Supporting information for

[{Cp'Fe(µ-OH)}₃]: The synthesis of A Unique Organometallic Iron Hydroxide

Marc D. Walter*, and Peter S. White

Contribution from the Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig (Germany) and the Department of Chemistry,

University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290 (USA)

E-mail: <u>mwalter@tu-bs.de</u>

Table of Content:

1.	Experimental Details	S 2
2.	Variable temperature NMR behavior of 2 , 2 -DMAP and 3 -OD	S 4
3.	Crystal Structure Determination of Complexes 2-DMAP and 3-OH	S 7
4.	References	S 9

1. Experimental Details

General Considerations. All manipulations were carried out using standard vacuum, Schlenk, cannula, or glovebox techniques. Argon was purified by passage through BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. ¹H and ²H NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer. Elemental analyses were carried out by analytical facilities at UC Berkeley and TU Braunschweig. Solid state magnetic susceptibility studies were performed as previously described.¹ The solution magnetic susceptibility was determined using a modified² Evans method.³

Materials. All solvents were deoxygenated and dried by passage over columns of activated alumina.^{4,5} C_6D_6 and C_7D_8 purchased from Cambridge Laboratories, Inc., were dried over Na, vacuum transferred to a Teflon sealable Schlenk flask containing 4 Å molecular sieves, and degassed via three freeze-pump-thaw cycles. [{Cp'FeI}₂] was synthesized as previously described.⁴

Synthesis of [Cp'FeN(SiMe₃)₂] (2). A mixture of [{Cp'FeI}₂] (1.41 g, 1.7 mmol) and LiN(SiMe₃)₂ · OEt₂ (0.81 g, 3.4 mmol) was dissolved in *ca*. 20 mL of pentane, and the reaction mixture turned immediately bright yellow. After having stirred for 10 min the solution was filtered and the pentane was removed under reduced pressure. The yellow residue was sublimed in diffusion pump vacuum at 60-70 °C to give yellow crystalline material (1.06 g, 2.36 mmol, 69 %). M.p. 122-124 °C (rev.). ¹H NMR (C₆D₆, 292K): δ 44.9 (18H, SiMe₃, v_{1/2} = 1100 Hz), -30.3 (18H, CMe₃, v_{1/2} = 1050 Hz), -42.6 (9H, CMe₃, v_{1/2} = 700 Hz). IR (Nujol mull; CsI windows; cm⁻¹): 1365m, 1260m, 1249vs, 1205vw, 1160vw, 1100vbr.vw., 1005sh, 970brvs, 875vs, 852m, 830brs, 798sh, 752w, 723w, 670s, 637vw, 615w, 545vw, 450br.w, 362vs, 418vw, 460s, 270vw, 238s. Anal. calcd. for C₂₃H₄₇NSi₂Fe: C, 61.43; H, 10.53; N, 3.12. Found: C, 61.17; H, 10.21; N, 2.95. The E.I. mass spectrum showed a molecular ion at m/e= 449 amu. The parent ion isotopic cluster was simulated: (calcd. %, observd. %): 447(6, 6), 448(2, 3), 449(100, 100), 450(38, 39), 451(14, 13), 452(3, 2).

