

*Supporting Information for*

***N-Heterocyclic carbene adducts to [Cp'FeI]<sub>2</sub>:***

***Synthesis and Molecular and Electronic Structure***

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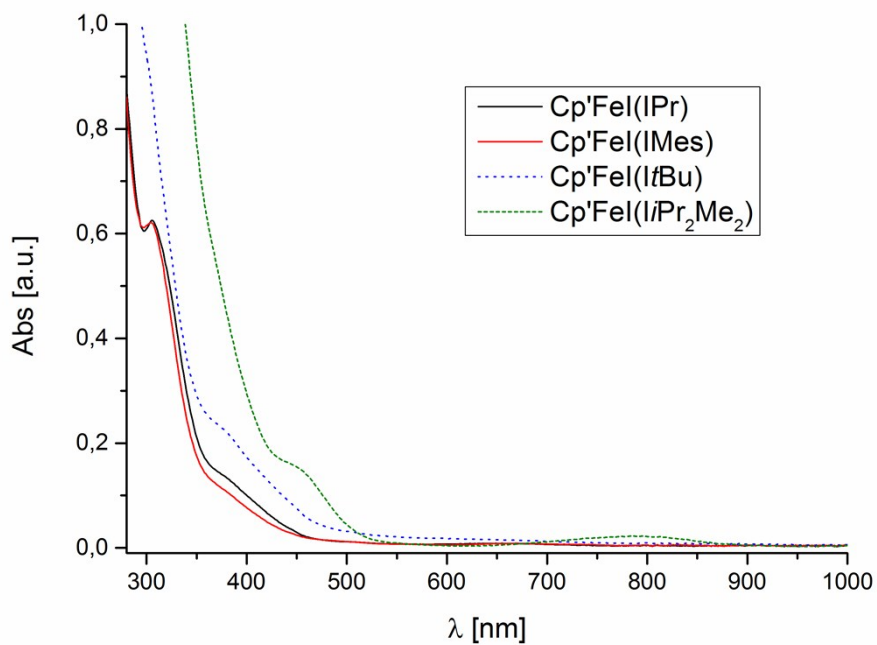
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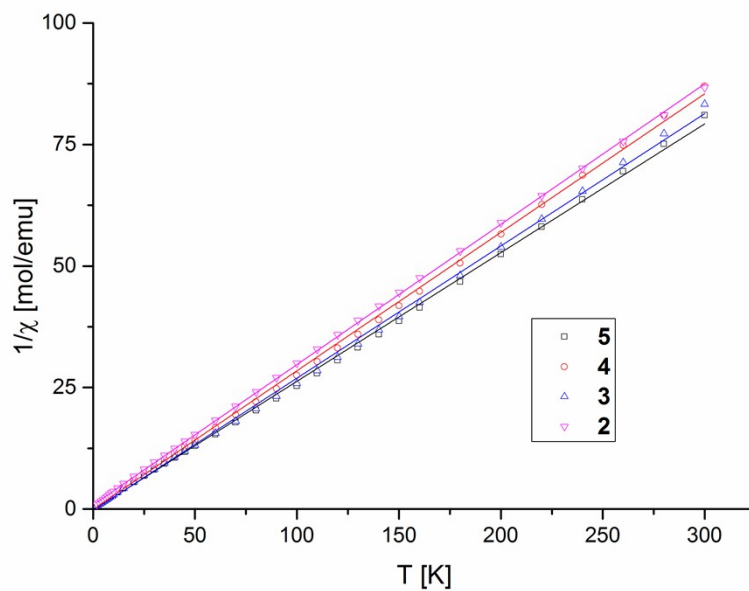
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## 1. UV/Vis Spectra of [Cp'FeI(L)]



