

**Lanthanide Hydroxide Cubane Clusters Anchoring Ferrocenes:  
Model Compounds for Fixation of Organometallic Fragments on a  
Lanthanide Oxide Surface.**

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**Supporting Information**

## CV Measurements

### *Experimental*

Voltammetric investigations on **1** were conducted in CH<sub>2</sub>Cl<sub>2</sub>/NBu<sub>4</sub>PF<sub>6</sub> (0.2 M) at ambient temperature; compound **5** was also studied in THF/NBu<sub>4</sub>PF<sub>6</sub> (0.2 M). The electrochemical experiments were performed in a home-built cylindrical vacuum tight one compartment cell. A spiral shaped Pt wire and a Ag wire as the counter and reference electrodes are sealed directly into opposite sides of the glass wall while the respective working electrode (Pt or glassy carbon 1.1 mm polished with 0.25 μm diamond paste (Buehler-Wirtz) before each experiment series) are introduced via a teflon screw cap with a suitable fitting. The cell may be attached to a conventional Schlenk line via two sidearms equipped with teflon screw valves. CH<sub>2</sub>Cl<sub>2</sub> and THF were obtained from Fluka (Burdick&Jackson Brand) and freshly distilled from CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>) or Na (THF) before use. NBu<sub>4</sub>PF<sub>6</sub> (0.25 mM) was used as the supporting electrolyte.

**1** gives a rather strange shaped response to cyclic and square wave voltammetric investigations. It consists of a quite well defined anodic wave (or peak) with signs of chemical reversibility, as is particularly evident from the square wave voltammetry (Fig S1 and S2). This wave has peak-to-peak separations of about 70 mV in cyclic voltammetry and a half-width  $W_{1/2}$  of about 100 mV, in good agreement with the data for the internal Cp\*<sub>2</sub>Fe<sup>0/+</sup> standard. This wave is superimposed on rather ill-defined, broad features at less positive potentials. Deconvolution was carried out on the  $i_{p,f} - i_{p,rev}$  plot from Osteryoung square wave voltammetry. Any satisfactory fit required three separate peaks, the sharper, reversible one being located at 140 to 150 mV with respect to the ferrocene/ferrocenium couple. This peak has a half width in the range of 70 to 100 mV. The additional features are significantly broadened and are located at ca. -20 to -35 mV and at 60 to 100 mV with the largest uncertainty for the latter peak with respect to half width and relative peak area. The broadening of these features points to slow kinetics associated with the underlying electron transfer processes (i. e. to at best quasireversible behavior). No changes apart from a further general broadening of all the features were obtained upon increasing the sweep rate or cooling. Changing the electrode material from platinum to glassy carbon or gold also had no effect on the general appearance of the voltammograms. Unfortunately, the low

resolution of the individual features and the large uncertainties involved in the deconvolution prevent us from drawing any safe conclusions as to the precise potentials of each of these processes and the number of electrons involved in each step. It is therefore not possible to make a statement as to the presence and the degree of any “electronic coupling” between the individual ferrocene based subunits.

