$	0.44
$BD^{*}2_{C14\text{-}C15}$	$BD^{*}1_{P1\text{-}C8}$	0.39
$BD1_{S3\text{-}C20}$	$BD^{*}1_{P1\text{-}C8}$	0.38
$BD^{*}2_{S3\text{-}C20}$	$BD^{*}1_{P1\text{-}C8}$	0.37
$LP2_{Fe1}$	$BD^{*}1_{P1\text{-}C8}$	0.37
$LP1_{C2}$	$BD^{*}1_{P1\text{-}C8}$	0.34
$BD^{*}1_{C1\text{-}O1}$	$BD^{*}1_{P1\text{-}C8}$	0.26
$BD^{*}2_{C2\text{-}O2}$	$BD^{*}1_{P1\text{-}C8}$	0.19
$LP1_{C4}$	$BD^{*}1_{P1\text{-}C8}$	0.05
$BD2_{C2\text{-}O2}$	$BD^{*}1_{P1\text{-}C8}$	0.03
$LP1_{P1}$	$BD^{*}1_{P1\text{-}C14}$	7.75
$BD1_{C15\text{-}C16}$	$BD^{*}1_{P1\text{-}C14}$	2.44
$BD1_{C18\text{-}C19}$	$BD^{*}1_{P1\text{-}C14}$	2.43
$BD1_{P1\text{-}C8}$	$BD^{*}1_{P1\text{-}C14}$	1.49
$LP1_{S1}$	$BD^{*}1_{P1\text{-}C14}$	1.41
$BD2_{S3\text{-}C20}$	$BD^{*}1_{P1\text{-}C14}$	1.37
$BD1_{P1\text{-}C20}$	$BD^{*}1_{P1\text{-}C14}$	1.21
$LP3_{S1}$	$BD^{*}1_{P1\text{-}C14}$	1.11
$BD1_{C14\text{-}C15}$	$BD^{*}1_{P1\text{-}C14}$	0.85
$BD1_{C14\text{-}C19}$	$BD^{*}1_{P1\text{-}C14}$	0.83
$LP1_{Fe1}$	$BD^{*}1_{P1\text{-}C14}$	0.8
$BD^{*}2_{S3\text{-}C20}$	$BD^{*}1_{P1\text{-}C14}$	0.62
$BD2_{C8\text{-}C9}$	$BD^{*}1_{P1\text{-}C14}$	0.55
$BD1_{P1\text{-}C14}$	$BD^{*}1_{P1\text{-}C14}$	0.54
$BD1_{Fe1\text{-}C1}$	$BD^{*}1_{P1\text{-}C14}$	0.51
$BD^{*}1_{S1\text{-}C5}$	$BD^{*}1_{P1\text{-}C14}$	0.48
$LP1_{C2}$	$BD^{*}1_{P1\text{-}C14}$	0.12
$BD^{*}1_{C2\text{-}O2}$	$BD^{*}1_{P1\text{-}C14}$	0.08
$LP1_{P1}$	$BD^{*}1_{P1\text{-}C20}$	10.68
$BD^{*}1_{S4\text{-}C20}$	$BD^{*}1_{P1\text{-}C20}$	8.78
$BD^{*}1_{Fe2\text{-}S3}$	$BD^{*}1_{P1\text{-}C20}$	5.4
$LP1_{S3}$	$BD^{*}1_{P1\text{-}C20}$	4.26
$LP2_{S4}$	$BD^{*}1_{P1\text{-}C20}$	2.74

$BD2_{C8\text{-}C9}$	$BD^{*}1_{P1\text{-}C20}$	1.54
$BD1_{S4\text{-}C21}$	$BD^{*}1_{P1\text{-}C20}$	1.36
$LP2_{Fe1}$	$BD^{*}1_{P1\text{-}C20}$	1.08
$BD1_{P1\text{-}C8}$	$BD^{*}1_{P1\text{-}C20}$	1.06
$BD1_{P1\text{-}C14}$	$BD^{*}1_{P1\text{-}C20}$	1.02
$BD1_{S3\text{-}C20}$	$BD^{*}1_{P1\text{-}C20}$	1.02
$BD^{*}2_{C8\text{-}C9}$	$BD^{*}1_{P1\text{-}C20}$	0.89
$LP1_{C2}$	$BD^{*}1_{P1\text{-}C20}$	0.87
$LP1_{S4}$	$BD^{*}1_{P1\text{-}C20}$	0.78
$BD1_{Fe1\text{-}Fe2}$	$BD^{*}1_{P1\text{-}C20}$	0.56
$BD^{*}1_{S1\text{-}C5}$	$BD^{*}1_{P1\text{-}C20}$	0.46
$BD1_{S4\text{-}C20}$	$BD^{*}1_{P1\text{-}C20}$	0.29
$LP1_{Fe1}$	$BD^{*}1_{P1\text{-}C20}$	0.26
$BD^{*}1_{C2\text{-}O2}$	$BD^{*}1_{P1\text{-}C20}$	0.1
$BD^{*}2_{C2\text{-}O2}$	$BD^{*}1_{P1\text{-}C20}$	0.09
$BD1_{C2\text{-}O2}$	$BD^{*}1_{P1\text{-}C20}$	0.03

Table S10. The stabilization energies between donors and acceptors of NBOs in complex [(μ-bdt)$Fe_2(CO)_5(PPh_2C_{60}(H))$] (**5**).

Donor (*i*)	Acceptor (*j*)	E^2, kcal/mol
$BD1_{P1\text{-}C12}$	$BD^{*}1_{C13\text{-}C14}$	3.89
$BD1_{P1\text{-}C12}$	$BD^{*}1_{C16\text{-}C17}$	3.63
$BD1_{P1\text{-}C12}$	$BD^{*}1_{C12\text{-}C17}$	1.69
$BD1_{P1\text{-}C12}$	$BD^{*}1_{C24\text{-}C25}$	1.68
$BD1_{P1\text{-}C12}$	$BD^{*}1_{C18\text{-}C23}$	1.6
$BD1_{P1\text{-}C12}$	$BD^{*}1_{C12\text{-}C13}$	1.43
$BD1_{P1\text{-}C12}$	$BD^{*}2_{C18\text{-}C23}$	1.02
$BD1_{P1\text{-}C12}$	$BD^{*}1_{P1\text{-}C24}$	0.66
$BD1_{P1\text{-}C12}$	$BD^{*}1_{Fe2\text{-}C5}$	0.64
$BD1_{P1\text{-}C12}$	$BD^{*}1_{P1\text{-}C18}$	0.57
$BD1_{P1\text{-}C12}$	$BD^{*}1_{Fe2\text{-}C4}$	0.49

$BD1_{P1-C12}$	$BD^*1_{Fe1-Fe2}$	0.25
$BD1_{P1-C12}$	BD^*2_{C4-O4}	0.09
$BD1_{P1-C18}$	$BD^*1_{C19-C20}$	3.96
$BD1_{P1-C18}$	$BD^*1_{C22-C23}$	3.49
$BD1_{P1-C18}$	$BD^*1_{C12-C13}$	2.24
$BD1_{P1-C18}$	$BD^*1_{C18-C23}$	1.94
$BD1_{P1-C18}$	$BD^*1_{C18-C19}$	1.2
$BD1_{P1-C18}$	$BD^*1_{C24-C29}$	0.84
$BD1_{P1-C18}$	BD^*1_{P1-C24}	0.8
$BD1_{P1-C18}$	BD^*1_{Fe2-C5}	0.41
$BD1_{P1-C18}$	BD^*1_{Fe2-C4}	0.23
$BD1_{P1-C18}$	LP^*4_{Fe2}	0.06
$BD1_{P1-C24}$	$BD^*2_{C28-C29}$	4.6
$BD1_{P1-C24}$	$BD^*2_{C53-C55}$	3.96
$BD1_{P1-C24}$	$BD^*2_{C12-C13}$	2.09
$BD1_{P1-C24}$	$BD^*1_{C18-C19}$	1.62
$BD1_{P1-C24}$	$BD^*1_{C25-C72}$	1.04
$BD1_{P1-C24}$	$BD^*1_{C25-H25}$	1
$BD1_{P1-C24}$	$BD^*1_{C25-C26}$	0.96
$BD1_{P1-C24}$	BD^*1_{P1-C18}	0.82
$BD1_{P1-C24}$	$BD^*1_{C28-C29}$	0.7
$BD1_{P1-C24}$	$BD^*1_{C53-C54}$	0.67
$BD1_{P1-C24}$	BD^*1_{Fe2-C4}	0.37
$BD1_{P1-C24}$	BD^*1_{Fe2-C5}	0.13
$BD1_{P1-C24}$	LP^*6_{Fe2}	0.1
$BD1_{P1-C24}$	BD^*2_{C4-O4}	0.06
$BD1_{P1-C24}$	BD^*1_{C4-O4}	0.05
BD^*1_{P1-D24}	$BD^*1_{C25-H25}$	0.92
BD^*1_{P1-D24}	BD^*1_{Fe2-C5}	0.49
BD^*1_{P1-D24}	LP^*6_{Fe2}	0.18
$LP1_{P1}$	$BD^*1_{Fe1-Fe2}$	54.92
$LP1_{P1}$	BD^*1_{Fe2-C5}	18.89
$LP1_{P1}$	BD^*1_{Fe2-C4}	17.68
$LP1_{P1}$	LP^*6_{Fe2}	12.83

$LP1_{P1}$	$BD^{*}2_{C18-C23}$	3.95
$LP1_{P1}$	$BD^{*}1_{C12-C17}$	3.46
$LP1_{P1}$	$BD^{*}1_{C24-C53}$	2.72
$LP1_{P1}$	$BD^{*}2_{C4-O4}$	2.64
$LP1_{P1}$	$BD^{*}2_{C5-O5}$	2.24
$LP1_{P1}$	$BD^{*}1_{C18-C23}$	1.8
$LP1_{P1}$	$BD^{*}1_{Fe1-C3}$	1.52
$LP1_{P1}$	$BD^{*}1_{Fe1-C2}$	1.5
$LP1_{P1}$	$BD^{*}1_{C4-O4}$	0.99
$LP1_{P1}$	$BD^{*}2_{C12-C13}$	0.77
$LP1_{P1}$	$BD^{*}3_{C4-O4}$	0.73
$LP1_{P1}$	$LP^{*}4_{Fe2}$	0.7
$LP1_{P1}$	$BD^{*}3_{C5-O5}$	0.69
$LP1_{P1}$	$BD^{*}1_{C5-O5}$	0.59
$LP1_{P1}$	$LP^{*}5_{Fe2}$	0.37
$LP1_{P1}$	$LP^{*}4_{Fe1}$	0.07
$BD1_{C16-C17}$	$BD^{*}1_{P1-C12}$	5.32
$BD1_{C13-C14}$	$BD^{*}1_{P1-C12}$	5.01
$BD2_{C18-C23}$	$BD^{*}1_{P1-C12}$	2.41
$LP2_{Fe2}$	$BD^{*}1_{P1-C12}$	2.18
$BD1_{C12-C13}$	$BD^{*}1_{P1-C12}$	1.97
$BD1_{C12-C17}$	$BD^{*}1_{P1-C12}$	1.85
$BD^{*}2_{C18-C23}$	$BD^{*}1_{P1-C12}$	1.34
$LP2_{S2}$	$BD^{*}1_{P1-C12}$	1.24
$BD1_{C25-H25}$	$BD^{*}1_{P1-C12}$	0.99
$LP2_{S1}$	$BD^{*}1_{P1-C12}$	0.55
$LP1_{S2}$	$BD^{*}1_{P1-C12}$	0.14
$BD^{*}1_{S2-C11}$	$BD^{*}1_{P1-C12}$	0.13
$BD1_{S1-C6}$	$BD^{*}1_{P1-C12}$	0.13
$BD^{*}2_{C4-O4}$	$BD^{*}1_{P1-C12}$	0.12
$BD^{*}1_{Fe1-Fe2}$	$BD^{*}1_{P1-C12}$	0.1
$BD^{*}1_{C5-O5}$	$BD^{*}1_{P1-C12}$	0.09
$BD1_{Fe2-C5}$	$BD^{*}1_{P1-C12}$	0.07
$BD1_{Fe2-C4}$	$BD^{*}1_{P1-C12}$	0.07

