Electronic Supplementary Material (ESI) for Dalton Transactions

Mechanistic Studies on Proton Transfer in Diiron Dithiolate Complex

Ying Wang and Mårten S. G. Ahlquist*
Division of Theoretical Chemistry & Biology, School of Biotechnology, KTH Royal Institute of Technology, 106 91 Stockholm, Sweden.

Computational studies

All Density Functional Theory (DFT) calculations were carried out with Jaguar 7.6 program package by Schrödinger LLC. For geometry optimizations, solvation energy, and frequency calculations, Becke's three-parameter hybrid functional and the LYP correlation functional (B3LYP)[i] was used with the LACVP** core potential and basis set, while single point energy corrections were performed with the M06[ii] functional using the LACV3P**++ basis set which, as suggested by Martin,[iii] was augmented with two f-polarization functions on Fe. Frequency calculations were performed on the optimized geometries to verify that the geometries correspond to minima or first-order saddle points (transition states) on the potential energy surface (PES). The Gibbs free energies were defined as the following equation G = E(M06/LACV3P**++ 2f on Fe) + G_{solv} + ZPE + H_{298} + TS_{298}. The enthalpic energies were defined as the following equation H = E(M06/LACV3P**++ 2f on Fe) + G_{solv} + ZPE + H_{298}. The entropic energies were defined as S = TS_{298}. Based on the gas-phase-optimized structures, the effect of solvent was evaluated by single-point calculations using the Poisson-Bolzmann reactive field implemented in Jaguar 7.6 (PBF)[iv] in dichloromethane.

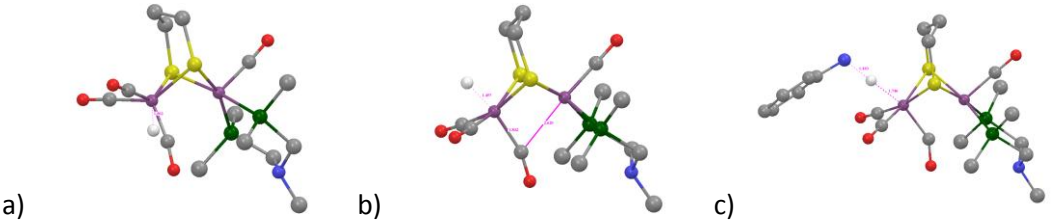

Figure S1. Optimized geometries of a) **ts1 [1(H_{Fe})]$^{1+}$**; b) [**1**(H_{Fe})]$^{1+}$; c) **ts2 [1-H_{Fe}-aniline]$^{1+}$**. Hydrogen atoms except the migrating H are omitted for clarity. (Purple = Fe; Red = O; Blue = N; Green = P; Yellow = S; Grey = C; White = H). The bond lengths are given in Å.

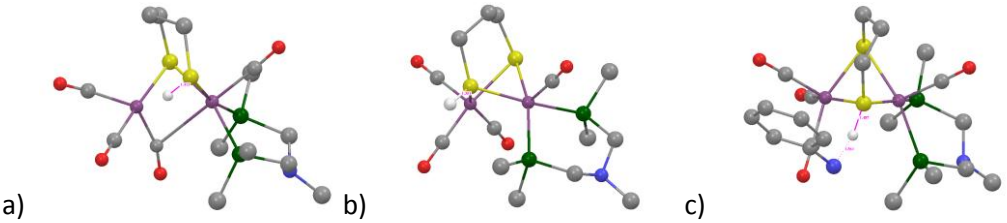

Figure S2. Optimized geometries of a) **ts1 [1(H$_S$)]$^{1+}$**; b) [**1**(H$_S$)]$^{1+}$; c) **ts2 [1-H$_S$-aniline]$^{1+}$**. Hydrogen atoms except the migrating H are omitted for clarity. (Purple = Fe; Red = O; Blue = N; Green = P; Yellow = S; Grey = C; White = H). The bond lengths are given in Å.

