Electronic Supplementary Information for

Ligand Engineering of Tetra N-Heterocyclic Carbenes for Boosting Catalytic Aziridination

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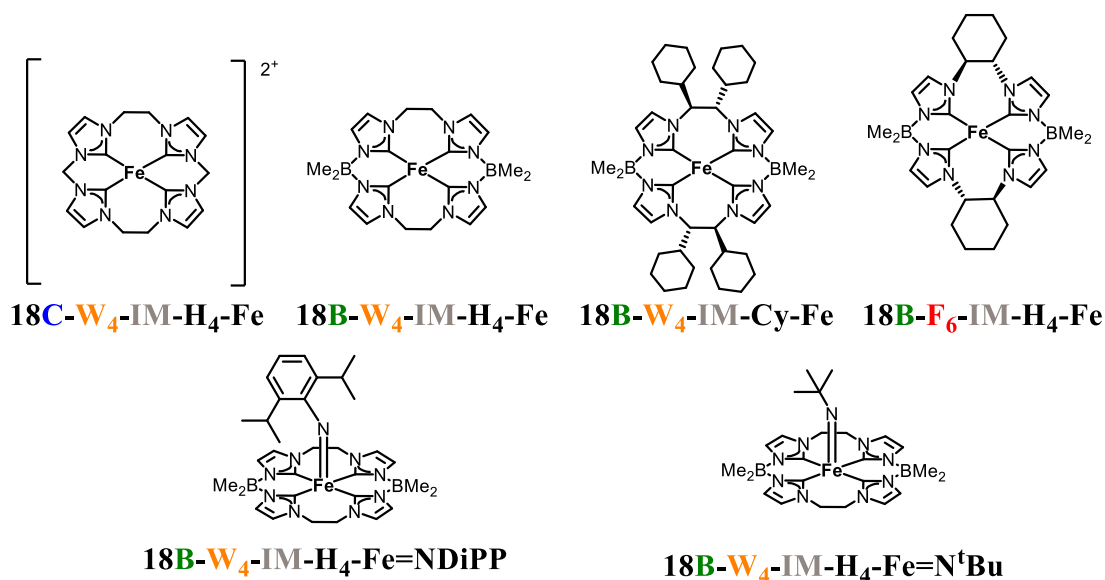
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Section S1. Density Functional Benchmarking

The use of density functional theory in computational catalysis has become a common practice, but careful consideration and benchmarking is of great importance to any study utilizing DFT. Aziridination with iron tetra-NHC catalysts have been studied using DFT in previous studies[1], where various density functionals were benchmarked (see their ESI documents). Since the publication of this study four additional iron tetra-NHC crystal structures have been isolated,[2–4] and we sought to re-evaluate the performance of various density functionals. Using the ORCA 5.0.2 software package[5] we have evaluated the performance of the BLYP, BP86, OLYP, PBE, RPBE, TPSS and SCAN density functionals. All calculations utilized Grimme's D3 dispersion correction with Becke-Johnson damping[6,7], def2-SVP was used for all non-iron atoms, and def2-TZVP was used for iron.[8,9] Key bond distances and bond angles were evaluated against the original crystal structure as a reference.

18C-W$_4$-IM-H$_4$-Fe   **18B-W$_4$-IM-H$_4$-Fe**   **18B-W$_4$-IM-Cy-Fe**   **18B-F$_6$-IM-H$_4$-Fe**

18B-W$_4$-IM-H$_4$-Fe=NDiPP   **18B-W$_4$-IM-H$_4$-Fe=N^{t}Bu**

Figure S - 1. Selected geometries with experimentally refined crystal structures used for DFT benchmarking.

The key bond distances and angles for the crystal structures that are not intermediates (iron(IV)-imides) are shown in **Table S - 1**. The key bond distances and angles for the remaining to iron(IV)-imide crystal structures can be found in **Table S - 2**.

Coordinate	18C-W$_4$-IM-H$_4$-Fe	18B-W$_4$-IM-H$_4$-Fe	18B-W$_4$-IM-Cy$_4$-Fe	18B-F$_6$-IM-H$_4$-Fe
Fe-C$_1$	2.052	1.941	2.046	1.951
Fe-C$_2$	1.986	1.941	1.984	2.006
Fe-C$_3$	2.029	1.943	1.992	1.938
Fe-C$_4$	1.977	1.934	2.031	2.005
C$_1$-Fe-C$_3$	3.286	3.461	3.379	3.477
C$_2$-Fe-C$_4$	3.287	3.439	3.384	3.351
C$_1$-Fe-C$_2$	1.931	179.197	171.291	120.193
C$_3$-Fe-C$_4$	1.917	178.265	167.254	157.593
[a]E-Fe-E	169.726	89.214	86.593	10.025

[a]E denotes the group that links together the dicarbene subunits, either BMe_3 or CH_2

Table S - 1. Key bond distances and angles for the various crystal structures used in benchmarking, in Å and degrees.

Coordinate	18B-W$_4$-IM-H$_4$-Fe=N^{t}Bu	18B-W$_4$-IM-H$_4$-Fe=NDiPP
Fe-C$_1$	1.933	1.986
Fe-C$_2$	1.929	1.980
Fe-C$_3$	1.987	1.973
Fe-C$_4$	1.996	1.978
Fe-N	1.655	1.730
Fe-N-R	150.067	163.041
C$_1$-Fe-C$_3$	143.063	150.826
C$_2$-Fe-C$_4$	141.191	152.798
C$_1$-Fe-C$_2$	86.776	86.388
C$_3$-Fe-C$_4$	83.716	86.280
^{a}E-Fe-E	109.083	129.001

^{a}E denotes the group that links together the dicarbene subunits, either BMe$_3$ or CH$_2$

Table S - 2. Key bond distances and angles for the various crystal imide structures used in benchmarking in Å and degrees

Bond Angles (degrees)		Bond Lengths (Å)	
Functional	MAE(deg)	Functional	MAE(Å)
BLYP	3.00	BLYP	0.026
BP86	2.03	BP86	0.025
OLYP	3.22	OLYP	0.040
PBE	1.42	PBE	0.023
Rpbe	2.96	Rpbe	0.032
TPSS	2.96	TPSS	0.024
SCANfunc	3.37	SCANfunc	0.025

Table S - 3. Overall density functional mean absolute error in bond lengths (right) and bond angles (left).

The top performers are PBE-D3(BJ), TPSS-D3(BJ), and BP86-D3(BJ), with PBE-D3(BJ) providing the both the most accurate bond angles and bond lengths. This has led us to conclude TPSS and PBE provide the most accurate results, but due to its' computational efficiency, PBE was chosen as our density functional of choice.

Section S1.1. Computational Details, Convergence Criteria and Transition State Optimization

All geometry optimizations and frequency calculations were carried using the ORCA 5.0.2 software package[1, 2]. All results shown herein were obtained with the PBE density functional[3], along with Grimme's D3 dispersion correction with Becke-Johnson Damping (D3(BJ))[4, 5] and the resolution of identity (RI)[6]. The def2-SVP basis set was used for all non-iron atoms, while iron employed the def2-TZVP basis set,[7, 8] with matching auxiliary basis sets. All calculations were carried out with an intermediate spin-state (S = 1), as it is the predicted ground state from

DFT, multireference methods and experimental methods[9-12]. Additionally the calculation of free volume was performed using SambVca 2.0[13]. All Natural Orbitals for Chemical Valence (NOCV) calculations were carried out in the Multiwfn software package[14]. In addition, the convergence criteria for the SCF and geometry optimization cycles are listed below:

Criteria	Tolerance	Units
Energy Change	5.00E-06	E_h
Max. Gradient	3.00E-04	E_h/Bohr
RMS Gradient	1.00E-04	E_h/Bohr
Max. Displacement	4.00E-03	Bohr
RMS Displacement	2.00E-03	Bohr

Table S 1. Convergence criteria

Identifying true minima in optimizations was done through analysing the vibrational frequencies for any imaginary frequencies. There were multiple approaches taken for identifying transition structures.

1. All transition structures began with a transition state relaxed surface scan of the internal coordinate of interest (ORCA keyword:ScanTS).

   TS1: [Fe-$N_1R=N_2=N_3$] N_1-N_2 was scanned from 1.2 to 1.8 angstroms with 10 steps of 0.06 angstroms each.

   TS2: [Fe=N_1R--C_{Decene}] N_1---C_{decene} was scanned from 1.5 to 2.0 angstroms with 10 steps of 0.05 angstroms each.

TS3: [Fe-N_1-C_{Tolyl} -C_{Decene}] the angle N_1-C_{tolyl}-C_{Decene} was scanned from 95 degrees to 55 degrees of steps of 2 degrees each

2. Each transition structure was further relaxed with a transition state optimization (ORCA Keyword: OptTS) using the same energy and geometry tolerances.

3. Manual inspection to ensure a single imaginary frequency and visual inspection of the vibrational mode to ensure expected stretches/bends.
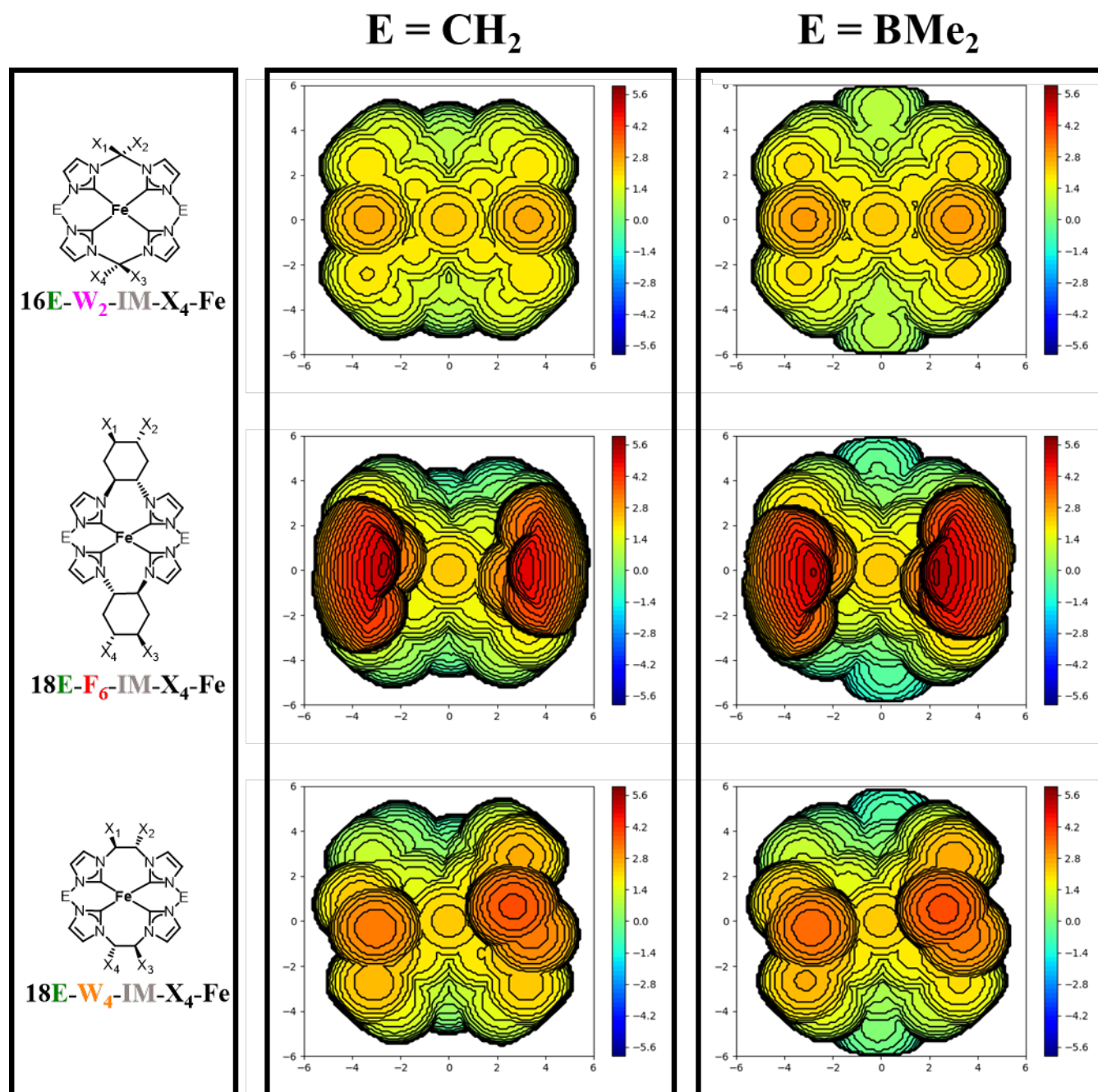
Section S2. Free Volume, Steric-Mapping, Key Bond Lengths and Tolman Electronic Parameters

