Supporting information for

Weak paramagnetism in compounds of the type Cp’$_2$Yb(bipy)

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1. $(C_5Me_5)_2Yb(py)_2$

The amount of Yb(III) impurity the following approach was determined in the following manner: The Yb(III) impurity was modelled by $[(C_5Me_5)_2Yb(bipy)][I]$. The amount of Yb(III) impurity, A, can be calculated by a least squares refinement of the following equation:

$\chi_{calc}[(C_5Me_5)_2Yb(py)_2]= A^* \chi[(C_5Me_5)_2Yb(bipy)I]$ and the minimization of the sum $\sum_i (\chi_{i\exp} - \chi_{i calc})^2$

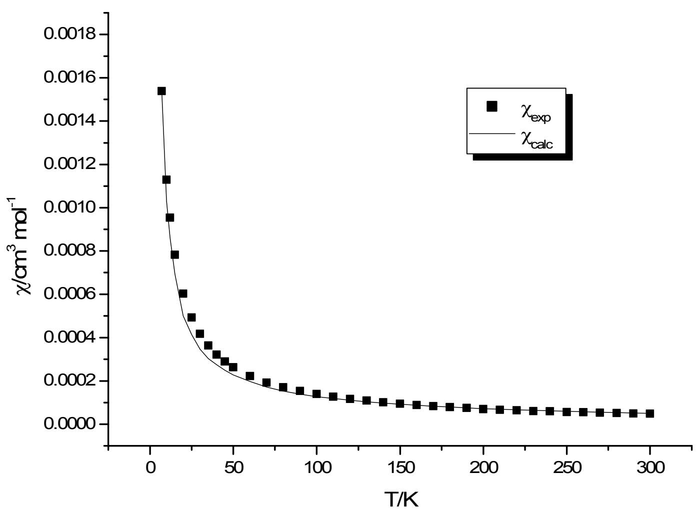


Figure S1a. Solid state magnetic susceptibility, χ vs. T plot of $(C_5Me_5)_2Yb(py)_2$ and the calculated magnetic susceptibility assuming a ~ 0.5 % impurity contribution (A = 0.0045).

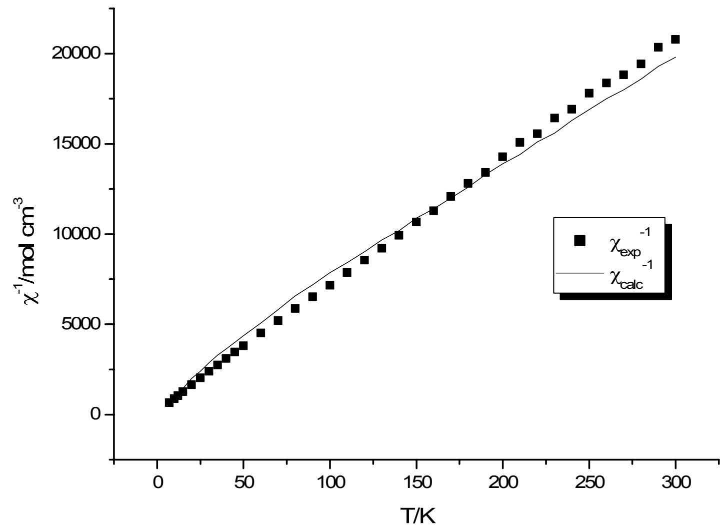


Figure S1b. Solid state magnetic susceptibility, χ^{-1} vs. T plot of $(C_5Me_5)_2Yb(py)_2$ and the calculated magnetic susceptibility assuming a ~ 0.5 % impurity contribution (A = 0.0045).

2. Variable temperature NMR studies

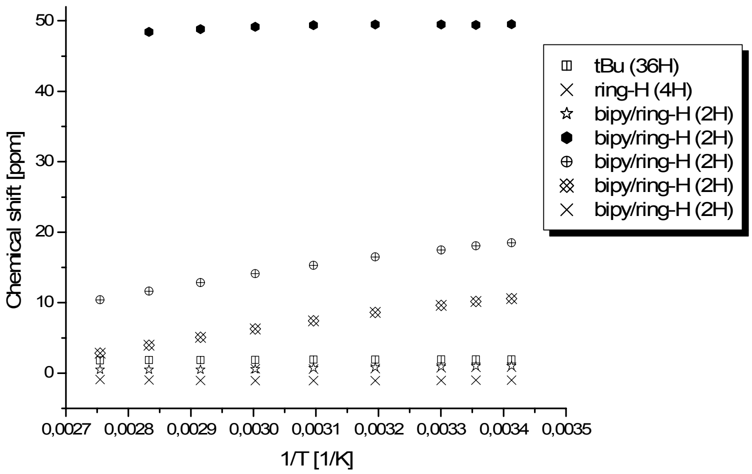


Figure S2. Chemical shift (δ) vs. 1/T plot of ^{1}H NMR resonances of $[1,3\text{-}(Me_3C)_2C_5H_3]_2Yb(bipy)$ in toluene-d_8 at temperatures from +20 to +90°C.