**Figure S1.** UV/Vis spectra of the NHC adducts recorded in THF at 22 °C.

## 2. $1/\chi$ vs. T plots for complexes 2-5

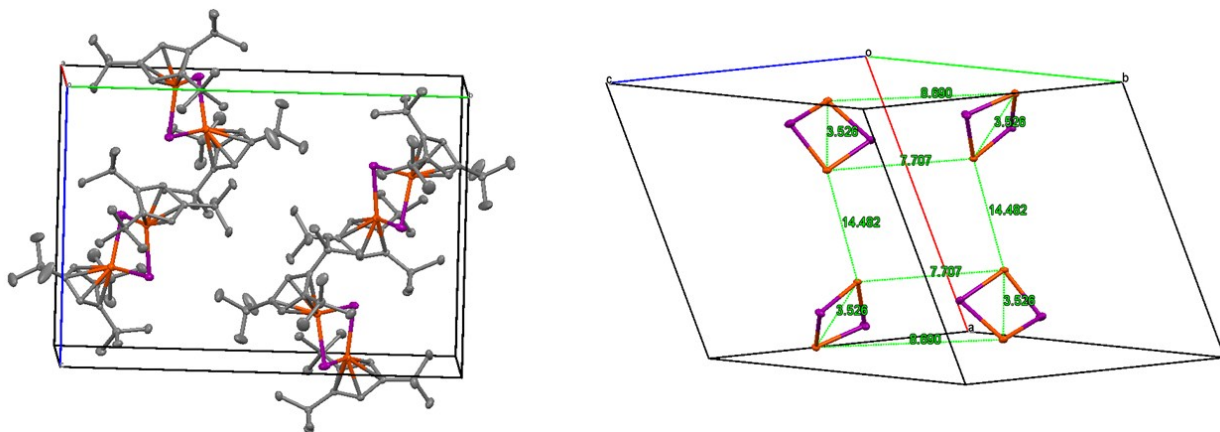


**Figure S2.**  $1/\chi$  vs. T plots for the NHC-adducts 2-5.

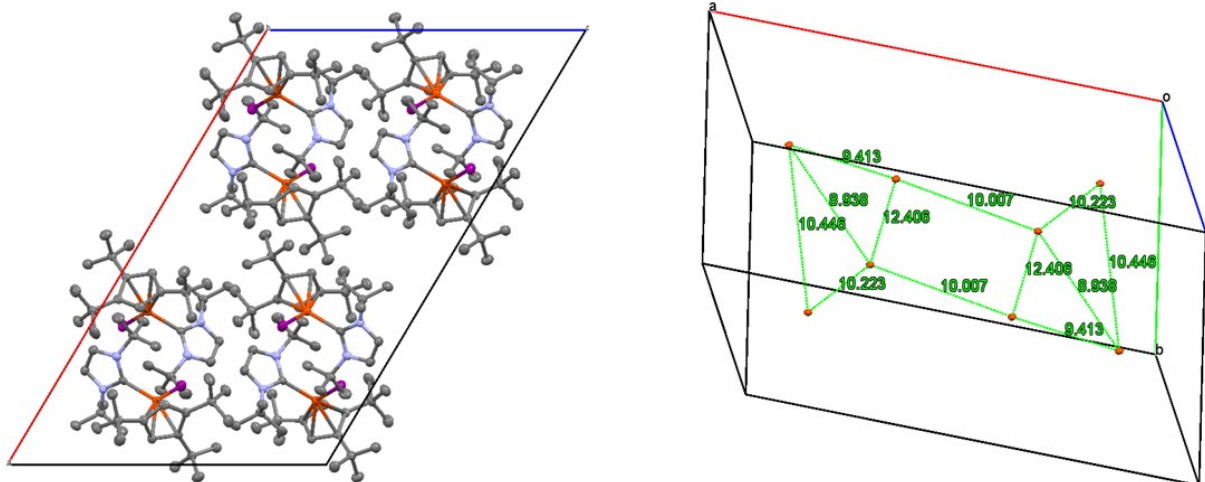
**Table S1.** Curie-Weiss constants for compounds 2-5.

Compound	C (emu K/mol)	$\Theta$ (K)
2	3.46(1)	-2.61(26)
3	3.67(2)	+0.11(66)
4	3.51(1)	+0.23(6)
5	3.78(2)	+0.83(62)