Free/Buried volume calculations have been used as a steric descriptor extensively for transition metal complexes with carbene ligands.
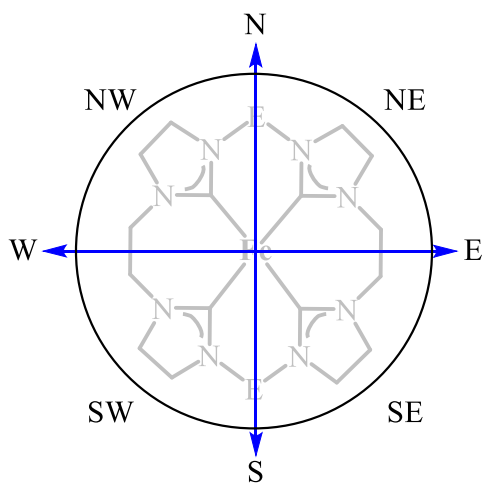

Scheme S - 1. Representation of the decomposition of regions for quadrant analysis, as an example 18E-W_4-IN-H_4-Fe has been shown.
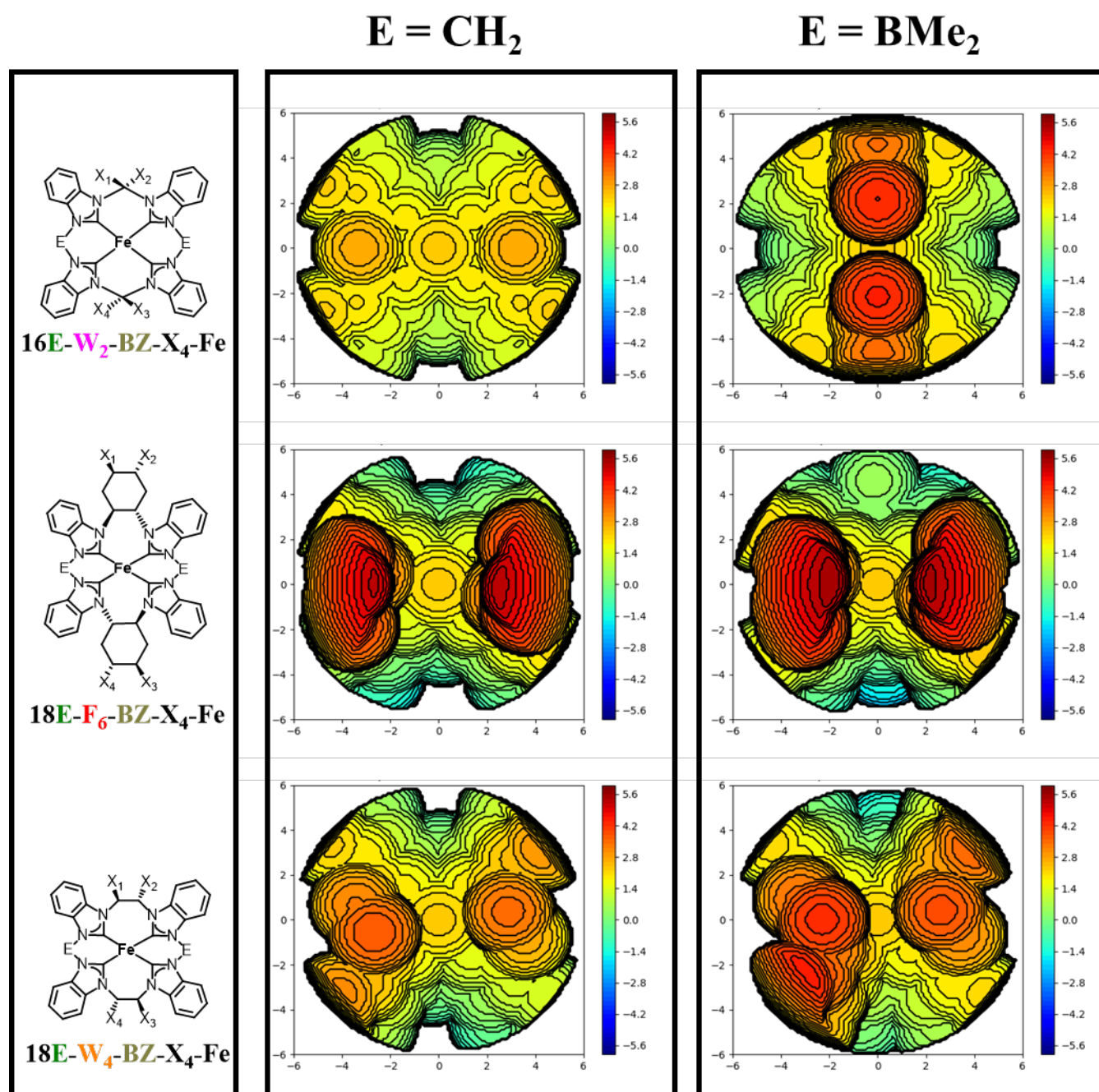
Figure S - 2. Steric mapping of complexes containing imidazole (IM) carbene subunits. Left panel showing the chemical structures, where the "E" can be either CH_2 (center panel) or BMe_2 (right panel). Steric maps shown for $16E-W_2-IM-H_4-Fe$ (top), $18E-F_6-IM-H_4-Fe$ (middle) and $18E-W_4-IM-H_4-Fe$ (bottom).
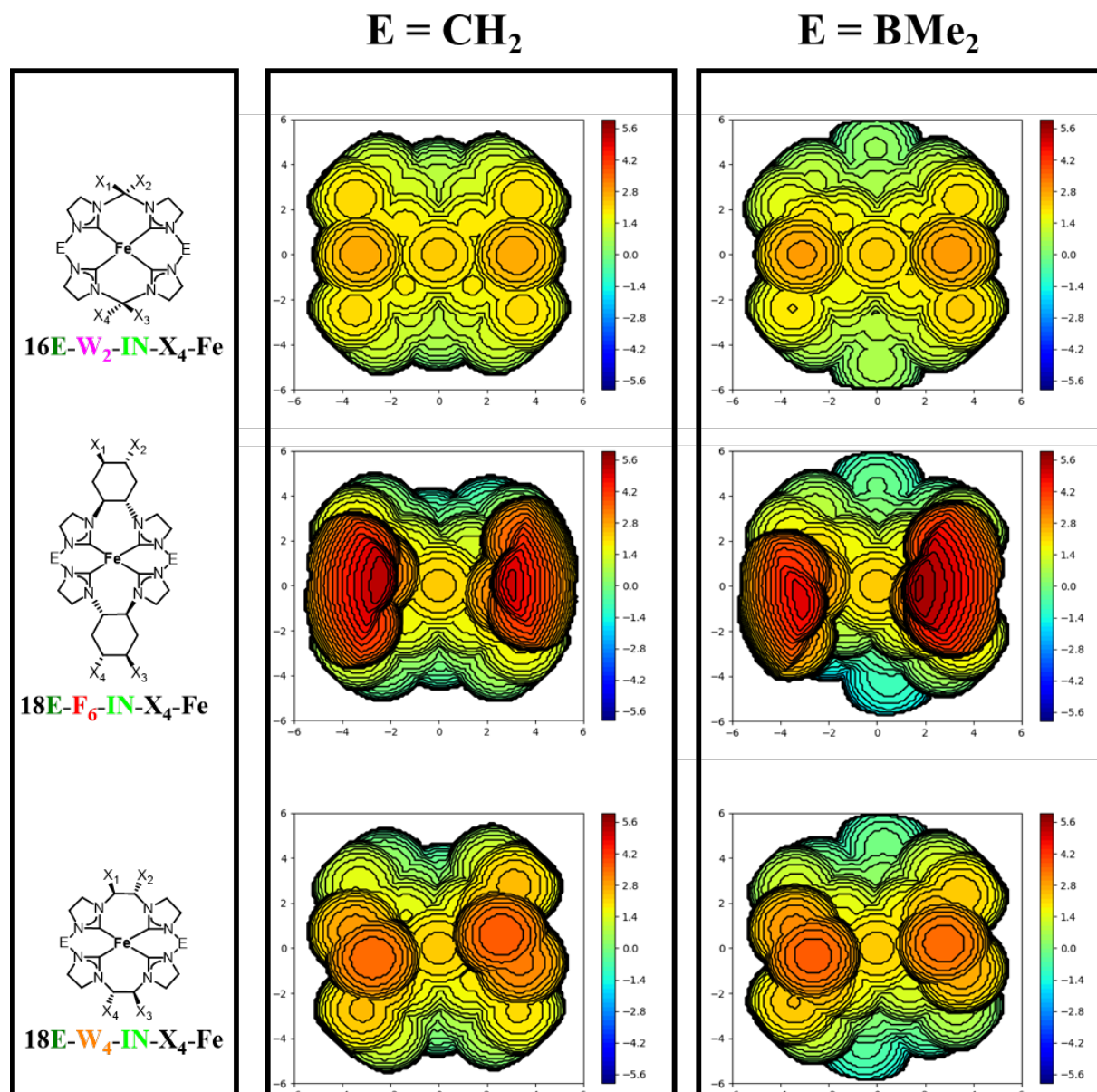
Figure S - 3. Steric mapping of complexes containing imidazole (IM) carbene subunits. Left panel showing the chemical structures, where the "E" can be either CH_2 (center panel) or BMe_2 (right panel). Steric maps shown for 16E-W_2-IM-H_4-Fe (top), 18E-F_6-IM-H_4-Fe (middle) and 18E-W_4-IM-H_4-Fe (bottom).

Figure S - 4. Steric mapping of complexes containing imidazole (IM) carbene subunits. Left panel showing the chemical structures, where the "E" can be either CH_2 (center panel) or BMe_2

(right panel). Steric maps shown for 16E-W_2-IM-H_4-Fe (top), 18E-F_6-IM-H_4-Fe (middle) and 18E-W_4-IM-H_4-Fe (bottom).

