SUPPORTING INFORMATION

The bonding situation in the dinuclear tetra-hydrido complex [{^{5}CpFe}$_2$(μ-H)$_4$] revisited by hard X-ray spectroscopy

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Section S1 – Treatment of experimental data

Since HERFD-XANES filters background photons with high efficiency (in contrast to conventional XANES and TFY XANES), all spectra were only area normalized and smoothed to reduce the white noise (not necessary).

VtC-XES spectra are superimposed by the high-energy slope of the $K\beta_{1,3}$ emission line and therefore need to be background corrected. There are multiple ways to do this, either the $K\beta_{1,3}$ emission line is measured within every VtC-XES scan or the $K\beta_{1,3}$ emission line is measured separately and only a section of the $K\beta_{1,3}$ high-energy slope is recorded within every VtC-XES spectra. The separate $K\beta_{1,3}$ and VtC-XES spectra can be joined together to obtain the whole $K\beta$-XES spectra. The $K\beta_{1,3}$ high-energy slope is subtracted, by either fitting the whole $K\beta_{1,3}$ line with any suitable function like a pseudo-voigt functions, or only a section of the $K\beta_{1,3}$ high-energy slope is fitted by any suited decay function. The resulting fit is subtracted to obtain the background corrected VtC-XES spectra. All VtC-XES data in this work were corrected by the latter method and area normalized for comparison.

Section S2 - Structural parameters

Table S1: Atomic and centroid distances in **1** and **1H**.

Distances	Compounds			
	1H (cryst.)	**1H** (DFT)	**1** (cryst.)	**1** (DFT)
^{5}Cp-Fe	1.67 Å	1.67 Å	1.66 Å	1.67 Å
	1.67 Å	1.67 Å	-	-
Cp-Fe	-	-	1.67 Å	1.69 Å
Fe-Fe	2.21 Å	2.17 Å	-	
Fe-H	1.64 Å	1.62 Å		
	1.66 Å	1.62 Å		
	1.54 Å	1.62 Å		
	1.55 Å	1.62 Å		
H-H	1.73 Å	1.71 Å		
	1.73 Å	1.71 Å		
	1.52 Å	1.71 Å		
	1.52 Å	1.71 Å		

Chart S1. Comparison of crystal (left) and DFT structure (right).

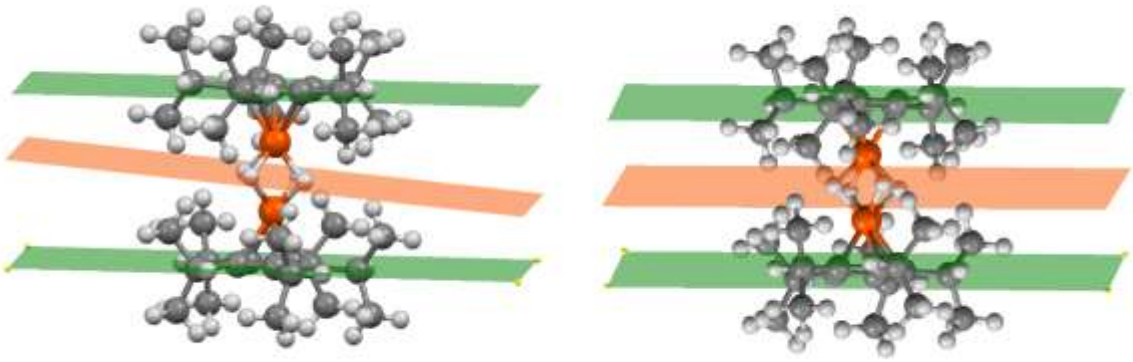


Chart S2. Molecule 1 from the X-ray crystal structure of **1**, distances/Å. Fe1–C1 2.063(3), Fe1–C5 2.056(3), Fe1–C9 2.054(3), Fe1–C13 2.056(3), Fe1–C17 2.065(3), Fe1–$^{5}Cp_{cent.}$ 1.661, Fe1–C61 2.062(3), Fe1–C62 2.063(3), Fe1–C63 2.059(3), Fe1–C64 2.066(3), Fe1–C65 2.069(3), Fe1–$Cp_{cent.}$ 1.673. Molecule 2: Fe2–C21 2.049(3), Fe2–C25 2.053(3), Fe2–C29 2.052(3), Fe2–C33 2.053(3), Fe2–C37 2.052(3), Fe2–$^{5}Cp_{cent.}$ 1.662, Fe2–C66 2.058(3), Fe2–C67 2.058(3), Fe2–C68 2.054(3), Fe2–C69 2.058(3), Fe2–C70 2.065(3), Fe2–$Cp_{cent.}$ 1.669. Molecule 3: Fe3–C41 2.053(3), Fe3–C45 2.056(3), Fe3–C49 2.063(3), Fe3–C53 2.064(3), Fe3–C57 2.057(3), Fe3–$^{5}Cp_{cent.}$ 1.666, Fe3–C71 2.057(3), Fe3–C6 22.053(3), Fe3–C73 2.059(3), Fe3–C74 2.056(3), Fe3–C75 2.063(3), Fe3–$Cp_{cent.}$ 1.667