$LP3_{Fe2}$	BD^*1_{P1-C12}	0.07
BD^*2_{C5-O5}	BD^*1_{P1-C12}	0.07
BD^*2_{C10-C1}	BD^*1_{P1-C12}	0.06
$BD3_{C4-O4}$	BD^*1_{P1-C12}	0.06
$BD1_{C22-C23}$	BD^*1_{P1-C18}	5.59
$BD1_{C19-C20}$	BD^*1_{P1-C18}	4.75
$BD1_{Fe2-C5}$	BD^*1_{P1-C18}	4.23
$LP2_{Fe2}$	BD^*1_{P1-C18}	0.24
$BD1_{C18-C23}$	BD^*1_{P1-C18}	2.18
$BD1_{C18-C19}$	BD^*1_{P1-C18}	1.93
$LP1_{Fe2}$	BD^*1_{P1-C18}	1.38
$BD1_{P1-C24}$	BD^*1_{P1-C18}	0.82
$BD2_{C28-C29}$	BD^*1_{P1-C18}	0.74
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C18}	0.7
$BD1_{C24-C29}$	BD^*1_{P1-C18}	0.68
$BD^*2_{C28-C29}$	BD^*1_{P1-C18}	0.66
BD^*2_{C5-O5}	BD^*1_{P1-C18}	0.6
$BD1_{P1-C12}$	BD^*1_{P1-C18}	0.57
$BD1_{Fe2-C4}$	BD^*1_{P1-C18}	0.52
$BD1_{C13-H13}$	BD^*1_{P1-C18}	0.51
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C18}	0.23
$LP2_{S1}$	BD^*1_{P1-C18}	0.21
$BD3_{C5-O5}$	BD^*1_{P1-C18}	0.21
$LP1_{S1}$	BD^*1_{P1-C18}	0.11
BD^*1_{C4-O4}	BD^*1_{P1-C18}	0.11
$LP2_{S2}$	BD^*1_{P1-C18}	0.1
$BD3_{C5-O5}$	BD^*1_{P1-C18}	0.09
BD^*1_{C5-O5}	BD^*1_{P1-C18}	0.06
$BD1_{Fe2-C4}$	BD^*1_{P1-C24}	5.71
$BD^*2_{C53-C54}$	BD^*1_{P1-C24}	5.18
$BD2_{C12-C13}$	BD^*1_{P1-C24}	4.61
$BD2_{C53-C54}$	BD^*1_{P1-C24}	4.23
$BD^*2_{C12-C13}$	BD^*1_{P1-C24}	3.95
$BD^*2_{C48-C49}$	BD^*1_{P1-C24}	3.86

BD*1$_{Fe1-Fe2}$	BD*1$_{P1-C24}$	3.32
BD2$_{C28-C29}$	BD*1$_{P1-C24}$	3.26
LP1$_{Fe2}$	BD*1$_{P1-C24}$	1.82
BD1$_{C24-C29}$	BD*1$_{P1-C24}$	1.32
BD1$_{C25-C72}$	BD*1$_{P1-C24}$	1.31
BD1$_{C24-C53}$	BD*1$_{P1-C24}$	1.24
BD1$_{C25-C26}$	BD*1$_{P1-C24}$	1.19
LP2$_{S1}$	BD*1$_{P1-C24}$	1.15
BD1$_{C52-C53}$	BD*1$_{P1-C24}$	1.13
BD*2$_{C18-C23}$	BD*1$_{P1-C24}$	1.02
BD*2$_{C4-O4}$	BD*1$_{P1-C24}$	1.02
BD1$_{C29-C30}$	BD*1$_{P1-C24}$	1
BD1$_{C53-C54}$	BD*1$_{P1-C24}$	0.87
BD1$_{P1-C18}$	BD*1$_{P1-C24}$	0.8
BD1$_{C19-H19}$	BD*1$_{P1-C24}$	0.79
BD1$_{C24-C25}$	BD*1$_{P1-C24}$	0.75
BD1$_{C28-C29}$	BD*1$_{P1-C24}$	0.75
BD1$_{C18-C19}$	BD*1$_{P1-C24}$	0.69
BD*1$_{C4-O4}$	BD*1$_{P1-C24}$	0.67
BD1$_{P1-C12}$	BD*1$_{P1-C24}$	0.66
BD1$_{Fe1-Fe2}$	BD*1$_{P1-C24}$	0.57
BD3$_{C4-O4}$	BD*1$_{P1-C24}$	0.33
BD1$_{Fe2-C5}$	BD*1$_{P1-C24}$	0.28
LP2$_{Fe2}$	BD*1$_{P1-C24}$	0.45
BD*1$_{C5-O5}$	BD*1$_{P1-C24}$	0.11
LP1$_{O4}$	BD*1$_{P1-C24}$	0.08
BD1$_{S1-C6}$	BD*1$_{P1-C24}$	0.08
BD2$_{C4-O4}$	BD*1$_{P1-C24}$	0.06
LP1$_{S2}$	BD*1$_{P1-C24}$	0.05
BD*2$_{C5-O5}$	BD*1$_{P1-C24}$	0.05
LP1$_{S1}$	BD*1$_{P1-C24}$	0.23

Table S11. The stabilization energies between donors and acceptors of alpha NBOs in complex [(μ-bdt)$Fe_2(CO)_5(PPh_2C_{60}(H))]^-$ (**5**$^-$).

Donor (i)	Acceptor (j)	E^2, kcal/mol
$BD1_{P1-C12}$	$BD^*1_{C13-C14}$	1.97
$BD1_{P1-C12}$	$BD^*1_{C16-C17}$	1.84
$BD1_{P1-C12}$	$BD^*1_{C12-C17}$	0.84
$BD1_{P1-C12}$	$BD^*1_{C24-C25}$	0.82
$BD1_{P1-C12}$	$BD^*1_{C18-C23}$	0.76
$BD1_{P1-C12}$	$BD^*1_{C12-C13}$	0.73
$BD1_{P1-C12}$	$BD^*2_{C18-C19}$	0.48
$BD1_{P1-C12}$	BD^*1_{Fe2-C5}	0.3
$BD1_{P1-C12}$	BD^*1_{P1-C24}	0.29
$BD1_{P1-C12}$	BD^*1_{P1-C18}	0.28
$BD1_{P1-C12}$	BD^*1_{Fe2-C4}	0.23
$BD1_{P1-C12}$	$BD^*1_{Fe1-Fe2}$	0.12
$BD1_{P1-C12}$	BD^*2_{C4-O4}	0.05
$BD1_{P1-C18}$	$BD^*1_{C19-C20}$	2
$BD1_{P1-C18}$	$BD^*1_{C22-C23}$	1.77
$BD1_{P1-C18}$	$BD^*1_{C12-C13}$	1.12
$BD1_{P1-C18}$	$BD^*1_{C18-C23}$	0.97
$BD1_{P1-C18}$	$BD^*1_{C18-C19}$	0.61
$BD1_{P1-C18}$	$BD^*1_{C24-C29}$	0.41
$BD1_{P1-C18}$	BD^*1_{P1-C24}	0.37
$BD1_{P1-C18}$	BD^*1_{Fe2-C5}	0.2
$BD1_{P1-C18}$	BD^*1_{Fe2-C4}	0.11
$BD1_{P1-C18}$	LP^*4_{Fe2}	0.03
$BD1_{P1-C24}$	$BD^*2_{C28-C29}$	2.16
$BD1_{P1-C24}$	$BD^*2_{C53-C54}$	1.85
$BD1_{P1-C24}$	$BD^*2_{C12-C13}$	1.05
$BD1_{P1-C24}$	$BD^*1_{C18-C19}$	0.84
$BD1_{P1-C24}$	$BD^*1_{C25-C72}$	0.51
$BD1_{P1-C24}$	$BD^*1_{C25-H25}$	0.49
$BD1_{P1-C24}$	$BD^*1_{C25-C26}$	0.47
$BD1_{P1-C24}$	BD^*1_{P1-C18}	0.4

$BD1_{P1-C24}$	$BD^*1_{C28-C29}$	0.33
$BD1_{P1-C24}$	$BD^*1_{C53-C54}$	0.31
$BD1_{P1-C24}$	BD^*1_{Fe2-C4}	0.19
$BD1_{P1-C24}$	BD^*1_{Fe2-C5}	0.06
$BD1_{P1-C24}$	LP^*6_{Fe2}	0.04
$BD1_{P1-C24}$	BD^*1_{C4-O4}	0.03
$BD1_{P1-C24}$	BD^*2_{C4-O4}	0.03
$LP1_{P1}$	$BD^*1_{Fe1-Fe2}$	26.81
$LP1_{P1}$	BD^*1_{Fe2-C5}	9.17
$LP1_{P1}$	BD^*1_{Fe2-C4}	8.61
$LP1_{P1}$	LP^*6_{Fe2}	5.85
$LP1_{P1}$	$BD^*2_{C18-C19}$	1.73
$LP1_{P1}$	$BD^*1_{C12-C17}$	1.71
$LP1_{P1}$	$BD^*1_{C24-C53}$	1.35
$LP1_{P1}$	BD^*2_{C4-O4}	1.32
$LP1_{P1}$	BD^*2_{C5-O5}	0.99
$LP1_{P1}$	$BD^*1_{C18-C23}$	0.98
$LP1_{P1}$	BD^*1_{Fe1-S1}	0.49
$LP1_{P1}$	BD^*1_{C4-O4}	0.47
$LP1_{P1}$	BD^*1_{Fe1-S2}	0.47
$LP1_{P1}$	LP^*5_{Fe2}	0.44
$LP1_{P1}$	$BD^*2_{C12-C13}$	0.41
$LP1_{P1}$	BD^*1_{C5-O5}	0.39
$LP1_{P1}$	BD^*3_{C4-O4}	0.37
$LP1_{P1}$	BD^*3_{C5-O5}	0.36
$LP1_{P1}$	LP^*4_{Fe2}	0.36
$LP1_{P1}$	$LP4_{Fe1}$	0.16
$LP1_{P1}$	LP^*6_{Fe1}	0.15
BD^*1_{P1-C24}	$BD^*1_{C25-H25}$	0.45
BD^*1_{P1-C24}	BD^*1_{Fe2-C5}	0.24
BD^*1_{P1-C24}	LP^*6_{Fe2}	0.08
$BD1_{C16-C17}$	BD^*1_{P1-C12}	2.63
$BD1_{C13-C14}$	BD^*1_{P1-C12}	2.48
$LP2_{Fe2}$	BD^*1_{P1-C12}	1.04

$BD1_{C12-C13}$	BD^*1_{P1-C12}	0.99
$BD2_{C18-C19}$	BD^*1_{P1-C12}	0.97
$BD1_{C12-C17}$	BD^*1_{P1-C12}	0.93
$BD^*2_{C18-C19}$	BD^*1_{P1-C12}	0.91
$LP2_{S2}$	BD^*1_{P1-C12}	0.6
$BD1_{C25-H25}$	BD^*1_{P1-C12}	0.54
$LP2_{S1}$	BD^*1_{P1-C12}	0.25
$LP1_{S2}$	BD^*1_{P1-C12}	0.07
$BD1_{S2-C11}$	BD^*1_{P1-C12}	0.07
BD^*2_{C4-O4}	BD^*1_{P1-C12}	0.06
$BD1_{S1-C6}$	BD^*1_{P1-C12}	0.06
BD^*1_{C5-O5}	BD^*1_{P1-C12}	0.04
BD^*2_{C5-O5}	BD^*1_{P1-C12}	0.04
$BD1_{Fe2-C4}$	BD^*1_{P1-C12}	0.04
$LP3_{Fe2}$	BD^*1_{P1-C12}	0.03
BD^*2_{C6-C7}	BD^*1_{P1-C12}	0.03
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C12}	0.03
$BD1_{Fe2-C5}$	BD^*1_{P1-C12}	0.03
$BD^*2_{C10-C11}$	BD^*1_{P1-C12}	0.03
$BD3_{C4-O4}$	BD^*1_{P1-C12}	0.03
$BD1_{C22-C23}$	BD^*1_{P1-C18}	2.77
$BD1_{C19-C20}$	BD^*1_{P1-C18}	2.35
$BD1_{Fe2-C5}$	BD^*1_{P1-C18}	2.05
$BD1_{C18-C23}$	BD^*1_{P1-C18}	1.08
$BD1_{C18-C19}$	BD^*1_{P1-C18}	0.96
$LP1_{Fe2}$	BD^*1_{P1-C18}	0.65
$BD^*2_{C28-C29}$	BD^*1_{P1-C18}	0.43
$BD1_{P1-C24}$	BD^*1_{P1-C18}	0.4
$BD1_{C24-C29}$	BD^*1_{P1-C18}	0.39
$BD2_{C28-C29}$	BD^*1_{P1-C18}	0.38
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C18}	0.32
$BD1_{P1-C12}$	BD^*1_{P1-C18}	0.28
BD^*2_{C5-O5}	BD^*1_{P1-C18}	0.26
$BD1_{Fe2-C4}$	BD^*1_{P1-C18}	0.23