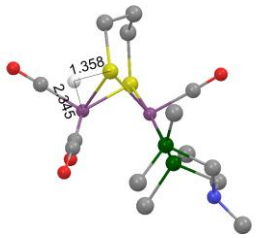

Figure S3. Optimized geometries of **ts1 [1(H$_{Fe\text{-}S}$)]$^{1+}$**. Hydrogen atoms except the migrating H are omitted for clarity. (Purple = Fe; Red = O; Blue = N; Green = P; Yellow = S; Grey = C; White = H). Hydrogen atoms except the migrating H are omitted for clarity. The bond lengths are given in Å.

Cartesian coordinates in Å and energies in atomic units unless stated otherwise of the calculated geometries.

Cartesian coordinates of **Figure S1a**

E (M06/LACV3P++ 2f(Fe)) = -2630.39307680883**

ZPE (kcal mol^{-1}) = 244.491

G$_{solv}$ = -0.0584488

DH$_{298}$ (kcal mol^{-1})= 21.354

DS$_{298}$ (cal K^{-1} mol^{-1})= 202.816

atom	x	y	z
S1	-6.1301237344	3.4884874766	-1.4042014392
Fe2	-5.8393005397	1.3080974896	-2.0117239565
S3	-7.9857838061	0.9534398593	-1.2628280960
Fe4	-6.7158241030	2.0609107897	0.4022031993
O5	-6.6540162865	4.6173237586	1.8797235344
C6	-6.6902223996	3.6414728329	1.2817215253
O7	-4.0906635593	1.2279288082	1.3423638901
C8	-5.0865485946	1.5875656241	0.8797239134
O9	-8.9387055659	1.2806136420	2.1867565055
C10	-8.0949027009	1.6021292210	1.4832716688
O11	-6.5583190043	1.3725774507	-4.8206251596
C12	-6.2388336879	1.3327343183	-3.7127536726
C13	-7.6944248675	4.2486197077	-2.0433295609
H14	-7.6445085395	5.2967688307	-1.7364982919
H15	-7.6087225284	4.2137794773	-3.1343755463
C16	-9.0030475719	3.6227179349	-1.5754691744
H17	-9.8253932804	4.2048276601	-2.0130031912
H18	-9.0979919811	3.7229602221	-0.4887639019

C19	-9.1920900570	2.1657328331	-1.9786535983
H20	-9.1371168919	2.0436747623	-3.0652432054
H21	-10.1717036453	1.8077356878	-1.6511393695
N22	-2.6984712623	-0.8064466579	-2.3000242807
C23	-1.4749095881	-1.6200831753	-2.2670638528
H24	-1.6299495623	-2.4824991795	-1.6135350531
H25	-1.1694468568	-1.9852617925	-3.2617728286
H26	-0.6569120486	-1.0278682304	-1.8487028391
C27	-3.8590272510	-1.5705644795	-2.7484651671
H28	-3.7405772466	-2.6154700681	-2.4445710675
H29	-3.9767928662	-1.5671782157	-3.8480331080
C30	-2.5241243442	0.4238183910	-3.0660556879
H31	-2.7166622123	0.2856559607	-4.1463749855
H32	-1.4884652220	0.7643054291	-2.9684460093
P33	-5.4498898264	-0.9786467816	-1.9773745343
P34	-3.6004780973	1.8155886978	-2.4464463982
C35	-6.7015525695	-1.9878169272	-2.8769113375
H36	-6.7563462087	-1.6750550547	-3.9230945261
H37	-6.4501835492	-3.0519845202	-2.8356410836
H38	-7.6828996885	-1.8367356820	-2.4212477112
C39	-5.3886534329	-1.7734431605	-0.3131777909
H40	-5.2395246739	-2.8529968342	-0.4141745352
H41	-4.5660329834	-1.3525800243	0.2690676402
H42	-6.3283798099	-1.6018994850	0.2176835292
C43	-3.4302467285	3.0508100102	-3.8052840443
H44	-3.9180710511	2.6916449900	-4.7148517172
H45	-3.9067401555	3.9861240738	-3.5018136739
H46	-2.3759544808	3.2471791048	-4.0221675853
C47	-2.5664625587	2.5550056691	-1.1099797769
H48	-1.6197710784	2.9079418565	-1.5302936087
H49	-3.0858167011	3.4030230825	-0.6568669204
H50	-2.3630499364	1.8121091871	-0.3374186692
H52	-6.4649423632	0.6143201828	0.7199829835

