Supporting Information for the manuscript

Electron Transfer in Tetramethylbiphosphinine Complexes of Cp^*_2Yb and Cp^*_2Sm

Arnaud Jaoul, Carine Clavaguéra,* and Grégory Nocton*

LCM, CNRS, Ecole polytechnique, Université Paris-Saclay, 91128 Palaiseau, France

Figure S1: ^{1}H NMR of **1** at room temperature in toluene-d_8. * are for solvents (toluene) and impurities (grease).

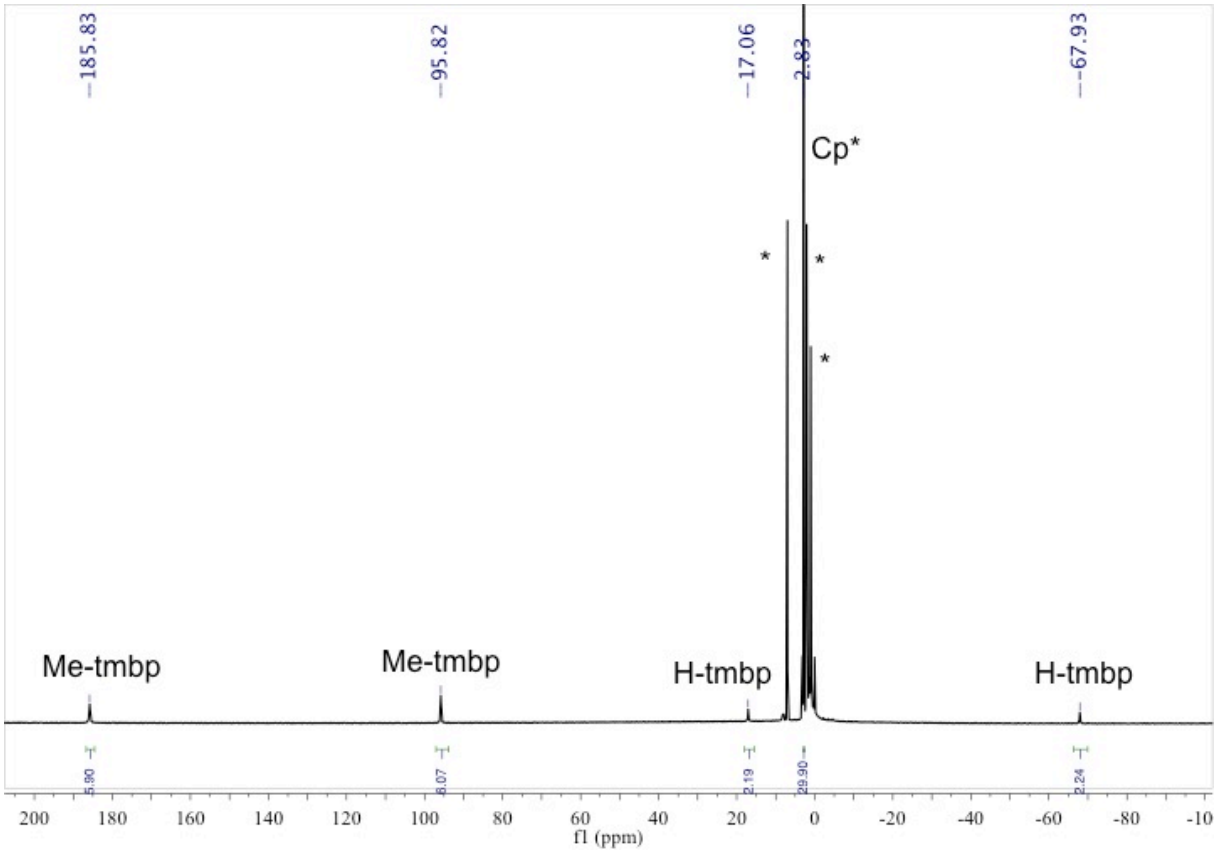


Figure S2: ^{1}H NMR of **2** at room temperature in toluene-d_8. * are for solvents (toluene) and impurities (grease).