Complex	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}	%V_{Buried}
16C-W_2-IM-H_4-Fe	562.9	341.1	904	62.3	37.7
18C-W_4-IM-H_4-Fe	529.8	374.2	904	58.6	41.4
18C-F_6-IM-H_4-Fe	470.4	433.6	904	52	48
16B-W_2-IM-H_4-Fe	498.2	405.8	904	55.1	44.9
18B-W_4-IM-H_4-Fe	465.7	438.3	904	51.5	48.5
18B-F_6-IM-H_4-Fe	400.3	503.7	904	44.3	55.7
16C-W_2-IN-H_4-Fe	554.9	349.1	904	61.4	38.6
18C-W_4-IN-H_4-Fe	522.2	381.8	904	57.8	42.2
18C-F_6-IN-H_4-Fe	457.4	446.7	904	50.6	49.4
16B-W_2-IN-H_4-Fe	488.6	415.4	904	54.0	46.0
18B-W_4-IN-H_4-Fe	455.7	448.3	904	50.4	49.6
18B-F_6-IN-H_4-Fe	380.3	523.7	904	42.1	57.9
16C-W_2-BZ-H_4-Fe	526.1	377.9	904	58.2	41.8
18C-W_4-BZ-H_4-Fe	495.5	408.5	904	54.8	45.2
18C-F_6-BZ-H_4-Fe	424.6	479.4	904	47.0	53.0
16B-W_2-BZ-H_4-Fe	461.9	442.2	904	51.1	48.9
18B-W_4-BZ-H_4-Fe	431.1	473	904	47.7	52.3
18B-F_6-IN-H_4-Fe	352.5	551.5	904	39.0	61.0

Table S - 4. Tabulated values from steric mapping and analysis. V_{Free}, V_{Buried} and V_{Total} are all shown in units of Å^3 and represent that calculated volumes. The percentage of free volume and buried volume are percentages in comparison to the total volumes. The total volume for each molecule is identical at 904 Å^3, which is a result of the chosen sphere radius.

16C-W_2-IM-H_4-Fe				
Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}
SW	140.8	85.2	226	62.3
NW	140.6	85.4	226	62.2
NE	140.6	85.4	226	62.2
SE	140.9	85.1	226	62.3
18C-W_4-IM-H_4-Fe				
Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}
SW	135.4	90.6	226	59.9
NW	132.7	93.3	226	58.7
NE	128.5	97.5	226	56.9

SE	133.1	92.9	226	58.9

18C-F₆-IM-H₄-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	115.8	110.2	226	51.2
NW	117.3	108.7	226	51.9
NE	114.5	111.5	226	50.7
SE	122.7	103.3	226	54.3

16B-W₂-IM-H₄-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	124.7	101.3	226	55.2
NW	124.7	101.3	226	55.2
NE	124.5	101.5	226	55.1
SE	124.3	101.7	226	55

18B-W₄-IM-H₄-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	116.6	109.4	226	51.6
NW	122.8	103.2	226	54.3
NE	107.6	118.4	226	47.6
SE	118.7	107.3	226	52.5

18B-F₆-IM-H₄-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	101.8	124.2	226	45
NW	103	123	226	45.6
NE	100	126	226	44.3
SE	95.6	130.4	226	42.3

Table S - 5. Steric analysis of IM based complexes, where quadrants decompose the steric map into four regions, Southwest (SW), Northwest(NW), Northeast (NE) and Southeast (SE).

16C-W₂-IN-H₄-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	138.6	87.4	226	61.3
NW	138.8	87.2	226	61.4
NE	138.9	87.1	226	61.4
SE	138.6	87.4	226	61.3

18C-W₄-IN-H₄-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	132	94	226	58.4
NW	130.7	95.3	226	57.8
NE	128.8	97.2	226	57
SE	130.7	95.3	226	57.8

18C-F₆-IN-H₄-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	112.6	113.4	226	49.8

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}
NW	113.6	112.4	226	50.2
NE	110.6	115.5	226	48.9
SE	120.6	105.4	226	53.4

16B-W$_2$-IN-H$_4$-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}
SW	123.4	102.6	226	54.6
NW	122.7	103.3	226	54.3
NE	121.2	104.8	226	53.6
SE	121.3	104.7	226	53.7

18B-W$_4$-IN-H$_4$-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}
SW	106.3	119.7	226	47
NW	118	108	226	52.2
NE	110.5	115.5	226	48.9
SE	120.9	105.1	226	53.5

18B-F$_6$-IN-H$_4$-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}
SW	97.7	128.3	226	43.3
NW	105.3	120.7	226	46.6
NE	92.4	133.6	226	40.9
SE	84.8	141.2	226	37.5

Table S - 6. Steric analysis of IN complexes, where quadrants decompose the steric map into four regions, Southwest (SW), Northwest(NW), Northeast (NE) and Southeast (SE).

16C-W$_2$-BZ-H$_4$-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}
SW	131.5	94.5	226	58.2
NW	131.5	94.5	226	58.2
NE	131.5	94.5	226	58.2
SE	131.5	94.5	226	58.2

18C-W$_4$-BZ-H$_4$-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}
SW	121.2	104.8	226	53.6
NW	124.5	101.5	226	55.1
NE	125.3	100.7	226	55.5
SE	124.4	101.6	226	55.1

18C-F$_6$-BZ-H$_4$-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	%V_{Free}
SW	89.9	136.1	226	39.8
NW	85	141	226	37.6
NE	84.8	141.2	226	37.5
SE	92.8	133.2	226	41

16B-W$_2$-BZ-H$_4$-Fe

Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	115.3	110.7	226	51
NW	115.7	110.3	226	51.2
NE	115.5	110.5	226	51.1
SE	115.3	110.7	226	51
18B-W$_4$-BZ-H$_4$-Fe				
Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	100.6	125.5	226	44.5
NW	109.5	116.5	226	48.5
NE	102.1	123.9	226	45.2
SE	118.8	107.2	226	52.6
18B-F$_6$-IN-H$_4$-Fe				
Quadrant	V_{Free} (Å^3)	V_{Buried} (Å^3)	V_{Total} (Å^3)	$\%V_{Free}$
SW	89.9	136.1	226	39.8
NW	85	141	226	37.6
NE	84.8	141.2	226	37.5
SE	92.8	133.2	226	41

Table S - 7. Steric analysis of BZ complexes , where quadrants decompose the steric map into four regions, Southwest (SW), Northwest(NW), Northeast (NE) and Southeast (SE).

Complex	μ(Fe-Carbene) (Å)	Fe=N (Å)	Fe=N-Tolyl (degrees)
16B-W$_2$-IM-H$_4$-Fe	1.945	1.707	145.56
16C-W$_2$-IM-H$_4$-Fe	1.929	1.718	156.46
18B-F$_6$-IM-H$_4$-Fe	1.975	1.713	142.58
18C-F$_6$-IM-H$_4$-Fe	1.958	1.711	149.34
18B-W$_4$-IM-H$_4$-Fe	1.977	1.713	143.33
18C-W$_4$-IM-H$_4$-Fe	1.969	1.716	149.58
16B-W$_2$-IN-H$_4$-Fe	1.958	1.701	148.3
16C-W$_2$-IN-H$_4$-Fe	1.949	1.715	153.82
18B-F$_6$-IN-H$_4$-Fe	1.970	1.713	144.87
18C-F$_6$-IN-H$_4$-Fe	1.964	1.707	149.88
18B-W$_4$-IN-H$_4$-Fe	1.967	1.712	145.11
18C-W$_4$-IN-H$_4$-Fe	1.971	1.712	149.26

16B-W$_2$-BZ-H$_4$-Fe	1.943	1.710	144.85
16C-W$_2$-BZ-H$_4$-Fe	1.931	1.716	154.61
18B-F$_6$-BZ-H$_4$-Fe	1.982	1.716	142.03
18C-F$_6$-BZ-H$_4$-Fe	1.961	1.711	150.64
18B-W$_4$-BZ-H$_4$-Fe	1.977	1.716	144.13
18C-W$_4$-BZ-H$_4$-Fe	1.965	1.716	148.82

Table S - 8. Key bond lengths and distances for the iron(IV) imide intermediate.

Complex	Fe=N (Å)	Fe=N-Tolyl (Å)	N-Radical (Å)	$V_{imaginary}$ (cm^{-1})
16B-W$_2$-IM-H$_4$-Fe	1.823	126.55	1.870	(i)639.8
16C-W$_2$-IM-H$_4$-Fe	1.794	127.02	1.917	(i)457.3
18B-F$_6$-IM-H$_4$-Fe	1.787	130.70	1.858	(i)553.4
18C-F$_6$-IM-H$_4$-Fe	1.821	131.01	1.947	(i)522.0
18B-W$_4$-IM-H$_4$-Fe	1.801	129.30	1.865	(i)572.6
18C-W$_4$-IM-H$_4$-Fe	1.817	132.82	1.920	(i)427.1
16B-W$_2$-IN-H$_4$-Fe	1.811	127.56	1.882	(i)492.9
16C-W$_2$-IN-H$_4$-Fe	1.794	129.12	1.924	(i)450.6
18B-F$_6$-IN-H$_4$-Fe	1.781	130.27	1.862	(i)555.7
18C-F$_6$-IN-H$_4$-Fe	1.821	130.04	1.941	(i)465.2
18B-W$_4$-IN-H$_4$-Fe	1.823	127.42	1.862	(i)440.3
18C-W$_4$-IN-H$_4$-Fe	1.806	129.90	1.929	(i)431.9
16B-W$_2$-BZ-H$_4$-Fe	1.792	127.62	1.862	(i)443.9
16C-W$_2$-BZ-H$_4$-Fe	1.793	128.49	1.938	(i)437.2
18B-F$_6$-BZ-H$_4$-Fe	1.788	130.97	1.893	(i)548.8

18C-F$_6$-BZ-H$_4$-Fe	1.823	130.27	1.957	(i)472.4
18B-W$_4$-BZ-H$_4$-Fe	1.846	126.47	1.891	(i)476.1
18C-W$_4$-BZ-H$_4$-Fe	1.808	129.8	1.930	(i)435.9

Table S - 9. Tabulated key bond lengths (Å), bond angles (degrees) for the iron(IV)-imide species and the activated complex (TS$_2$). Additionally, the imaginary frequency corresponding to the N-C$_{radical}$ bond formation for TS$_2$ is included, values displayed in cm^{-1}.
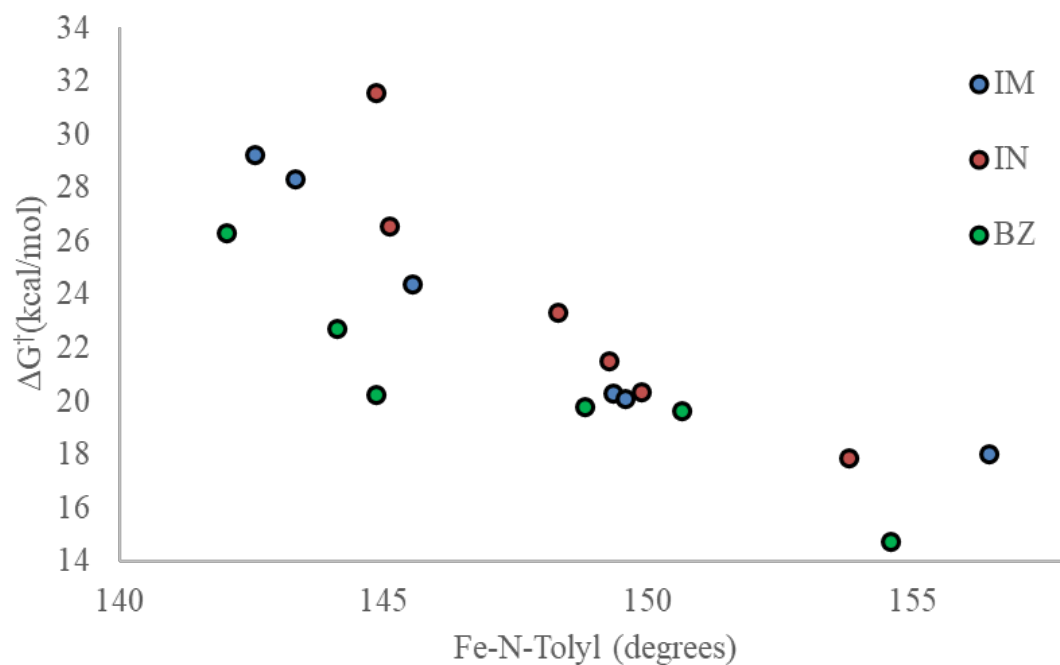
Figure S - 5. Scatter plot of the Fe=N-Tolyl bond angle vs $\Delta G^{\dagger}$, with imidazole subunits in blue, imidazoline subunits in red and benzimidazole subunits in green.