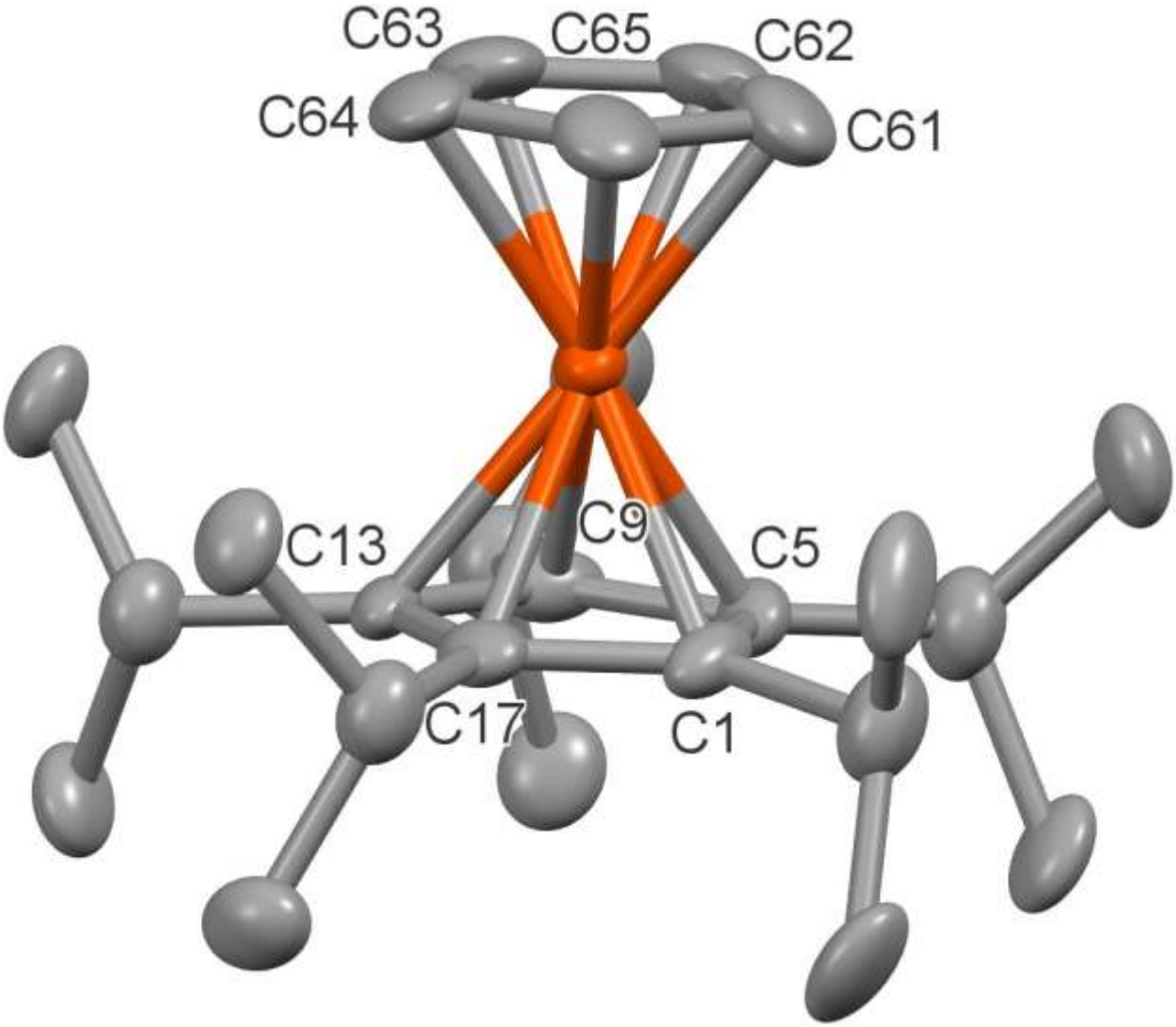
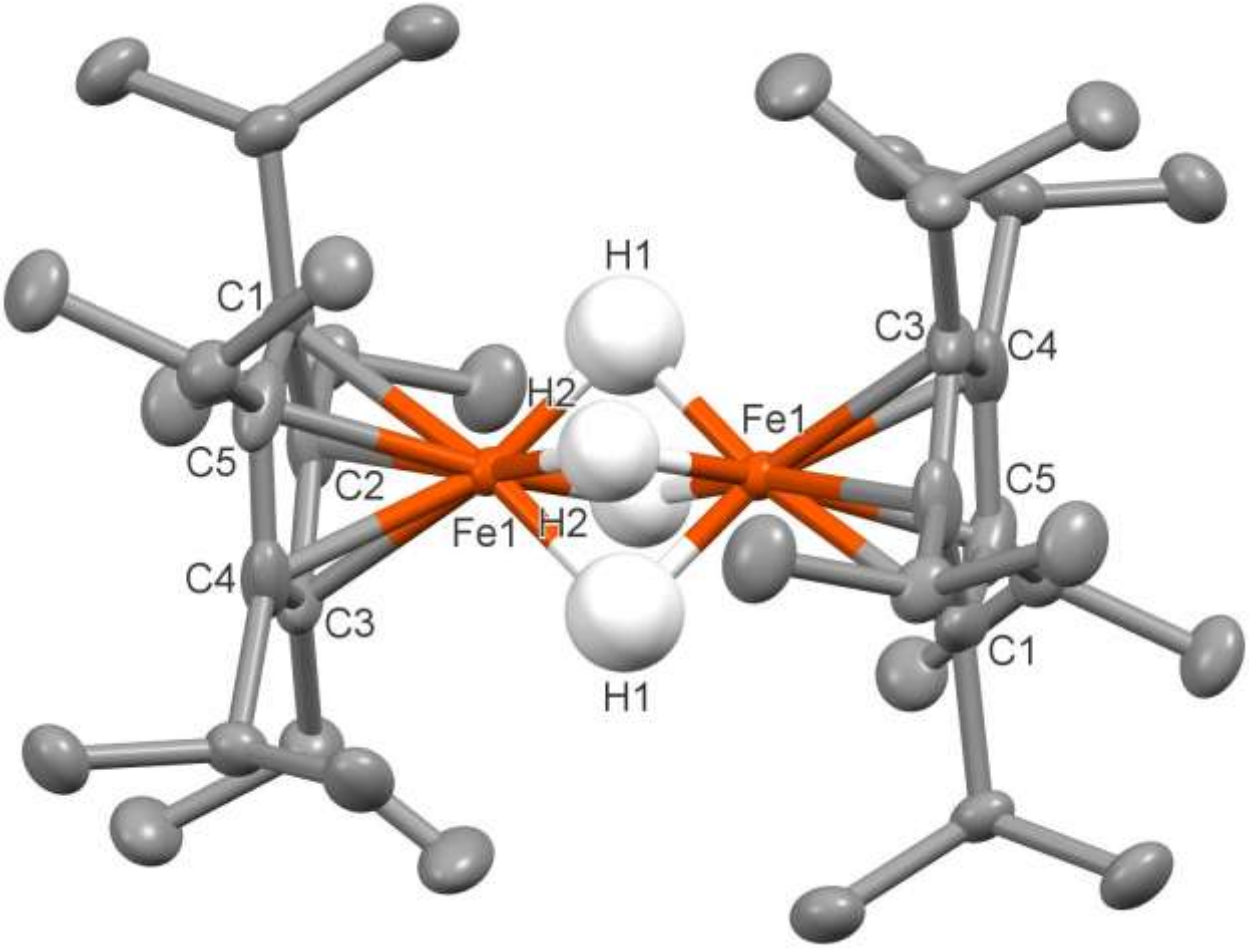


Chart S3. X-ray crystal structure of **1H**, distances/Å. Fe1–Fe1# 2.2145(6), Fe1–C1 2.074(2), Fe1–C2 2.061(2), Fe1–C3 2.048(2), Fe1–C4 2.060(2), Fe1–C5 2.072(2), Fe1–$^{5}Cp_{cent.}$ 1.673. The five-membered rings are disordered, only one of two possible orientations of isopropyl groups around the ring is shown for each ^{5}Cp ligand.