Cartesian coordinates of **Figure S1b**

E (M06/LACV3P++ 2f(Fe)) = -2630.42542590131**

ZPE (kcal mol^{-1}) = 246.006

G_{solv} = -0.0582507

DH_{298} (kcal mol^{-1})= 21.353

DS_{298} (cal K^{-1} mol^{-1})= 202.554

atom	x	y	z
S1	-5.9415680941	3.4256163874	-1.5147724437
Fe2	-5.6989238574	1.2035964773	-2.0786187880
S3	-7.7947604281	0.8893838186	-1.1725143512
Fe4	-6.4823571189	2.1045283322	0.3546078041

O5	-4.0968483507	0.4311737795	0.8292384344
C6	-4.9977630941	1.0344914148	0.4402006899
O7	-5.3586806277	4.2513552647	2.0188710318
C8	-5.7628930437	3.3911075977	1.3839408551
O9	-7.9399499277	0.7103507051	2.4931802965
C10	-7.3372689634	1.2312836276	1.6734540642
O11	-6.3282442750	1.2773172648	-4.9078366739
C12	-6.0767824716	1.2473938767	-3.7824254926
N13	-2.6814361546	-1.0460312633	-2.4372568579
C14	-1.4925819723	-1.9112101319	-2.4142117056
H15	-1.6895043965	-2.7825587937	-1.7843336909
H16	-1.1935112478	-2.2639543783	-3.4154267439
H17	-0.6541536096	-1.3648645124	-1.9745232923
C18	-3.8655894836	-1.7547447445	-2.9154845804
H19	-3.7931668004	-2.8085179500	-2.6281087944
H20	-3.9628426184	-1.7297232212	-4.0169769750
C21	-2.4440479885	0.1913144633	-3.1759410067
H22	-2.6335983309	0.0845423283	-4.2604197096
H23	-1.3937271085	0.4789898542	-3.0650060748
P24	-5.4530545811	-1.1147079742	-2.1713096011
P25	-3.4529372501	1.6286553431	-2.5432490782
C26	-6.7232111531	-1.9374979859	-3.2227146499
H27	-6.7048897620	-1.5313104228	-4.2370284989
H28	-6.5476852825	-3.0165765360	-3.2692283436
H29	-7.7119595385	-1.7578949217	-2.7938865999
C30	-5.5714622048	-2.0554821575	-0.5884348051
H31	-5.6380254828	-3.1269869978	-0.7999482965
H32	-4.6898167122	-1.8667336593	0.0261601328
H33	-6.4648740920	-1.7521402502	-0.0363896151
C34	-3.2156335435	2.8757841652	-3.8790093426
H35	-3.7201167832	2.5596177079	-4.7953135388
H36	-3.6431432005	3.8285549034	-3.5577101914
H37	-2.1516862215	3.0185596441	-4.0911205549
C38	-2.4049353936	2.2970311551	-1.1793888380
H39	-1.4452161128	2.6341530345	-1.5825691979
H40	-2.9025896558	3.1468625215	-0.7049652094
H41	-2.2260642022	1.5236718919	-0.4306582061
C42	-7.5462390983	4.1686292702	-2.0660990309
H43	-7.9532007678	4.6834631647	-1.1919349860
H44	-7.2591596396	4.9289709160	-2.7979071447
C45	-9.0648317441	2.0899350058	-1.7864843438
H46	-9.7834331669	1.4729186362	-2.3333005087
H47	-9.5664578697	2.4760058371	-0.8953326135
C48	-8.5658523985	3.2176536759	-2.6836135349

H49	-9.4409704532	3.8189929546	-2.9661401543
H50	-8.1701149677	2.8034514037	-3.6152970998
H53	-7.6695906493	2.9966125999	0.5464454520