Complex	ν_{CO} (cm^{-1})
18B-F$_6$-BZ-H$_4$-Fe	1887.27
18B-W$_4$-BZ-H$_4$-Fe	1924.10
16B-W$_2$-BZ-H$_4$-Fe	1964.60
18C-F$_6$-BZ-H$_4$-Fe	1973.42
18C-W$_4$-BZ-H$_4$-Fe	1993.36
16C-W$_2$-BZ-H$_4$-Fe	2031.24
18B-F$_6$-IM-H$_4$-Fe	1890.20
18B-W$_4$-IM-H$_4$-Fe	1914.06
16B-W$_2$-IM-H$_4$-Fe	1955.48
18C-F$_6$-IM-H$_4$-Fe	1983.99
18C-W$_4$-IM-H$_4$-Fe	1999.98
16C-W$_2$-IM-H$_4$-Fe	2036.72
18B-F$_6$-IN-H$_4$-Fe	1909.26
18B-W$_4$-IN-H$_4$-Fe	1926.57
16B-W$_2$-IN-H$_4$-Fe	1959.93
18C-F$_6$-IN-H$_4$-Fe	1988.34
18C-W$_4$-IN-H$_4$-Fe	1999.97
16C-W$_2$-IN-H$_4$-Fe	2043.17

Table S - 10. Calculated vibrational frequencies for the A$_1$ carbonyl stretching vibration in cm^{-1}.

Section S3. Frontier Molecular Orbital Analysis

Section S3.1. Orbital Energies and Orbital Energy Differences.

Complex	16C-W$_2$-IM-H$_4$-Fe	18C-W$_4$-IM-H$_4$-Fe	18C-F$_6$-IM-H$_4$-Fe
(α)HOMO-5	-11.54	-11.46	-11.25
(α)HOMO-4	-11.50	-11.35	-11.17
(α)HOMO-3	-10.97	-10.96	-10.76
(α)HOMO-2	-10.85	-10.83	-10.64
(α)HOMO-1	-10.08	-10.34	-10.16
(α)HOMO	-9.20	-9.20	-8.97
(α)LUMO	-8.90	-8.86	-8.64
(α)LUMO+1	-6.79	-6.77	-6.63
(β)HOMO-3	-11.51	-11.28	-11.09
(β)HOMO-2	-11.04	-11.20	-11.06
(β)HOMO-1	-10.57	-10.48	-10.27
(β)HOMO	-10.28	-10.20	-10.02
(β)LUMO	-8.93	-8.94	-8.78
(β)LUMO+1	-8.56	-8.45	-8.23
(β)LUMO+2	-8.05	-8.18	-8.01
Complex	16B-W$_2$-IM-H$_4$-Fe	18B-W$_4$-IM-H$_4$-Fe	18B-F$_6$-IM-H$_4$-Fe
(α)HOMO-5	-5.56	-5.37	-5.30
(α)HOMO-4	-5.34	-5.29	-5.24
(α)HOMO-3	-5.20	-5.21	-5.16
(α)HOMO-2	-4.81	-4.68	-4.61
(α)HOMO-1	-4.24	-4.35	-4.28
(α)HOMO	-3.30	-3.43	-3.42
(α)LUMO	-2.77	-2.64	-2.60
(α)LUMO+1	-0.74	-0.86	-0.94
(β)HOMO-3	-5.54	-5.34	-5.25
(β)HOMO-2	-5.21	-5.12	-5.08
(β)HOMO-1	-4.64	-4.70	-4.69
(β)HOMO	-4.15	-4.01	-3.96
(β)LUMO	-2.86	-2.83	-2.78
(β)LUMO+1	-2.40	-2.51	-2.51
(β)LUMO+2	-2.32	-2.15	-2.11

Table S - 11. Orbital energies from DFT optimization of the imidazole(IM) based Iron(IV)-imide species. All values listed in eV.

Complex	16C-W$_2$-IN-H$_4$-Fe	18C-W$_4$-IN-H$_4$-Fe	18C-F6-IN-H$_4$-Fe
(α)HOMO-5	-11.26	-11.13	-10.93
(α)HOMO-4	-11.12	-11.08	-10.84
(α)HOMO-3	-11.00	-10.95	-10.75
(α)HOMO-2	-10.94	-10.91	-10.70
(α)HOMO-1	-10.26	-10.48	-10.29
(α)HOMO	-9.23	-9.12	-8.92
(α)LUMO	-8.95	-8.78	-8.59
(α)LUMO+1	-6.69	-6.77	-6.68
(β)HOMO-3	-11.23	-11.06	-10.84
(β)HOMO-2	-11.09	-10.95	-10.75
(β)HOMO-1	-10.65	-10.46	-10.26
(β)HOMO	-10.26	-10.43	-10.26
(β)LUMO	-8.93	-8.95	-8.77
(β)LUMO+1	-8.59	-8.37	-8.17
(β)LUMO+2	-8.09	-8.13	-7.99
Complex	16B-W$_2$-IN-H$_4$-Fe	18B-W$_4$-IN-H$_4$-Fe	18B-F6-IN-H$_4$-Fe
(α)HOMO-5	-5.10	-4.97	-4.91
(α)HOMO-4	-5.06	-4.90	-4.84
(α)HOMO-3	-4.85	-4.77	-4.72
(α)HOMO-2	-4.67	-4.54	-4.48
(α)HOMO-1	-4.26	-4.28	-4.21
(α)HOMO	-3.30	-3.32	-3.34
(α)LUMO	-2.70	-2.45	-2.47
(α)LUMO+1	-0.78	-0.83	-0.89
(β)HOMO-3	-4.92	-4.72	-4.66
(β)HOMO-2	-4.78	-4.66	-4.61
(β)HOMO-1	-4.65	-4.51	-4.46
(β)HOMO	-4.18	-4.16	-4.13
(β)LUMO	-2.88	-2.80	-2.74
(β)LUMO+1	-2.43	-2.45	-2.47
(β)LUMO+2	-2.24	-1.97	-1.97

Table S - 12. Orbital energies from DFT optimization of the imidazoline(IN) based Iron(IV)-imide species. All values listed in eV.

Complex	16C-W$_2$-BZ-H$_4$-Fe	18C-W$_4$-BZ-H$_4$-Fe	18C-F6-BZ-H$_4$-Fe
(α)HOMO-5	-10.93	-10.84	-10.70
(α)HOMO-4	-10.87	-10.81	-10.67
(α)HOMO-3	-10.68	-10.69	-10.53
(α)HOMO-2	-10.57	-10.54	-10.42
(α)HOMO-1	-9.85	-10.12	-9.97
(α)HOMO	-8.97	-8.96	-8.83

(α)LUMO	-8.68	-8.63	-8.50
(α)LUMO+1	-6.88	-6.86	-6.80
(β)HOMO-3	-10.90	-10.80	-10.66
(β)HOMO-2	-10.66	-10.73	-10.60
(β)HOMO-1	-10.34	-10.25	-10.12
(β)HOMO	-10.02	-9.98	-9.85
(β)LUMO	-8.74	-8.76	-8.64
(β)LUMO+1	-8.35	-8.22	-8.10
(β)LUMO+2	-7.87	-7.98	-7.88
Complex	16B-W$_2$-BZ-H$_4$-Fe	18B-W$_4$-BZ-H$_4$-Fe	18B-F6-BZ-H$_4$-Fe
(α)HOMO-5	-5.64	-5.51	-5.49
(α)HOMO-4	-5.52	-5.50	-5.45
(α)HOMO-3	-5.46	-5.33	-5.19
(α)HOMO-2	-5.15	-5.07	-4.95
(α)HOMO-1	-4.59	-4.73	-4.62
(α)HOMO	-3.65	-3.80	-3.80
(α)LUMO	-3.16	-3.02	-2.92
(α)LUMO+1	-1.62	-1.52	-1.55
(β)HOMO-3	-5.59	-5.47	-5.42
(β)HOMO-2	-5.42	-5.31	-5.18
(β)HOMO-1	-5.00	-5.04	-5.04
(β)HOMO	-4.53	-4.45	-4.37
(β)LUMO	-3.23	-3.21	-3.13
(β)LUMO+1	-2.79	-2.89	-2.92
(β)LUMO+2	-2.73	-2.55	-2.45

Table S - 13. Orbital energies from DFT optimization of the benzimidazole (BZ) based Iron(IV)-imide species. All values listed in eV.

Complex	$\Delta E_{H(\alpha)-L(\alpha)}$	$\Delta E_{H(\beta)-L(\beta)}$	$\Delta E_{H(\alpha)-L(\beta)}$	$\Delta E_{L(\alpha)-L(\beta)}$	$\Delta E_{\sigma*(\alpha)-\pi*(\beta)}$	$\Delta G^{\ddagger}_{Act}$
16B-W$_2$-IM-H$_4$-Fe	-0.525	-1.289	-0.436	0.089	-0.451	24.40
16C-W$_2$-IM-H$_4$-Fe	-0.294	-1.344	-0.265	0.029	-0.343	18.21
18B-F$_6$-IM-H$_4$-Fe	-0.817	-1.180	-0.642	0.175	-0.498	29.16
18C-F$_6$-IM-H$_4$-Fe	-0.325	-1.243	-0.190	0.134	-0.411	20.30
18B-W$_4$-IM-H$_4$-Fe	-0.790	-1.186	-0.602	0.188	-0.494	28.35
18C-W$_4$-IM-H$_4$-Fe	-0.342	-1.266	-0.265	0.077	-0.408	20.07
16B-W$_2$-IN-H$_4$-Fe	-0.597	-1.303	-0.422	0.175	-0.466	23.35
16C-W$_2$-IN-H$_4$-Fe	-0.279	-1.326	-0.297	-0.018	-0.361	17.78
18B-F$_6$-IN-H$_4$-Fe	-0.868	-1.384	-0.598	0.270	-0.502	31.58
18C-F$_6$-IN-H$_4$-Fe	-0.327	-1.483	-0.148	0.179	-0.420	20.36
18B-W$_4$-IN-H$_4$-Fe	-0.871	-1.362	-0.523	0.348	-0.481	26.60
18C-W$_4$-IN-H$_4$-Fe	-0.342	-1.485	-0.175	0.167	-0.411	21.51
16B-W$_2$-BZ-H$_4$-Fe	-0.491	-1.295	-0.424	0.067	-0.438	20.23
16C-W$_2$-BZ-H$_4$-Fe	-0.289	-1.276	-0.228	0.062	-0.337	14.75
18B-F$_6$-BZ-H$_4$-Fe	-0.875	-1.240	-0.668	0.207	-0.474	26.28
18C-F$_6$-BZ-H$_4$-Fe	-0.339	-1.214	-0.199	0.140	-0.393	19.61
18B-W$_4$-BZ-H$_4$-Fe	-0.773	-1.241	-0.582	0.191	-0.474	22.68
18C-W$_4$-BZ-H$_4$-Fe	-0.337	-1.221	-0.201	0.136	-0.406	19.72