Synthesis of [Cp'FeN(SiMe₃)₂(dmap)] (2-DMAP). A mixture of [Cp'FeN(SiMe₃)₂] (0.441 g, 1 mmol) and *p*-dimethylaminopyridine (DMAP) (0.122 g, 1 mmol) was dissolved in pentane (10 mL) and stirred at room temperature for 15 min. The solvent was removed under dynamic vacuum and the residue was dissolved in hexamethyldisiloxane (10 mL). The yellow-green solution was filtered and concentrated to *ca*. 5 mL. Complex **2-**DMAP was crystallized at -30 °C to give yellow-green crystals (0.25 g, 0.44 mmol, 44 %). M.p. 126-129 °C (rev.). ¹H NMR (C₆D₆, 292K): δ 32.2 (18H, SiMe₃, v_{1/2} = 1070 Hz), 20.6 (4H, α-β-CH-DMAP, v_{1/2} = 580 Hz), 2.83 (6H, NMe₂-DMAP, v_{1/2} = 30 Hz), -26.5 (18H, CMe₃, v_{1/2} = 920 Hz), -31.3 (9H, CMe₃, v_{1/2} = 340 Hz). IR (Nujol mull; CsI windows; cm⁻¹): 1620s, 1517s, 1380w, 1262s, 1240vs, 1228s, 1200w, 1168vw, 1158vw, 1115vw, 1068s, 1010vs, 970brvs, 878vs, 848sh, 830brs, 810s, 785m, 760m, 670s, 620w, 610w, 540m, 450w, 380s, 280vw, 240w. Anal. calcd. for C₃₀H₅₇N₃Si₂Fe: C, 63.01; H, 10.05; N, 7.35. Found: C, 63.17; H, 10.21; N, 7.15.

Synthesis of [{Cp'Fe(μ -OH)}₃] (3-OH). A pentane solution (10 mL) of [Cp'FeN(SiMe₃)₂] (0.45 g, 1 mmol) was transferred with a cannula to the mixture of degassed H₂O (18 μ L, 1 mmol) and pentane (10 mL). The color of the light yellow solution changed slowly to green and a small amount of a colorless precipitate formed. After stirring at RT for 15 min the solvent was removed under reduced pressure to give a green, slightly sticky solid. The residue was dissolved in (Me₃Si)₂O, and the solution was filtered, concentrated and cooled to -30°C. Green block-like crystals were isolated on filtration. Yield: 0.12 g (0.13 mmol, 39 %). ¹H NMR (C₆D₆, 292K): δ 502.5 (1H, OH, $v_{1/2}$ = 810 Hz), -3.3 (18H, CMe₃, $v_{1/2}$ = 58 Hz), -6.1 (9H, CMe₃, $v_{1/2}$ = 58 Hz), -33.5 (2H, ring-CH, $v_{1/2}$ = 275 Hz). ²H NMR (C₆H₆, RT): δ 502.5 (1H, OD, $v_{1/2}$ = 62 Hz). IR (Nujol mull; KBr windows; cm⁻¹): 3653m (O-H), 2690m (O-D). Anal. calcd. for C₅₁H₉₀O₃Fe₃: C, 66.67; H, 9.87. Found: C, 66.45; H, 9.72.

2. Variable temperature NMR behavior of 2, 2-DMAP and 3-OD



Figure S1. Chemical Shift (δ) vs. T⁻¹ plot for the ¹H NMR resonances of [Cp'FeN(SiMe₃)₂] (**2**) in toluene-d₈ from -90 to +104 °C.



Figure S2. Chemical Shift (δ) vs. T⁻¹ plot for the ¹H NMR resonances of [Cp'FeN(SiMe₃)₂(DMAP)] (2-DMAP) in toluene-d₈ from -90 to +104 °C.



Figure S3. Comparison of the chemical Shift (δ) vs. T⁻¹ plots of [Cp'FeN(SiMe₃)₂] (**2**) and [Cp'FeN(SiMe₃)₂(DMAP)] (**2**-DMAP) in toluene-d₈ from -90 to +104 °C.



Figure S4. Chemical Shift (δ) vs. T⁻¹ plot for the ¹H NMR resonances of [{Cp'Fe(OD)}₃] (**3**-OD) in methylcyclohexane-d₁₂ from -100 to +104 °C (only the tBu resonances of the Cp'rings are shown). At elevated temperatures some sample degradation was observed.

3. Crystal Structure Determination of 2-DMAP and 3-OH

Table S1. X-Ray Crystal Structure Data for 2-DMAP (internal number: c09219)

$C_{30}H_{57}FeN_3Si_2$	
571.82	
Orthorhombic, <i>Pna</i> 2 ₁	
100	
20.6031 (4), 11.4977 (3), 14.2483 (3)	
3375.26 (13)	
4	
Μο Κα	
0.54	
$0.25\times0.25\times0.05$	
CCD area detector diffractometer	
Empirical (using intensity measurements)	
Blessing (1995)	
0.877, 0.974	
25199, 7963, 5804	
0.058	
0.038, 0.062, 0.86	
7963	
374	
1	
H-atom parameters constrained	
0.29, -0.35	
Flack H D (1983), Acta Cryst. A39, 876-881	
0.396 (11)	

Computer programs: Bruker SMART, Bruker SAINT, Bruker SHELXTL.