Cartesian coordinates of **Figure S1c**

E (M06/LACV3P++ 2f(Fe)) = -2917.88608062108**

ZPE (kcal mol^{-1}) = 318.968

G_{solv} = -0.0642833

DH_{298} (kcal mol^{-1})= 25.27

DS_{298} (cal K^{-1} mol^{-1})= 233.571

atom	x	y	z
S1	-6.1179447763	3.6242458167	-1.6568658308
Fe2	-5.7582888040	1.3340048733	-2.0595816568
S3	-8.0939524282	1.1349552753	-1.8647001787
Fe4	-7.1284540147	2.2524663635	-0.0439699191
O5	-5.0028085029	0.5454633552	0.9272580107
C6	-5.6942583933	1.1324713886	0.1954831083
O7	-6.1856450747	4.1514596967	1.9704323783
C8	-6.5672255017	3.3964047563	1.1910983735
O9	-8.9091623478	0.7176649459	1.6865584926
C10	-8.1846257905	1.3176713800	1.0203575611
O11	-5.5485586738	1.3593666856	-4.9646727989
C12	-5.6467709920	1.3636522441	-3.8138483032
N13	-2.8176369514	-1.0058974562	-1.7068032099
C14	-1.6940230704	-1.9096035202	-1.4252326304
H15	-2.0581567136	-2.7838549311	-0.8791756119
H16	-1.1766991885	-2.2572846685	-2.3358892705
H17	-0.9671024296	-1.3986734535	-0.7883322255
C18	-3.8756805829	-1.6679935045	-2.4645561590
H19	-3.9051458711	-2.7265099025	-2.1868125458
H20	-3.7042937661	-1.6287221084	-3.5571042578
C21	-2.3769154811	0.2341678540	-2.3394762242
H22	-2.3041088051	0.1468891854	-3.4402301485
H23	-1.3754532300	0.4849287521	-1.9752191505
P24	-5.5803574832	-0.9866135398	-2.1174971052
P25	-3.4637946398	1.7004113978	-1.9414129978
C26	-6.5658069990	-1.7735063961	-3.4625182798
H27	-6.2822717027	-1.3661905133	-4.4359897466
H28	-6.4115460991	-2.8568591316	-3.4716061440
H29	-7.6253129352	-1.5666896513	-3.2946138828
C30	-6.1075207576	-1.9480138178	-0.6345216243
H31	-6.1310308974	-3.0154605303	-0.8739025835
H32	-5.4116313048	-1.7754851015	0.1875284352
H33	-7.1070650288	-1.6341058467	-0.3228188154
C34	-2.8552540657	2.9446608682	-3.1579993554

H35	-3.1212654516	2.6504742469	-4.1760420742
H36	-3.3199127302	3.9093926772	-2.9418336896
H37	-1.7681687318	3.0505307898	-3.0912037135
C38	-2.7492112932	2.3200755612	-0.3587349697
H39	-1.7050326399	2.6090419129	-0.5116956594
H40	-3.3100842931	3.1925557847	-0.0137246778
H41	-2.8025310742	1.5421283194	0.4040362904
C42	-7.4084386820	4.3624982808	-2.7561761314
H43	-8.0730521066	4.9345699372	-2.0998773458
H44	-6.8735860063	5.0876316713	-3.3761480805
C45	-9.0123195959	2.3413691564	-2.9264216411
H46	-9.5415280480	1.7262963715	-3.6597855761
H47	-9.7736933645	2.7950920389	-2.2829016385
C48	-8.2032335255	3.4144336443	-3.6478112847
H49	-8.9093138125	4.0227333974	-4.2309765252
H50	-7.5374931049	2.9487316220	-4.3779959964
H53	-8.5256094876	3.2710226102	0.2002223916
C53	-9.8234520448	5.6154953473	4.3265110400
C54	-9.3566104072	6.4048111350	3.2741599848
C55	-9.3417934873	5.9053158710	1.9724945849
C56	-9.8012258112	4.6091307612	1.7308837169
C57	-10.2687585330	3.8096826077	2.7765945296
C58	-10.2801997261	4.3209121591	4.0740805030
H59	-9.8342224193	6.0085870731	5.3382245178
H60	-9.0033470776	7.4136116780	3.4638111848
H61	-8.9770708170	6.5214799246	1.1540181549
H62	-10.6192759824	2.7993220020	2.5830470096
H63	-10.6483009286	3.7035893943	4.8877861806
H64	-10.4809999230	3.4086407040	0.2060096569
N64	-9.7191574621	4.0578480922	0.3993202105
H65	-9.7254604764	4.7842068713	-0.3143484747