Table S - 14. Orbital energy differences used to correlate electronics with reactivity, all values listed in eV. $\Delta E_{H(\alpha)-L(\alpha)}$ is the HOMO-LUMO gap for α orbitals, $\Delta E_{H(\beta)-L(\beta)}$ is the HOMO-LUMO gap for the β molecular orbitals. The $\Delta E_{\sigma*(\alpha)-\pi*(\beta)}$ column represents the two "competing" orbitals in radical formation, the α-d$_z{}^2$ orbital and the β-d$_{xz}$, and the last column contains the activation barrier for the formation of the radical intermediate (TS2) ($\Delta G^{\ddagger}_{Act}$ values in kcal/mol).
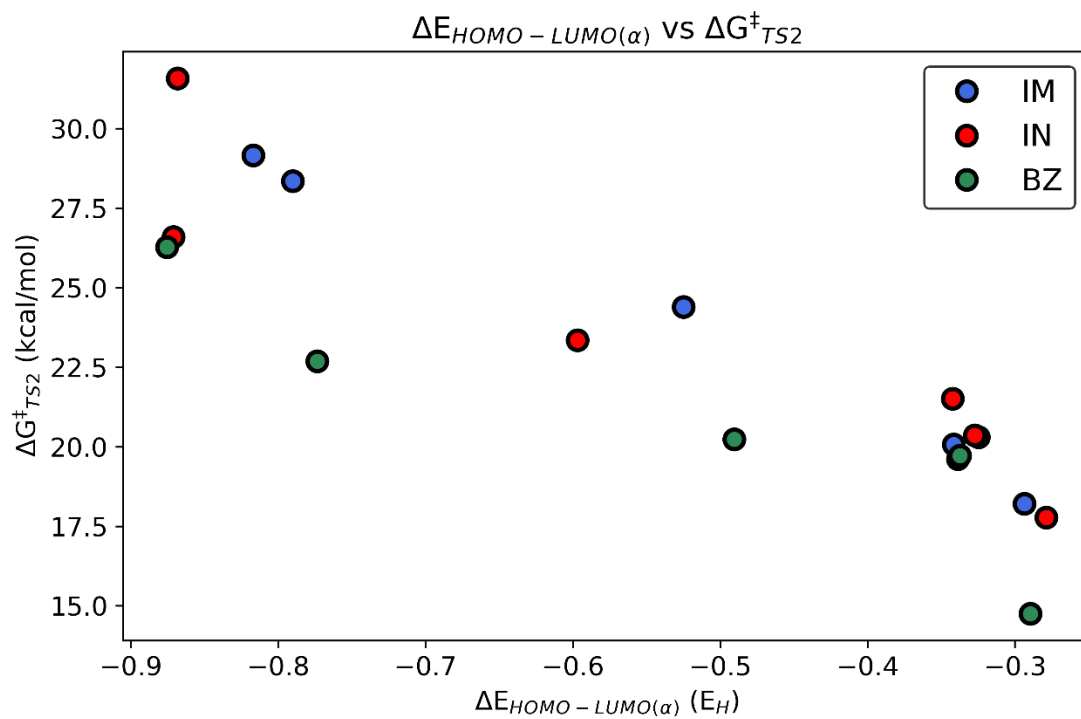
Figure S - 6. Scatter plot of the HOMO-LUMO gap of α molecular orbitals, orbital energies displayed in Hartree and activation barriers are presented in kcal/mol. The data points are

separated based on the NHC subunits, imidazoles (IM) shown in blue, imidazolines (IN) shown in red and benzimidazoles (BZ) shown in green.
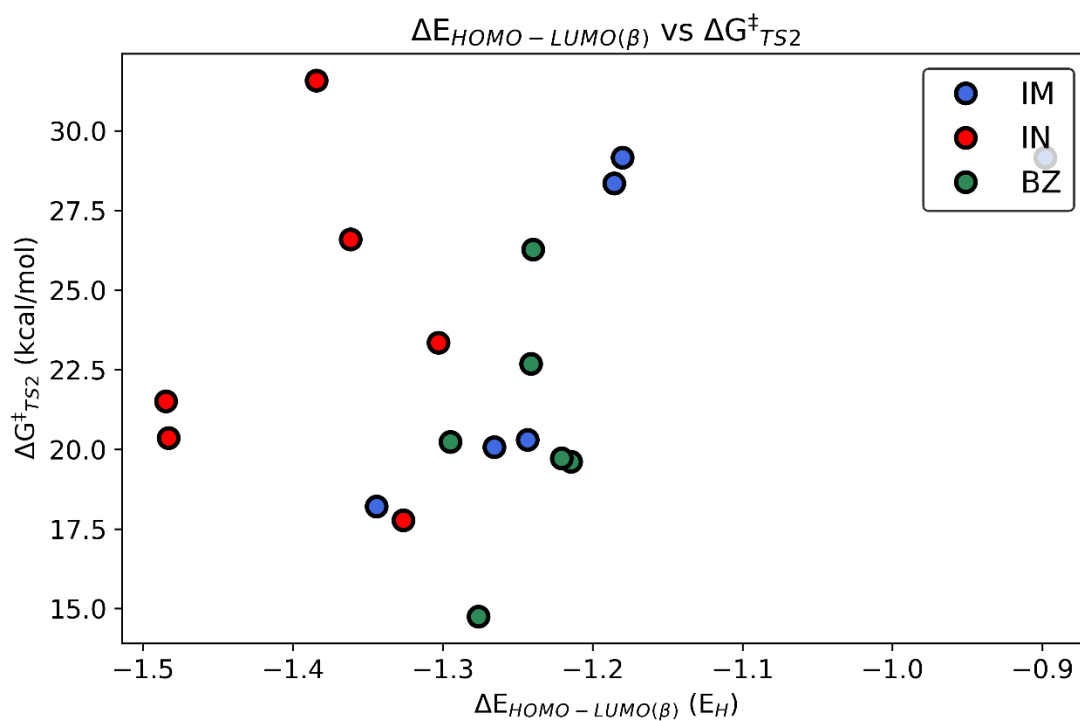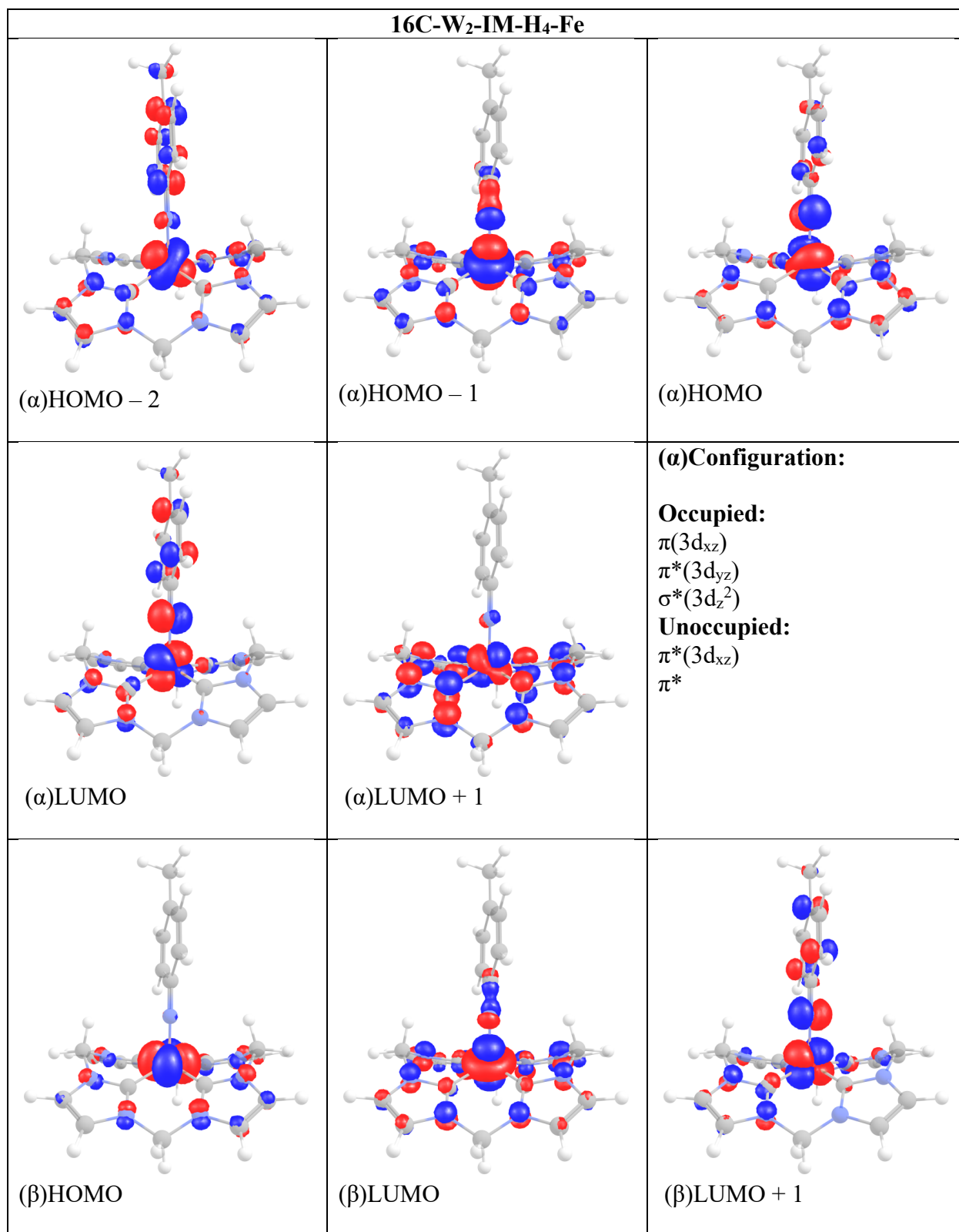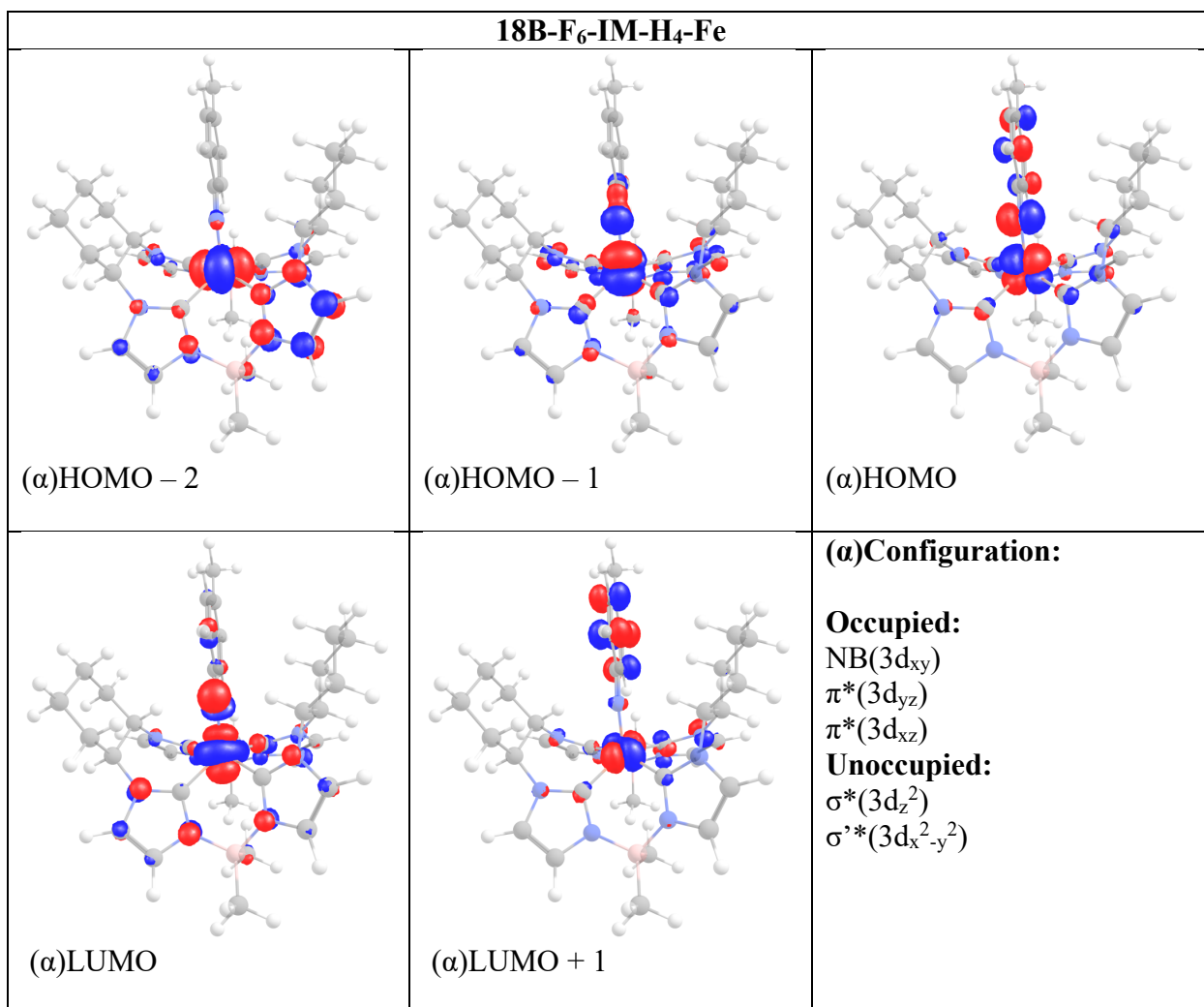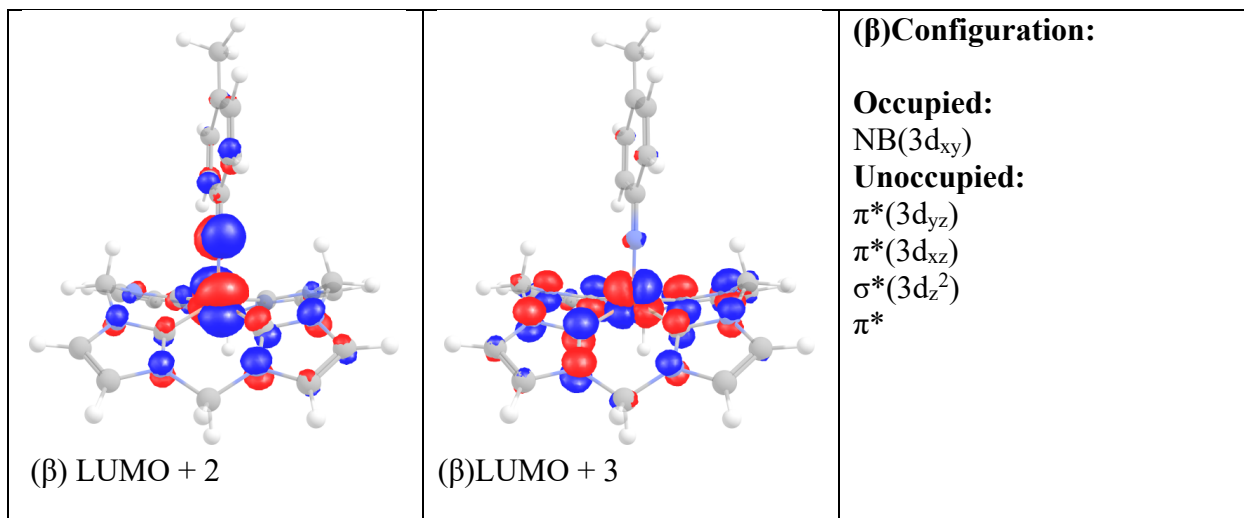