$LP2_{Fe2}$	$BD^{*}1_{P1-C18}$	0.12
$LP2_{S1}$	$BD^{*}1_{P1-C18}$	0.11
$BD1_{Fe1-Fe2}$	$BD^{*}1_{P1-C18}$	0.11
$BD3_{C5-O5}$	$BD^{*}1_{P1-C18}$	0.1
$LP1_{S1}$	$BD^{*}1_{P1-C18}$	0.06
$LP2_{S2}$	$BD^{*}1_{P1-C18}$	0.05
$BD^{*}1_{Fe1-S1}$	$BD^{*}1_{P1-C18}$	0.05
$BD^{*}1_{C4-O4}$	$BD^{*}1_{P1-C18}$	0.05
$BD^{*}1_{C5-O5}$	$BD^{*}1_{P1-C18}$	0.05
$BD2_{C5-O5}$	$BD^{*}1_{P1-C18}$	0.05
$BD^{*}2_{C53-C54}$	$BD^{*}1_{P1-C24}$	3.17
$BD1_{Fe2-C4}$	$BD^{*}1_{P1-C24}$	2.77
$BD^{*}2_{C28-C29}$	$BD^{*}1_{P1-C24}$	2.38
$BD2_{C12-C13}$	$BD^{*}1_{P1-C24}$	2.18
$BD2_{C53-C54}$	$BD^{*}1_{P1-C24}$	2.17
$BD^{*}2_{C12-C13}$	$BD^{*}1_{P1-C24}$	1.8
$BD2_{C28-C29}$	$BD^{*}1_{P1-C24}$	1.69
$BD^{*}1_{Fe1-Fe2}$	$BD^{*}1_{P1-C24}$	1.24
$LP1_{Fe2}$	$BD^{*}1_{P1-C24}$	0.85
$BD1_{C25-C72}$	$BD^{*}1_{P1-C24}$	0.66
$BD1_{C24-C29}$	$BD^{*}1_{P1-C24}$	0.63
$BD1_{C24-C53}$	$BD^{*}1_{P1-C24}$	0.6
$BD1_{C44-C46}$	$BD^{*}1_{P1-C24}$	0.6
$BD1_{C52-C53}$	$BD^{*}1_{P1-C24}$	0.58
$LP2_{S1}$	$BD^{*}1_{P1-C24}$	0.54
$BD2_{C29-C30}$	$BD^{*}1_{P1-C24}$	0.51
$BD^{*}2_{C4-O4}$	$BD^{*}1_{P1-C24}$	0.46
$BD1_{C53-C54}$	$BD^{*}1_{P1-C24}$	0.44
$BD1_{C19-H19}$	$BD^{*}1_{P1-C24}$	0.39
$BD1_{C28-C29}$	$BD^{*}1_{P1-C24}$	0.38
$BD1_{P1-C18}$	$BD^{*}1_{P1-C24}$	0.37
$BD1_{C18-C19}$	$BD^{*}1_{P1-C24}$	0.34
$BD1_{C24-C25}$	$BD^{*}1_{P1-C24}$	0.34
$BD2_{C18-C19}$	$BD^{*}1_{P1-C24}$	0.32

$BD1_{Fe1-Fe2}$	BD^*1_{P1-C24}	0.3
$BD1_{P1-C12}$	BD^*1_{P1-C24}	0.29
BD^*1_{C4-O4}	BD^*1_{P1-C24}	0.28
$LP2_{Fe2}$	BD^*1_{P1-C24}	0.17
$BD3_{C4-O4}$	BD^*1_{P1-C24}	0.16
$BD1_{Fe2-C5}$	BD^*1_{P1-C24}	0.15
BD^*1_{Fe1-S2}	BD^*1_{P1-C24}	0.2
$LP1_{S1}$	BD^*1_{P1-C24}	0.11
BD^*1_{C5-O5}	BD^*1_{P1-C24}	0.06
$LP1_{O4}$	BD^*1_{P1-C24}	0.04
$BD1_{S1-C6}$	BD^*1_{P1-C24}	0.04
$BD2_{C4-O4}$	BD^*1_{P1-C24}	0.03
BD^*1_{Fe1-S1}	BD^*1_{P1-C24}	0.03

Table S12. The stabilization energies between donors and acceptors of beta NBOs in complex $[(\mu\text{-bdt})Fe_2(CO)_5(PPh_2C_{60}(H))]^-$ (**5**$^-$).

Donor (*i*)	Acceptor (*j*)	E^2, kcal/mol
$BD1_{P1-C12}$	$BD^*1_{C13-C14}$	1.97
$BD1_{P1-C12}$	$BD^*1_{C16-C17}$	1.84
$BD1_{P1-C12}$	$BD^*1_{C12-C17}$	0.84
$BD1_{P1-C12}$	$BD^*1_{C24-C25}$	0.82
$BD1_{P1-C12}$	$BD^*1_{C18-C23}$	0.76
$BD1_{P1-C12}$	$BD^*1_{C12-C13}$	0.73
$BD1_{P1-C12}$	$BD^*2_{C18-C19}$	0.48
$BD1_{P1-C12}$	BD^*1_{P1-C24}	0.3
$BD1_{P1-C12}$	BD^*1_{Fe2-C5}	0.3
$BD1_{P1-C12}$	BD^*1_{P1-C18}	0.28
$BD1_{P1-C12}$	BD^*1_{Fe2-C4}	0.23
$BD1_{P1-C12}$	$BD^*1_{Fe1-Fe2}$	0.12
$BD1_{P1-C12}$	BD^*2_{C4-O4}	0.05
$BD1_{P1-C18}$	$BD^*1_{C19-C20}$	2

$BD1_{P1-C18}$	$BD^*1_{C22-C23}$	1.77
$BD1_{P1-C18}$	$BD^*1_{C12-C13}$	1.12
$BD1_{P1-C18}$	$BD^*1_{C18-C23}$	0.97
$BD1_{P1-C18}$	$BD^*1_{C18-C19}$	0.61
$BD1_{P1-C18}$	$BD^*1_{C24-C29}$	0.42
$BD1_{P1-C18}$	BD^*1_{P1-C24}	0.37
$BD1_{P1-C18}$	BD^*1_{Fe2-C5}	0.2
$BD1_{P1-C18}$	BD^*1_{Fe2-C4}	0.11
$BD1_{P1-C18}$	LP^*4_{Fe2}	0.03
$BD1_{P1-C24}$	$BD^*2_{C28-C29}$	2.11
$BD1_{P1-C24}$	$BD^*2_{C53-C54}$	1.81
$BD1_{P1-C24}$	$BD^*2_{C12-C13}$	1.04
$BD1_{P1-C24}$	$BD^*1_{C18-C19}$	0.84
$BD1_{P1-C24}$	$BD^*1_{C25-C72}$	0.51
$BD1_{P1-C24}$	$BD^*1_{C25-H25}$	0.49
$BD1_{P1-C24}$	$BD^*1_{C25-C26}$	0.47
$BD1_{P1-C24}$	BD^*1_{P1-C18}	0.4
$BD1_{P1-C24}$	$BD^*1_{C28-C29}$	0.34
$BD1_{P1-C24}$	$BD^*1_{C53-C54}$	0.32
$BD1_{P1-C24}$	BD^*1_{Fe2-C4}	0.19
$BD1_{P1-C24}$	BD^*1_{Fe2-C5}	0.06
$BD1_{P1-C24}$	LP^*6_{Fe2}	0.04
$BD1_{P1-C24}$	BD^*1_{C4-O4}	0.03
$BD1_{P1-C24}$	BD^*2_{C4-O4}	0.03
$LP1_{P1}$	$BD^*1_{Fe1-Fe2}$	26.79
$LP1_{P1}$	BD^*1_{Fe2-C5}	9.17
$LP1_{P1}$	BD^*1_{Fe2-C4}	8.61
$LP1_{P1}$	LP^*6_{Fe2}	5.85
$LP1_{P1}$	$BD^*2_{C18-C19}$	1.73
$LP1_{P1}$	$BD^*1_{C12-C17}$	1.71
$LP1_{P1}$	$BD^*1_{C24-C53}$	1.36
$LP1_{P1}$	BD^*2_{C4-O4}	1.32
$LP1_{P1}$	BD^*2_{C5-O5}	1
$LP1_{P1}$	$BD^*1_{C18-C23}$	0.98

LP1$_{P1}$	BD*$_{Fe1-S1}$	0.49
LP1$_{P1}$	BD*1$_{Fe1-S2}$	0.47
LP1$_{P1}$	BD*1$_{C4-O4}$	0.47
LP1$_{P1}$	LP*5$_{Fe2}$	0.44
LP1$_{P1}$	BD*2$_{C12-C13}$	0.41
LP1$_{P1}$	BD*1$_{C5-O5}$	0.38
LP1$_{P1}$	BD*3$_{C4-O4}$	0.37
LP1$_{P1}$	LP*4$_{Fe2}$	0.35
LP1$_{P1}$	BD*3$_{C5-O5}$	0.35
LP1$_{P1}$	LP4$_{Fe1}$	0.16
LP1$_{P1}$	LP*6$_{Fe1}$	0.15
BD*1$_{P1-C12}$	BD*1$_{P1-C18}$	2.12
BD*1$_{P1-C12}$	BD*1$_{Fe2-C4}$	0.37
BD*1$_{P1-C12}$	BD*1$_{C13-H13}$	0.34
BD*1$_{P1-C12}$	BD*1$_{C17-H17}$	0.32
BD*1$_{P1-C12}$	BD*1$_{Fe2-C5}$	0.18
BD*1$_{P1-C12}$	LP*6$_{Fe2}$	0.05
BD*1$_{P1-C12}$	LP*4$_{Fe2}$	0.03
BD*1$_{P1-C18}$	BD*1$_{C19-H19}$	0.36
BD*1$_{P1-C18}$	BD*1$_{C23-H23}$	0.33
BD*1$_{P1-C18}$	BD*1$_{Fe2-C4}$	0.15
BD*1$_{P1-C18}$	LP*6$_{Fe2}$	0.06
BD*1$_{P1-C24}$	BD*1$_{C25-H25}$	0.45
BD*1$_{P1-C24}$	BD*1$_{Fe2-C5}$	0.24
BD*1$_{P1-C24}$	LP*6$_{Fe2}$	0.08
BD1$_{C16-C17}$	BD*1$_{P1-C12}$	2.63
BD1$_{C13-C14}$	BD*1$_{P1-C12}$	2.48
BD2$_{C12-C13}$	BD*1$_{P1-C12}$	2.18
LP2$_{Fe2}$	BD*1$_{P1-C12}$	1.04
BD1$_{C12-C13}$	BD*1$_{P1-C12}$	0.99
BD2$_{C18-C19}$	BD*1$_{P1-C12}$	0.97
BD1$_{C12-C17}$	BD*1$_{P1-C12}$	0.93
BD*2$_{C18-C19}$	BD*1$_{P1-C12}$	0.9
BD1$_{C25-H25}$	BD*1$_{P1-C12}$	0.53

$LP2_{S1}$	BD^*1_{P1-C12}	0.25
$BD1_{S2-C11}$	BD^*1_{P1-C12}	0.07
$LP1_{S2}$	BD^*1_{P1-C12}	0.07
$LP2_{S2}$	BD^*1_{P1-C12}	0.6
BD^*2_{C4-O4}	BD^*1_{P1-C12}	0.06
$BD1_{S1-C6}$	BD^*1_{P1-C12}	0.06
BD^*1_{C5-O5}	BD^*1_{P1-C12}	0.04
BD^*2_{C5-O5}	BD^*1_{P1-C12}	0.04
$BD1_{Fe2-C4}$	BD^*1_{P1-C12}	0.04
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C12}	0.03
$BD1_{Fe2-C5}$	BD^*1_{P1-C12}	0.03
$LP3_{Fe2}$	BD^*1_{P1-C12}	0.03
BD^*2_{C6-C7}	BD^*1_{P1-C12}	0.03
$BD^*2_{C10-C11}$	BD^*1_{P1-C12}	0.03
$BD1_{C22-C23}$	BD^*1_{P1-C18}	2.77
$BD1_{C19-C20}$	BD^*1_{P1-C18}	2.35
BD^*1_{P1-C12}	BD^*1_{P1-C18}	2.12
$BD1_{Fe2-C5}$	BD^*1_{P1-C18}	2.05
$BD1_{C18-C23}$	BD^*1_{P1-C18}	1.08
$BD1_{C18-C19}$	BD^*1_{P1-C18}	0.96
$LP1_{Fe2}$	BD^*1_{P1-C18}	0.67
$BD2_{C28-C29}$	BD^*1_{P1-C18}	0.41
$BD1_{P1-C24}$	BD^*1_{P1-C18}	0.4
$BD1_{C24-C29}$	BD^*1_{P1-C18}	0.39
$BD^*2_{C28-C29}$	BD^*1_{P1-C18}	0.38
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C18}	0.32
$BD1_{P1-C12}$	BD^*1_{P1-C18}	0.28
BD^*2_{C5-O5}	BD^*1_{P1-C18}	0.26
$BD1_{Fe2-C4}$	BD^*1_{P1-C18}	0.23
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C18}	0.11
$LP2_{S1}$	BD^*1_{P1-C18}	0.11
$LP2_{Fe2}$	BD^*1_{P1-C18}	0.1
BD^*3_{C5-O5}	BD^*1_{P1-C18}	0.1
$LP2_{S2}$	BD^*1_{P1-C18}	0.05