Cartesian coordinates of **Figure S2a**

E (M06/LACV3P++ 2f(Fe)) = -2630.37402261872**

ZPE (kcal mol^{-1}) = 242.682

G_{solv} = -0.0604903

DH_{298} (kcal mol^{-1})= 22.035

DS_{298} (cal K^{-1} mol^{-1})=210.5

atom	x	y	z
S1	-6.6984572717	4.4479332749	-1.6876672394
Fe2	-5.7145790416	1.0236912031	-1.7113012044
S3	-7.8521643226	1.1080334981	-0.8511629266
Fe4	-6.3955813844	2.7223984543	0.0194474147

O5	-8.4276515555	3.9708658263	1.8078244071
C6	-7.6400989033	3.4828017588	1.1399307783
O7	-4.0839712498	4.3696704953	0.7991024615
C8	-4.9901893847	3.7339885496	0.4987983728
O9	-5.4316934562	0.5945295096	1.8026320772
C10	-5.8047701987	1.4037260567	1.0729608038
O11	-6.2990825054	1.3829903879	-4.5249726261
C12	-6.0559368130	1.2269011843	-3.4068776672
C13	-8.1587135964	4.0367000606	-2.7317250178
H14	-8.4896483760	5.0299430440	-3.0505034625
H15	-7.8252229115	3.5043890132	-3.6267441966
C16	-9.3178072551	3.2992999930	-2.0593269445
H17	-10.2200853734	3.4821951209	-2.6586321482
H18	-9.5182864990	3.7183695985	-1.0681268039
C19	-9.1584665565	1.7826546803	-1.9867817479
H20	-8.9648425462	1.3676911884	-2.9801872848
H21	-10.0798312631	1.3315879579	-1.6095810378
N22	-2.9046932827	-1.2962595109	-2.6442752848
C23	-1.7968471019	-2.1928416084	-3.0078637208
H24	-1.9749208386	-3.1833933781	-2.5812554939
H25	-1.6682781970	-2.2993535096	-4.0978184840
H26	-0.8649110351	-1.8094909006	-2.5846655113
C27	-4.1942449962	-1.8267649590	-3.0797839879
H28	-4.1793204438	-2.9173582314	-2.9819633494
H29	-4.4216124637	-1.6004572614	-4.1387348942
C30	-2.6657625730	0.0776059408	-3.0889197190
H31	-3.0035139620	0.2621528657	-4.1253528424
H32	-1.5892980559	0.2749546998	-3.0638695791
P33	-5.6102548864	-1.2149341914	-2.0357408751
P34	-3.4751365518	1.3224928403	-1.9611147543
C35	-7.0700943440	-2.0279340189	-2.8037922838
H36	-7.2559182466	-1.6113083734	-3.7972600073
H37	-6.9149433490	-3.1075988696	-2.8924246614
H38	-7.9479606038	-1.8435877977	-2.1798640939
C39	-5.3889629652	-2.0833555667	-0.4276040364
H40	-5.4162152477	-3.1675691066	-0.5774721187
H41	-4.4261488291	-1.8105728287	0.0093110136
H42	-6.1870444977	-1.8007818195	0.2628781603
C43	-2.9664855432	2.9290021453	-2.7028253710
H44	-3.4430515494	3.0611532477	-3.6775428154
H45	-3.2834185434	3.7516470803	-2.0580264910
H46	-1.8799324273	2.9733000363	-2.8254789172
C47	-2.4489970412	1.1818097059	-0.4346641669
H48	-1.3914279187	1.3246121708	-0.6790191561