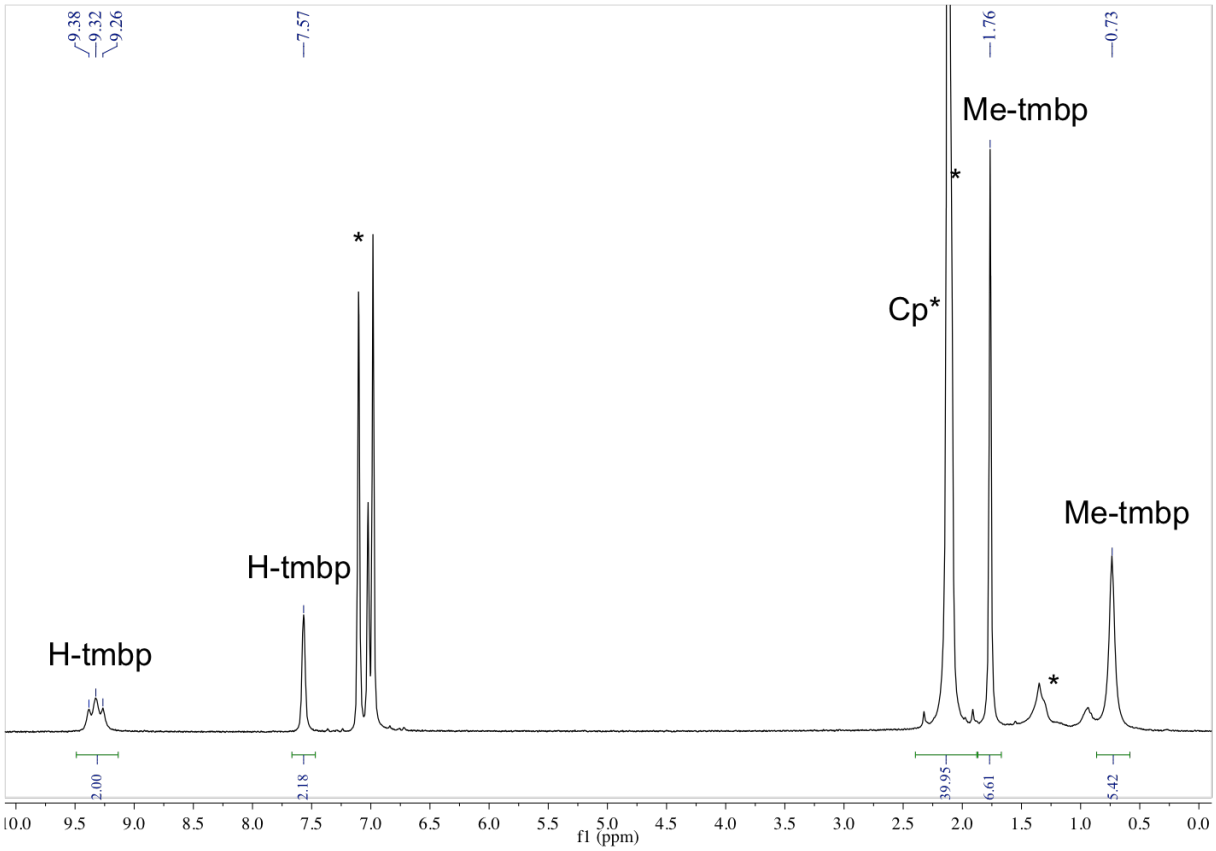


Figure S3: ^{1}H NMR of **2** at room temperature in thf-d_8. * are for solvents (thf and benzene) and and impurities (grease).