$LP1_{S1}$	BD^*1_{P1-C18}	0.06
BD^*1_{C4-O4}	BD^*1_{P1-C18}	0.05
$BD2_{C5-O5}$	BD^*1_{P1-C18}	0.05
BD^*1_{Fe1-S1}	BD^*1_{P1-C18}	0.05
BD^*1_{C5-O5}	BD^*1_{P1-C18}	0.05
$BD^*2_{C53-C54}$	BD^*1_{P1-C24}	2.78
$BD1_{Fe2-C4}$	BD^*1_{P1-C24}	2.78
$BD2_{C53-C54}$	BD^*1_{P1-C24}	2.24
$BD2_{C12-C13}$	BD^*1_{P1-C24}	2.18
$BD^*2_{C28-C29}$	BD^*1_{P1-C24}	2.09
$BD^*2_{C12-C13}$	BD^*1_{P1-C24}	1.8
$BD2_{C28-C29}$	BD^*1_{P1-C24}	1.75
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C24}	1.24
$LP1_{Fe2}$	BD^*1_{P1-C24}	0.82
$BD1_{C25-C26}$	BD^*1_{P1-C24}	0.66
$BD1_{C24-C29}$	BD^*1_{P1-C24}	0.63
$BD1_{C24-C53}$	BD^*1_{P1-C24}	0.6
$BD1_{C25-C26}$	BD^*1_{P1-C24}	0.6
$BD1_{C52-C53}$	BD^*1_{P1-C24}	0.58
$LP2_{S1}$	BD^*1_{P1-C24}	0.54
$BD1_{C29-C30}$	BD^*1_{P1-C24}	0.51
BD^*2_{C4-O4}	BD^*1_{P1-C24}	0.45
$BD1_{C53-C54}$	BD^*1_{P1-C24}	0.45
$BD1_{C19-H19}$	BD^*1_{P1-C24}	0.39
$BD^*1_{C28-C29}$	BD^*1_{P1-C24}	0.39
$BD1_{P1-C18}$	BD^*1_{P1-C24}	0.37
$BD1_{C18-C19}$	BD^*1_{P1-C24}	0.34
$BD1_{C24-C25}$	BD^*1_{P1-C24}	0.34
$BD2_{C18-C19}$	BD^*1_{P1-C24}	0.32
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C24}	0.3
$BD1_{P1-C12}$	BD^*1_{P1-C24}	0.3
BD^*1_{C4-O4}	BD^*1_{P1-C24}	0.27
BD^*1_{Fe1-S2}	BD^*1_{P1-C24}	0.2
$LP2_{Fe2}$	BD^*1_{P1-C24}	0.19

$BD3_{C4-O4}$	$BD^{*}1_{P1-C24}$	0.16
$BD1_{Fe2-C5}$	$BD^{*}1_{P1-C24}$	0.15
$LP1_{S1}$	$BD^{*}1_{P1-C24}$	0.11
$BD^{*}1_{C5-O5}$	$BD^{*}1_{P1-C24}$	0.05
$BD1_{S1-C6}$	$BD^{*}1_{P1-C24}$	0.04
$LP1_{O4}$	$BD^{*}1_{P1-C24}$	0.04
$BD2_{C4-O4}$	$BD^{*}1_{P1-C24}$	0.03
$BD^{*}1_{Fe1-S1}$	$BD^{*}1_{P1-C24}$	0.03

Table S13. The stabilization energies between donors and acceptors of NBOs in complex [(μ-pdt)$Fe_2(CO)_5$(mppf)] (**6**).

Donor (*i*)	Acceptor (*j*)	E^2, kcal/mol
$BD1_{P1-C9}$	$BD^{*}1_{C9-C13}$	2
$BD1_{P1-C9}$	$BD^{*}1_{C19-C24}$	1.93
$BD1_{P1-C9}$	$BD^{*}1_{C9-C10}$	1.91
$BD1_{P1-C9}$	$BD^{*}1_{C12-C13}$	1.69
$BD1_{P1-C9}$	$BD^{*}1_{C10-C1}$	1.67
$BD1_{P1-C9}$	$BD^{*}2_{C25-C30}$	1.49
$BD1_{P1-C9}$	$BD^{*}1_{P1-C19}$	0.53
$BD1_{P1-C9}$	$BD^{*}1_{Fe2-C4}$	0.43
$BD1_{P1-C9}$	$LP^{*}6_{Fe3}$	0.51
$BD1_{P1-C9}$	$BD^{*}1_{Fe2-C5}$	0.22
$BD1_{P1-C9}$	$LP^{*}9_{Fe3}$	0.16
$BD1_{P1-C9}$	$BD^{*}1_{Fe1-Fe2}$	0.05
$BD1_{P1-C19}$	$BD^{*}1_{C23-C24}$	3.88
$BD1_{P1-C19}$	$BD^{*}1_{C20-C21}$	3.6
$BD1_{P1-C19}$	$BD^{*}2_{C9-C10}$	2.18
$BD1_{P1-C19}$	$BD^{*}1_{C25-C30}$	2.1
$BD1_{P1-C19}$	$BD^{*}1_{C19-C20}$	1.46
$BD1_{P1-C19}$	$BD^{*}1_{C19-C24}$	1.07
$BD1_{P1-C19}$	$BD^{*}1_{C9-C10}$	0.6

$BD1_{P1-C19}$	$BD^*1_{C24-H24}$	0.55
$BD1_{P1-C19}$	$BD^*1_{C20-H20}$	0.53
$BD1_{P1-C19}$	BD^*1_{Fe2-C5}	0.47
$BD1_{P1-C19}$	BD^*1_{Fe2-C4}	0.28
$BD1_{P1-C19}$	LP^*9_{Fe3}	0.09
$BD1_{P1-C19}$	LP^*6_{Fe3}	0.08
$BD1_{P1-C19}$	$BD^*1_{Fe1-Fe2}$	0.07
$BD1_{P1-C25}$	$BD^*1_{C29-C30}$	3.92
$BD1_{P1-C25}$	$BD^*1_{C26-C27}$	3.69
$BD1_{P1-C25}$	BD^*1_{C9-C10}	2.39
$BD1_{P1-C25}$	$BD^*1_{C25-C26}$	1.36
$BD1_{P1-C25}$	$BD^*1_{C19-C20}$	1.26
$BD1_{P1-C25}$	$BD^*2_{C19-C20}$	1.24
$BD1_{P1-C25}$	$BD^*1_{C25-C30}$	1.18
$BD1_{P1-C25}$	BD^*1_{Fe2-C5}	0.58
$BD1_{P1-C25}$	BD^*1_{P1-C19}	0.57
$BD1_{P1-C25}$	$BD^*1_{C26-H26}$	0.54
$BD1_{P1-C25}$	BD^*1_{Fe2-C4}	0.44
$BD1_{P1-C25}$	$BD^*1_{Fe1-Fe2}$	0.24
$BD1_{P1-C25}$	BD^*2_{C4-O4}	0.09
$LP1_{P1}$	$BD^*1_{Fe1-Fe2}$	59.81
$LP1_{P1}$	BD^*1_{Fe2-C5}	19.34
$LP1_{P1}$	BD^*1_{Fe2-C4}	17.75
$LP1_{P1}$	LP^*6_{Fe2}	13.3
$LP1_{P1}$	BD^*1_{C9-C13}	5.26
$LP1_{P1}$	$BD^*2_{C19-C20}$	3.74
$LP1_{P1}$	$BD^*1_{C25-C26}$	3.24
$LP1_{P1}$	BD^*2_{C4-O4}	2.13
$LP1_{P1}$	$BD^*1_{C19-C20}$	2.04
$LP1_{P1}$	BD^*2_{C5-O5}	1.79
$LP1_{P1}$	BD^*1_{C4-O4}	1.7
$LP1_{P1}$	BD^*1_{Fe1-C3}	1.67
$LP1_{P1}$	BD^*1_{Fe1-C2}	1.66
$LP1_{P1}$	LP^*4_{Fe2}	1.49

$LP1_{P1}$	BD^*3_{C5-O5}	1.02
$LP1_{P1}$	$BD^*2_{C25-C30}$	0.9
$LP1_{P1}$	BD^*3_{C4-O4}	0.86
$LP1_{P1}$	BD^*1_{C5-O5}	0.52
$LP1_{P1}$	LP^*6_{Fe3}	0.1
$LP1_{P1}$	LP^*9_{Fe3}	0.07
$LP1_{P1}$	LP^*4_{Fe1}	0.06
$BD1_{C10-C11}$	BD^*1_{P1-C9}	6.65
$BD1_{C12-C13}$	BD^*1_{P1-C9}	6.59
$BD1_{Fe2-C4}$	BD^*1_{P1-C9}	4.3
$BD1_{C25-C30}$	BD^*1_{P1-C9}	3.31
$BD1_{C9-C10}$	BD^*1_{P1-C9}	2.57
$LP1_{C13}$	BD^*1_{P1-C9}	2.47
$BD1_{C9-C13}$	BD^*1_{P1-C9}	2.29
$LP1_{Fe2}$	BD^*1_{P1-C9}	1.52
$BD^*2_{C25-C30}$	BD^*1_{P1-C9}	1.86
$BD1_{C11-C12}$	BD^*1_{P1-C9}	0.86
BD^*2_{C9-C10}	BD^*1_{P1-C9}	0.79
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C9}	0.7
$BD2_{C9-C10}$	BD^*1_{P1-C9}	0.59
$LP1_{Fe3}$	BD^*1_{P1-C9}	0.55
$LP2_{S1}$	BD^*1_{P1-C9}	0.55
$BD2_{C11-C12}$	BD^*1_{P1-C9}	0.52
$BD1_{C24-H24}$	BD^*1_{P1-C9}	0.5
BD^*1_{C4-O4}	BD^*1_{P1-C9}	0.36
BD^*2_{C4-O4}	BD^*1_{P1-C9}	0.33
$BD3_{C4-O4}$	BD^*1_{P1-C9}	0.26
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C9}	0.2
$BD2_{C16-C17}$	BD^*1_{P1-C9}	0.18
$LP3_{Fe3}$	BD^*1_{P1-C9}	0.17
$LP2_{Fe2}$	BD^*1_{P1-C9}	0.16
$BD2_{C14-C15}$	BD^*1_{P1-C9}	0.15
$BD1_{Fe2-C5}$	BD^*1_{P1-C9}	0.15
$LP1_{S1}$	BD^*1_{P1-C9}	0.14