Section S3 – Additional figures and charts

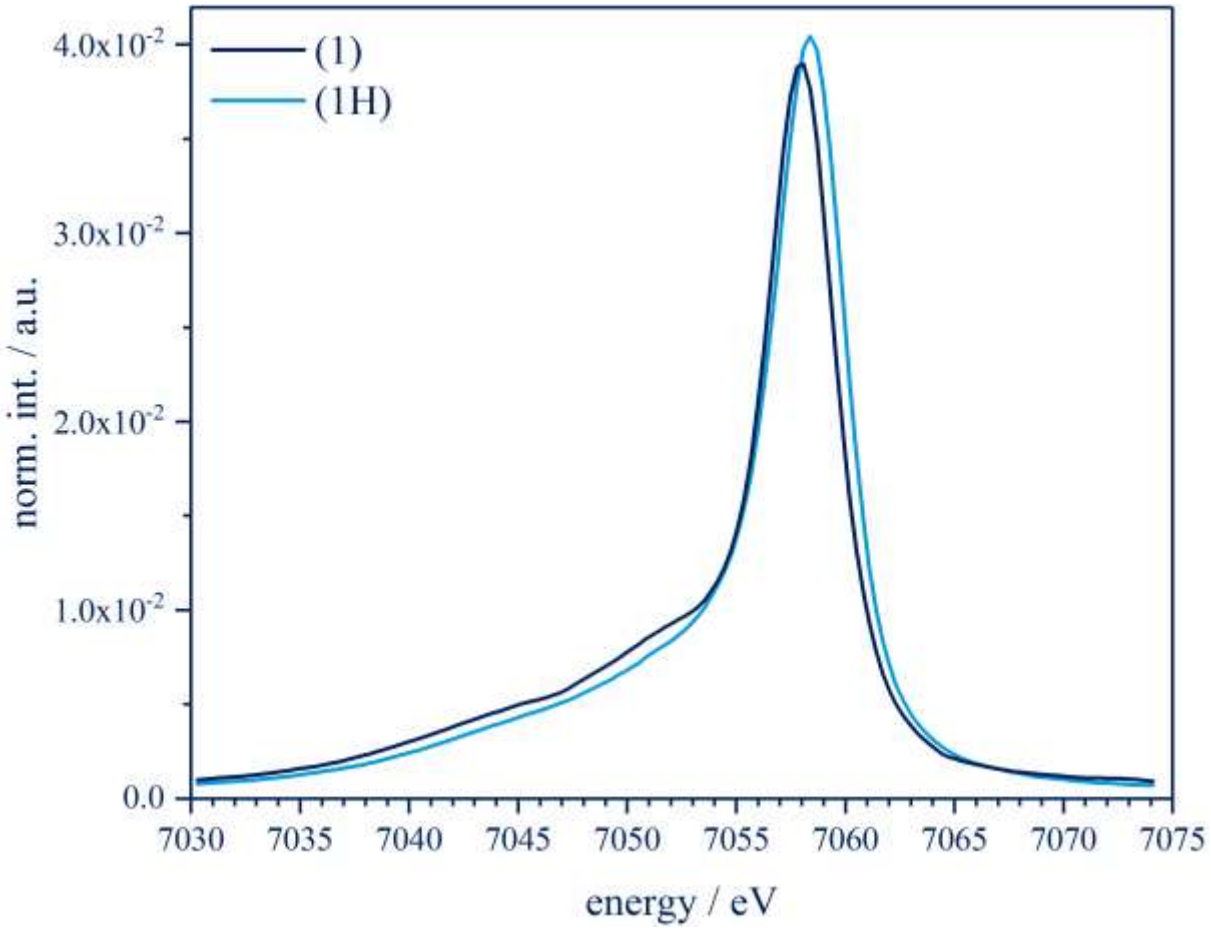


Figure S1. Experimental CtC-XES spectra of complexes **1** and **1H**.

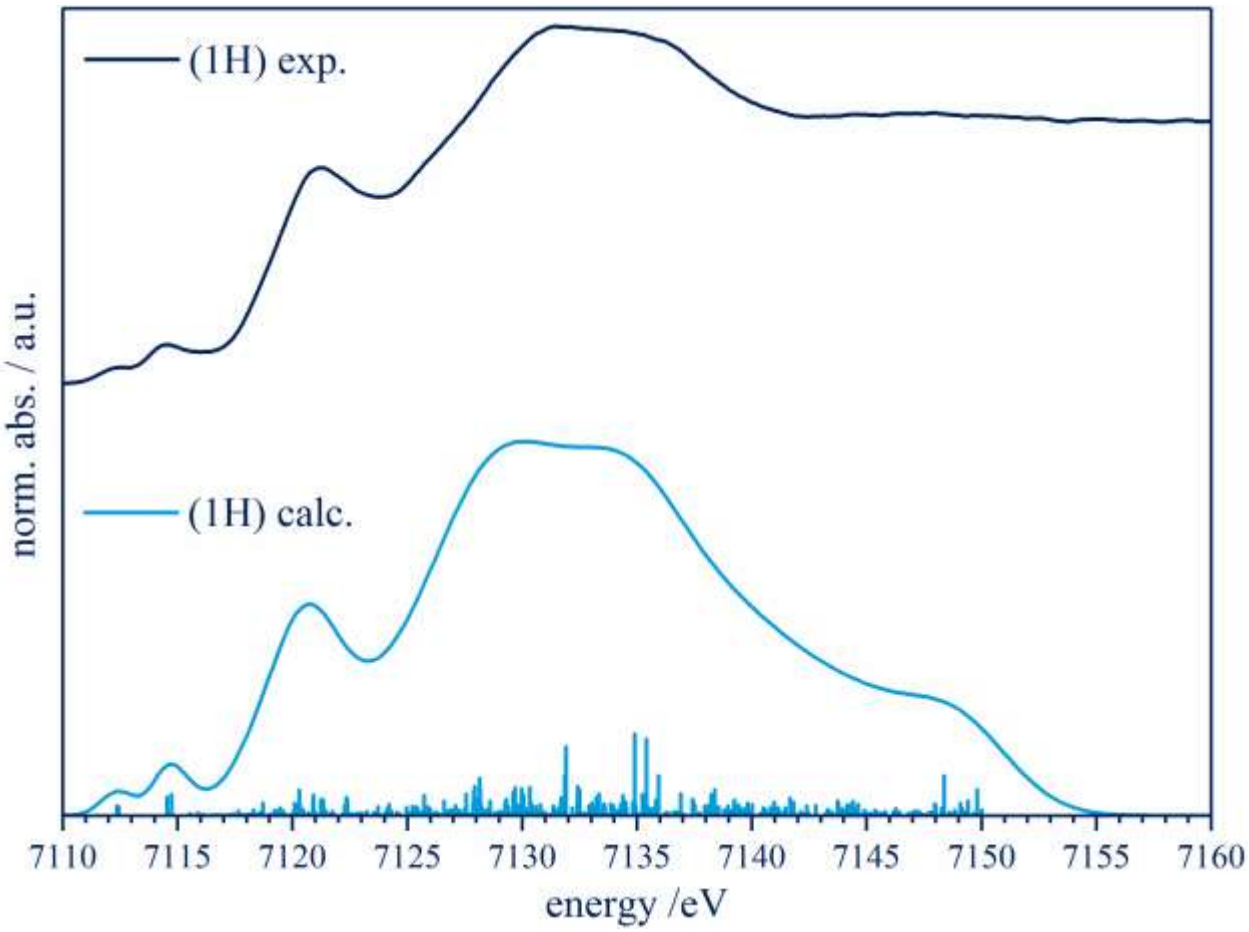


Figure S2. Comparison of experimental (top) and theoretical (M_S = 1, bottom) Fe K-edge XANES spectra of **1H**. Transitions were incremental broadened as a function of the absorption energy.