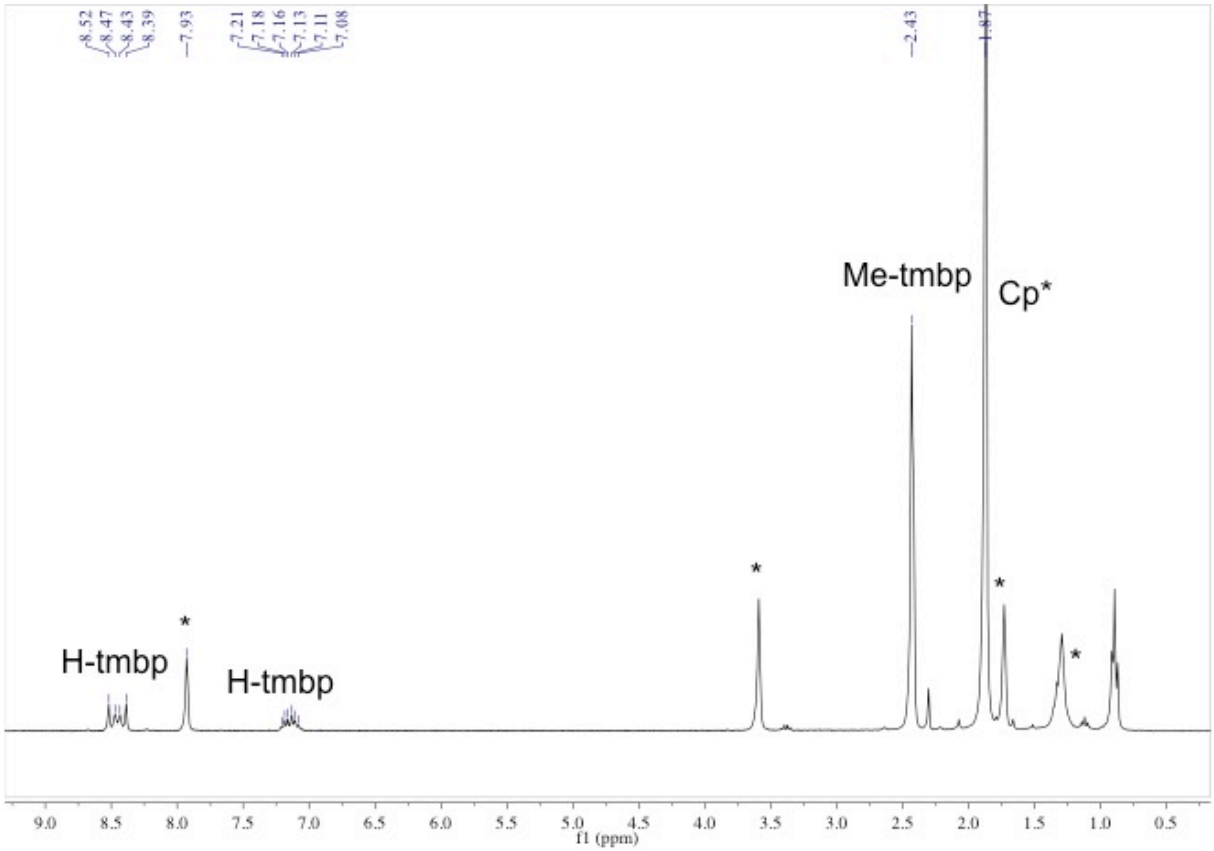


Figure S4: ^{13}C NMR of **2** at room temperature in toluene-d_8. The rather low concentration in toluene-d_8 did not allow observing all resonances after one weekend of acquiring the spectrum.

