Electronic Supplementary Information

for

An old workhorse for new applications: $Fe(dpm)_3$ as precursor for low- temperature PECVD of iron(III) oxide

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NMR spectra of $Fe(dpm)_3$

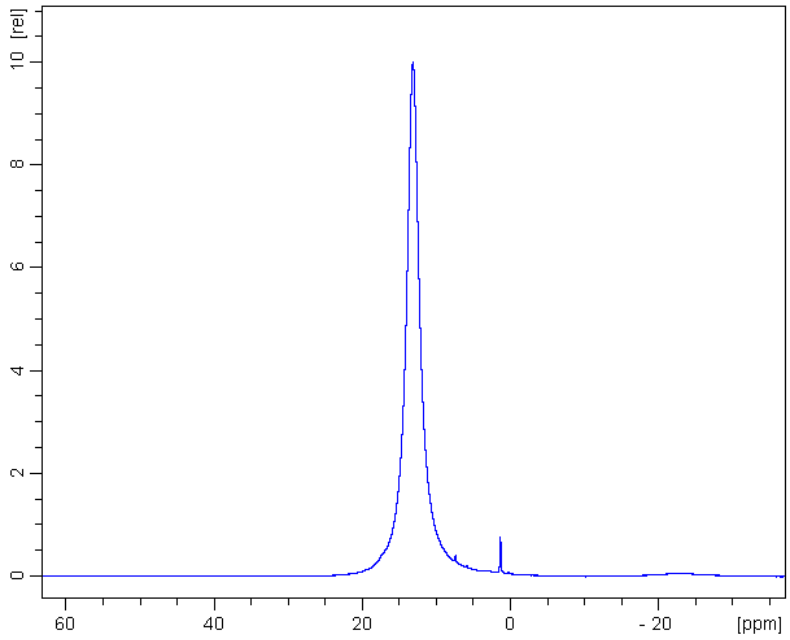


Fig. S1. ^{1}H-NMR spectrum of $Fe(dpm)_3$ in $CDCl_3$. Experimental conditions: number of scans = 8, relaxation delay = 1 s, sweep width = 40 KHz, time domain = 256 Kwords. The chemical shift values are δ ≈13.04 and ≈–22.8 for CH_3 and CH protons, respectively. The signal at δ 1.4 is due to some residual H_2O.

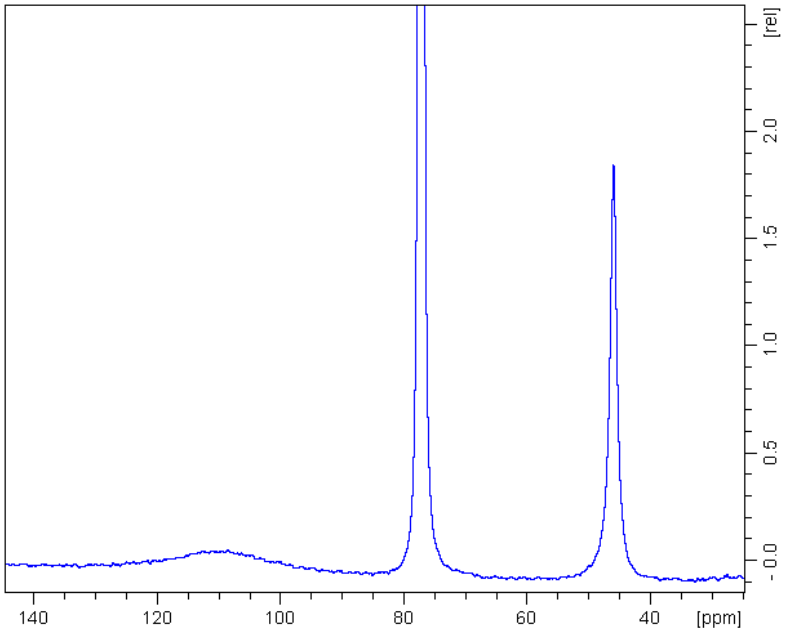
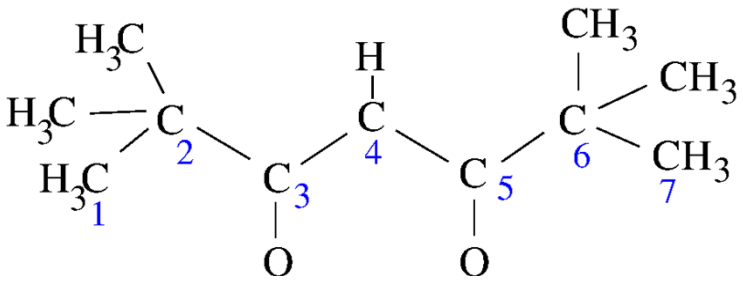