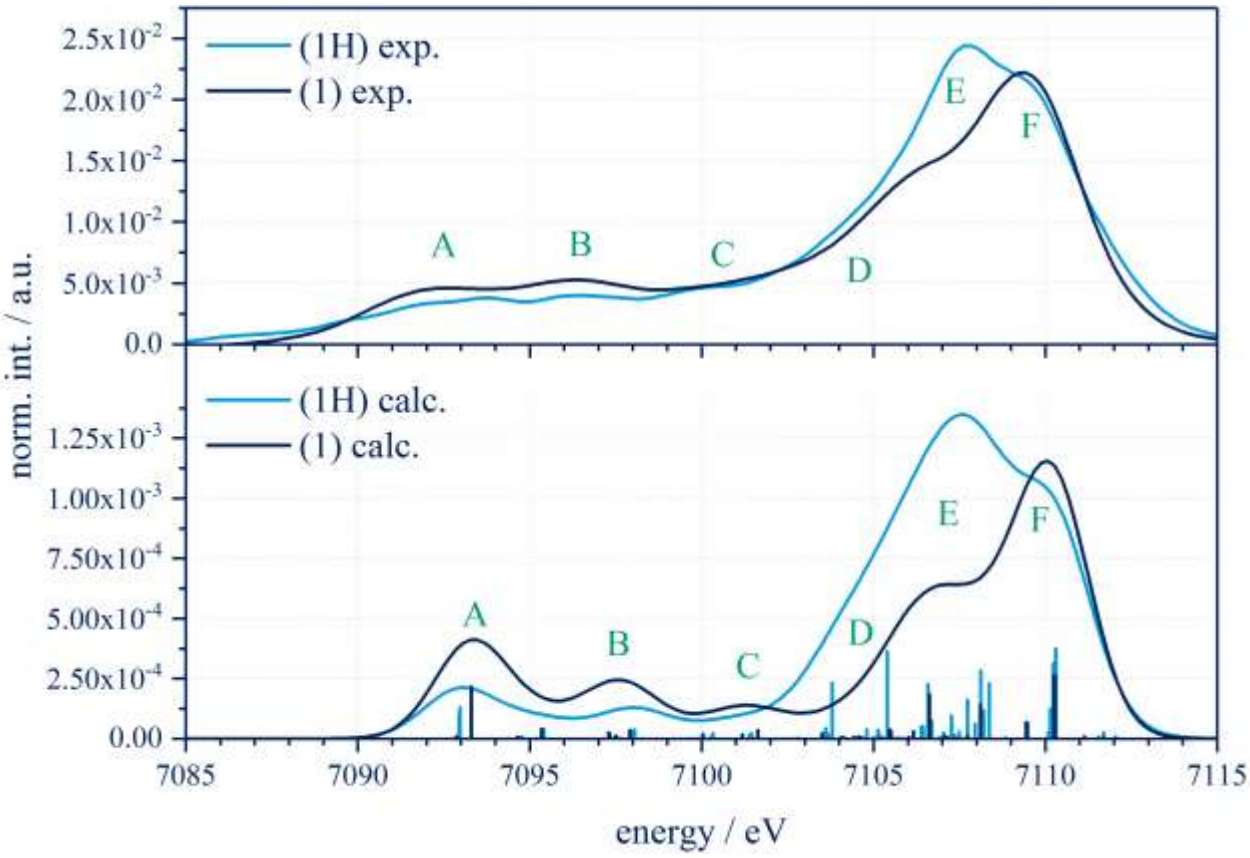


Figure S3. Comparison of experimental (top) and theoretical (M_S = 1, bottom) Fe K-edge VtC-XES spectra of **1** and **1H**.

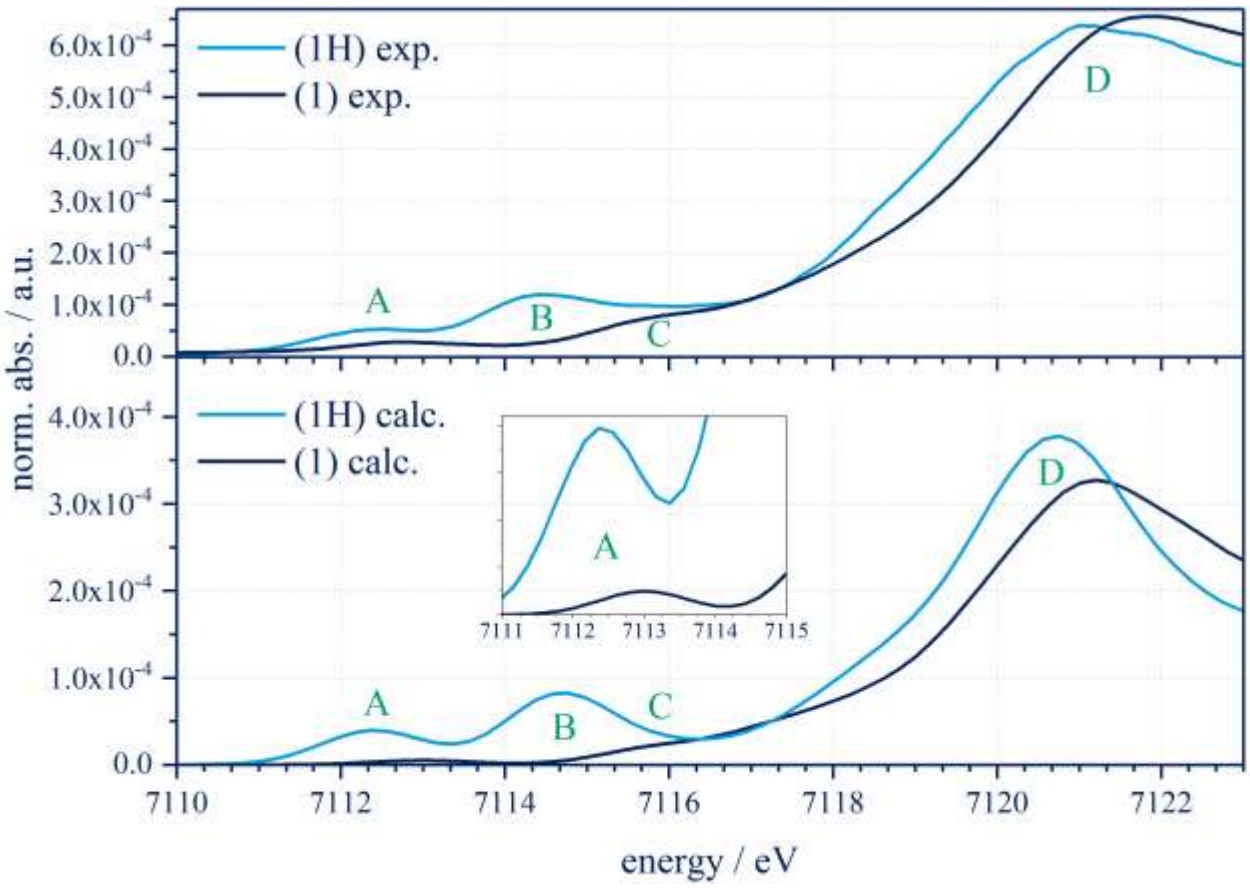


Figure S4. Comparison of experimental (top) and theoretical (M_S = 1, bottom) Fe K-edge HERFD-XANES spectra of **1** and **1H**.

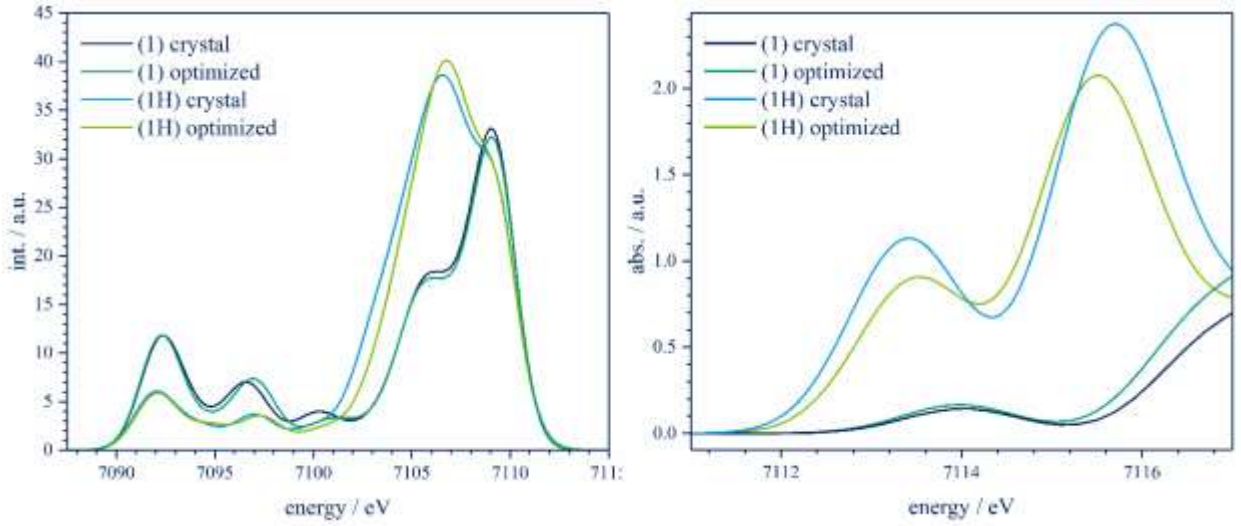


Figure S5. Comparison of calculated VtC-XES (left) and XANES (right) spectra utilizing crystal and optimized structures of **1** and **1H**.