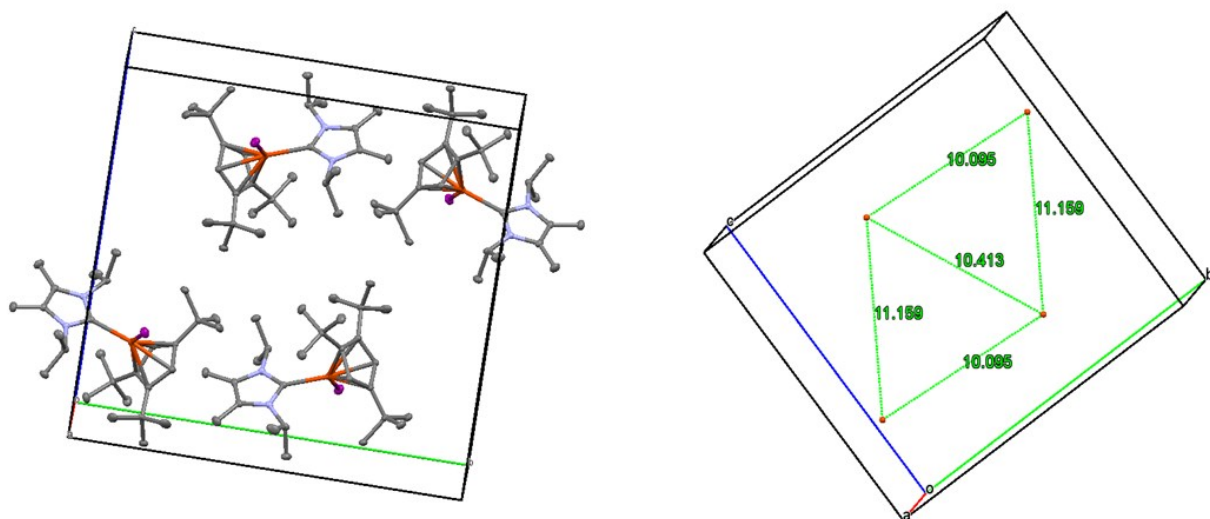
### 3. Packing diagram of compounds 1-5



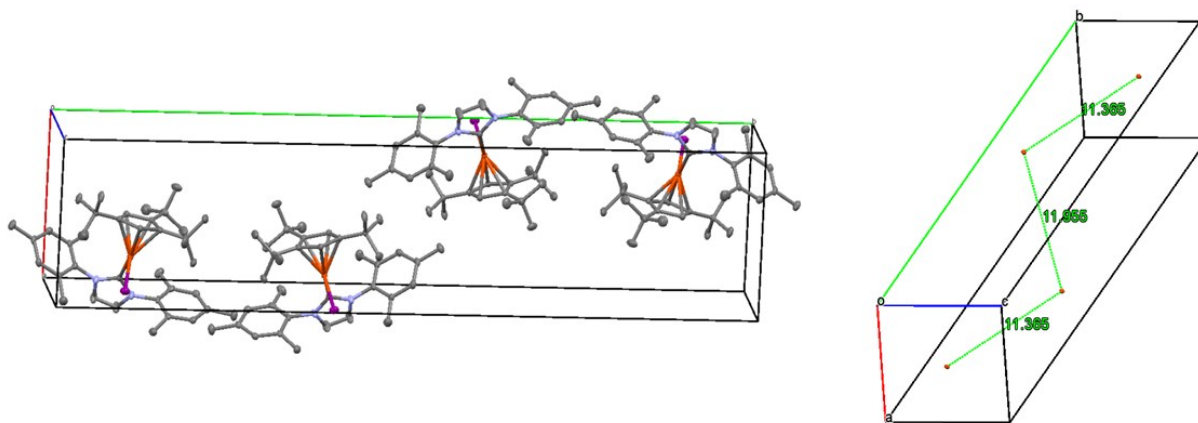
**Figure S3.** Packing diagram of half-sandwich complex 1 (left) and arrangement of the Fe- and I-atoms in (including intermolecular Fe...Fe distances (in Å)) (right).