Table S2. X-Ray Crystal Structure Data for 3-OH (internal number: c09205)

Crystal data			
Chemical formula	$C_{51}H_{90}Fe_3O_3$		
M _r	918.78		
Crystal system, space group	Monoclinic, $P2_1/c$		
Temperature (K)	100		
a, b, c (Å)	10.3786 (2), 23.9595 (5), 21.2188 (5)		
β (°)	92.417 (1)		
$V(\text{\AA}^3)$	5271.70 (19)		
Ζ	4		
Radiation type	Μο Κα		
$\mu (mm^{-1})$	0.85		
Crystal size (mm)	$0.25 \times 0.10 \times 0.10$		
Data collection			
Diffractometer	Bruker APEX-II CCD diffractometer		
Absorption correction	Multi-scan SADABS		
T_{\min}, T_{\max}	0.816, 0.920		
No. of measured, independent and observed			
$[I > 2\sigma(I)]$ reflections	34016, 10522, 6802		
$R_{\rm int}$	0.059		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.051, 0.118, 1.02		
No. of reflections	10522		
No. of parameters	541		
No. of restraints	0		
H-atom treatment	H-atom parameters constrained		
$\Delta \rangle_{\rm max}, \Delta \rangle_{\rm min} (e {\rm \AA}^{-3})$	1.47, -0.45		

Computer programs: Bruker APEX2, Bruker SAINT, SHELXS97 (Sheldrick, 2008), SHELXL97 (Sheldrick, 2008), Bruker SHELXTL.

O3 is disordered and was therefore refined isotropically in two positions (O3A and O3B). The O-H protons were not unambiguously assigned in the Fourier map and therefore not included in the refinement. Their presence was verified by other spectroscopic methods (IR and NMR spectroscopy).

4. Magnetic Susceptibility Studies on 2, 2-DMAP and 3-OD



Figure S5. Solid state magnetic susceptibility (χ) vs. T plot for [Cp'FeN(SiMe₃)₂] (**2**). Simulation: S=2, g= 2.19, |D|= 1.83 cm⁻¹.



Figure S6. Solid state magnetic susceptibility (χ) vs. T plot for [Cp'FeN(SiMe₃)₂(DMAP)] (**2**-DMAP). Simulation: S=2, g= 1.93, |D|= 2.91 cm⁻¹.



Figure S7. Comparison between the magnetic susceptibility of **3**-OD obtained in solid state (SQUID) and in solution (Evans method).



Figure S6a. Solid state magnetic susceptibility (χT) vs. T plot for $[\{Cp'Fe(\mu-OD)\}_3]$ (3-OD). Simulation ($S = S_1 = S_2 = S_3 = 2$): $J_1 = J_2 = J_3 = -19.35$ cm⁻¹, $g_1 = g_2 = g_3 = 2.31$, PI(S=2)= 8.0%. The relatively large contribution of a paramagnetic impurity (PI) is due to the high thermal, moisture and airsensitivity of this molecule. Furthermore, it is unclear what magnetic signature the thermal degradation product would exhibit, so the assumption of a PI with S=2 might be a rather crude approximation.

5. References

- 1. M. D. Walter, M. Schultz and R. A. Andersen, New. J. Chem., 2006, 30, 238-246.
- 2. K. Sur, J. Magn. Reson., 1989, 82, 169-173.
- 3. D. F. Evans, J. Chem. Soc., 1959, 2003.
- 4. P. J. Alaimo, D. W. Peters, J. Arnold and R. G. Bergman, J. Chem. Educ., 2001, 78, 64.
- 5. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.