$LP2_{S2}$	$BD^{*}1_{P1-C9}$	0.08
$BD2_{C4-O4}$	$BD^{*}1_{P1-C9}$	0.08
$BD^{*}1_{C5-O5}$	$BD^{*}1_{P1-C9}$	0.06
$LP1_{O5}$	$BD^{*}1_{P1-C9}$	0.06
$BD1_{C20-C21}$	$BD^{*}1_{P1-C19}$	5.07
$BD1_{C23-C24}$	$BD^{*}1_{P1-C19}$	4.51
$BD1_{Fe2-C5}$	$BD^{*}1_{P1-C19}$	3.38
$BD^{*}2_{C9-C10}$	$BD^{*}1_{P1-C19}$	3.09
$BD2_{C9-C10}$	$BD^{*}1_{P1-C19}$	2.95
$BD1_{C19-C20}$	$BD^{*}1_{P1-C19}$	1.74
$BD1_{C19-C24}$	$BD^{*}1_{P1-C19}$	1.64
$LP2_{Fe2}$	$BD^{*}1_{P1-C19}$	1.4
$BD^{*}1_{Fe1-Fe2}$	$BD^{*}1_{P1-C19}$	0.62
$BD^{*}2_{C5-O5}$	$BD^{*}1_{P1-C19}$	0.61
$BD2_{C25-C30}$	$BD^{*}1_{P1-C19}$	0.6
$BD1_{P1-C25}$	$BD^{*}1_{P1-C19}$	0.57
$BD1_{P1-C9}$	$BD^{*}1_{P1-C19}$	0.53
$BD1_{Fe2-C4}$	$BD^{*}1_{P1-C19}$	0.28
$LP2_{S1}$	$BD^{*}1_{P1-C19}$	0.25
$LP1_{Fe2}$	$BD^{*}1_{P1-C19}$	0.22
$BD1_{Fe1-Fe2}$	$BD^{*}1_{P1-C19}$	0.18
$BD2_{C5-O5}$	$BD^{*}1_{P1-C19}$	0.13
$BD3_{C5-O5}$	$BD^{*}1_{P1-C19}$	0.13
$BD^{*}1_{C4-O4}$	$BD^{*}1_{P1-C19}$	0.11
$LP1_{S1}$	$BD^{*}1_{P1-C19}$	0.08
$BD1_{C7-H7}$	$BD^{*}1_{P1-C19}$	0.07
$BD^{*}1_{C5-O5}$	$BD^{*}1_{P1-C19}$	0.07
$LP1_{Fe3}$	$BD^{*}1_{P1-C19}$	0.05
$BD1_{C26-C27}$	$BD^{*}1_{P1-C25}$	4.97
$BD1_{C29-C30}$	$BD^{*}1_{P1-C25}$	4.69
$BD2_{C19-C20}$	$BD^{*}1_{P1-C25}$	2.62
$BD1_{C25-C30}$	$BD^{*}1_{P1-C25}$	1.69
$BD^{*}2_{C19-C20}$	$BD^{*}1_{P1-C25}$	1.58
$BD1_{C25-C26}$	$BD^{*}1_{P1-C25}$	1.57

$BD2_{C9-C10}$	BD^*1_{P1-C25}	1.35
$LP2_{Fe2}$	BD^*1_{P1-C25}	1.14
$LP2_{S2}$	BD^*1_{P1-C25}	1.04
$LP1_{Fe2}$	BD^*1_{P1-C25}	1.03
$LP2_{S1}$	BD^*1_{P1-C25}	0.6
$BD1_{C7-H7}$	BD^*1_{P1-C25}	0.51
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C25}	0.15
BD^*2_{C4-O4}	BD^*1_{P1-C25}	0.11
$LP3_{Fe2}$	BD^*1_{P1-C25}	0.11
BD^*2_{C5-O5}	BD^*1_{P1-C25}	0.1
BD^*1_{C5-O5}	BD^*1_{P1-C25}	0.06
$LP1_{S2}$	BD^*1_{P1-C25}	0.06
$BD1_{S1-C6}$	BD^*1_{P1-C25}	0.05

Table S14. The stabilization energies between donors and acceptors of alpha NBOs in complex $[(\mu\text{-pdt})Fe_2(CO)_5(mppf)]^+$ (**6**$^+$).

Donor (*i*)	Acceptor (*j*)	E^2, kcal/mol
$BD1_{P1-C9}$	$BD^*1_{C10-C11}$	1
$BD1_{P1-C9}$	BD^*1_{C9-C13}	0.95
$BD1_{P1-C9}$	$BD^*1_{C19-C24}$	0.93
$BD1_{P1-C9}$	$BD^*1_{C12-C13}$	0.92
$BD1_{P1-C9}$	BD^*1_{C9-C10}	0.86
$BD1_{P1-C9}$	$BD^*2_{C25-C26}$	0.82
$BD1_{P1-C9}$	BD^*1_{P1-C19}	0.29
$BD1_{P1-C9}$	LP^*6_{Fe3}	0.28
$BD1_{P1-C9}$	BD^*1_{Fe2-C4}	0.21
$BD1_{P1-C9}$	BD^*1_{Fe2-C5}	0.11
$BD1_{P1-C9}$	LP^*9_{Fe3}	0.07
$BD1_{P1-C9}$	$BD^*1_{Fe1-Fe2}$	0.03
$BD1_{P1-C19}$	$BD^*1_{C23-C24}$	1.93
$BD1_{P1-C19}$	$BD^*1_{C20-C21}$	1.69

$BD1_{P1-C19}$	$BD^{*}1_{C25-C30}$	1.05
$BD1_{P1-C19}$	$BD^{*}1_{C19-C20}$	0.74
$BD1_{P1-C19}$	$BD^{*}1_{C19-C24}$	0.46
$BD1_{P1-C19}$	$BD^{*}1_{C9-C10}$	0.33
$BD1_{P1-C19}$	$BD^{*}1_{C24-H24}$	0.27
$BD1_{P1-C19}$	$BD^{*}1_{Fe2-C5}$	0.23
$BD1_{P1-C19}$	$BD^{*}1_{Fe2-C4}$	0.15
$BD1_{P1-C19}$	$LP^{*}9_{Fe3}$	0.06
$BD1_{P1-C19}$	$BD^{*}1_{Fe1-Fe2}$	0.03
$BD1_{P1-C19}$	$LP^{*}6_{Fe3}$	0.03
$BD1_{P1-C19}$	$LP^{*}4_{Fe2}$	0.03
$BD1_{P1-C25}$	$BD^{*}1_{C29-C30}$	1.93
$BD1_{P1-C25}$	$BD^{*}1_{C26-C27}$	1.77
$BD1_{P1-C25}$	$BD^{*}1_{C9-C10}$	1.16
$BD1_{P1-C25}$	$BD^{*}1_{C25-C26}$	0.66
$BD1_{P1-C25}$	$BD^{*}1_{C19-C20}$	0.64
$BD1_{P1-C25}$	$BD^{*}1_{C19-C20}$	0.62
$BD1_{P1-C25}$	$BD^{*}1_{C25-C30}$	0.56
$BD1_{P1-C25}$	$BD^{*}1_{Fe2-C5}$	0.33
$BD1_{P1-C25}$	$BD^{*}1_{P1-C19}$	0.27
$BD1_{P1-C25}$	$BD^{*}1_{P1-C9}$	0.27
$BD1_{P1-C25}$	$BD^{*}1_{C26-H26}$	0.25
$BD1_{P1-C25}$	$BD^{*}1_{Fe2-C4}$	0.25
$BD1_{P1-C25}$	$BD^{*}1_{Fe1-Fe2}$	0.13
$BD1_{P1-C25}$	$BD^{*}2_{C4-O4}$	0.04
$LP1_{P1}$	$BD^{*}1_{Fe1-Fe2}$	28.9
$LP1_{P1}$	$BD^{*}1_{Fe2-C5}$	10.44
$LP1_{P1}$	$BD^{*}1_{Fe2-C4}$	9.23
$LP1_{P1}$	$LP^{*}6_{Fe2}$	7.05
$LP1_{P1}$	$BD^{*}1_{C9-C13}$	2.63
$LP1_{P1}$	$BD^{*}2_{C19-C20}$	1.78
$LP1_{P1}$	$BD^{*}1_{C25-C26}$	1.63
$LP1_{P1}$	$BD^{*}1_{C19-C20}$	1.07
$LP1_{P1}$	$BD^{*}1_{C4-O4}$	0.96

$LP1_{P1}$	$BD^{*}2_{C4-O4}$	0.91
$LP1_{P1}$	$BD^{*}1_{Fe1-C3}$	0.86
$LP1_{P1}$	$BD^{*}2_{C5-O5}$	0.77
$LP1_{P1}$	$LP^{*}4_{Fe2}$	0.64
$LP1_{P1}$	$BD^{*}1_{Fe1-S2}$	0.57
$LP1_{P1}$	$BD^{*}3_{C5-O5}$	0.57
$LP1_{P1}$	$BD^{*}3_{C4-O4}$	0.43
$LP1_{P1}$	$BD^{*}2_{C25-C26}$	0.36
$LP1_{P1}$	$LP^{*}6_{Fe1}$	0.09
$LP1_{P1}$	$BD^{*}1_{C5-O5}$	0.2
$LP1_{P1}$	$LP^{*}4_{Fe1}$	0.05
$LP1_{P1}$	$LP^{*}6_{Fe3}$	0.04
$BD1_{C12-C13}$	$BD^{*}1_{P1-C9}$	3.14
$BD1_{C10-C11}$	$BD^{*}1_{P1-C9}$	2.99
$BD1_{Fe2-C4}$	$BD^{*}1_{P1-C9}$	2.14
$BD2_{C25-C26}$	$BD^{*}1_{P1-C9}$	1.74
$BD^{*}2_{C25-C26}$	$BD^{*}1_{P1-C9}$	1.28
$BD1_{C9-C10}$	$BD^{*}1_{P1-C9}$	1.12
$BD1_{C9-C13}$	$BD^{*}1_{P1-C9}$	0.98
$LP1_{Fe2}$	$BD^{*}1_{P1-C9}$	0.69
$LP^{*}1_{C10}$	$BD^{*}1_{P1-C9}$	0.53
$BD^{*}1_{Fe1-Fe2}$	$BD^{*}1_{P1-C9}$	0.44
$BD1_{C11-C12}$	$BD^{*}1_{P1-C9}$	0.41
$LP2_{Fe2}$	$BD^{*}1_{P1-C9}$	0.4
$LP2_{S1}$	$BD^{*}1_{P1-C9}$	0.33
$BD1_{C24-H24}$	$BD^{*}1_{P1-C9}$	0.31
$LP1_{C13}$	$BD^{*}1_{P1-C9}$	0.7
$BD^{*}1_{C4-O4}$	$BD^{*}1_{P1-C9}$	0.29
$BD1_{P1-C25}$	$BD^{*}1_{P1-C9}$	0.27
$BD^{*}1_{Fe2-S2}$	$BD^{*}1_{P1-C9}$	0.21
$BD^{*}2_{C4-O4}$	$BD^{*}1_{P1-C9}$	0.15
$LP1_{Fe3}$	$BD^{*}1_{P1-C9}$	0.13
$BD3_{C4-O4}$	$BD^{*}1_{P1-C9}$	0.13
$BD1_{Fe1-Fe2}$	$BD^{*}1_{P1-C9}$	0.12

$LP1_{S1}$	BD^*1_{P1-C9}	0.07
LP^*1_{C16}	BD^*1_{P1-C9}	0.06
$LP2_{S2}$	BD^*1_{P1-C9}	0.05
BD^*1_{C5-O5}	BD^*1_{P1-C9}	0.04
BD^*2_{C5-O5}	BD^*1_{P1-C9}	0.04
$BD1_{Fe2-C5}$	BD^*1_{P1-C9}	0.04
$LP3_{Fe3}$	BD^*1_{P1-C9}	0.03
$LP1_{O4}$	BD^*1_{P1-C9}	0.03
LP^*1_{C15}	BD^*1_{P1-C9}	0.03
$BD1_{C4-O4}$	BD^*1_{P1-C9}	0.03
$BD2_{C4-O4}$	BD^*1_{P1-C9}	0.03
$BD1_{C20-C21}$	BD^*1_{P1-C19}	2.67
$BD1_{C23-C24}$	BD^*1_{P1-C19}	2.29
$LP1_{C9}$	BD^*1_{P1-C19}	2.18
$BD1_{Fe2-C5}$	BD^*1_{P1-C19}	1.9
$LP2_{Fe2}$	BD^*1_{P1-C19}	0.9
$BD1_{C19-C20}$	BD^*1_{P1-C19}	0.87
$BD1_{C19-C24}$	BD^*1_{P1-C19}	0.81
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C19}	0.38
BD^*2_{C5-O5}	BD^*1_{P1-C19}	0.35
$BD1_{P1-C9}$	BD^*1_{P1-C19}	0.29
$BD1_{P1-C25}$	BD^*1_{P1-C19}	0.27
$BD1_{Fe2-C4}$	BD^*1_{P1-C19}	0.26
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C19}	0.14
$LP2_{S1}$	BD^*1_{P1-C19}	0.11
$BD2_{C5-O5}$	BD^*1_{P1-C19}	0.08
$BD3_{C5-O5}$	BD^*1_{P1-C19}	0.06
BD^*1_{P1-C9}	BD^*1_{P1-C19}	0.05
BD^*1_{C4-O4}	BD^*1_{P1-C19}	0.04
LP^*1_{C16}	BD^*1_{P1-C19}	0.03
$LP1_{Fe3}$	BD^*1_{P1-C19}	0.03
$BD1_{C7-H7}$	BD^*1_{P1-C19}	0.03
$LP1_{S1}$	BD^*1_{P1-C19}	0.03
$BD1_{C26-C27}$	BD^*1_{P1-C25}	2.56

$BD1_{C29-C30}$	$BD^{*}1_{P1-C25}$	2.37
$BD2_{C19-C20}$	$BD^{*}1_{P1-C25}$	1.38
$LP1_{Fe2}$	$BD^{*}1_{P1-C25}$	0.9
$BD^{*}2_{C19-C20}$	$BD^{*}1_{P1-C25}$	0.89
$BD1_{C25-C30}$	$BD^{*}1_{P1-C25}$	0.82
$BD1_{C25-C26}$	$BD^{*}1_{P1-C25}$	0.77
$LP1_{C9}$	$BD^{*}1_{P1-C25}$	0.65
$LP2_{S2}$	$BD^{*}1_{P1-C25}$	0.6
$LP2_{Fe2}$	$BD^{*}1_{P1-C25}$	0.28
$LP2_{S1}$	$BD^{*}1_{P1-C25}$	0.26
$BD1_{C7-H7}$	$BD^{*}1_{P1-C25}$	0.2
$BD^{*}1_{Fe1-Fe2}$	$BD^{*}1_{P1-C25}$	0.09
$LP3_{Fe2}$	$BD^{*}1_{P1-C25}$	0.06
$BD^{*}2_{C5-O5}$	$BD^{*}1_{P1-C25}$	0.05
$BD^{*}2_{C4-O4}$	$BD^{*}1_{P1-C25}$	0.05
$BD^{*}1_{C5-O5}$	$BD^{*}1_{P1-C25}$	0.04
$LP1_{S2}$	$BD^{*}1_{P1-C25}$	0.04
$BD1_{Fe2-C4}$	$BD^{*}1_{P1-C25}$	0.03

Table S15. The stabilization energies between donors and acceptors of beta NBOs in complex $[(\mu\text{-pdt})Fe_2(CO)_5(mppf)]^+$ (**6**$^+$).