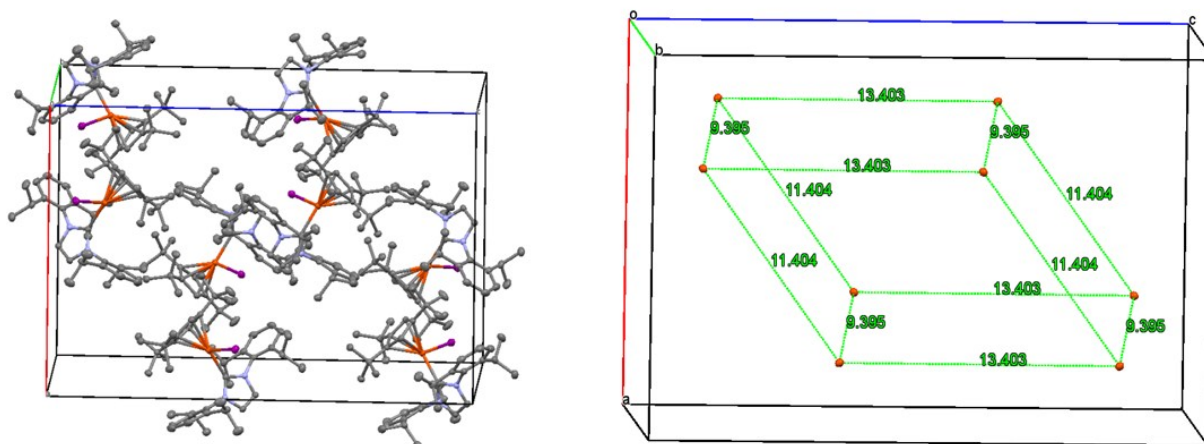
**Figure S4.** Packing diagram of NHC-adduct **2** (left) and arrangement of the Fe-atoms in the unit cell (including intermolecular Fe  $\cdots$ Fe distances (in Å)) (right).



**Figure S5.** Packing diagram of NHC-adduct **3** (left) and arrangement of the Fe-atoms in the unit cell (including intermolecular Fe  $\cdots$ Fe distances (in Å)) (right).

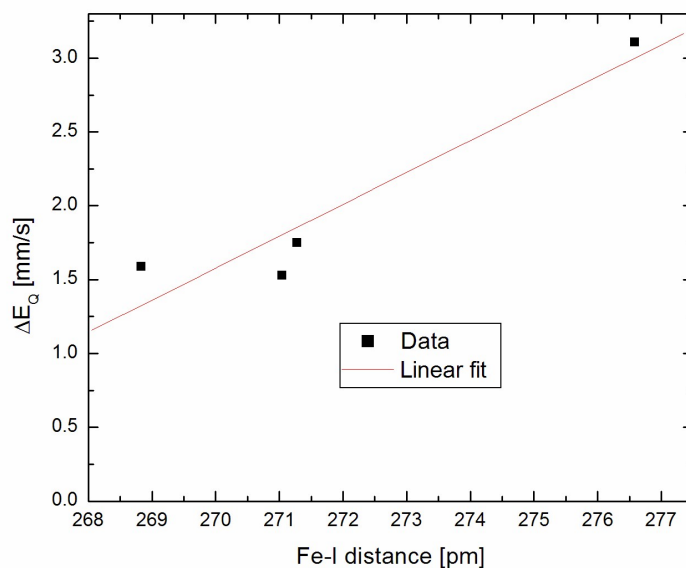


**Figure S6.** Packing diagram of NHC-adduct **4** (left) and arrangement of the Fe-atoms in the unit cell (including intermolecular Fe...Fe distances (in Å)) (right).



**Figure S7.** Packing diagram of NHC-adduct **5** (left) and arrangement of the Fe-atoms in the unit cell (including intermolecular Fe...Fe distances (in Å)) (right).