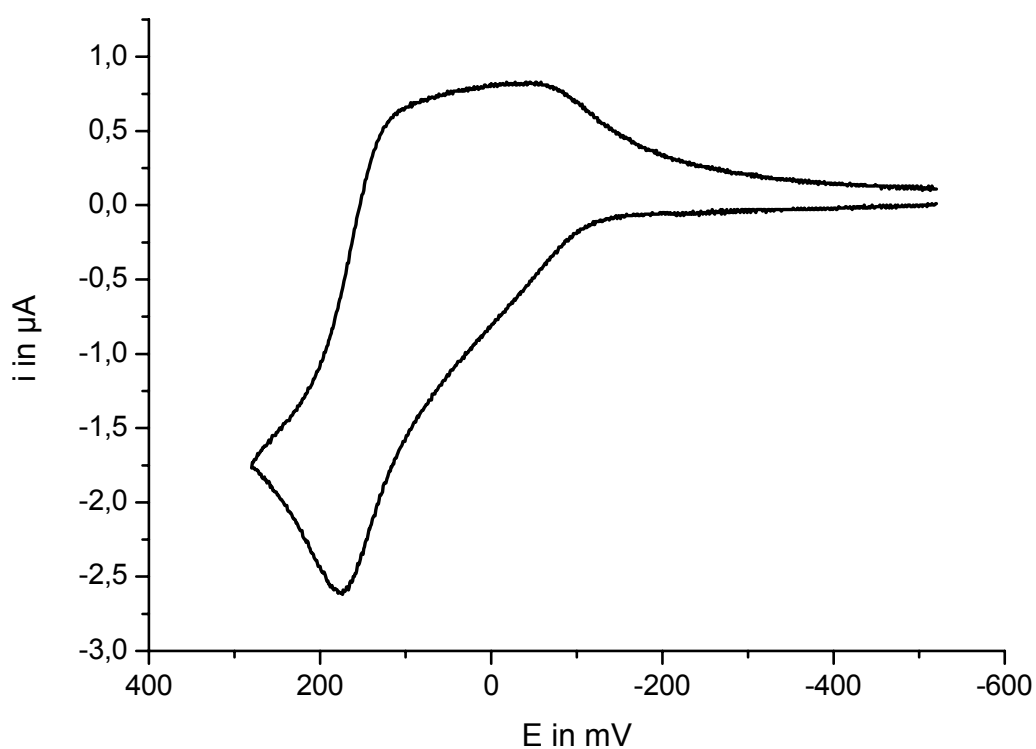


Figure S1. CV of Yb4 in CH<sub>2</sub>Cl<sub>2</sub>/NBu<sub>4</sub>PF<sub>6</sub>, 0.1 V/s at 293 K and at a Pt electrode