H49	-2.7424857423	1.9371075494	0.2961695292
H50	-2.5767924596	0.1904199835	0.0051209875
H52	-5.9053806158	2.9295147302	-1.5686955886

Cartesian coordinates of **Figure S2b**

E (M06/LACV3P++ 2f(Fe)) = -2630.40607168213**

ZPE (kcal mol^{-1}) = 246.077

G_{solv} = -0.0648938

DH_{298} (kcal mol^{-1})= 21.748

DS_{298} (cal K^{-1} mol^{-1})= 207.879

atom	x	y	z
S1	-6.3224479856	3.2982084515	-1.7686394726
Fe2	-5.6638464630	1.1251445713	-2.0637459096
S3	-7.7231149925	0.7991458401	-1.0027754966
Fe4	-6.3488516447	2.2493149764	0.2307771711
O5	-5.3753462797	-0.0183558207	1.8000443011
C6	-5.7413948389	0.8508975776	1.1365065248
O7	-4.2036997198	3.9498824822	1.2873149174
C8	-5.0428000926	3.2703950595	0.8856180733
O9	-8.5171125505	3.2507912547	1.9583202919
C10	-7.6733392842	2.8953219266	1.2654110743
O11	-6.0978642597	0.9649930476	-4.9433495594
C12	-5.9147353833	0.9986332061	-3.8028196379
N13	-2.6477074894	-1.0944305656	-2.8469986722
C14	-1.5262678512	-1.9266536788	-3.3028133908
H15	-1.6136033925	-2.9252691617	-2.8667881506
H16	-1.4813052531	-2.0272996984	-4.4004898617
H17	-0.5853020467	-1.4912698676	-2.9561470115
C18	-3.9383961462	-1.6892511298	-3.1795825924
H19	-3.8590038095	-2.7770351131	-3.0860630447
H20	-4.2566877089	-1.4768376467	-4.2175820548
C21	-2.5212660784	0.2864942469	-3.3043739189
H22	-2.8811169963	0.4366690731	-4.3396553675
H23	-1.4630495475	0.5664375020	-3.2850045421
P24	-5.3076768170	-1.1611490713	-2.0254868756
P25	-3.4097465684	1.4753656704	-2.1741527816
C26	-6.7313515924	-2.1084329809	-2.7150449631
H27	-7.0014900300	-1.7233056218	-3.7013971731
H28	-6.4792861997	-3.1699757631	-2.8010495552
H29	-7.5926367980	-1.9993021000	-2.0527499610
C30	-4.9127187198	-2.0934588312	-0.4874359587
H31	-4.7831682980	-3.1532632255	-0.7281378982
H32	-3.9939490527	-1.7161554148	-0.0359344851
H33	-5.7235576613	-1.9908284369	0.2351443525
C34	-2.8668123093	3.1040735336	-2.8572861988

H35	-3.3523141811	3.2964816415	-3.8178154181
H36	-3.1273882215	3.9077767337	-2.1622916124
H37	-1.7816594321	3.1246779320	-2.9971698391
C38	-2.4078086024	1.3230595589	-0.6342565094
H39	-1.3430868294	1.4340439844	-0.8634863171
H40	-2.6969242463	2.0900580329	0.0849667799
H41	-2.5706866081	0.3409304974	-0.1880636230
C42	-7.9222305125	3.9061424540	-2.4796035395
H43	-8.3668168171	4.5507739547	-1.7166877171
H44	-7.6723552187	4.5013783675	-3.3609334789
C45	-9.1484554854	1.7643114827	-1.7065000949
H46	-9.8490948561	1.0057080224	-2.0651016894
H47	-9.6248874981	2.2790003973	-0.8668299826
C48	-8.8278422516	2.7312009027	-2.8469976915
H49	-9.7708545147	3.1615636362	-3.2085465081
H50	-8.3945322843	2.1821183808	-3.6881230828
H53	-5.5393401236	4.3791139938	-1.9761148480