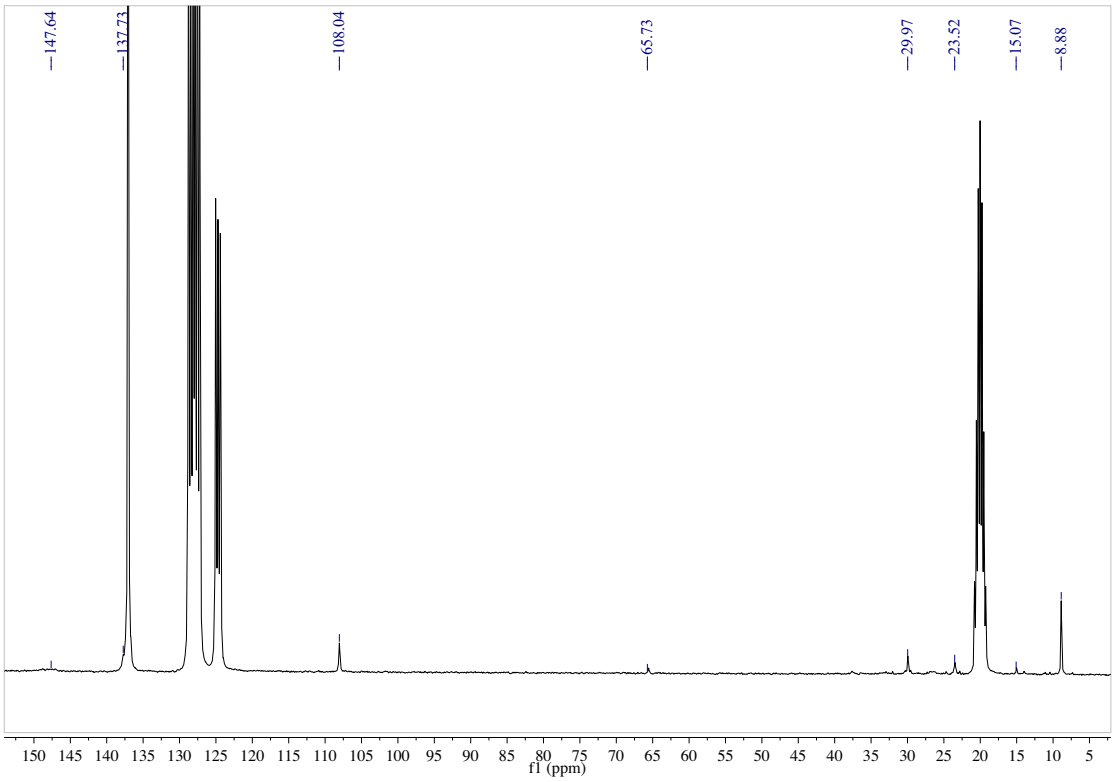


Figure S5: UV-Vis spectrum of **2** recorded in toluene at room temperature.