Fig. S2. ^{13}C NMR spectrum of $Fe(dpm)_3$ in $CDCl_3$. Experimental conditions: number of scans = 54040, relaxation delay = 0.15 s, sweep width = 75 KHz, time domain = 8196 words. The chemical shift values are $\delta \approx 45.9$ and ≈ 110 for CH_3 and CH carbons, respectively. The intense signal at $\delta \approx 77$ is due to the solvent.

Structural properties of $Fe(dpm)_3$



Scheme 1. Numbering of the carbon atoms in the dpm unit.

	Exp. ref.[a]	**PBE (U=0)** $S_z = 1/2\ \hbar$	**PBE U=4** $S_z = 1/2\ \hbar$	**PBE U=4** $S_z = 5/2\ \hbar$
C_1-C_2 Distance	1.44	1.53	1.53	1.54
C_2-C_3 Distance	1.52	1.54	1.55	1.55
C_3-C_4 Distance	1.39	1.40	1.40	1.40
C_3-O Distance	1.29	1.28	1.28	1.28
O-O Distance	2.71	2.79	2.83	2.81
Fe-O Distance	2.00	2.03	1.98	1.95
C_3-C_4-C_5 Angle	125°	125°	125°	125°

[a] reference [S1].

Table S1. Selected bond length (in Å) and bond angle values from experiment and simulation. The numbering according to Scheme 1 is used.

Detailed assignments of theoretical vibrational lines for $Fe(dpm)_3$

	$Fe(dpm)_3$	
assignment	**ν [cm^{-1}]**	**I [km/mol]**
$\gamma(CH_3)$ asym. $\gamma(CH_3)$ symm. $\gamma(CH_3)$ [a]	3027-3190 (39) 2962-2976 (18) 2964[a], 2866[a]	$\Sigma = 918$ $\Sigma = 572$
γ(C=O)	1543, 1549	768, 817
γ(C-C)	1546[a]	-
β(H)	1499, 1501, 1502 1506[a]	332, 270, 981
$\delta_a[CH_3]$	1441	75
γ(C=O)	1399, 1408, 1419	85, 67, 171
$\delta_s[CH_3]$	1336-1373(18) 1396[a]	$\Sigma = 207$
θ[ring]	1257, 1258	25, 15
$C(CH_3)_3$ internal	1212, 1222, 1223	73, 36, 32
β[C-H]	1158, 1161, 1166	15, 22, 23
θ[ring]	1029, 1030	114,100
$\gamma[C\text{-}C(CH_3)_3]$	853, 854, 856 872[a]	36, 46, 75
π[C-H]	788, 792 820, 794[a]	20,15
γ[Fe-O]	603, 604 623[a]	66, 74
γ[Fe-O]	485, 487 480, 502[a]	64, 62

[a] reference [S2].

Table S2. Main IR transitions for the $Fe(dpm)_3$ complex. Symbols: γ = in-plane stretching; β = in-plane bending; δ_s = symmetric bending; δ_a = asymmetric bending; π = out-of-plane bending; θ = breathing mode. The values in brackets denote the multiplicity of the IR-transitions forming a band of similar character. The band intensity I is summed up accordingly.