Cartesian coordinates of **Figure S2c**

E (M06/LACV3P++ 2f(Fe)) = -2917.88413161487**

ZPE (kcal mol^{-1}) = 319.799

G_{solv} = -0.062562

DH_{298} (kcal mol^{-1})= 25.389

DS_{298} (cal K^{-1} mol^{-1})= 237.469

atom	x	y	z
S1	-5.2329670063	3.4222327001	-2.2988560141
Fe2	-5.2650556541	1.0992363413	-2.2660611593
S3	-7.5153215816	1.4703135275	-1.8414872895
Fe4	-6.1781755023	2.6705897043	-0.3539692956
O5	-7.0337135900	0.8230660164	1.7501162211
C6	-6.6694016250	1.5270167257	0.9137636171
O7	-3.7644820605	3.5179686044	1.0620096727
C8	-4.7186041713	3.1342637263	0.5233194744
O9	-7.9927579167	4.8780273798	0.3658119992
C10	-7.2928739273	4.0155732777	0.0661471188
O11	-5.4034600036	0.3770047518	-5.0868192246
C12	-5.3278535403	0.6496695466	-3.9651978008
N13	-2.8642556583	-1.8967755934	-2.1121780595
C14	-1.9803745152	-3.0618591794	-2.2391055763
H15	-2.3475839512	-3.8690210606	-1.5997345325
H16	-1.9096869846	-3.4405292235	-3.2732329978
H17	-0.9757180495	-2.7957535730	-1.8990915951
C18	-4.2484524702	-2.2228461288	-2.4461349115
H19	-4.4647863853	-3.2346438382	-2.0886999826
H20	-4.4426874316	-2.2142717641	-3.5350709964

C21	-2.3568136461	-0.7483402820	-2.8545441585
H22	-2.5989575372	-0.7888308546	-3.9336571107
H23	-1.2653918726	-0.7290126593	-2.7682155896
P24	-5.4796111842	-1.0950024654	-1.6085211001
P25	-2.9792891912	0.8721098945	-2.1684288923
C26	-7.0650615720	-1.9089276840	-2.0793573533
H27	-7.2370945348	-1.7934614992	-3.1526513227
H28	-7.0390879250	-2.9737967758	-1.8281521970
H29	-7.8945475026	-1.4350392501	-1.5510888932
C30	-5.2644927953	-1.5826706040	0.1561126781
H31	-5.3128947558	-2.6721887106	0.2493000480
H32	-4.2943044615	-1.2404411642	0.5200131115
H33	-6.0473098362	-1.1403692428	0.7720357567
C34	-2.0584904479	2.0552753952	-3.2510118377
H35	-2.4613935930	2.0200614469	-4.2665380634
H36	-2.1770901551	3.0732638863	-2.8734017384
H37	-0.9911862707	1.8153457314	-3.2787323062
C38	-2.0518312622	0.9622847005	-0.5756744571
H39	-0.9741512091	0.8921277649	-0.7555954915
H40	-2.2696791594	1.8922610617	-0.0493657099
H41	-2.3553542431	0.1267130276	0.0584303481
C42	-6.4108739013	4.3357358071	-3.3948545501
H43	-6.8682137227	5.1159811709	-2.7806119626
H44	-5.8071481399	4.8093893881	-4.1731177057
C45	-8.3377320653	2.6580165379	-3.0097124692
H46	-9.0657906674	2.0523867324	-3.5565986367
H47	-8.8994498154	3.3598799613	-2.3854675315
C48	-7.4495663469	3.4001434010	-4.0089008018
H49	-8.0994142713	4.0133137492	-4.6477517976
H50	-6.9537828486	2.6846021450	-4.6717030231
H53	-4.1438538655	4.4064901699	-2.0592514719
H52	-2.3200244260	5.5738840636	-2.1284092853
H55	-2.9484230993	5.3194669974	-0.6236231983
N55	-3.1838584999	5.5440841716	-1.5900732649
C55	-5.4289730663	9.1150954603	-1.9306647905
C56	-5.5031411961	8.3490338315	-0.7665357531
C57	-4.7449710386	7.1843743673	-0.6381760269
C58	-3.9066264874	6.7902964269	-1.6841419152
C59	-3.8269182461	7.5513025600	-2.8528878879
C60	-4.5875212986	8.7148969844	-2.9698439938
H61	-6.0178072418	10.0220150499	-2.0248823980
H62	-6.1486400774	8.6581874034	0.0498775433
H63	-4.7977304828	6.5943145738	0.2735309279
H64	-3.1690989491	7.2444848297	-3.6631279639