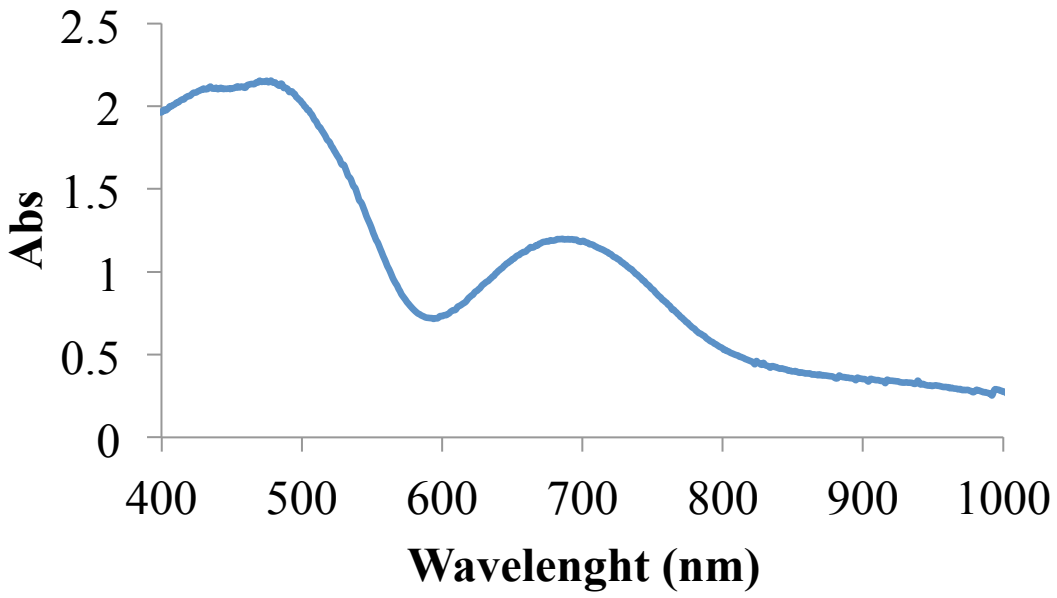


Figure S6: Temperature dependent magnetic data for **1**. χ vs T is given as unfilled red dots, μ_{eff} vs. T as filled blue dots.

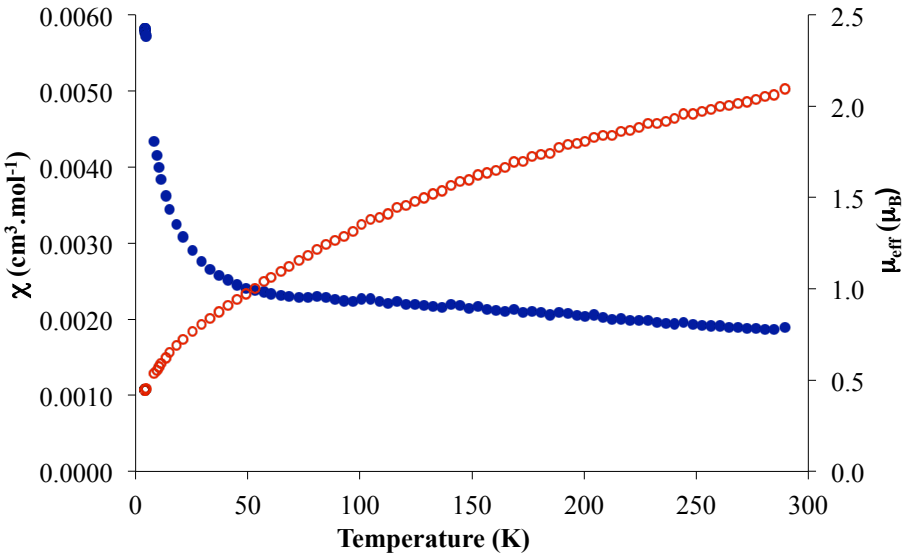
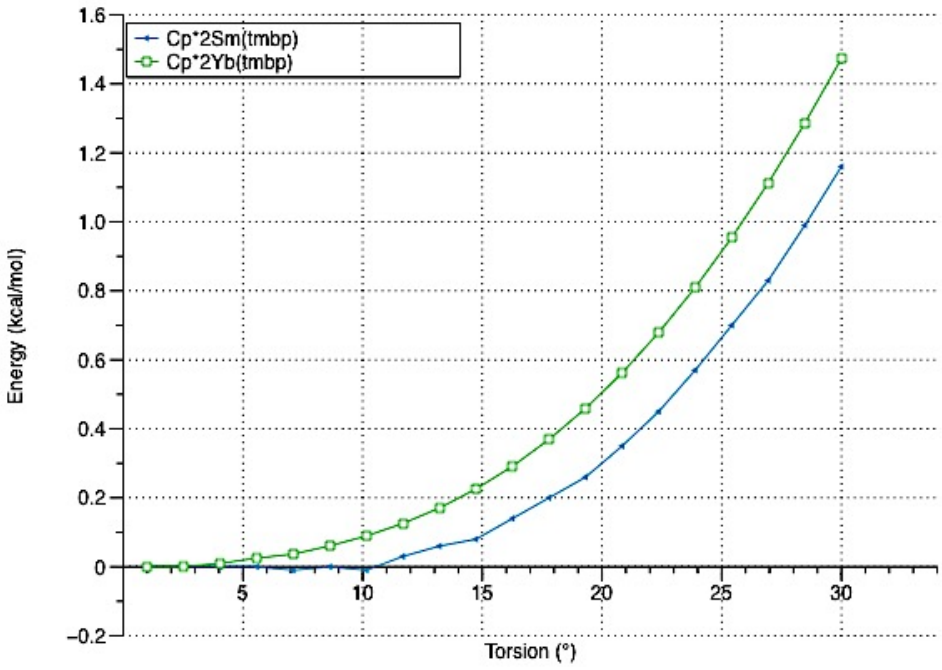


Figure S7: Energy profile as a function of the PCCP angle for both Sm and Yb complexes at the PBE-D3/SVP level.