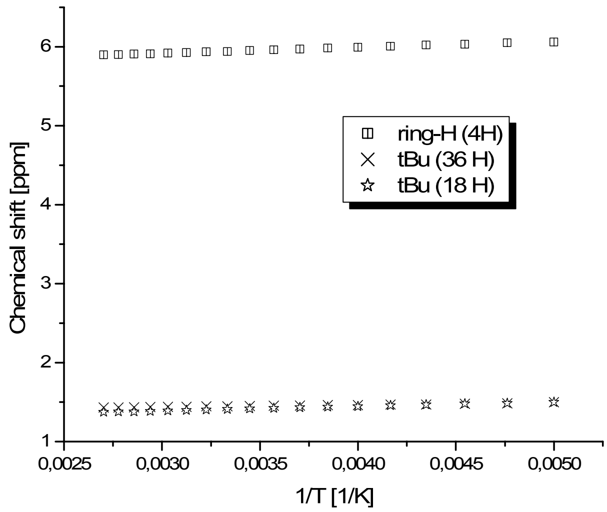
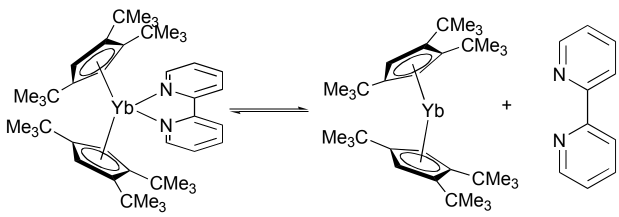


Figure S3. Chemical shift (δ) vs 1/T plot of [1]H NMR resonances of $[1,2,4\text{-}(Me_3C)_3C_5H_2]_2Yb$ in toluene-d_8 at temperatures from -70 to +100°C.

3. Thermodynamics of the equilibrium



Concentration [Yb] = [bipy]

The equilibrium can be described as a [Yb(bipy)] = 2 [Yb] problem with the equilibrium constant: K_x= $[Yb]^2$/[Yb(bipy)]

[1]H NMR studies at variable temperature give ratio: [Yb]/[Yb(bipy)] = X

→ [Yb(bipy)]=[Yb]/X

Total concentration (in mole fractions): 2 [Yb] + [Yb(bipy)] = 1

➔ 2 [Yb] + [Yb]/X = 1 → [Yb] (2 + 1/X) = 1 ➔ $[Yb] = \frac{X}{(2X+1)}$

$$K_x = \frac{[Yb]^2}{[Yb(bipy)]} = X[Yb] = \frac{X^2}{(2X+1)}$$

Table S1. X determined in the temperature regime 270-220 K

T^{-1}/K^{-1}	X	K_x	ln K_x
0.0037037	0.71022727	0.20840002	-1.56829587
0.00377358	0.55991041	0.1478897	-1.91128854
0.00384615	0.42992261	0.09938109	-2.30879338
0.00392157	0.330033	0.06561292	-2.7239826
0.004	0.2399808	0.0389137	-3.24640885
0.00416667	0.1549907	0.01833775	-3.99879326
0.00425532	0.1200048	0.01161374	-4.45556619
0.00434783	0.0900009	0.00686453	-4.98138718
0.00444444	0.07500188	0.00489153	-5.32024953
0.00454545	0.05	0.00227273	-6.08677473

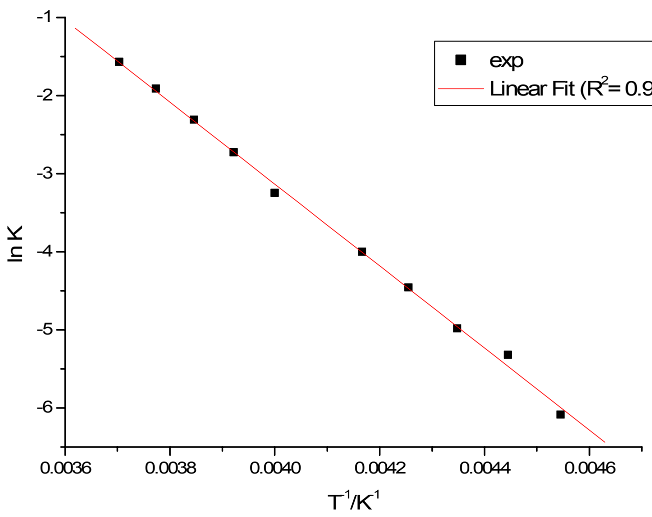


Figure S4. ln K_x vs. T^{-1} plot for $[1,2,4\text{-}(Me_3C)_3C_5H_2]_2Yb(bipy)$.

Linear fit to equation ln K_x= A + B(T^{-1}): A= 17.8607 ± 0.34846; B= -5248.38502 ± 84.78444

$$\ln K_x = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

ΔH= 10.43 ± 0.17 kcal mol^{-1}

ΔS= 35.49 ± 0.69 cal mol^{-1} K^{-1}

ΔG(300K) = –0.22 ± 0.01 kcal mol^{-1}