Electronic structure of $Fe(dpm)_3$

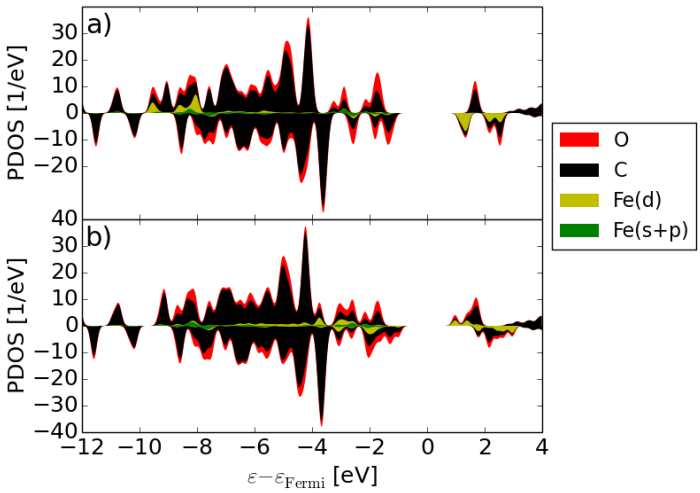


Fig. S3. Projected density of states (PDOS) of the $Fe(dpm)_3$ complex in the relaxed configurations of each spin state: a) $S_z = 5/2\hbar$ and b) $S_z = \hbar/2$. Majority and minority spin PDOS are plotted as positive and negative numbers, respectively.

Correlation between bond order and bond length

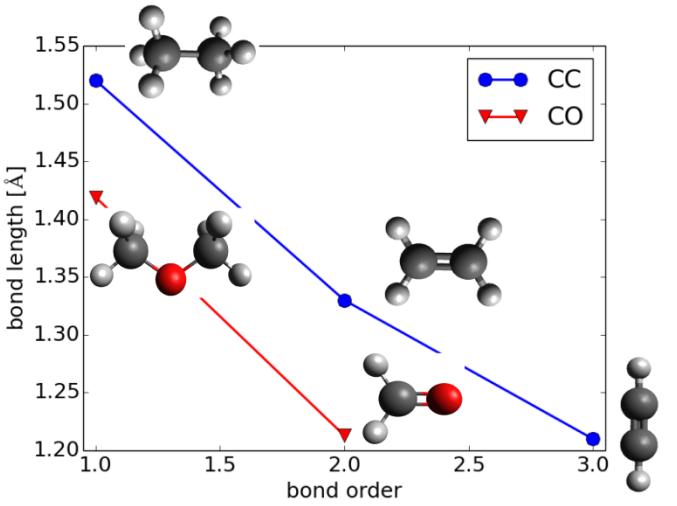


Fig. S4. PBE bond lengths depending on the nominal bond order (reproduction of Fig. 5c in the main text), showing the near linear correlation between CC and CO bond length and theoretical bond order. The displayed PBE bond lengths are for: ethane, C_2H_6 (single bond, R_{CC} = 1.52 Å); ethylene, C_2H_4 (double bond, R_{CC} = 1.33 Å); acetylene, C_2H_2 (triple bond, R_{CC} = 1.21 Å); dimethyl ether, CH_3OCH_3 (single bond, R_{CO} = 1.42 Å); formaldehyde, H_2CO (double bond, R_{CO} = 1.21 Å).

References

[S1] M. A. K. Ahmed, H. Fjellvåg, A. Kjekshus and D. S. Wragg, *Z. Anorg. Allg. Chem.*, 2013, **639**, 770-778.

[S2] Y. Jiang, M. Liu, Y. Wang, H. Song, J. Gao and G. Meng, *J. Phys. Chem. A*, 2006, **110**, 13479-13486.