The single-point energy calculations were performed at the DFT/PBE-D3/SVP level of theory with the ORCA 3.03 package.[1,2] Scalar relativistic effects were taken into account using ZORA Hamiltonian.

Table S1. Crystallographic parameters for **1** and **2**.

	[Cp^*_2Sm(tmbp)] (**1**)	[Cp^*_2Yb(tmbp)] (**2**)
Formula	$C_{34}H_{46}P_2Sm$	$C_{34}H_{46}P_2Yb$
Crystal size (mm)	0.6 x 0.06 x 0.03	0.16x0.14x0.12
cryst system	Monoclinic	triclinic
space group	P 21/c	P -1
volume (Å)	V = 3098.5(5)	V = 1526.9(2)
a (Å)	*a* = 15.389(1)	*a* = 9.821(1)
b (Å)	b = 11.081(1)	b = 10.697(1)
c (Å)	*c* =18.832(1)	*c* =15.776(1)
a (deg)	90.00	77.407(1)
b (deg)	105.234(1)	74.304(1)
g (deg)	90.00	75.918(1)
Z	4	2
formula weight (g/mol)	667	689.69
density (calcd) (g cm^{-3})	1.43	1.500
absorption coefficient (mm^{-1})	2.02	3.188
F(000)	1368	700
temp (K)	150(1)	150(1)
diffractometer[a]	SMART APEX	SMART APEX
θ range for data collection (deg)	2.24 to 26.37	2.84 to 27.48
transmission range	0.865 - 0.941	0.6295 - 0.7009
absorption correction	Multi-scan	Multi-scan
total no. reflections	15409	12166
unique reflections [R_{int}]	6266 [0.072]	6658 [0.053]
final R[b] indices [$I > 2\sigma(I)$]	R = 0.062, R_w = 0.1152	R = 0.0490, R_w = 0.1101
R indices (all data)	R = 0.0904, R_w = 0.1300	R = 0.0590, R_w = 0.1175
largest diff. peak and hole (e.A^{-3})	0.85 and -0.81	2.054 and -1.355
GooF	1.06	1.084

Figure S8: ORTEP and labeling scheme for **1**. Thermal ellipsoids are at 50%.