Figure S - 7. Scatter plot of the HOMO-LUMO gap of β molecular orbitals, orbital energies displayed in Hartree and activation barriers are presented in kcal/mol. The data points are

separated based on the NHC subunits, imidazoles (IM) shown in blue, imidazolines (IN) shown in red and benzimidazoles (BZ) shown in green.
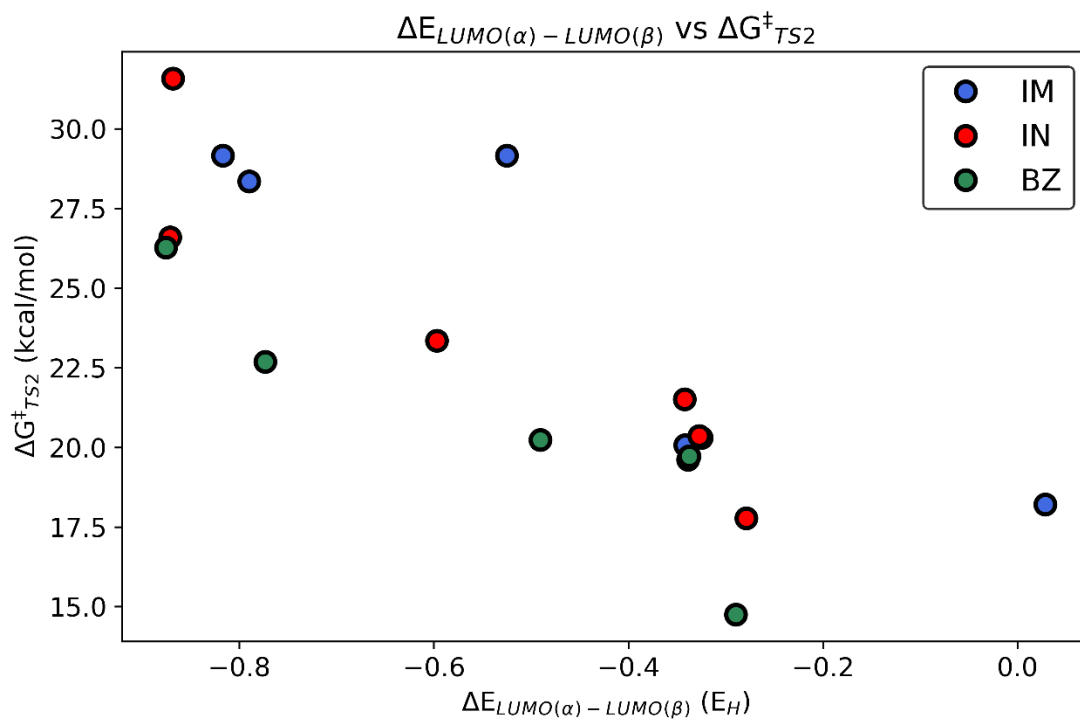
Figure S - 8. Scatter plot of the HOMO-LUMO gap of α and β molecular orbitals, orbital energies displayed in Hartree and activation barriers are presented in kcal/mol. In these cases, the HOMO is of α-spin and the LUMO is of β-spin. The data points are separated based on the NHC subunits, imidazoles (IM) shown in blue, imidazolines (IN) shown in red and benzimidazoles (BZ) shown in green.
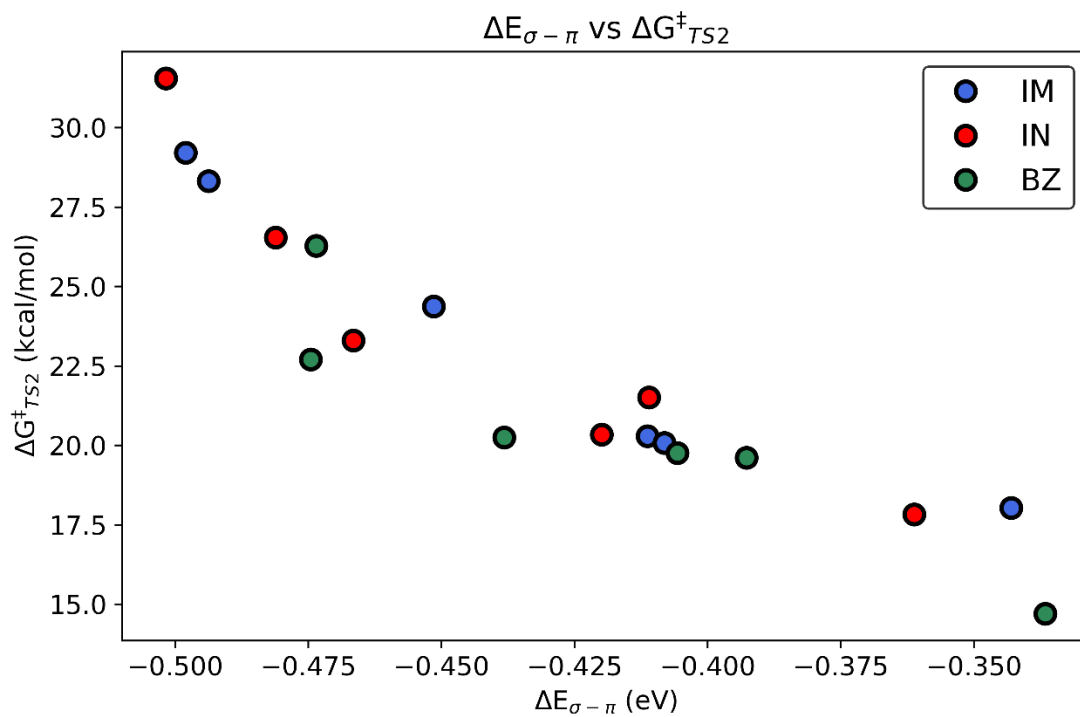
Figure S - 9. Scatter plot of the σ* (dz^2) orbital with α-spin subtracted from the π*(d$_{xz/yz}$) orbital with β-spin. In the carbon-based complexes this is LUMO(α) and LUMO+1(β), and in the complexes linked with dimethyl borates this is LUMO(α) and LUMO+2(β). The data points are separated based on the NHC subunits, imidazoles (IM) shown in blue, imidazolines (IN) shown in red and benzimidazoles (BZ) shown in green.

Section S3.1. Molecular Orbital Visualization and Selected Spin Densities

Frontier molecular orbitals of each iron(IV)-imide species. For α-spin orbitals this is the HOMO-2 up to LUMO+1, and for the β-spin orbitals this is HOMO up to the LUMO+3. All isosurfaces have been rendered at an isovalue of 0.08

16B-W$_2$-IM-H$_4$-Fe		
(α)HOMO – 2	(α)HOMO – 1	(α)HOMO
		(α)Configuration: **Occupied:** NB(3d$_{xy}$) π*(3d$_{yz}$) π*(3d$_{xz}$) **Unoccupied:** σ*(3d$_{z^2}$) σ'*(3d$_{x^2-y^2}$)
(α)LUMO	(α)LUMO + 1	

(β)HOMO	(β)LUMO	(β)LUMO + 1
(β) LUMO + 2	(β)LUMO + 3	**(β)Configuration:** **Occupied:** NB($3d_{xy}$) **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_{z^2})$ $\sigma'^*(3d_{x^2-y^2})$

16C-W₂-IM-H₄-Fe

(α)HOMO − 2

(α)HOMO − 1

(α)HOMO

(α)LUMO

(α)LUMO + 1

(α)Configuration:

Occupied:
$\pi(3d_{xz})$
$\pi^*(3d_{yz})$
$\sigma^*(3d_z^2)$
Unoccupied:
$\pi^*(3d_{xz})$
π^*

(β)HOMO

(β)LUMO

(β)LUMO + 1

		(β)Configuration: **Occupied:** NB($3d_{xy}$) **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_{z^2})$ π^*
(β) LUMO + 2	(β)LUMO + 3	

18B-F$_6$-IM-H$_4$-Fe

(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
		(α)Configuration: **Occupied:** NB($3d_{xy}$) $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ **Unoccupied:** $\sigma^*(3d_{z^2})$ $\sigma'^*(3d_{x^2-y^2})$
(α)LUMO	(α)LUMO + 1	