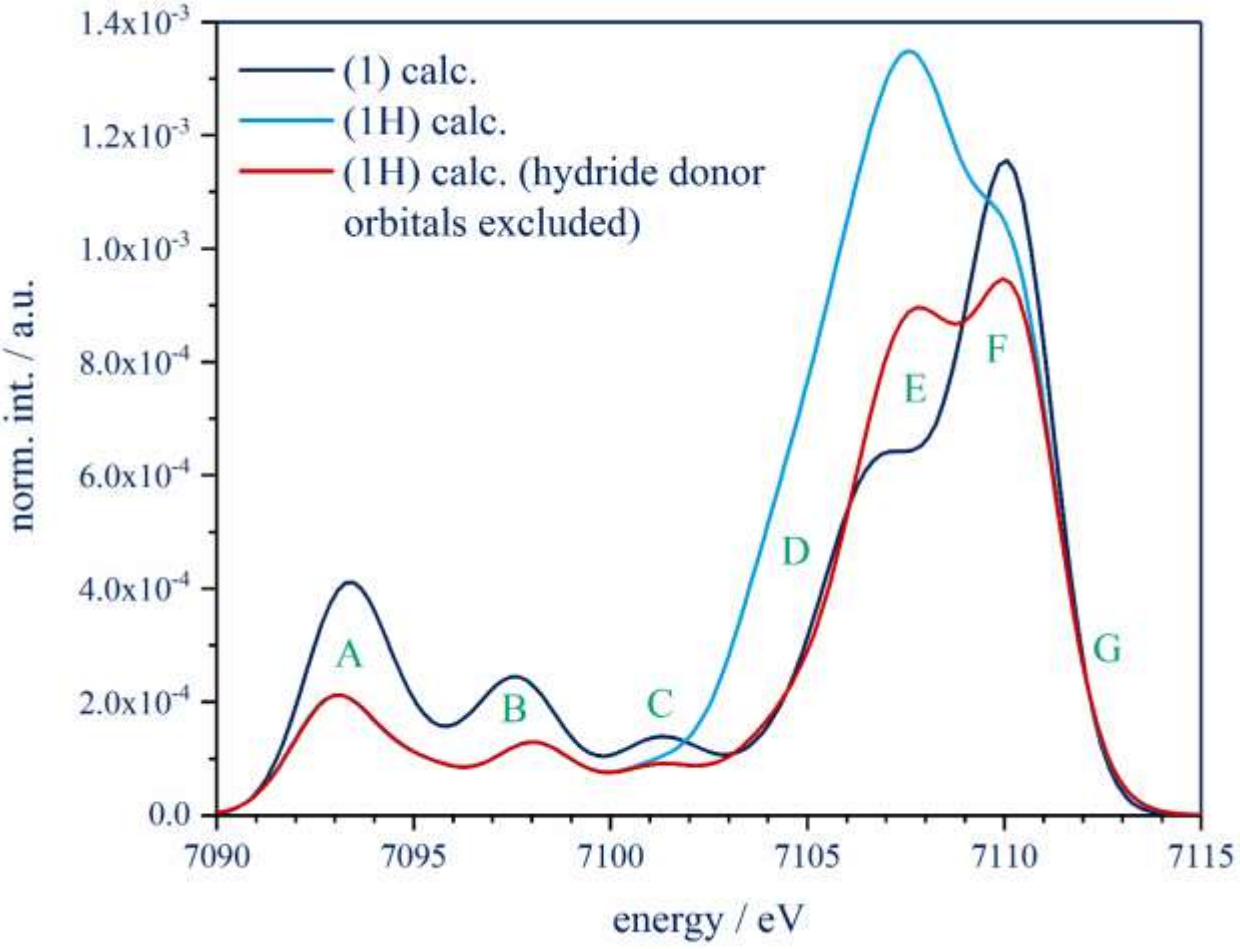
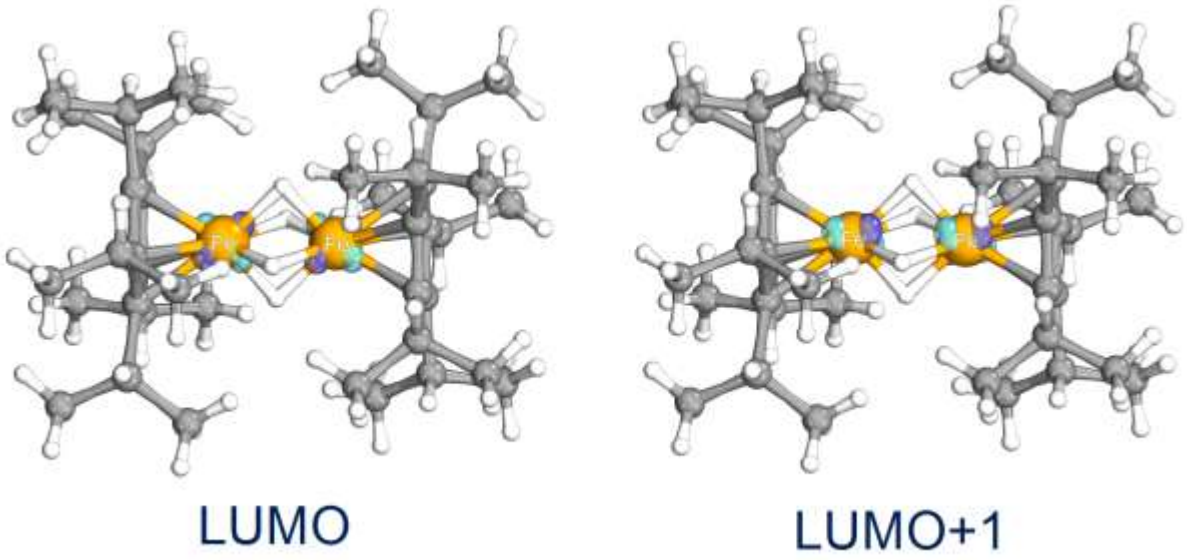


Figure S6. Comparison of theoretical Fe K-edge VtC-XES spectra of complexes **1** (dark blue), **1H** (light blue) and **1H** excluding all transitions of donor orbitals with significant hydride density (red).

Chart S4. LUMO and LUMO+1 of **1H**.