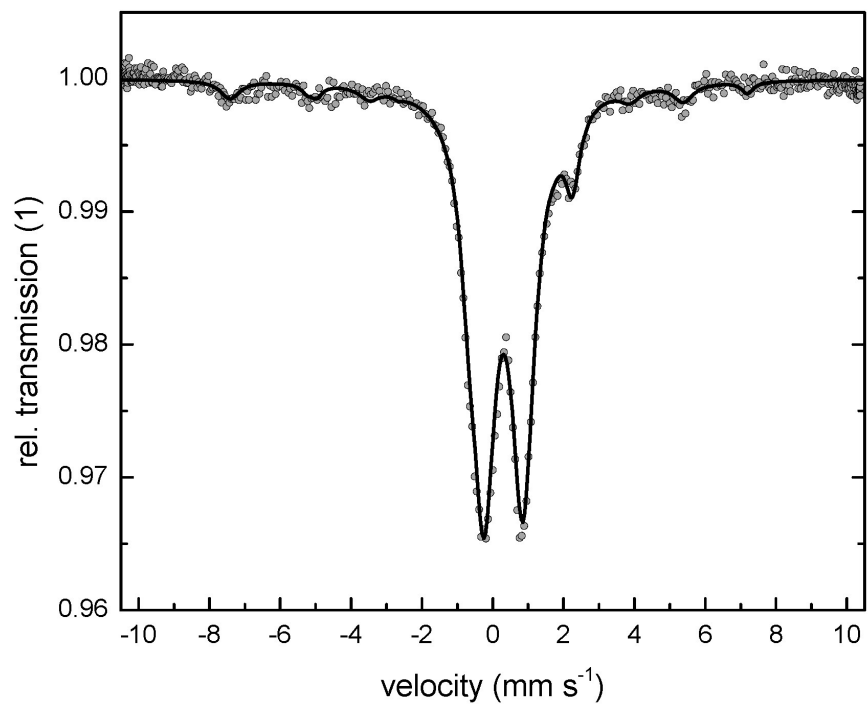
## 4. Mössbauer Spectroscopy



**Figure S8.** Correlation between  $\Delta E_Q$  and the Fe-I distance for NHC-adducts **2-5**.

### Decomposition studies on complex **4**

To exclude, that the second sub-spectrum found at low temperatures for complex **4** is attributed to a partial sample decomposition as result of accidental air contact, we measured the same sample after deliberate exposure to air at  $T = 20$  K. The colour of the powder changes within *approx.* 5 min from orange to dark brown. The main components of the spectrum were analyzed by two Lorentzian doublets with isomer shift ( $\delta$  *approx.* 0.42 and 0.91 mm/s, respectively) and quadrupole splitting values ( $\Delta E_Q$  *approx.* 1.10 and 2.92 mm/s), which are consistent with *approx.* 81% of an Fe(III) high-spin and *approx.* 10% of an Fe(II) high-spin form (Figure S9). The Fe(II) high-spin sub-spectrum may be related to the original complex **4**, but the  $\delta$  and  $\Delta E_Q$  values change significantly and no indication of slow paramagnetic relaxation is observable. A reliable fit of the residual magnetically split hyperfine pattern ( $H_{\text{hf}}$  *approx.* 39.5 and 37.5 T) with a volume fraction of *approx.* 10% was not possible. Furthermore simulation of this hyperfine pattern on basis of the parameters of the original complex **4** does not account for the experimental data.



**Figure S9.** Mössbauer spectrum of complex **4** measured at  $T = 20$  K, after deliberate exposure of **4** to air for *ca.* five minutes.

Hence we conclude that the signature of the sample **4** after decomposition in air no longer shows paramagnetic relaxation and the decomposition product is dominated by an Fe(III) high-spin Lorentzian doublet. Therefore we exclude that the second sub-spectrum observed at low temperatures for the original complex **4** is associated with sample decomposition after accidental air contact.

## 5. Computational Details

All computations were performed using the DFT functional method B97D and B3LYP as implemented in the Gaussian09 program.<sup>[1]</sup> The all-electron triple- $\zeta$  basis set (6-311G\*\*)<sup>[2]</sup> was applied for all elements (Fe, N, C and H), whereas a Stuttgart-Dresden pseudopotential (SDD)<sup>[3]</sup> was used for iodine (I).

### 5.1 Energies of the optimized structures

**Table S2.** Energies of the optimized structures

Compound	E(0 K) <sup>a</sup>	H(298 K) <sup>b</sup>	G(298 K) <sup>b</sup>
	[Ha]	[Ha]	[Ha]
<b>B3LYP:</b>			
[Cp*FeCl(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <i>S</i> = 0)	-2654.215575	-2654.183190	-2654.275695
[Cp*FeCl(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <i>S</i> = 1)	-2654.237983	-2654.204942	-2654.300576
[Cp*FeCl(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <i>S</i> = 2)	-2654.238347	-2654.204382	-2654.304542
[Cp*FeCl(IMes)] ( <i>S</i> = 0)	-3037.587294	-3037.546969	-3037.658517
[Cp*FeCl(IMes)] ( <i>S</i> = 1)	-3037.611522	-3037.570542	-3037.685142
[Cp*FeCl(IMes)] ( <i>S</i> = 2)	-3037.614295	-3037.572526	-3037.690884
[Cp'FeI(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <b>3</b> , <i>S</i> = 0)	-2480.748042	-2480.706821	-2480.818705
[Cp'FeI(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <b>3</b> , <i>S</i> = 1)	-2480.775392	-2480.733752	-2480.847675
[Cp'FeI(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <b>3</b> , <i>S</i> = 2)	-2480.778516	-2480.736422	-2480.852389
[Cp'FeI(IMes)] ( <b>4</b> , <i>S</i> = 0)	-2864.190333	-2864.140967	-2864.271987
[Cp'FeI(IMes)] ( <b>4</b> , <i>S</i> = 1)	-2864.220116	-2864.170548	-2864.303123
[Cp'FeI(IMes)] ( <b>4</b> , <i>S</i> = 2)	-2864.227514	-2864.177296	-2864.312655
<b>B97D:</b>			
[Cp*FeCl(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <i>S</i> = 0)	-2654.079887	-2654.047670	-2654.138960
[Cp*FeCl(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <i>S</i> = 1)	-2654.084336	-2654.051338	-2654.145844
[Cp*FeCl(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <i>S</i> = 2)	-2654.074011	-2654.040381	-2654.137513
[Cp*FeCl(IMes)] ( <i>S</i> = 0)	-3037.164612	-3037.124451	-3037.234381