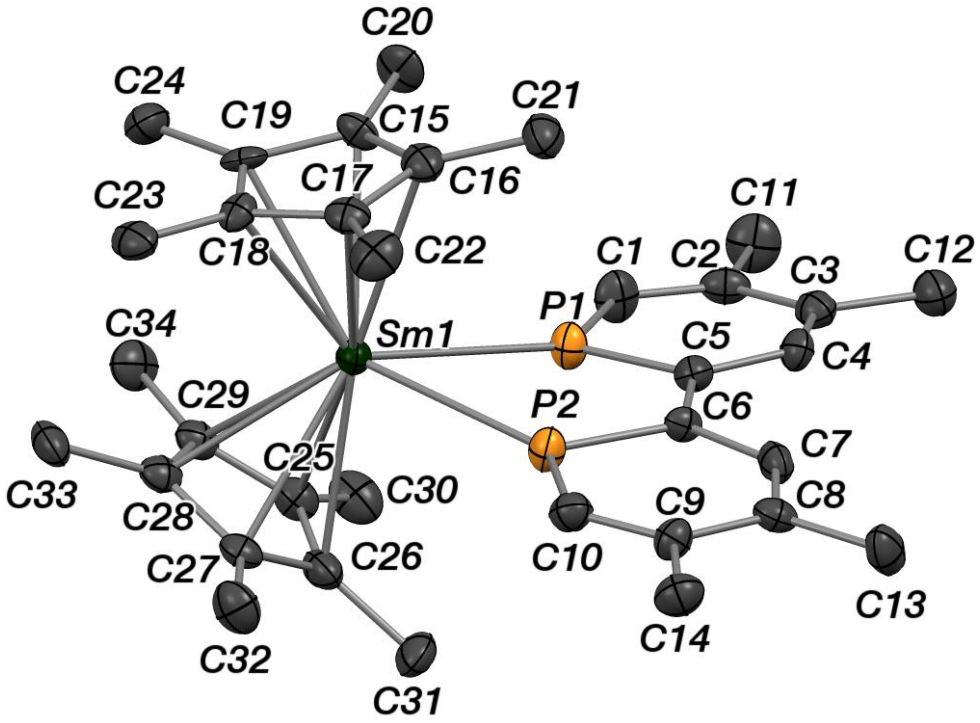
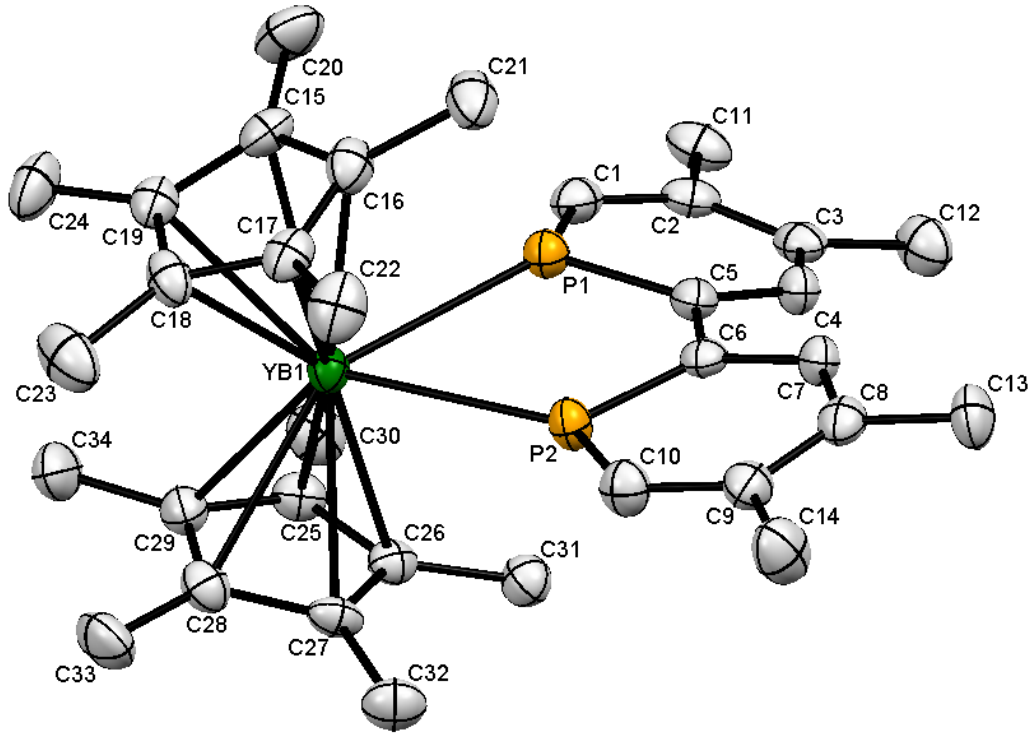


Figure S9: ORTEP and labeling scheme for **2**. Thermal ellipsoids are at 50%.



References:

1. Neese, F. (2012) The ORCA program system, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2, 73–78 .
2. Pantazis, D. A.; Neese, F. (2009) All-Electron Scalar Relativistic Basis Sets for the Lanthanides, J. Chem. Theory Comput., 5, 2229–2238.