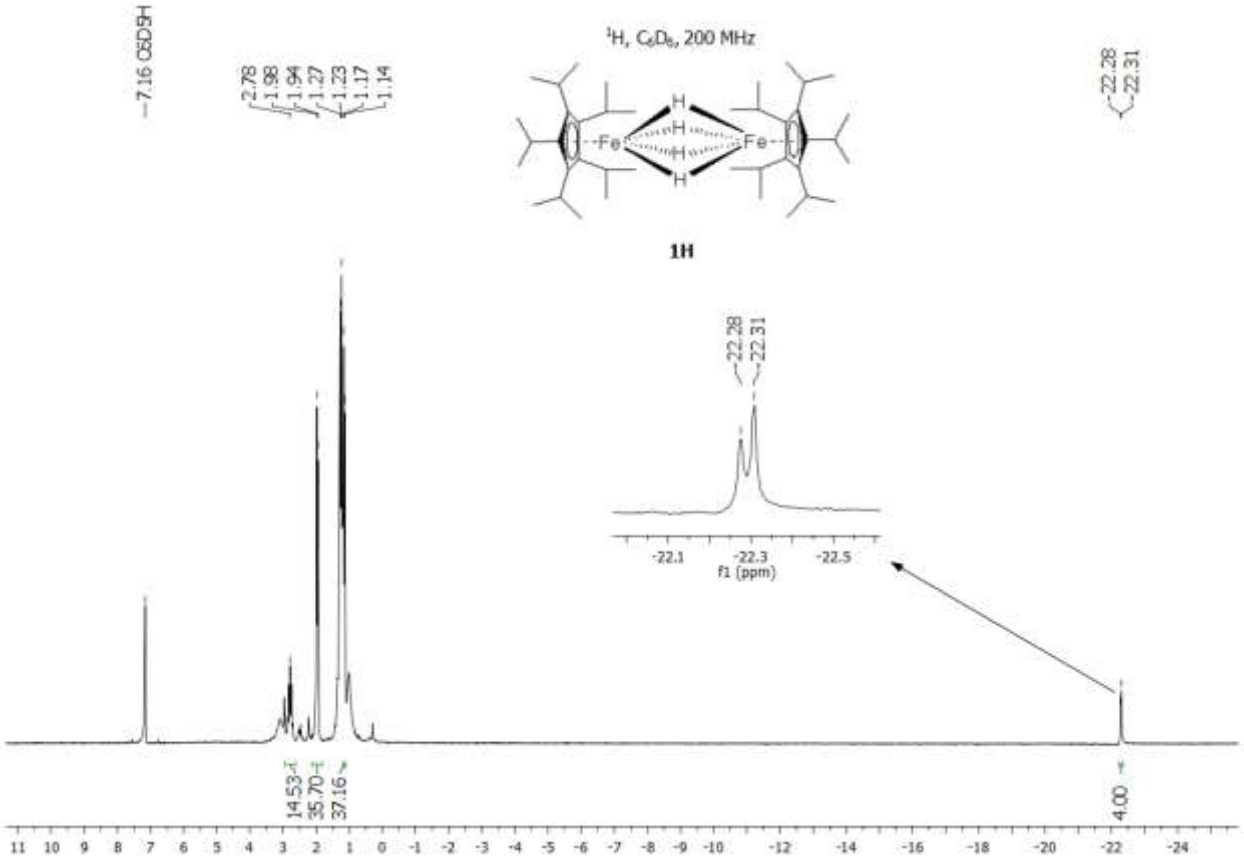


Figure S7. ^{1}H NMR of **1H** in C_6D_6.

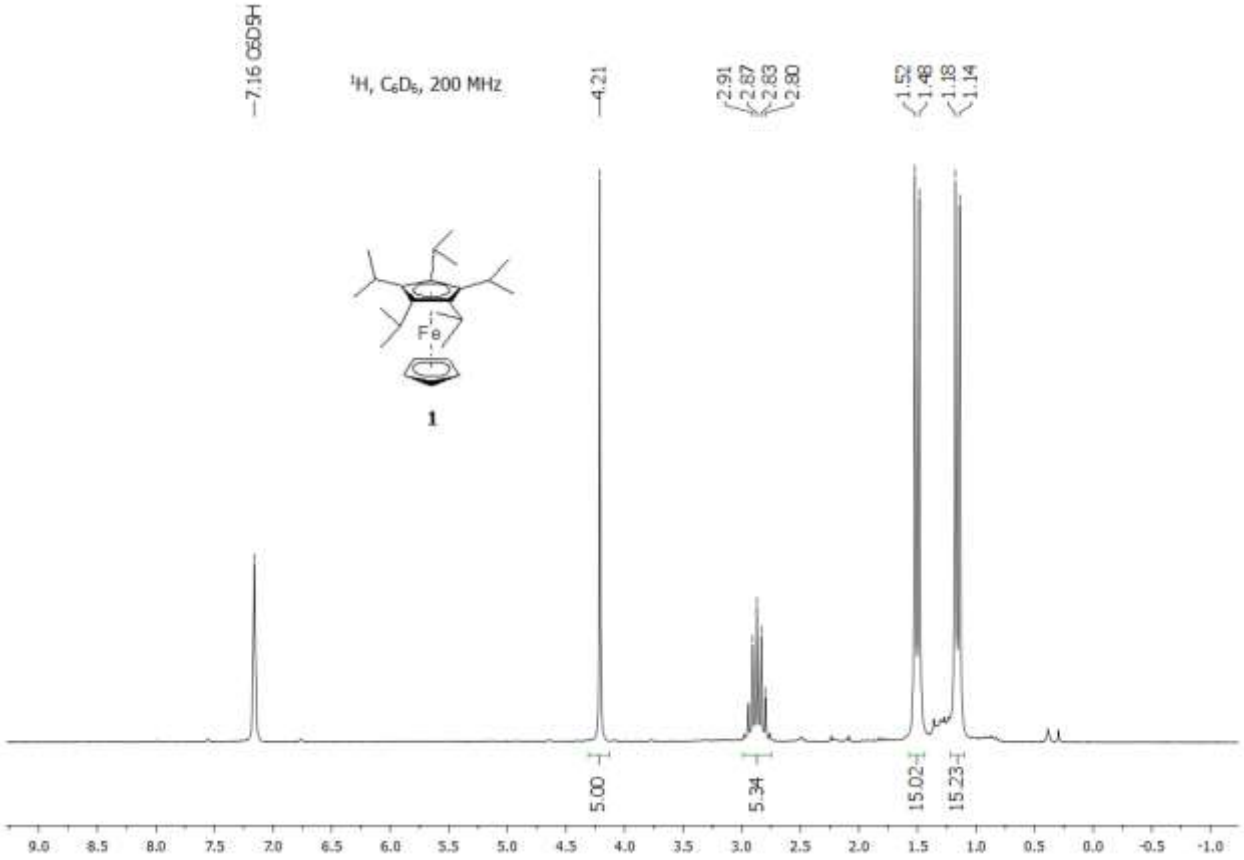


Figure S8. ^{1}H NMR of **1** in C_6D_6.

Section S4 – Composition of {H_4} and Fe localized orbitals

Table S2. AO populations of hydride localized orbitals of **1H**.

Element / fragment (orbital)	Population[a] / %							
	H-82[b] (1_o)	H-54 (2_o)	H-41 (3_o)	H-20 (4_o)	H-14 (5_o)	H-9 (6_o)	L+2[c] (1_u)	L+3 (2_u)
Fe (s, p, d)	23.4	13.2	34.8	30.6	10.8	60.8	49.6	46.8
Fe (s)	12.4	3.4	0.2	0	0	0.6	0	0
Fe (p)	8.2	7	7	5.2	5.4	0.2	8	9.8
Fe (d)	2.8	2.8	27.6	25.4	5.4	60	41.6	37
H_4 (s, p)	29	16.2	26.6	16.4	11.2	13.2	13	12.8

[a] Population of the given element via Loewdin reduced orbital population analysis. All given values are the sum over all AOs of a given element or fragment.

[b] H : HOMO, [c] L : LUMO

Table S3. AO populations of Fe localized orbitals of 1H.

Element (orbital)	Population[a] / %									
	H-9[b]	H-7	H-3	H-2	H-1	H	L[c]	L+1	L+2	L+3
Fe (s, p, d)	60.8	68	84.8	87.4	87.6	85.8	72.2	72.4	49.6	46.8
Fe (s)	0.6	1.2	0.2	2.4	0	0	0	0	0	0
Fe (p)	0.2	0.8	0.2	1.2	0	0.2	3	2.8	8	9.8
Fe (d)	60	66	84.4	83.8	87.6	85.6	69.2	69.6	41.6	37

[a] Population of the given element via Loewdin reduced orbital population analysis. All given values are the sum over all AOs of a given element.