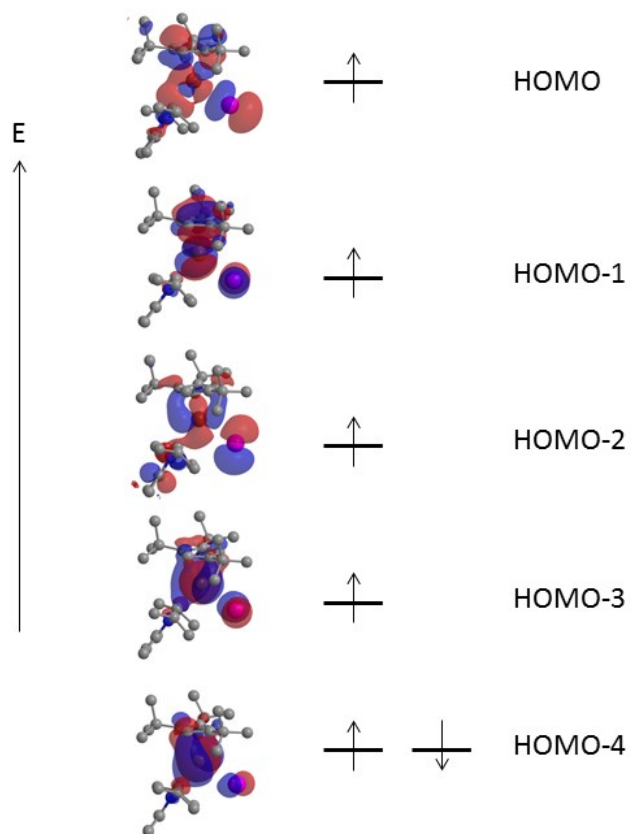


[Cp*FeCl(IMes)] ( $S = 1$ )	-3037.170839	-3037.130067	-3037.241951
[Cp*FeCl(IMes)] ( $S = 2$ )	-3037.162118	-3037.120549	-3037.236218
[Cp'FeI(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <b>3</b> , $S = 0$ )	-2480.476173	-2480.435599	-2480.543406
[Cp'FeI(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <b>3</b> , $S = 1$ )	-2480.483350	-2480.442457	-2480.552800
[Cp'FeI(IiPr <sub>2</sub> Me <sub>2</sub> )] ( <b>3</b> , $S = 2$ )	-2480.475911	-2480.434172	-2480.547817
[Cp'FeI(IMes)] ( <b>4</b> , $S = 0$ )	-2863.632326	-2863.583740	-2863.708612
[Cp'FeI(IMes)] ( <b>4</b> , $S = 1$ )	-2863.646512	-2863.597731	-2863.724354
[Cp'FeI(IMes)] ( <b>4</b> , $S = 2$ )	-2863.638530	-2863.588502	-2863.720436

<sup>a</sup>DFT energy incl. ZPE.

<sup>b</sup>standard conditions  $T = 298.15$  K and  $p = 1$  atm.

## 5.2 (Biorthogonalized) Kohn-Sham molecular orbitals for complex 3



## 6. References

- [1] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [2] X. Cao and M. Dolg, *J. Chem. Phys.* 2001, **115**, 7348.
- [3] A. Bergner, M. Dolg, W. Küchle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431-41.