Donor (*i*)	Acceptor (*j*)	E^2, kcal/mol
$BD1_{P1-C9}$	$BD^{*}1_{C10-C11}$	0.99
$BD1_{P1-C9}$	$BD^{*}1_{C19-C24}$	0.93
$BD1_{P1-C9}$	$BD^{*}1_{C9-C13}$	0.92
$BD1_{P1-C9}$	$BD^{*}1_{C12-C13}$	0.91
$BD1_{P1-C9}$	$BD^{*}1_{C9-C10}$	0.85
$BD1_{P1-C9}$	$BD^{*}2_{C25-C26}$	0.81
$BD1_{P1-C9}$	$BD^{*}1_{P1-C19}$	0.3
$BD1_{P1-C9}$	$LP^{*}5_{Fe3}$	0.26
$BD1_{P1-C9}$	$BD^{*}1_{Fe2-C4}$	0.21

$BD1_{P1-C9}$	$BD^{*}1_{Fe2-C5}$	0.11
$BD1_{P1-C9}$	$LP^{*}9_{Fe3}$	0.07
$BD1_{P1-C9}$	$BD^{*}1_{Fe1-Fe2}$	0.03
$BD1_{P1-C19}$	$BD^{*}1_{C23-C24}$	1.93
$BD1_{P1-C19}$	$BD^{*}1_{C20-C21}$	1.69
$BD1_{P1-C19}$	$BD^{*}2_{C9-C10}$	1.14
$BD1_{P1-C19}$	$BD^{*}1_{C25-C30}$	1.05
$BD1_{P1-C19}$	$BD^{*}1_{C19-C20}$	0.74
$BD1_{P1-C19}$	$BD^{*}1_{C19-C24}$	0.46
$BD1_{P1-C19}$	$BD^{*}1_{C9-C10}$	0.33
$BD1_{P1-C19}$	$BD^{*}1_{C24-H24}$	0.27
$BD1_{P1-C19}$	$BD^{*}1_{Fe2-C5}$	0.23
$BD1_{P1-C19}$	$BD^{*}1_{Fe2-C4}$	0.15
$BD1_{P1-C19}$	$LP^{*}9_{Fe3}$	0.05
$BD1_{P1-C19}$	$LP^{*}4_{Fe2}$	0.03
$BD1_{P1-C19}$	$BD^{*}1_{Fe1-Fe2}$	0.03
$BD1_{P1-C19}$	$LP^{*}5_{Fe3}$	0.03
$BD1_{P1-C25}$	$BD^{*}1_{C29-C30}$	1.93
$BD1_{P1-C25}$	$BD^{*}1_{C26-C27}$	1.77
$BD1_{P1-C25}$	$BD^{*}1_{C9-C10}$	1.17
$BD1_{P1-C25}$	$BD^{*}1_{C25-C26}$	0.66
$BD1_{P1-C25}$	$BD^{*}2_{C19-C20}$	0.63
$BD1_{P1-C25}$	$BD^{*}1_{C19-C20}$	0.62
$BD1_{P1-C25}$	$BD^{*}1_{C25-C30}$	0.56
$BD1_{P1-C25}$	$BD^{*}1_{Fe2-C5}$	0.33
$BD1_{P1-C25}$	$BD^{*}1_{P1-C9}$	0.27
$BD1_{P1-C25}$	$BD^{*}1_{P1-C19}$	0.27
$BD1_{P1-C25}$	$BD^{*}1_{C26-H26}$	0.25
$BD1_{P1-C25}$	$BD^{*}1_{Fe2-C4}$	0.25
$BD1_{P1-C25}$	$BD^{*}1_{Fe1-Fe2}$	0.13
$BD1_{P1-C25}$	$BD^{*}2_{C4-O4}$	0.04
$LP1_{P1}$	$BD^{*}1_{Fe1-Fe2}$	28.75
$LP1_{P1}$	$BD^{*}1_{Fe2-C5}$	10.44
$LP1_{P1}$	$BD^{*}1_{Fe2-C4}$	9.22

$LP1_{P1}$	$LP^{*}6_{Fe2}$	7.04
$LP1_{P1}$	$BD^{*}1_{C4-O4}$	0.96
$LP1_{P1}$	$BD^{*}2_{C4-O4}$	0.91
$LP1_{P1}$	$BD^{*}1_{Fe1-C3}$	0.86
$LP1_{P1}$	$BD^{*}2_{C5-O5}$	0.77
$LP1_{P1}$	$LP^{*}4_{Fe2}$	0.63
$LP1_{P1}$	$BD^{*}1_{Fe1-S2}$	0.57
$LP1_{P1}$	$BD^{*}3_{C4-O4}$	0.43
$LP1_{P1}$	$BD^{*}1_{C5-O5}$	0.2
$LP1_{P1}$	$BD^{*}1_{S1-C6}$	0.18
$LP1_{P1}$	$LP^{*}6_{Fe1}$	0.09
$LP1_{P1}$	$LP^{*}4_{Fe1}$	0.05
$BD^{*}1_{P1-C9}$	$BD^{*}1_{P1-C25}$	3.21
$BD^{*}1_{P1-C9}$	$BD^{*}1_{P1-C19}$	1.74
$BD^{*}1_{P1-C9}$	$BD^{*}1_{C9-C13}$	0.4
$BD^{*}1_{P1-C9}$	$BD^{*}1_{C10-H10}$	0.29
$BD^{*}1_{P1-C9}$	$BD^{*}1_{C13-H13}$	0.28
$BD^{*}1_{P1-C19}$	$BD^{*}1_{C24-H24}$	0.38
$BD^{*}1_{P1-C19}$	$BD^{*}1_{C20-H20}$	0.36
$BD^{*}1_{P1-C19}$	$BD^{*}1_{C20-C21}$	0.26
$BD^{*}1_{P1-C19}$	$BD^{*}1_{Fe2-C4}$	0.17
$BD^{*}1_{P1-C19}$	$LP^{*}6_{Fe2}$	0.09
$BD^{*}1_{P1-C19}$	$BD^{*}1_{Fe1-C3}$	0.03
$BD^{*}1_{P1-C25}$	$BD^{*}1_{P1-C19}$	2.74
$BD^{*}1_{P1-C25}$	$BD^{*}1_{Fe2-C4}$	0.37
$BD^{*}1_{P1-C25}$	$BD^{*}1_{C26-H26}$	0.34
$BD^{*}1_{P1-C25}$	$BD^{*}1_{C30-H30}$	0.37
$BD^{*}1_{P1-C25}$	$BD^{*}1_{Fe2-C5}$	0.19
$BD^{*}1_{P1-C25}$	$LP^{*}6_{Fe2}$	0.06
$BD^{*}1_{P1-C25}$	$BD^{*}1_{C7-H7}$	0.04
$BD^{*}1_{P1-C25}$	$LP^{*}4_{Fe2}$	0.04
$BD1_{C12-C13}$	$BD^{*}1_{P1-C9}$	3.18
$BD1_{C10-C11}$	$BD^{*}1_{P1-C9}$	3.08
$BD1_{Fe2-C4}$	$BD^{*}1_{P1-C9}$	2.14

$BD2_{C25-C26}$	BD^*1_{P1-C9}	1.75
$BD^*2_{C25-C26}$	BD^*1_{P1-C9}	1.29
$BD1_{C9-C10}$	BD^*1_{P1-C9}	1.12
$BD1_{C9-C13}$	BD^*1_{P1-C9}	0.98
$LP1_{Fe2}$	BD^*1_{P1-C9}	0.67
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C9}	0.44
$LP2_{Fe2}$	BD^*1_{P1-C9}	0.42
$BD1_{C11-C12}$	BD^*1_{P1-C9}	0.41
$LP2_{S1}$	BD^*1_{P1-C9}	0.33
$BD1_{C4-O4}$	BD^*1_{P1-C9}	0.33
$BD1_{C24-H24}$	BD^*1_{P1-C9}	0.31
BD^*1_{C4-O4}	BD^*1_{P1-C9}	0.29
$BD1_{P1-C25}$	BD^*1_{P1-C9}	0.27
BD^*1_{Fe1-S2}	BD^*1_{P1-C9}	0.21
$LP1_{Fe3}$	BD^*1_{P1-C9}	0.17
BD^*2_{C4-O4}	BD^*1_{P1-C9}	0.15
$BD3_{C4-O4}$	BD^*1_{P1-C9}	0.13
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C9}	0.12
$BD2_{C16-C17}$	BD^*1_{P1-C9}	0.08
$LP1_{S1}$	BD^*1_{P1-C9}	0.07
$LP2_{S2}$	BD^*1_{P1-C9}	0.05
BD^*2_{C5-O5}	BD^*1_{P1-C9}	0.04
BD^*1_{C5-O5}	BD^*1_{P1-C9}	0.04
$BD1_{Fe2-C5}$	BD^*1_{P1-C9}	0.04
$BD2_{C14-C15}$	BD^*1_{P1-C9}	0.04
$LP2_{Fe3}$	BD^*1_{P1-C9}	0.03
$BD2_{C4-O4}$	BD^*1_{P1-C9}	0.03
$LP1_{O4}$	BD^*1_{P1-C9}	0.03
BD^*1_{P1-C25}	BD^*1_{P1-C19}	2.74
$BD1_{C20-C21}$	BD^*1_{P1-C19}	2.67
$BD1_{C23-C24}$	BD^*1_{P1-C19}	2.28
$BD1_{Fe2-C5}$	BD^*1_{P1-C19}	1.91
BD^*1_{P1-C9}	BD^*1_{P1-C19}	1.74
$BD1_{C9-C10}$	BD^*1_{P1-C19}	1.17

BD^*2_{C9-C10}	BD^*1_{P1-C19}	0.92
$LP1_{Fe2}$	BD^*1_{P1-C19}	0.9
$BD1_{C19-C20}$	BD^*1_{P1-C19}	0.87
$BD1_{C19-C24}$	BD^*1_{P1-C19}	0.81
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C19}	0.38
BD^*2_{C5-O5}	BD^*1_{P1-C19}	0.35
$BD1_{P1-C9}$	BD^*1_{P1-C19}	0.3
$BD1_{P1-C25}$	BD^*1_{P1-C19}	0.27
$BD1_{Fe2-C4}$	BD^*1_{P1-C19}	0.26
$BD1_{Fe1-Fe2}$	BD^*1_{P1-C19}	0.14
$LP2_{S1}$	BD^*1_{P1-C19}	0.11
$BD2_{C5-O5}$	BD^*1_{P1-C19}	0.08
$BD3_{C5-O5}$	BD^*1_{P1-C19}	0.06
BD^*1_{Fe1-S2}	BD^*1_{P1-C19}	0.05
BD^*1_{C4-O4}	BD^*1_{P1-C19}	0.04
$LP1_{S1}$	BD^*1_{P1-C19}	0.03
$BD1_{C7-H7}$	BD^*1_{P1-C19}	0.03
$LP1_{Fe3}$	BD^*1_{P1-C19}	0.03
BD^*1_{P1-C9}	BD^*1_{P1-C25}	3.21
$BD1_{C26-C27}$	BD^*1_{P1-C25}	2.56
$BD1_{C29-C30}$	BD^*1_{P1-C25}	2.37
$BD2_{C19-C20}$	BD^*1_{P1-C25}	1.38
$LP1_{Fe2}$	BD^*1_{P1-C25}	0.92
$BD^*2_{C19-C20}$	BD^*1_{P1-C25}	0.89
$BD1_{C25-C30}$	BD^*1_{P1-C25}	0.82
$BD1_{C25-C26}$	BD^*1_{P1-C25}	0.77
$LP2_{S2}$	BD^*1_{P1-C25}	0.6
$BD2_{C9-C10}$	BD^*1_{P1-C25}	0.5
$LP2_{S1}$	BD^*1_{P1-C25}	0.26
$LP2_{Fe2}$	BD^*1_{P1-C25}	0.26
$BD1_{C7-H7}$	BD^*1_{P1-C25}	0.2
$BD^*1_{Fe1-Fe2}$	BD^*1_{P1-C25}	0.09
$LP3_{Fe2}$	BD^*1_{P1-C25}	0.06
BD^*2_{C4-O4}	BD^*1_{P1-C25}	0.05

BD*2$_{C5-O5}$	BD*1$_{P1-C25}$	0.05
LP1$_{S2}$	BD*1$_{P1-C25}$	0.04
BD*1$_{C5-O5}$	BD*1$_{P1-C25}$	0.04
BD1$_{Fe2-C4}$	BD*1$_{P1-C25}$	0.03
BD1$_{Fe1-Fe2}$	BD*1$_{P1-C25}$	0.03

Table S16. Cartesian coordinates of all calculated species.