[b] H : HOMO, [c] L : LUMO

Section S5 – VtC-XES and XANES transitions

Table S4. Comparison of all relevant TD-DFT core-excited states of complexes **1** and **1H** concerning relevant ligand/element populations (acceptor orbitals), energies and normalized intensities.

Cmpd	Feature	Transition	Calc. energy[a] / eV	Norm. Int.[b] / a.u.	Element / Ligand character	Core-excited state contribution	LUMOs
1	A	1	7113.01	0.031	Fe	0.95	LUMO
		2	7113.02	0.029	Fe	0.95	LUMO+1
1H	A	1	7112.36	0.037	Fe	0.95	LUMO
		2	7112.36	0.452	Fe	0.95	LUMO
		3	7112.45	0.040	Fe	0.96	LUMO+1
		4	7112.45	0.411	Fe	0.96	LUMO+1
	B	5	7114.55	0.891	H	0.95	LUMO+2
		6	7114.55	0.009	H	0.95	LUMO+2
		7	7114.74	1.000	H	0.94	LUMO+3
		8	7114.74	0.008	H	0.94	LUMO+3

[a] all values were shifted by 151.5 eV, [b] normalized to 1 (all values were divided by the overall highest value)

Section S6 – XYZ coordinates of all optimized structures

Optimized structure of **1**:

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C	-0.69031348669412	0.57916726436960	3.35226642791718
C	-2.02822227933197	-0.11195172502580	3.50369946205010
H	-2.78949493221171	0.66673803313256	3.46743526503396
C	-2.16044294740801	-0.75178920112325	4.88944888143739
H	-3.18621363776691	-1.08363555197968	5.06077362219491
H	-1.90401824809028	-0.04130289331655	5.67584224214847
H	-1.51510765574581	-1.62166848624367	5.01142381656186
C	-2.40821625040898	-1.09291365804791	2.39535202404328
H	-2.48337841449341	-0.58649088970671	1.43488596584003
H	-3.38082937676755	-1.54032954949821	2.60950011444572
H	-1.69555415019484	-1.90873225668506	2.27884153135634
C	-0.50070495904181	1.99476827992464	3.34266379978662
C	-1.57099514619745	3.05587262788961	3.48132728537491
H	-1.06447472508726	4.01967156727870	3.43694676879424
C	-2.22332487042046	2.99724480955863	4.86636186843562
H	-2.85058950271611	3.87534297840647	5.03105079615727
H	-1.47000718521270	2.97264027872101	5.65425744392445
H	-2.85715648160097	2.11954601153845	4.99232787827538
C	-2.61961016944984	3.10501433771316	2.37081881835632
H	-2.16050273136676	3.32741732930430	1.40942159098344
H	-3.34718547087638	3.89213000726988	2.57850908946627
H	-3.17372979431881	2.17373423536562	2.25978037080228

C	0.90416030033973	2.25166351678567	3.33277526394200
C	1.58106204269609	3.59929145570450	3.46069547333384
H	2.65457388743697	3.41614241526454	3.42264859771915
C	1.31717748169555	4.21508924218134	4.83862423401136
H	1.95630640700496	5.08578868736948	4.99684136352778
H	1.52455599745871	3.49969868542559	5.63488188683754
H	0.28548244163912	4.54604978099177	4.95725951700541
C	1.30670744173649	4.60096553283959	2.33970720130831
H	0.25022304456388	4.84140537800468	2.22615216478712
H	1.65915534654700	4.22275996724966	1.38200403071261
H	1.83237031345562	5.53707864796065	2.53823989123397
C	1.58289536786193	0.99503738169314	3.33515898039129
C	3.07350929580845	0.76840122952040	3.46800110174405
H	3.23111257741411	-0.30949822480039	3.43779646644422
C	3.57353225738287	1.21856865078948	4.84442142675621
H	3.56632896037291	2.30270023378768	4.95702629095311
H	4.59960880355479	0.88329008689531	5.00699043246904
H	2.95618259539131	0.80246029852901	5.64107781805204
C	3.94511502552957	1.32994273944355	2.34538986595905
H	3.85209462828064	2.40875122294571	2.22576423362209
H	3.69432077550643	0.87352664423655	1.38972873858118
H	4.99663943803757	1.11620400914903	2.54692747185462
C	0.59725973017274	-0.03872387699632	3.34751046904731
C	0.84134961703321	-1.52520713824850	3.49346129354660
H	-0.13577901528353	-2.00702810908667	3.46945495513323

C	1.42725517413390	-1.85126861214964	4.87097703222035
H	1.42194242522218	-2.92921464750900	5.04304943500132
H	0.84548984617130	-1.38355061609883	5.66575239579989
H	2.45773417368372	-1.51244140433285	4.97716577575862
C	1.64177937965512	-2.18945273820819	2.37396778166792
H	1.12187162463688	-2.10866196324568	1.42129070229326
H	1.77386899391980	-3.25183458831073	2.58829963411451
H	2.63421103728213	-1.76029581467742	2.24100584375627
C	-0.84232987332067	1.18409039598041	-0.00333095568286
H	-1.92131544520422	1.22656904185419	-0.00473503222618
C	0.03187827525934	2.29699114800591	-0.01270358283144
H	-0.26075662493195	3.33631793884980	-0.02334738446791
C	1.36051500029294	1.80949198627114	-0.01595094641128
H	2.25825420662008	2.40936664804779	-0.02902439846449
C	1.30747816917311	0.39525175134754	-0.00886025891824
H	2.15502735922081	-0.27371605771207	-0.01530865865580
C	-0.05393112188583	0.00879953377432	-0.00099895792133
H	-0.42791075816943	-1.00410464541081	-0.00105208736604
Fe	0.36873581200579	1.14733063704288	1.67914942997429

Optimized structure of **1H**:

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C	21.51928780380988	6.17812288097676	0.84322755088373
C	21.92550736967012	7.43256924032492	0.29807995089237
C	21.50190158032535	8.46013483541147	1.19300362435185

C	20.83215575265969	7.84040563212945	2.29053726297167
C	20.84413089086837	6.42984303610021	2.07443519629508
C	21.84898014085696	4.80389174949904	0.30276256151382
H	21.38233319046510	4.08278392302140	0.97278401852348
C	22.76897053367083	7.60026301054379	-0.94696947316360
H	22.89144486340011	6.60706687119410	-1.37775772557946
C	21.81691912711941	9.93060504623455	1.03163324630250
H	22.33628448164981	10.03609458114317	0.07979432513688
C	20.30258732942430	8.57025559570757	3.50475490170575
H	20.44457336280479	9.63395124747487	3.31605167241902
C	20.33133413475116	5.39962179178807	3.05647761129643
H	19.86576777173837	5.94987047130504	3.87347697095859
C	23.35379434484575	4.52944750295172	0.38731963142962
H	23.73568038402600	4.74121077917978	1.38657473780167
H	23.56287242565723	3.48145459018656	0.16535799178949
H	23.92935617419859	5.12986323121091	-0.31698851064768
C	21.29108479157982	4.48160317559094	-1.08254494816975
H	20.20357347007941	4.53572976941127	-1.08363306013311
H	21.65002061552646	5.15660501440395	-1.85879611666527
H	21.57593366748886	3.46894054615426	-1.37485007166085
C	24.18125993504452	8.07432877160585	-0.59082312319909
H	24.62299446534298	7.44687018142687	0.18394654443720
H	24.83097795709074	8.03030766367414	-1.46675830205848
H	24.19687806294811	9.10209910879611	-0.22802621260572
C	22.15417795858527	8.44509944371932	-2.06158785899856