H65	-4.5174692451	9.3104920438	-3.8750016436

Cartesian coordinates of **Figure S3**

E (M06/LACV3P++ 2f(Fe)) = -2630.38871729887**

ZPE (kcal mol^{-1}) = 244.794

G_{solv} = -0.0633896

DH_{298} (kcal mol^{-1})= 21.838

DS_{298} (cal K^{-1} mol^{-1})= 208.434

atom	x	y	z
S1	-5.9779868027	3.6080894996	-1.5991946512
Fe2	-5.5843896235	1.2376507036	-1.9771262514
S3	-7.8259720288	0.8792704222	-1.5090636787
Fe4	-6.6573491982	1.8446911623	0.2244021766
O5	-7.2549463521	-0.5667865535	1.7428968503
C6	-7.0063470204	0.3927540021	1.1594017995
O7	-4.0085480884	2.0171082148	1.4841419135
C8	-5.0248677411	1.9627072533	0.9364449172
O9	-8.5072838416	3.4957221883	1.8326658064
C10	-7.8030988137	2.8544458121	1.1890517628
O11	-6.0087695528	1.0279969790	-4.8579924265
C12	-5.8018275969	1.1228995587	-3.7260114359
N13	-2.5519458184	-0.9676414178	-2.8481774716
C14	-1.4654118077	-1.8152113048	-3.3581156554
H15	-1.4800854367	-2.7771507283	-2.8389601020
H16	-1.5371625867	-2.0027308843	-4.4428761709
H17	-0.5037918962	-1.3379725305	-3.1517966903
C18	-3.8542807182	-1.6086681930	-2.9983318913
H19	-3.7413351273	-2.6799559092	-2.8031783075
H20	-4.2749528088	-1.5061497204	-4.0163114721
C21	-2.5099401653	0.3735222600	-3.4198308913
H22	-2.9841357904	0.4345777877	-4.4174314029
H23	-1.4635461777	0.6704364783	-3.5434062049
P24	-5.1071065326	-0.9859143825	-1.7644204525
P25	-3.2936681588	1.6595654739	-2.3141433598
C26	-6.4947643442	-2.1650027560	-2.0359110603
H27	-6.9418052223	-1.9975990743	-3.0188308331
H28	-6.1300767947	-3.1947968672	-1.9714691328
H29	-7.2699036142	-2.0135191581	-1.2824284838
C30	-4.3689447150	-1.5494286341	-0.1716664208
H31	-4.0365226899	-2.5883359219	-0.2621997706
H32	-3.5123886889	-0.9269156879	0.0889156887
H33	-5.1085899701	-1.4875052152	0.6273403455
C34	-2.9825680142	3.1814424974	-3.3170308821
H35	-3.6156257566	3.1841640090	-4.2082024379
H36	-3.2094287696	4.0750530187	-2.7313842295

H37	-1.9335952919	3.2253784518	-3.6256663104
C38	-2.0352070685	1.8069350711	-0.9732721933
H39	-1.0569126103	2.0286408543	-1.4112214061
H40	-2.3014781887	2.6019506382	-0.2756774672
H41	-1.9685173366	0.8687497825	-0.4194868101
C42	-7.6403344717	4.3013524761	-2.0736361450
H43	-8.1801277292	4.5300158073	-1.1523129689
H44	-7.4201373779	5.2342089479	-2.5967803509
C45	-8.9918031768	2.1088325136	-2.2652463328
H46	-9.5757822948	1.5278252842	-2.9842950814
H47	-9.6708026040	2.4084595311	-1.4605857026
C48	-8.4164294769	3.3383220274	-2.9669045338
H49	-9.2596335507	3.9052734955	-3.3829886155
H50	-7.8040587974	3.0425397938	-3.8255293736
H53	-5.9206363265	4.0081666099	-0.3022309185

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