Supplementary material

Experimental

Compound preparation: The compound was prepared in a similar way to that described in reference 12.

NMR spectroscopy: All NMR experiments were performed on an INOVA 500 MHz spectrometer using standard pulse sequences. The data were processed with VNMR or MestRe-C using cosine squared apodization in both dimensions for the phase sensitive experiment and unshifted sinbell for in both dimensions for the AV experiments.

XANES: Measurements of X-ray Near Edge Absorption Spectroscopy (XANES) of the Pt L3-edge were performed at the BM26 beamline in ESRF. The optics comprises a collimator mirror, a double crystal Si (111) monochromator, and a focusing mirror. Samples were placed in an aluminium frame with polimide windows inside a He continuos flow cryostat (CF 1204-Oxford) operating at about 15 K. Fluorescence data was collected with a 9 elements Ge detector.

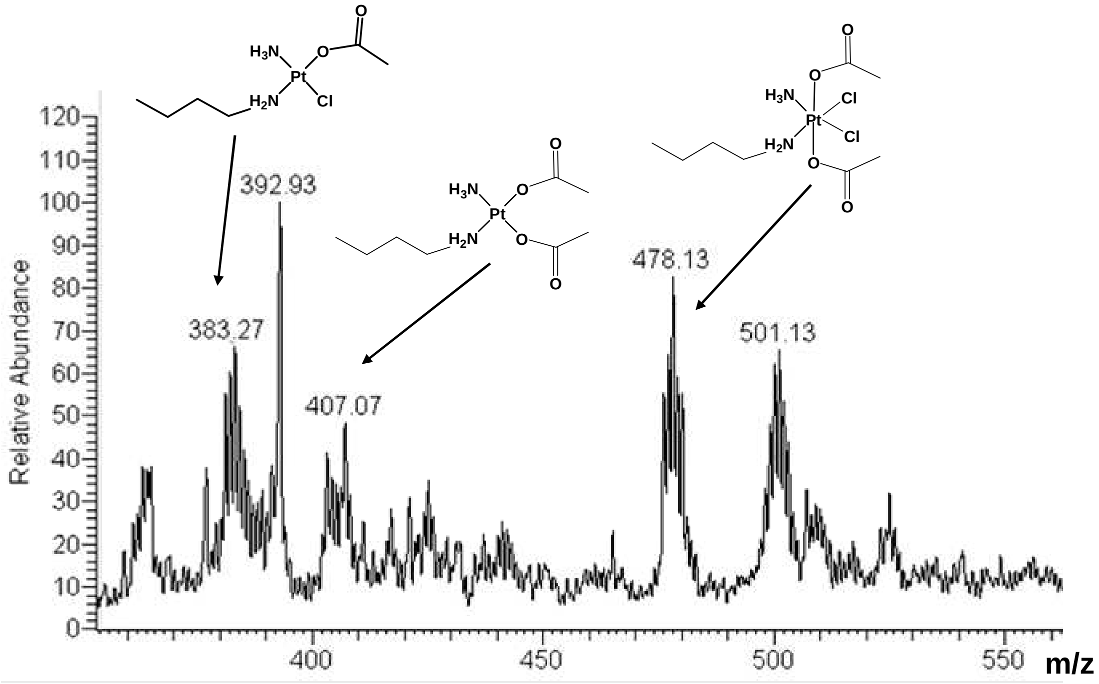
The energy was calibrated by setting the maximum of the first derivative of the Pt metal foil at 11563.4 eV. The code Athena[18] was used for the data reduction as in Mijovilovich et al.[19] The model compound calibration curves were determined by measuring the XANES of the pure compounds (100% Pt II and 100% Pt IV) and taking the height between the highest point of the absorption edge and the lowest point of the oscillation between the absorption edge and the following resonance as proportional to 100% of the corresponding oxidation state.[16] A calibration curve was built to determine the concentration of PtII in the intermediates samples.

References for XANES

B. Ravel and M. Newville, *J Synchrotron Radiat*, 2005, **12**, 537-541.

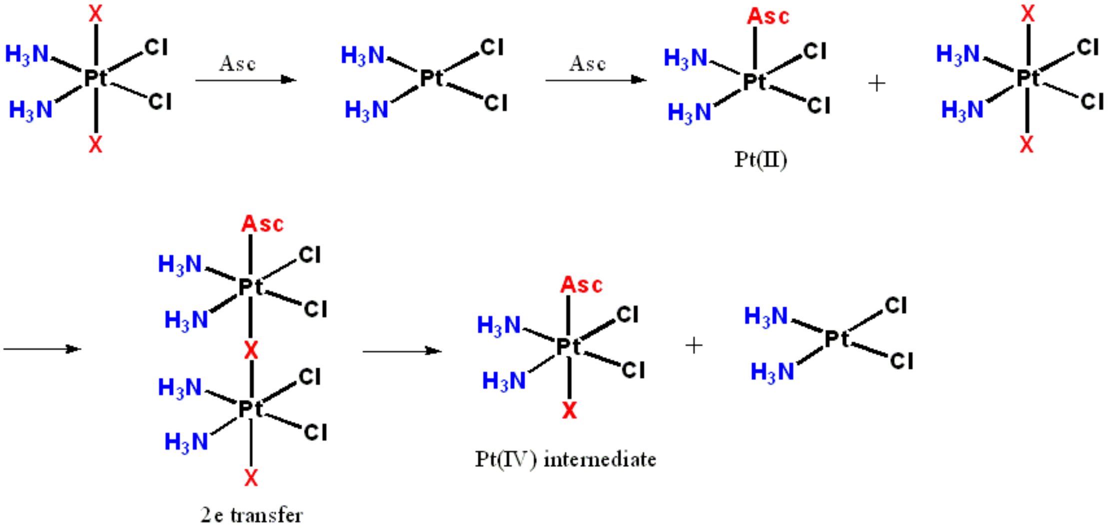
A. Mijovilovich, L. G. Pettersson, S. Mangold, M. Janousch, J. Susini, M. Salome, F. M. de Groot and B. M. Weckhuysen, *J Phys Chem A*, 2009, **113**, 2750-2756.

ESIMS



The spectrum was measured on an Thermo LCQ Duo in the positive ion mode using standard parameters. The peak at 501 is the sodiated form of the parent compound that appears at 478 amu. These peaks show the typical isotopic patterns of Pt.

Pt(II) catalyzed reduction of Pt(IV) complexes with chloride or hydroxide axilligands



Octahedral Pt(IV) is reduced by ascorbate to square planar Pt(II). An ascorbate binds the Pt(II) forming a square pyramidal complex that can then interact with the octahedral Pt(IV) to form a chloride.hydroxido bridged dimmer. Then two electrons are transferred from the Pt(II) to the Pt(IV) and the dimmer collapses to give a Pt(IV) ascorbate complex and a Pt(II). The Pt(IV) ascorbate is then reduced to Pt(II) releasing the ascorbate and a chloride/hydroxide.