(β)HOMO	(β)LUMO	(β)LUMO + 1
(β) LUMO + 2	(β)LUMO + 3	**(β)Configuration:** **Occupied:** NB($3d_{xy}$) **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_{z^2})$ $\sigma'^*(3d_{x^2-y^2})$

18C-F₆-IM-H₄-Fe

(α)HOMO – 2	(α)HOMO – 1	(α)HOMO
(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** NB($3d_{xy}$) $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ **Unoccupied:** $\sigma^*(3d_z^2)$ $\sigma'^*(3d_{x^2-y^2})$
(β)HOMO	(β)LUMO	(β)LUMO + 1

		(β)Configuration:
		Occupied: NB($3d_{xy}$) **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_{z^2})$ π^*
(β) LUMO + 2	(β)LUMO + 3	

18B-W$_4$-IM-H$_4$-Fe

(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
		(α)Configuration: **Occupied:** NB($3d_{xy}$) $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ **Unoccupied:** $\sigma^*(3d_{z^2})$ $\sigma'^*(3d_{x^2-y^2})$

(α)LUMO	(α)LUMO + 1	
(β)HOMO	(β)LUMO	(β)LUMO + 1
		(β)Configuration: **Occupied:** NB($3d_{xy}$) **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_{z^2})$ $\sigma'^*(3d_{x^2-y^2})$
(β) LUMO + 2	(β)LUMO + 3	

18C-W$_4$-IM-H$_4$-Fe

(α)HOMO – 2	(α)HOMO – 1	(α)HOMO
(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** NB(3d$_{xy}$) π*(3d$_{yz}$) π*(3d$_{xz}$) **Unoccupied:** σ*(3d$_z^2$) σ'*(3d$_{x^2-y^2}$)

(β)HOMO

(β)LUMO

(β)LUMO + 1

(β) LUMO + 2

(β)LUMO + 3

(β)Configuration:

Occupied:
NB($3d_{xy}$)
Unoccupied:
$\pi^*(3d_{yz})$
$\pi^*(3d_{xz})$
$\sigma^*(3d_{z^2})$
$\sigma'^*(3d_{x^2-y^2})$

16B-W₂-IN-H₄-Fe

(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** $NB(3d_{xy})$ $\pi*(3d_{yz})$ $\pi*(3d_{xz})$ **Unoccupied:** $\sigma*(3d_{z^2})$ $\sigma'*(3d_{x^2-y^2})$
(β)HOMO	(β)LUMO	(β)LUMO + 1

		(β)Configuration:
		Occupied: NB($3d_{xy}$) **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_{z^2})$ $\sigma'^*(3d_{x^2-y^2})$
(β) LUMO + 2	(β)LUMO + 3	

16C-W$_2$-IN-H$_4$-Fe		
(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
		(α)Configuration: **Occupied:** **NB($3d_{xy}$)** **$\pi^*(3d_{yz})$** **$\pi^*(3d_{xz})$** **Unoccupied:** **$\sigma^*(3d_{z^2})$** **$\sigma'^*(3d_{x^2-y^2})$**
(α)LUMO	(α)LUMO + 1	

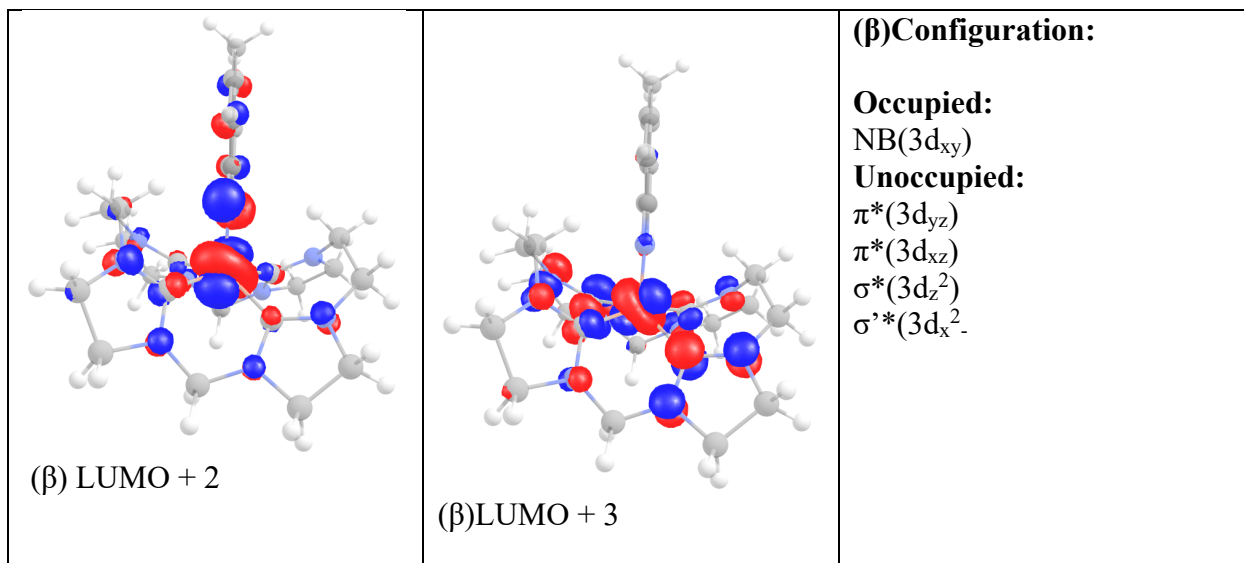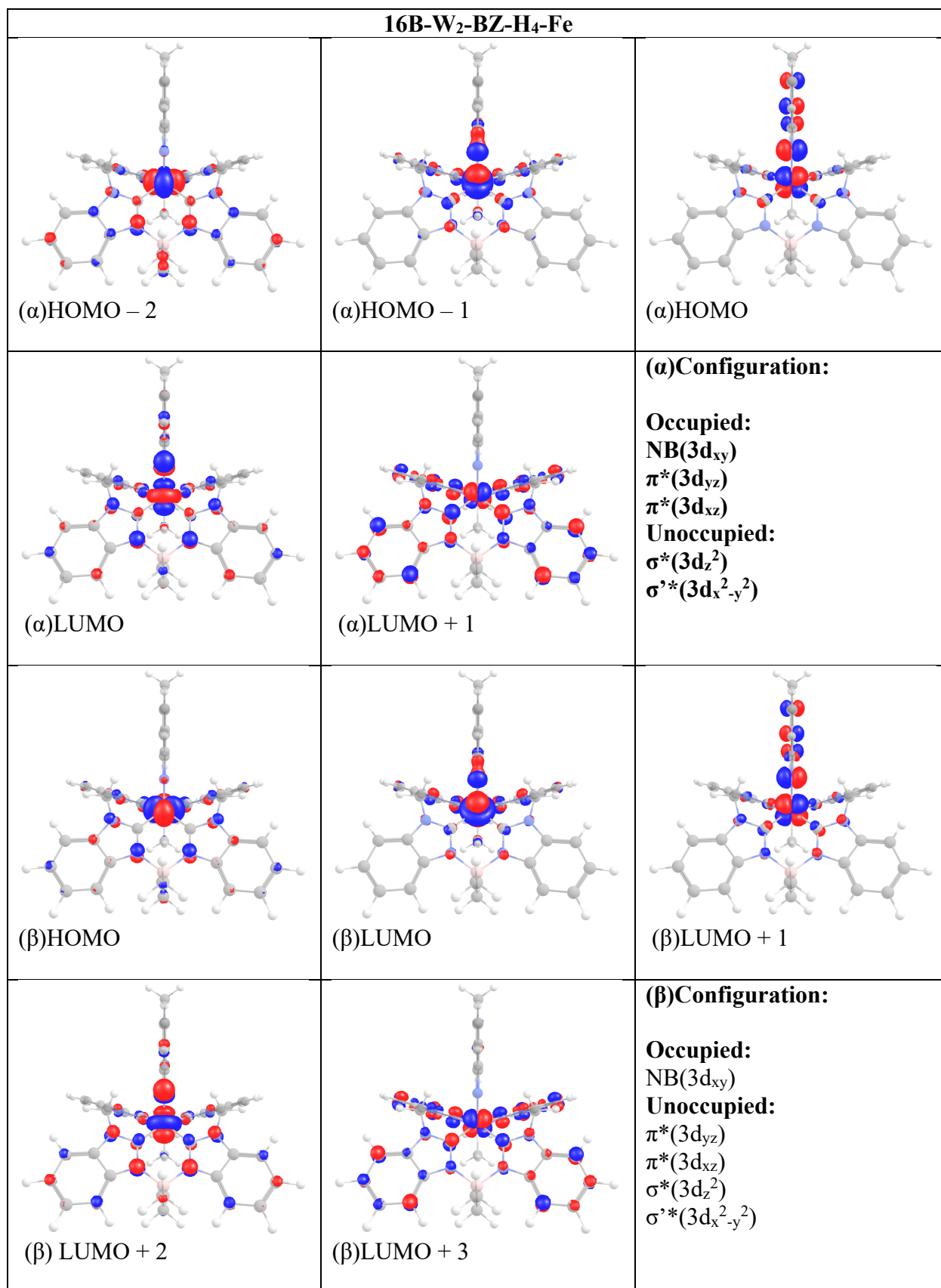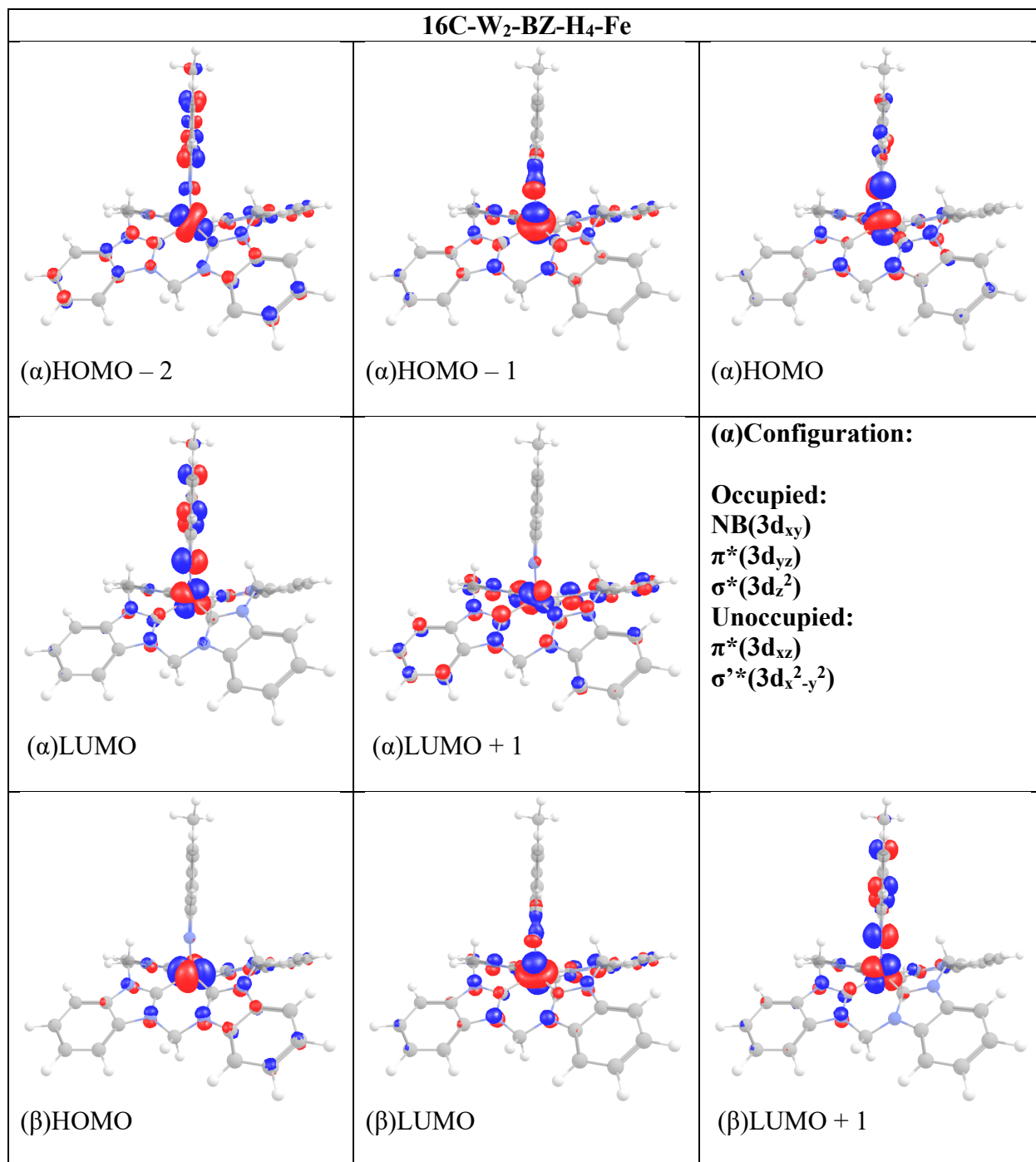|		
(β)HOMO	(β)LUMO	(β)LUMO + 1
(β) LUMO + 2	(β)LUMO + 3	**(β)Configuration:** **Occupied:** NB($3d_{xy}$) **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_{z^2})$ $\sigma'^*(3d_{x^2-y^2})$