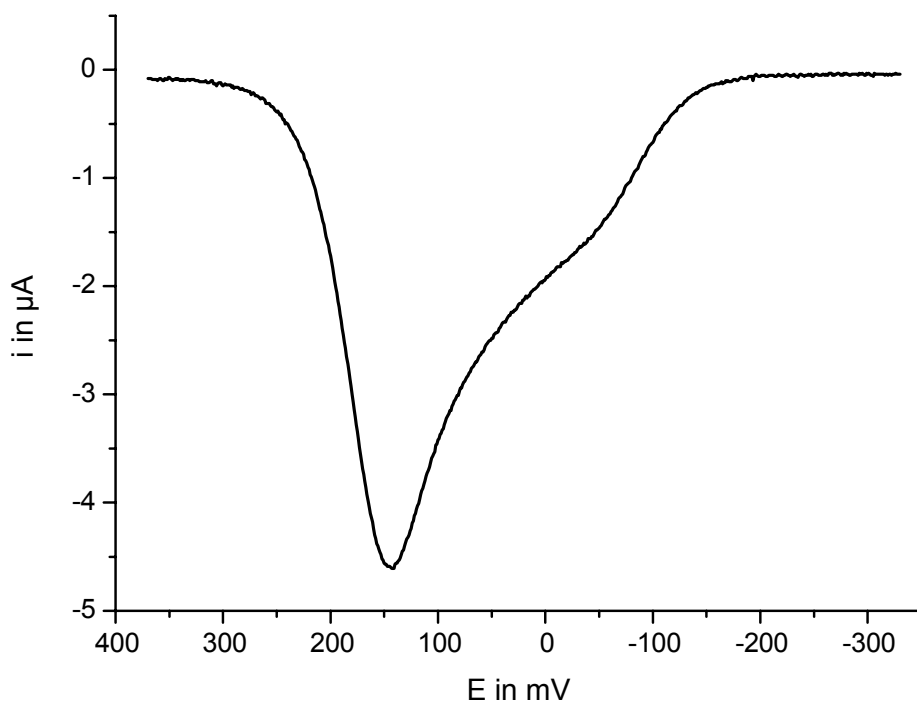
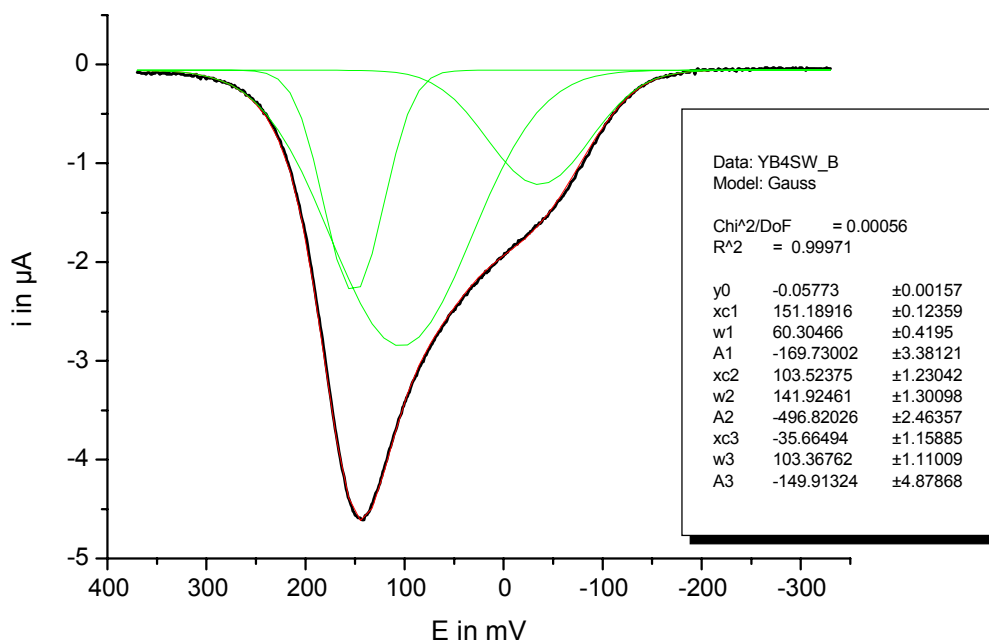
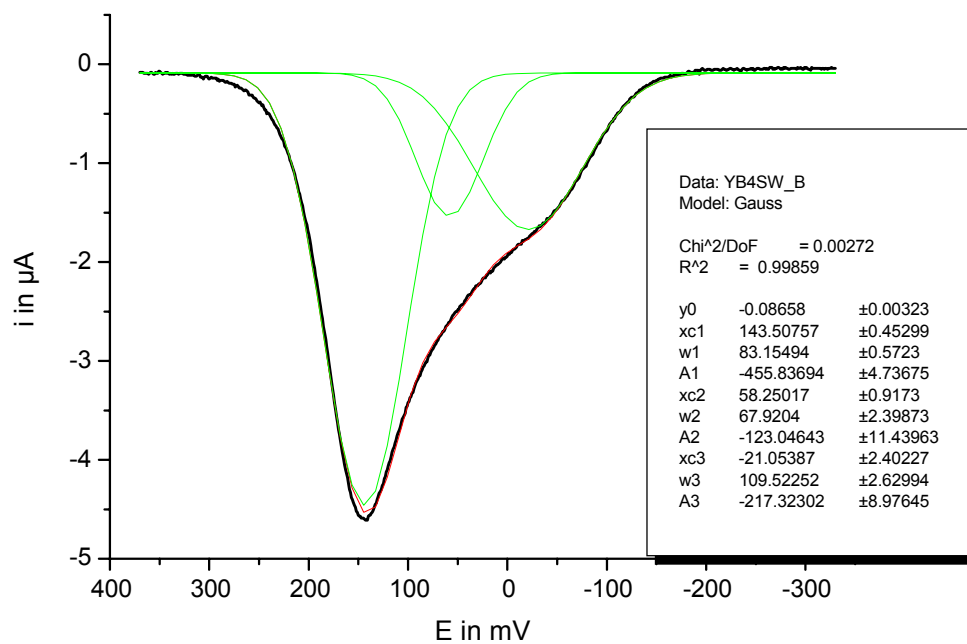


Fig. S2. Osteryoung square wave of Yb4 in  $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ , 10 Hz at 293 K and at a Pt electrode

Figures S3 and S4: Two different deconvolutions of the square wave voltammogram of Figure S2.





Perspective ORTEP view of the molecular structure of **1**. Thermal ellipsoids are drawn to encompass 30 % probability. Hydrogen atoms are omitted for clarity.