H	21.19643304263221	8.03445037610006	-2.37627920363958
H	21.98427502264677	9.48148903064772	-1.77157406599234
H	22.81657691960026	8.45651612115932	-2.92942765243026
C	22.80877887192471	10.40353766083400	2.09797607154863
H	23.68265410819139	9.75232711685461	2.13760067743871
H	23.15563877381996	11.41410841611302	1.87499421407512
H	22.37115295779155	10.42481327162024	3.09597220352461
C	20.60469339965250	10.85505635309351	0.93086884660342
H	19.96340362507582	10.56120933006104	0.10174643873613
H	19.99159497384631	10.85605703919534	1.83165073573339
H	20.93010416821331	11.88289851026985	0.75870043452614
C	21.13985665153094	8.25494816343506	4.74741302128963
H	22.20234911963695	8.40605642666378	4.55343806869398
H	20.85578709083494	8.90721130372109	5.57515514156469
H	21.01198878252852	7.22725403626020	5.08716225307340
C	18.80675477618765	8.40656810304601	3.76953543794170
H	18.22411782900931	8.73261649377367	2.90965030582669
H	18.51860166233258	7.37831533217033	3.98632097283487
H	18.50958667783986	9.01326538738113	4.62717546374541
C	21.48941745123578	4.62267055926112	3.68987847668519
H	22.24472272587583	5.30049411891314	4.08902031111068
H	21.12842736308319	4.00338497879418	4.51298813294194
H	21.98613033828302	3.96019252721362	2.98096660679438
C	19.24222910536295	4.46624241138649	2.53094306528691
H	18.37527670635528	5.03341960615496	2.19572237655014

H	19.57042624225813	3.84968262463083	1.69474083462588
H	18.91460682521049	3.78980314488633	3.32279453427188
Fe	19.87173383341726	7.39932791319625	0.52532636893478
H	19.15762689603367	6.46039426605174	-0.58741504956827
H	19.47235044267032	8.11289302379530	-0.87673967114769
C	16.33311496780368	8.79968476327896	-0.84328473426608
C	15.92682144085438	7.54524960312094	-0.29817551228982
C	16.35037424685934	6.51769707772912	-1.19313479985379
C	17.02023503002546	7.13739766784899	-2.29061394371271
C	17.00829349035346	8.54795379482935	-2.07448507138891
C	16.00357593997545	10.17392491052512	-0.30273938976848
H	16.47044786776511	10.89501871560504	-0.97262482104478
C	15.08343870680607	7.37749268422917	0.94691217459961
H	14.96056472916205	8.37072838389223	1.37750046103316
C	16.03537266677280	5.04721844177008	-1.03177932437920
H	15.51686724085257	4.94156362601903	-0.07949082417352
C	17.54991670373235	6.40752645359381	-3.50475940300350
H	17.40646057758165	5.34390836918684	-3.31670197439584
C	17.52103909976698	9.57823304425392	-3.05649104723970
H	17.98695779823536	9.02807426507122	-3.87334353097281
C	14.49882568341193	10.44864551814494	-0.38750226234090
H	14.11706481670742	10.23706229009473	-1.38684368871850
H	14.28989334933179	11.49664985981602	-0.16545485891283
H	13.92304711915376	9.84824882831391	0.31664371818164
C	16.56130082013670	10.49599801685311	1.08268327436402

H	17.64880008871084	10.44163734433558	1.08397252557165
H	16.20207124855425	9.82103324671574	1.85882913544313
H	16.27662477633868	11.50870622653839	1.37499980782682
C	13.67134447190239	6.90277398215747	0.59085510095236
H	13.22932555277941	7.52997476103032	-0.18395977097921
H	13.02162787661080	6.94659516867196	1.46680194912208
H	13.65615952915674	5.87496501535715	0.22813913341798
C	15.69860234940590	6.53315771370864	2.06170767231916
H	16.65614877956205	6.94431149906048	2.37635124571996
H	15.86899806891830	5.49679129765699	1.77190325031016
H	15.03618376471720	6.52159874135484	2.92953035443176
C	15.04243456313794	4.57454760660425	-2.09723406795189
H	14.16861231342510	5.22588758480776	-2.13595660595610
H	14.69563790327640	3.56400780120137	-1.87401424906029
H	15.47909374470317	4.55328772827450	-3.09564634351360
C	17.24764727667538	4.12268087766873	-0.93244904138893
H	17.88981160413037	4.41630057557735	-0.10392489266604
H	17.85981468424518	4.12187898251039	-1.83387259258845
H	16.92236605857818	3.09481092811423	-0.76019737159291
C	16.71412832787431	6.72457138166660	-4.74796957471479
H	15.65128618755192	6.57460576870667	-4.55503905138854
H	16.99817523610834	6.07248702556511	-5.57586089029586
H	16.84350438509146	7.75233674867496	-5.08696001348005
C	19.04621204971813	6.56934336666599	-3.76810596022755
H	19.62763107649644	6.24199708817159	-2.90788207605812

H	19.33595918608345	7.59731782783299	-3.98403844210500
H	19.34333294212452	5.96273490736024	-4.62582355125164
C	16.36289637958959	10.35475191759491	-3.69031895917724
H	15.60792158106105	9.67663823505172	-4.08959491700559
H	16.72394608749883	10.97402986697871	-4.51340815512813
H	15.86576382817328	11.01718102704094	-2.98166137709938
C	18.60965399927665	10.51201895126426	-2.53066844997411
H	19.47670856041000	9.94517302364101	-2.19514792012399
H	18.28095016912831	11.12847987822353	-1.69458671452159
H	18.93728721208089	11.18855046053461	-3.32243709710582
Fe	17.98051944817920	7.57843316933972	-0.52539525776617
H	18.69546506692720	8.51733008289644	0.58770536368641
H	18.38067235780038	6.86495253941716	0.87725561519476

Section S7 – Crystallographic data

Table S5. Crystallographic data, data collection and refinement.

	1	**1H**
empirical formula	$C_{25}H_{40}Fe$	$C_{40}H_{74}Fe_2$
formula weight	396.42	666.69
crystal size [mm]	0.440x0.201x0.077	0.283x0.183x0.038
T [K]	150(2)	150(2)
λ [Å]	1.54184	1.54184
crystal system	Triclinic	Monoclinic
space group	P-1	C2/c
a [Å]	15.7706(8)	25.2350(7)
b [Å]	16.5484(7)	9.9852(2)
c [Å]	16.6794(9)	16.5066(3)
α [°]	61.161(5)	90
β [°]	64.820(7)	112.144(2)
γ [°]	86.338(4)	90
V [Å^3]	3395.5(3)	3852.48(16)
Z	6	4
$\rho_{calcd.}$ [g cm^{-3}]	1.163	1.149
μ [mm^{-1}]	5.350	6.193
θ-range [º]	3.241-62.760	3.782-62.745
refl. coll.	25620	12301
indep. refl.	10806 [R_{int} = 0.0487]	3086 [R_{int} = 0.0360]
data/restr./param.	10806/0/805	3086/0/244
final R indices [$I>2\sigma(I)$] [a]	0.0451, 0.1046	0.0336, 0.0852
R indices (all data)	0.0579, 0.1136	0.0364, 0.0872
GooF [b]	1.021	1.073
$\Delta\rho_{max/min}$ (e·Å^{-3})	0.815/-0.342	0.307/-0.316

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $\omega R2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega F_o^2]^{1/2}$. [b] $GooF = [\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$.