18B-F$_6$-IN-H$_4$-Fe

(α)HOMO – 2	(α)HOMO – 1	(α)HOMO

 (α)LUMO	 (α)LUMO + 1	**(α)Configuration:** **Occupied:** **NB(3d$_{xy}$)** **π*(3d$_{yz}$)** **π*(3d$_{xz}$)** **Unoccupied:** **σ*(3d$_z^2$)** **σ'*(3d$_{x^2-y^2}$)**
 (β)HOMO	 (β)LUMO	 (β)LUMO + 1
 (β) LUMO + 2	 (β)LUMO + 3	**(β)Configuration:** **Occupied:** NB(3d$_{xy}$) **Unoccupied:** π*(3d$_{yz}$) π*(3d$_{xz}$) σ*(3d$_z^2$) σ'*(3d$_{x^2-y^2}$)

18C-F$_6$-IN-H$_4$-Fe

(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** **π(3d$_{xz}$)** **π*(3d$_{yz}$)** **π*(3d$_{xz}$)** **Unoccupied:** **σ*(3d$_z{}^2$)** **σ'*(3d$_{x^2\text{-}y^2}$)**
(β)HOMO	(β)LUMO	(β)LUMO + 1
(β) LUMO + 2	(β)LUMO + 3	**(β)Configuration:** **Occupied:** NB(3d$_{xy}$) **Unoccupied:** π*(3d$_{yz}$) π*(3d$_{xz}$) σ*(3d$_z{}^2$) σ'*(3d$_{x^2\text{-}y^2}$)

18B-W$_4$-IN-H$_4$-Fe

(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** **NB(3d$_{xy}$)** **π*(3d$_{yz}$)** **π*(3d$_{xz}$)** **Unoccupied:** **σ*(3d$_z^2$)** **σ'*(3d$_{x^2-y^2}$)**

(β)HOMO

(β)LUMO

(β)LUMO + 1

(β) LUMO + 2

(β)LUMO + 3

(β)Configuration:

Occupied:
NB($3d_{xy}$)
Unoccupied:
$\pi^*(3d_{yz})$
$\pi^*(3d_{xz})$
$\sigma^*(3d_{z^2})$
$\sigma'^*(3d_{x^2-y^2})$

18C-W$_4$-IN-H$_4$-Fe

(α)HOMO − 2

(α)HOMO − 1

(α)HOMO

(α)LUMO

(α)LUMO + 1

(α)Configuration:

Occupied:
$\pi(3d_{yz})$
$\pi^*(3d_{yz})$
$\pi^*(3d_{xz})$
Unoccupied:
$\sigma^*(3d_{z^2})$
$\sigma'^*(3d_{x^2-y^2})$

(β)HOMO

(β)LUMO

(β)LUMO + 1

(β) LUMO + 2

(β)LUMO + 3

(β)Configuration:

Occupied:
NB($3d_{xy}$)
Unoccupied:
$\pi^*(3d_{yz})$
$\pi^*(3d_{xz})$
$\sigma^*(3d_z{}^2)$
$\sigma'^*(3d_x{}^2{}_-$

16B-W₂-BZ-H₄-Fe

(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** **NB(3d$_{xy}$)** **π*(3d$_{yz}$)** **π*(3d$_{xz}$)** **Unoccupied:** **σ*(3d$_z^2$)** **σ'*(3d$_{x^2-y^2}$)**
(β)HOMO	(β)LUMO	(β)LUMO + 1
(β) LUMO + 2	(β)LUMO + 3	**(β)Configuration:** **Occupied:** NB(3d$_{xy}$) **Unoccupied:** π*(3d$_{yz}$) π*(3d$_{xz}$) σ*(3d$_z^2$) σ'*(3d$_{x^2-y^2}$)

16C-W₂-BZ-H₄-Fe		
(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** **NB(3d$_{xy}$)** **π*(3d$_{yz}$)** **σ*(3d$_{z^2}$)** **Unoccupied:** **π*(3d$_{xz}$)** **σ'*(3d$_{x^2-y^2}$)**
(β)HOMO	(β)LUMO	(β)LUMO + 1

		(β)Configuration: **Occupied:** NB($3d_{xy}$) **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_{z^2})$ $\sigma'^*(3d_{x^2-y^2})$
(β) LUMO + 2	(β)LUMO + 3	

18B-F$_6$-BZ-H$_4$-Fe		
(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
		(α)Configuration: **Occupied:** **NB($3d_{xy}$)** **$\pi^*(3d_{yz})$** **$\pi^*(3d_{xz})$** **Unoccupied:** **$\sigma^*(3d_{z^2})$** **$\sigma'^*(3d_{x^2-y^2})$**
(α)LUMO	(α)LUMO + 1	

(β)HOMO

(β)LUMO

(β)LUMO + 1

(β) LUMO + 2

(β)LUMO + 3

(β)Configuration:

Occupied:
NB($3d_{xy}$)
Unoccupied:
$\pi^*(3d_{yz})$
$\pi^*(3d_{xz})$
$\sigma^*(3d_{z^2})$
$\sigma'^*(3d_{x^2-y^2})$

18C-F₆-BZ-H₄-Fe

(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** **NB(3d$_{xy}$)** **π*(3d$_{yz}$)** **π*(3d$_{xz}$)** **Unoccupied:** **σ*(3d$_z{}^2$)** **σ'*(3d$_{x^2-y^2}$)**
(β)HOMO	(β)LUMO	(β)LUMO + 1

(β) LUMO + 2	(β)LUMO + 3	**(β)Configuration:** **Occupied:** $NB(3d_{xy})$ **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_z^2)$ $\sigma'^*(3d_{x^2-y^2})$

18B-W$_4$-BZ-H$_4$-Fe		
(α)HOMO − 2	(α)HOMO − 1	(α)HOMO
(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** **$NB(3d_{xy})$** **$\pi^*(3d_{yz})$** **$\pi^*(3d_{xz})$** **Unoccupied:** **$\sigma^*(3d_z^2)$** **$\sigma'^*(3d_{x^2-y^2})$**

(β)HOMO	(β)LUMO	(β)LUMO + 1
(β) LUMO + 2	(β)LUMO + 3	**(β)Configuration:** **Occupied:** NB($3d_{xy}$) **Unoccupied:** $\pi^*(3d_{yz})$ $\pi^*(3d_{xz})$ $\sigma^*(3d_z^2)$ $\sigma'^*(3d_{x^2-y^2})$

18C-W$_4$-BZ-H$_4$-Fe

(α)HOMO − 2	(α)HOMO − 1	(α)HOMO

(α)LUMO	(α)LUMO + 1	**(α)Configuration:** **Occupied:** **NB(3d$_{xy}$)** **π*(3d$_{yz}$)** **π*(3d$_{xz}$)** **Unoccupied:** **σ*(3d$_z^2$)** **σ'*(3d$_{x^2-y^2}$)**
(β)HOMO	(β)LUMO	(β)LUMO + 1
(β)LUMO + 2	(β)LUMO + 3	**(β)Configuration:** **Occupied:** NB(3d$_{xy}$) **Unoccupied:** π*(3d$_{yz}$) π*(3d$_{xz}$) σ*(3d$_z^2$) σ'*(3d$_{x^2-y^2}$)

Section S3.2 Spin Densities

Spin densities displayed are from TS2 (alkene addition), all isosurfaces have been rendered at an isovalue of 0.08.

Complex	
16B-W$_2$-IM-H$_4$-Fe	
16C-W$_2$-IM-H$_4$-Fe	
18B-F$_6$-IM-H$_4$-Fe	
18C-F$_6$-IM-H$_4$-Fe	
18B-W$_4$-IM-H$_4$-Fe	

18C-W$_4$-IM-H$_4$-Fe	
16B-W$_2$-IN-H$_4$-Fe	
16C-W$_2$-IN-H$_4$-Fe	
18B-F$_6$-IN-H$_4$-Fe	
18C-F$_6$-IN-H$_4$-Fe	
18B-W$_4$-IN-H$_4$-Fe	

18C-W$_4$-IN-H$_4$-Fe	
16B-W$_2$-BZ-H$_4$-Fe	
16C-W$_2$-BZ-H$_4$-Fe	
18B-F$_6$-BZ-H$_4$-Fe	
18C-F$_6$-BZ-H$_4$-Fe	

18B-W$_4$-BZ-H$_4$-Fe	
18C-W$_4$-BZ-H$_4$-Fe	
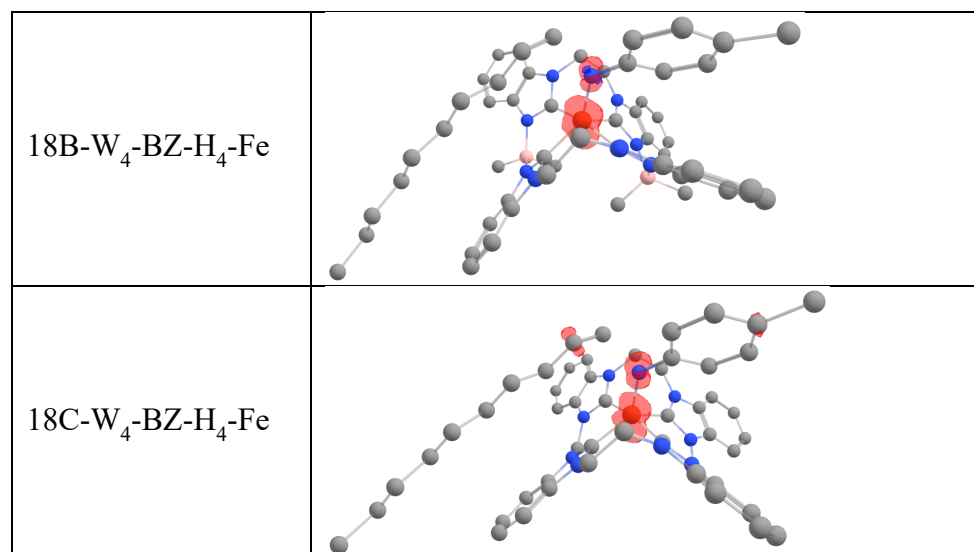
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