Electronic Supplementary Information (ESI)

Spin modification in iron(II) complexes via covalent (dative) and dispersion guided non-covalent bonding with N-heterocyclic carbenes: DFT, DLPNO-CCSD(T) and MCSCF studies

Debashree Manna,[a,b†] Rabindranath Lo, [a,b†] and Pavel Hobza [*a,b]

[a]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo nám. 2, 16610 Prague 6, Czech Republic.
[b]Regional Centre of Advanced Technologies and Materials, Palacký University, 77146 Olomouc, Czech Republic.
† Both authors contributed equally to this work and can be considered as the first author.
Email: pavel.hobza@uochb.cas.cz

Table S1: Relative energies (kcal/mol) of Carbenes at singlet (S) and triplet (T) in various levels of theory and HOMO-LUMO gap (eV) of singlet carbenes are given.

		B97-D3	BLYP-D3	PBE-D3	B3LYP-D3	PBE0-D3	B2-PLYP-D3	DLPNO-CCSD(T)	CCSD(T)	H-L Gap
$ImNH_2$	S	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.624
	T	83.7	84.2	83.9	85.4	84.3	81.9	88.7	73.0	
$ImN(CH_3)_2$	S	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.337
	T	82.2	82.3	82.4	84.5	84.4	83.8	91.0	99.0	
$ImN(CF_3)_2$	S	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.561
	T	74.6	75.9	75.5	76.2	76.4	74.5	84.1	92.6	
$ImN(CCl_3)_2$	S	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.271
	T	60.5	62.1	64.2	66.6	70.3	71.8	89.7	81.7	

Table S2: Mulliken and ESP charges on carbene carbon, first proton affinities (kcal/mol) and dimerization energies (kcal/mol) for the studied carbenes.

	Mulliken	ESP	First PA	Dimerization energy
$ImNH_2$	-0.249	-0.802	263.3	-13.1
$ImN(CH_3)_2$	-0.325	-0.948	272.3	-3.9
$ImN(CF_3)_2$	-0.265	-0.760	246.9	-0.1
$ImN(CCl_3)_2$	-0.242	-0.685	254.9	-3.3

Table S3: Interaction energies (kcal/mol) of FePc carbene complexes at B97-D3/TZVPP level.

	ΔE_{int}
FePc…$ImNH_2$	-45.5
FePc…$ImN(CH_3)_2$	-35.7
FePc…$ImN(CF_3)_2$	-12.4
FePc…$ImN(CCl_3)_2$	-14.5

Table S4: Relative energies (kcal/mol) of FePz…carbenes at various levels. CASPT2 values are given in parenthesis.

		B97-D3	BLYP-D3	PBE-D3	B3LYP-D3	PBE0-D3	B2-PLYP-D3	CASSCF	DLPNO-CCSD(T)
FePz…$ImNH_2$	S	0.0	0.0	0.0	0.0	0.0	8.6	0.0	0.0
	T	15.9	19.8	21.2	9.2	6.6	0.0	10.7 (12.3)	44.4
	Q	27.5	33.0	34.0	18.1	13.2	10.3	38.6	11.6
FePz…$ImN(CH_3)_2$	S	0.0	0.0	0.0	0.7	2.5	32.2	0.0	0.0
	T	6.2	11.0	12.8	0.0	0.0	16.0	20.6 (28.6)	39.2
	Q	13.2	28.7	30.0	6.4	2.7	0.0	---	51.4
FePz…$ImN(CF_3)_2$	S	1.4	0.0	0.0	8.4	10.6	41.9	2.2	2.9
	T	0.0	4.5	5.3	0.0	0.0	13.6	0.0	0.0
	Q	6.4	21.5	21.9	6.9	1.8	0.0	----	31.3
FePz…$ImN(CCl_3)_2$	S	6.8	1.9	2.2	21.5	26.4	57.8	64.5	15.3
	T	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Q	10.4	21.0	21.1	14.3	11.5	4.1	26.7	35.0

Table S5: Wiberg Bond Index and out-plane displacement (in Å) of Fe atom from the plane of FePz for FePz...Carbene complexes.

	Spin State	Wiberg Bond index (WBI)	Out-of-plane displacement	
			B97-D3	B3LYP-D3
FePz…$ImNH_2$	S	0.955	0.145	0.154
FePz…$ImN(CH_3)_2$	S	0.910	0.433	0.458
FePz…$ImN(CF_3)_2$	T	0.390	0.464	0.369
FePz…$ImN(CCl_3)_2$	T	0.053	0.106	0.091

Table S6: NBO and ESP charge transfer from carbenes to FePz molecule. The second order perturbation energy (kcal/mol), $E^{(2)}$ for back-bonding contribution for selected complexes.