The species **3A**

Fe	-0.73959692	-0.41080087	-1.12992083
Fe	-2.07646790	0.72177741	0.60266932
S	-1.50096049	-1.53283110	0.75427791
S	-2.93724992	0.16491710	-1.42717305
S	-0.48685100	1.05790978	2.22932939
S	2.28882744	0.11386174	2.81062974
P	1.20223444	-0.09249053	-0.06595226
C	-0.38203831	0.86300078	-2.30077915
C	-0.40879331	-1.79097591	-2.17015970
C	-1.93025338	2.38784938	0.03281962
C	-3.48504936	0.91598166	1.64980122
C	-2.85078492	-2.71478776	0.32317118
H	-2.46616669	-3.37540490	-0.45711074
H	-3.00065423	-3.31430261	1.22223985
C	-4.16068147	-2.06833902	-0.10172439
H	-4.52866341	-1.42026038	0.69810849
H	-4.91033603	-2.86010323	-0.22736672
C	-4.07913838	-1.28818775	-1.40411750
H	-5.05765498	-0.87926645	-1.66192050
H	-3.76353584	-1.93323349	-2.22789046
C	2.44297973	-1.46129736	0.03715904
C	1.97800752	-2.78280540	0.06708768
H	0.91521163	-2.98489963	0.01839464
C	2.87365234	-3.84447547	0.16512597
H	2.49834139	-4.86206294	0.18650961

C	4.24457310	-3.60116833	0.22924279
H	4.94192539	-4.42937796	0.29898516
C	4.71656082	-2.29023407	0.20082245
H	5.78222809	-2.09262773	0.24923122
C	3.82323662	-1.22543713	0.10910919
H	4.20714846	-0.21328203	0.08715472
C	2.18770686	1.33625362	-0.69295553
C	2.89881940	1.16166460	-1.88884166
H	2.92073026	0.19211028	-2.37473232
C	3.58308565	2.22861152	-2.46316100
H	4.13235677	2.07781302	-3.38639467
C	3.55850335	3.48431565	-1.85741112
H	4.09066449	4.31609269	-2.30655435
C	2.84216010	3.66727452	-0.67727108
H	2.81123630	4.64256808	-0.20330148
C	2.15666713	2.60068446	-0.09770944
H	1.59667787	2.76723956	0.81423002
C	0.96165558	0.39096690	1.74838540
C	1.70640510	0.71979577	4.42453632
H	2.52333403	0.52509249	5.11816825
H	0.81519504	0.17478753	4.73296783
H	1.49802131	1.78742675	4.38240524
O	-0.21189541	1.67521966	-3.09599912
O	-0.22423539	-2.69289618	-2.86282153
O	-1.84051612	3.47246104	-0.33643922
O	-4.43657712	1.06893981	2.27812158

The species **3A**$^{-}$

Fe	0.78137200	0.54278297	-1.00283467
Fe	2.11073582	-0.84934808	0.53452489
S	1.63323326	1.38006413	0.99681309
S	2.96210294	-0.06665458	-1.44138572
S	0.51479435	-1.37014671	2.16494088
S	-2.38748521	-0.79109094	2.77227288

P	-1.18121653	0.14908811	0.06638638
C	0.34764689	-0.56205406	-2.30030587
C	0.48268500	2.05227663	-1.83929824
C	1.77155483	-2.39199793	-0.23397207
C	3.50809471	-1.29014897	1.50126756
C	3.01406443	2.56055940	0.65931185
H	2.63940806	3.32085367	-0.03116170
H	3.20972658	3.05077053	1.61495972
C	4.29211505	1.92908143	0.12707133
H	4.64238795	1.16400063	0.82599409
H	5.07365118	2.70037619	0.09318370
C	4.15646638	1.33294640	-1.26524413
H	5.11632323	0.93463500	-1.60092693
H	3.84680182	2.09576589	-1.98463983
C	-2.27994243	1.61123992	0.41794970
C	-1.70097604	2.87142833	0.61613169
H	-0.62666444	2.98405756	0.54718285
C	-2.48941279	3.98173449	0.91220547
H	-2.01911433	4.94839818	1.06259129
C	-3.87358495	3.85315907	1.00979112
H	-4.48889380	4.71856455	1.23492014
C	-4.46238651	2.60454009	0.81658138
H	-5.53947486	2.49188052	0.89253037
C	-3.67281092	1.49304391	0.52833065
H	-4.14654133	0.53035672	0.38546811
C	-2.29674373	-0.94586566	-0.92953836
C	-3.04346327	-0.43134322	-1.99741096
H	-3.04825607	0.63607044	-2.19132299
C	-3.78300110	-1.27936895	-2.81845234
H	-4.35919821	-0.86477442	-3.63975973
C	-3.78003266	-2.65546456	-2.59003856
H	-4.35527119	-3.31609857	-3.23078521
C	-3.02688587	-3.17728536	-1.54000952
H	-3.00850400	-4.24787264	-1.36181594

C	-2.28744745	-2.32791981	-0.71793421
H	-1.68616345	-2.74030609	0.08423072
C	-0.99866204	-0.68747337	1.66684881
C	-2.54814238	-2.58793857	3.12482433
H	-3.34234059	-2.67963630	3.86731744
H	-1.62216093	-2.98419240	3.53671737
H	-2.82697373	-3.13721940	2.22614920
O	0.12720653	-1.26417762	-3.18866126
O	0.31678885	3.04327325	-2.41248345
O	1.54205456	-3.41511063	-0.71646616
O	4.45489589	-1.61709809	2.07742464

The species **5**

Fe	5.60563600	-1.92563600	-0.29485900
Fe	3.92324400	-0.11914400	-0.56286800
S	3.40145500	-2.23321600	0.30488200
S	5.55060900	-0.09189300	1.10549300
P	2.39953100	1.48999100	0.03694500
C	6.37455000	-3.12187900	0.77010100
C	5.28958000	-2.96763900	-1.71372700
C	7.06787700	-1.21677400	-1.04332300
C	3.20895600	-0.69524600	-2.06978800
C	4.96706200	1.01083600	-1.42376000
C	3.26488400	-2.34910800	2.14238700
H	2.24204900	-2.68146600	2.32476400
H	3.93184600	-3.15484700	2.45693700
C	3.54285100	-1.06687000	2.90742900
H	2.84454500	-0.29291100	2.58508900
H	3.33104400	-1.24850700	3.96895500
C	4.96584800	-0.54439600	2.79742200
H	5.68551000	-1.26878200	3.18625200
H	5.07340400	0.37203500	3.37947900
C	2.87216700	2.41063200	1.57235100
C	4.09432000	3.10367400	1.53825400

H	4.68268100	3.12890100	0.62836400
C	4.56572200	3.76909900	2.66404700
H	5.51022300	4.30010700	2.61406900
C	3.83187900	3.74893500	3.85132100
H	4.20183600	4.26573900	4.73032600
C	2.62478600	3.05984700	3.89884300
H	2.04452000	3.03387200	4.81502800
C	2.14839700	2.39459500	2.76763300
H	1.21207600	1.86283500	2.84485000
C	2.29167800	2.86550100	-1.20818500
C	2.21084400	4.21485200	-0.83263700
H	2.24257400	4.49590900	0.21218400
C	2.11270100	5.21908200	-1.79365100
H	2.05843100	6.25560700	-1.47811900
C	2.08904400	4.89540100	-3.14778800
H	2.01684800	5.67791400	-3.89556200
C	2.16369300	3.55952800	-3.53531800
H	2.14781500	3.29330700	-4.58669400
C	2.26410900	2.55526700	-2.57617400
H	2.32019000	1.52761000	-2.90795700
C	0.49196500	1.04916800	0.18617300
C	0.12942500	0.37924100	-1.14621100
C	0.09600900	-1.04621400	-0.99521800
C	0.14806900	-1.35547900	0.41534400
C	0.22018400	-0.11958600	1.14652900
C	-0.50171700	-0.00680000	2.31533500
C	-1.25181800	-1.12636800	2.83267600
C	-1.26964300	-2.34363400	2.14990200
C	-0.55146200	-2.45963000	0.90866800
C	-1.33416700	-3.28739000	0.00735900
C	-1.37597500	-2.99128300	-1.34979100
C	-2.63002600	-3.07095800	-2.07406300
C	-3.79533600	-3.44154400	-1.40727600
C	-3.75224500	-3.75215800	0.01057400

C	-2.54558600	-3.67785500	0.70302600
C	-2.50525700	-3.09309800	2.03119500
C	-3.67432600	-2.60343800	2.60936400
C	-3.65492600	-1.34597900	3.33622100
C	-2.47022400	-0.62344900	3.43843800
C	-2.48274900	0.81870500	3.30141500
C	-1.27837000	1.21651100	2.61251800
C	-1.30611100	2.24588400	1.70630600
C	-2.54791800	2.90808600	1.42723400
C	-3.71919700	2.55753300	2.10271300
C	-3.68648200	1.48503800	3.06416500
C	-4.91934000	0.73329000	2.94193400
C	-4.90469100	-0.65384900	3.07443900
C	-5.68908000	-1.47713200	2.17843800
C	-4.92886400	-2.68338800	1.89173900
C	-4.96768500	-3.24407900	0.61676200
C	-5.76321100	-2.62086500	-0.42488000
C	-6.49179800	-1.46630500	-0.15024700
C	-6.45658900	-0.88363900	1.17853800
C	-6.47086500	0.55940500	1.03584400
C	-6.51383300	0.86971900	-0.38211700
C	-6.52649100	-0.38205500	-1.11422400
C	-5.82464200	-0.49410100	-2.31269700
C	-5.08322600	0.63788400	-2.82741200
C	-5.07266100	1.84307900	-2.12796500
C	-5.80340700	1.96041300	-0.87848300
C	-5.01665400	2.78184300	0.02211300
C	-4.97642700	2.48475000	1.38039100
C	-5.71988400	1.35244400	1.89995300
C	-5.03723100	-2.74232400	-1.67542300
C	-5.06450000	-1.69997100	-2.59986900
C	-3.85272900	-1.31222200	-3.29037400
C	-2.65873400	-1.98366600	-3.03668400
C	-1.42345900	-1.23753400	-2.90207200

C	-0.63742000	-1.85305000	-1.86609800
C	-2.58905400	3.22054000	0.01343200
C	-1.37041200	2.75642700	-0.58765300
C	-0.37003700	2.35481300	0.50120100
H	0.31935800	3.18640300	0.66743500
C	-0.64041400	0.96686600	-2.12260100
C	-1.41022300	2.19660700	-1.83946700
C	-2.65935600	2.10361400	-2.55836000
C	-2.67419400	0.84900500	-3.28443500
C	-1.43055000	0.15410700	-3.01484100
C	-3.80303800	3.16765500	-0.67633600
C	-3.83983700	2.59454600	-1.99710000
C	-3.85949900	0.13430200	-3.42611100
O	6.86060200	-3.88939000	1.46692400
O	5.08386200	-3.64342800	-2.61362300
O	8.01173400	-0.76839900	-1.50952500
O	2.81557400	-1.11812800	-3.06360400
O	5.68322500	1.71632700	-1.97877800