		NBO	ESP	$E^{(2)}$
FePz…$ImNH_2$	S	-0.657	-0.248	55.2
	T	-0.393	-0.232	
	Q	-0.427	-0.269	
FePz…$ImN(CH_3)_2$	S	-0.647	-0.217	39.2
	T	-0.387	-0.188	
	Q	-0.394		
FePz…$ImN(CF_3)_2$	S	-0.440	-0.045	
	T	-0.247	-0.121	12.3
	Q	-0.198	-0.103	
FePz…$ImN(CCl_3)_2$	S	-0.293	0.054	
	T	-0.038	0.005	0.9
	Q	-0.115	-0.045	

Table S7: Calculated interaction energies (ΔE, kcal/mol) and their decomposition into reference and correlation energies from DLPNO-CCSD(T) method.

		ΔE	$\Delta E_{geo\text{-}prep}$	ΔE_{int}^{ref}	$\Delta E_{el-prep}^{ref}$	E_{elstat}	E_{exch}	ΔE_{int}^{Corr}	E_{disp}	$\Delta E_{int}^{C-(T)}$	$\Delta E_{no\text{-}disp}$
FePz…$ImNH_2$	S	-33.5	31.0	-9.9	717.9	-634.6	-93.2	-54.6	-25.5	-6.7	-22.4
	T	10.5	0.5	49.2	613.2	-507.3	-56.7	-39.2	-14.2	-4.8	-20.3
FePz…$ImN(CH_3)_2$	S	-26.8	39.7	-10.8	607.2	-534.7	-83.3	-55.8	-28.6	-6.7	-20.4
	T	12.1	4.4	46.3	525.9	-428.2	-51.4	-38.6	-18.6	-5.4	-14.6
FePz…$ImN(CF_3)_2$	S	-7.6	52.8	1.4	623.3	-534.3	-87.6	-61.8	-31.6	-228.2	198.1
	T	-10.1	5.5	6.5	186.7	-149.2	-31.0	-22.1	-16.5	-2.0	-3.6
FePz…$ImN(CCl_3)_2$	S	4.6	76.3	10.7	787.8	-664.5	-112.6	-82.4	-44.2	-11.2	-27.0
	T	-11.6	0.42	7.0	57.3	-38.6	-11.7	-19.1	-15.2	-1.6	-2.3

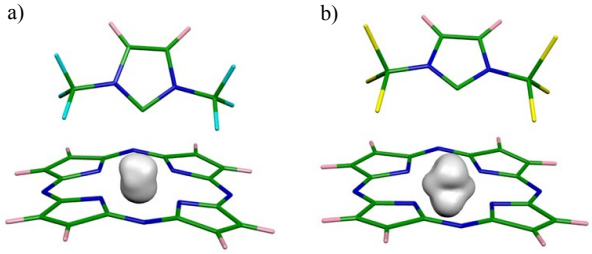

Fig. S1 Spin density difference for triplet a) Fe(II)-porphyrazine…$ImN(CF_3)_2$ and b) Fe(II)-porphyrazine…$ImN(CCl_3)_2$ (C- green, H- pink, N- blue, Fe- dark orange, Cl- yellow, F- cyan).

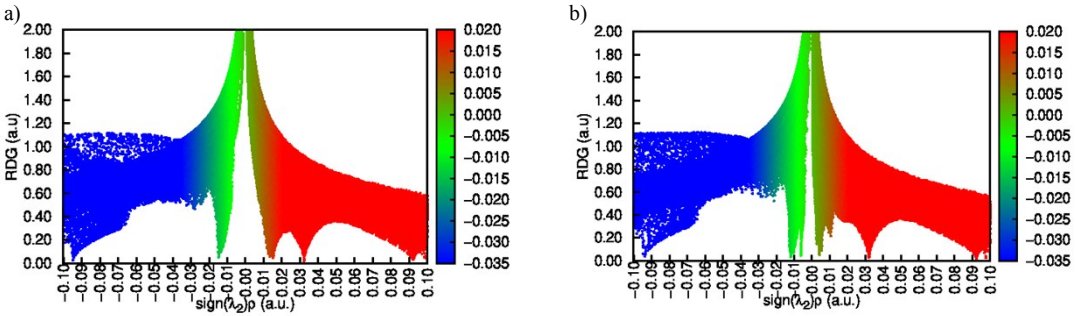

Fig. S2 Plots of reduced density gradient (RDG) against sign(λ2)ρ(r) for the a) FePz...$ImNH_2$ and b) FePz…$ImN(CCl_3)_2$ complexes, using Multiwfn 3.6.