The species **5**⁻

Fe	5.63975900	-1.91820100	-0.30104500
Fe	3.94512800	-0.11836200	-0.56671100
S	3.42704800	-2.24763200	0.25199300
S	5.54470800	-0.10766700	1.12946800
P	2.39404700	1.47414400	0.04419300
C	6.39475400	-3.12580000	0.75812100
C	5.34876500	-2.92873700	-1.74486800
C	7.10214000	-1.18127600	-1.01551300
C	3.23833800	-0.66708100	-2.08825000
C	4.98781800	1.03451400	-1.39504200
C	3.25388400	-2.39860600	2.08316100
H	2.22713700	-2.73391300	2.23545100
H	3.91608000	-3.20916500	2.39640200
C	3.51199300	-1.12963500	2.87663700

H	2.81416300	-0.35503100	2.55567800
H	3.28183400	-1.33170700	3.93077900
C	4.93381100	-0.59739900	2.80209100
H	5.65125500	-1.32482400	3.18986200
H	5.02497100	0.30841200	3.40350400
C	2.87429400	2.37547100	1.59124900
C	4.09516600	3.07126500	1.57085600
H	4.68498900	3.11100500	0.66238200
C	4.56375900	3.72132900	2.70691700
H	5.50738900	4.25510600	2.66625700
C	3.82803000	3.68235800	3.89269400
H	4.19528000	4.18707000	4.78006900
C	2.62205800	2.99045400	3.92690500
H	2.03913700	2.95027100	4.84108400
C	2.14855000	2.34104200	2.78502400
H	1.21186100	1.80801400	2.85079300
C	2.30803100	2.86680000	-1.18593000
C	2.24256100	4.21326300	-0.79801000
H	2.27176600	4.48324300	0.24978700
C	2.15816900	5.22862200	-1.74878200
H	2.11327900	6.26248700	-1.42254200
C	2.13214100	4.91925600	-3.10619700
H	2.06843400	5.70999300	-3.84631200
C	2.18933900	3.58624900	-3.50627800
H	2.16714300	3.33001100	-4.56017600
C	2.27604300	2.57150400	-2.55681500
H	2.31279400	1.54614100	-2.89773400
C	0.49443400	1.03007500	0.18105100
C	0.12844200	0.37230400	-1.15766600
C	0.08704900	-1.05275000	-1.01385000
C	0.14176400	-1.37235900	0.38865800
C	0.22069600	-0.14804000	1.13087600
C	-0.50027400	-0.03379300	2.30428100
C	-1.26636500	-1.15344900	2.81441800

C	-1.29037400	-2.36448900	2.11448100
C	-0.57018600	-2.48208400	0.88064800
C	-1.37372200	-3.28610600	-0.02546200
C	-1.41894400	-2.97909200	-1.38045200
C	-2.67215800	-3.05446000	-2.10634300
C	-3.84525500	-3.43245300	-1.43349800
C	-3.79925000	-3.75224800	-0.02638100
C	-2.58404700	-3.68471400	0.67134700
C	-2.53602800	-3.10887700	1.99490800
C	-3.70007700	-2.61303600	2.59056300
C	-3.67318300	-1.37528600	3.33464400
C	-2.46797600	-0.65181300	3.44013600
C	-2.47412800	0.78293700	3.30297100
C	-1.26376600	1.18630900	2.61374500
C	-1.29221000	2.22726700	1.71660900
C	-2.52420900	2.90491300	1.44708900
C	-3.70302200	2.55138600	2.13072200
C	-3.67360800	1.46637300	3.06822300
C	-4.91718800	0.72092900	2.94438400
C	-4.90801400	-0.67103100	3.07250300
C	-5.70989000	-1.47931900	2.17016100
C	-4.96054500	-2.68538300	1.87164100
C	-5.00597200	-3.23790100	0.59250700
C	-5.80294200	-2.60012500	-0.43974700
C	-6.52289900	-1.44313800	-0.15298400
C	-6.47894000	-0.86978400	1.17993100
C	-6.48839600	0.57406200	1.04606800
C	-6.53533700	0.89510000	-0.36130900
C	-6.55233900	-0.34776800	-1.10541600
C	-5.85293100	-0.45850600	-2.30751500
C	-5.09571800	0.67275600	-2.81683400
C	-5.07790200	1.87190800	-2.09978400
C	-5.80756400	1.98887200	-0.85650700
C	-5.00362500	2.78785800	0.04800000

C	-4.95946700	2.47922900	1.40414400
C	-5.71781200	1.35345900	1.92024700
C	-5.07843800	-2.71706300	-1.69253900
C	-5.10379400	-1.66296100	-2.60604100
C	-3.88784200	-1.26962300	-3.29855500
C	-2.69748300	-1.95779800	-3.04741300
C	-1.45199100	-1.21766000	-2.91101000
C	-0.66248100	-1.84770400	-1.89466700
C	-2.56894100	3.22616900	0.04175900
C	-1.35943500	2.75653100	-0.57132200
C	-0.35830400	2.33834400	0.50987600
H	0.33854000	3.16267300	0.68159000
C	-0.64559500	0.97699600	-2.12270700
C	-1.40362300	2.20572400	-1.82813400
C	-2.66016400	2.12006100	-2.54672700
C	-2.68327000	0.88463800	-3.28981700
C	-1.45360600	0.17775100	-3.01956500
C	-3.79065300	3.18544700	-0.65222500
C	-3.83480600	2.61729100	-1.96782000
C	-3.88862800	0.16949000	-3.43331600
O	6.87516600	-3.90209700	1.45081800
O	5.15937800	-3.58538600	-2.66338800
O	8.04855100	-0.71443100	-1.46084900
O	2.85531600	-1.07298400	-3.09276300
O	5.70506100	1.75511700	-1.93072300

The species **6**

Fe	3.50341960	-0.91014045	0.20114663
Fe	1.16686654	-0.16645473	0.56950565
Fe	-3.37571361	-1.44583093	-0.91321373
S	2.82820733	1.25815907	-0.22655159
S	1.80365080	-1.53658530	-1.23252258
P	-0.82474552	0.88438057	0.11285671
C	4.90104500	-1.02539055	-0.88978952

C	4.31277321	-0.28079102	1.66359018
C	3.48515042	-2.57937606	0.83640669
C	1.39268205	0.62276442	2.12793118
C	0.56967814	-1.64233028	1.31445212
C	2.77417909	1.61360752	-2.03831507
H	2.52898396	2.67474063	-2.10139279
H	3.79608773	1.48907144	-2.40467922
C	1.79002949	0.80354537	-2.86741191
H	0.77163404	1.01081504	-2.53559395
H	1.85301449	1.15786260	-3.90441696
C	2.02653244	-0.69600015	-2.86396808
H	3.03234982	-0.94480547	-3.20932986
H	1.32080095	-1.18863747	-3.53480129
C	-2.01374048	0.12514110	-1.04520911
C	-1.71716512	-0.88579657	-2.02069460
H	-0.80281540	-1.45603468	-2.06968889
C	-2.84479160	-1.03386949	-2.87297025
H	-2.93792954	-1.74753102	-3.67906685
C	-3.85362525	-0.12744420	-2.43464766
H	-4.84596296	-0.03066698	-2.85192214
C	-3.35428046	0.57844776	-1.30656412
H	-3.89262565	1.32090285	-0.73691523
C	-5.11784842	-2.04365399	0.03542109
H	-6.03716352	-1.47592340	0.01520065
C	-4.06997286	-1.90515566	0.98925488
H	-4.05660953	-1.21695712	1.82084258
C	-3.02064316	-2.80062890	0.62349275
H	-2.07764415	-2.92040167	1.13378242
C	-3.42120718	-3.49029543	-0.55602658
H	-2.82962687	-4.21220215	-1.10057184
C	-4.71676439	-3.02111448	-0.92215866
H	-5.27902955	-3.32403383	-1.79386753
C	-0.59478687	2.58448063	-0.58881947
C	-1.03800412	2.94353845	-1.86562150

H	-1.56806454	2.22711825	-2.48109659
C	-0.80666355	4.22828158	-2.36074562
H	-1.15561883	4.48910823	-3.35460111
C	-0.13772534	5.16977746	-1.58387570
H	0.03917196	6.16891675	-1.96803985
C	0.30397325	4.82132490	-0.30612454
H	0.82515829	5.54813484	0.30803759
C	0.08240006	3.53895889	0.18476051
H	0.43556209	3.28415147	1.17806254
C	-1.86965848	1.24913320	1.60421811
C	-2.69644142	2.38022357	1.65037730
H	-2.70192513	3.08480573	0.82782193
C	-3.50734197	2.62574821	2.75668152
H	-4.13721975	3.50915984	2.77326583
C	-3.50515506	1.74622434	3.83728726
H	-4.13161480	1.94060962	4.70144585
C	-2.68866250	0.61775425	3.80249241
H	-2.67597541	-0.07337726	4.63864707
C	-1.88005257	0.37089485	2.69460613
H	-1.26143047	-0.51725254	2.69142725
O	5.79888199	-1.09202780	-1.59788775
O	4.84159107	0.13036006	2.59209001
O	3.47451294	-3.65364319	1.23173583
O	1.58432865	1.13103019	3.14003708
O	0.26163355	-2.63489199	1.81005053

The species **6**$^+$

Fe	3.47407233	-0.97873335	0.17413269
Fe	1.15672758	-0.19528363	0.53681124
Fe	-3.38337884	-1.39426411	-0.98436233
S	2.90788299	1.25628225	0.02000845
S	1.82964033	-1.32608460	-1.41299102
P	-0.78755796	0.92712187	0.15110700
C	4.92525939	-0.98579173	-0.85553094

C	4.24210594	-0.59697724	1.74531463
C	3.39799562	-2.72821309	0.54795191
C	1.34731833	0.38609073	2.19271174
C	0.53109101	-1.74425673	1.07565962
C	2.98497142	1.84973569	-1.72733740
H	2.80171623	2.92273538	-1.65934840
H	4.02010756	1.71097416	-2.04756880
C	2.01532083	1.21755371	-2.71272747
H	0.99070029	1.44947508	-2.41790483
H	2.16811566	1.69854392	-3.68726659
C	2.17138918	-0.28143269	-2.90013579
H	3.17915950	-0.53932139	-3.23208186
H	1.47763913	-0.63889141	-3.66292746
C	-1.99523556	0.23838367	-1.07497859
C	-1.68933334	-0.69021267	-2.11485675
H	-0.76504492	-1.24236747	-2.20257038
C	-2.81861859	-0.82360586	-2.95955558
H	-2.89909035	-1.49437466	-3.80266779
C	-3.84760108	0.01911283	-2.45608884
H	-4.84348617	0.11880432	-2.86275643
C	-3.35172568	0.66509712	-1.28754512
H	-3.90197223	1.35863957	-0.67037771
C	-5.17877802	-2.12103195	-0.05736441
H	-6.10846555	-1.57062977	-0.05948610
C	-4.14801563	-2.00644280	0.90841213
H	-4.16324021	-1.36187969	1.77453655
C	-3.06294022	-2.83531151	0.49951064
H	-2.12444674	-2.96227471	1.01560702
C	-3.43221238	-3.46462232	-0.72707242
H	-2.82085099	-4.14187527	-1.30455715
C	-4.74012754	-3.01668219	-1.06976534
H	-5.28659707	-3.27362204	-1.96546098
C	-0.59112033	2.65928914	-0.46729226
C	-1.05048946	3.10262281	-1.71147650

H	-1.57834030	2.43343154	-2.37976111
C	-0.82804173	4.41952010	-2.11679579
H	-1.18813835	4.74810496	-3.08584570
C	-0.15196065	5.30562767	-1.28327298
H	0.01776802	6.32936890	-1.59879513
C	0.30732703	4.87084286	-0.03908242
H	0.83429046	5.55420308	0.61789268
C	0.09516284	3.55713196	0.36442438
H	0.46152718	3.23548010	1.33316054
C	-1.87389486	1.17804451	1.63297262
C	-2.70398836	2.30238102	1.74749995
H	-2.69091999	3.07257473	0.98622161
C	-3.53597895	2.45931303	2.85411832
H	-4.16629030	3.33894013	2.92873368
C	-3.55090472	1.49891499	3.86358883
H	-4.19271076	1.62657280	4.72852943
C	-2.72767052	0.37927948	3.76156699
H	-2.72284180	-0.36870276	4.54694070
C	-1.89591609	0.22011398	2.65496242
H	-1.26192305	-0.65569271	2.60308060
O	5.85187263	-0.97511311	-1.52562928
O	4.74194030	-0.34575984	2.74208467
O	3.35460135	-3.84829399	0.77265654
O	1.52104400	0.75779310	3.26387166
O	0.19092372	-2.78484443	1.43548823

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