Supplementary Information: Koch *et al*

Experimental

HPLC grade acetonitrile was obtained from Merck (608-001-00-3). All aqueous solutions were prepared using ultrapure Milli-Q water (› 18MΩ). Analytical grade purity tetrabutyl-ammonium nitrate ($TBA^+NO_3^-$), sodium acetate and glacial acetic acid were obtained from Sigma-Aldrich.

Mobile phases were prepared by the addition of acetonitrile to stock solutions of 0.05 M tetrabutyl-ammonium nitrate and 0.1 M acetate buffer (pH = 4.6) to give 55% (v/v) CH_3CN:H_2O solutions. All mobile phases were filtered through 0.45 µm HV filters (Millipore Corporation, HVLP04700) under vacuum and degassed for 15 min in an ultrasonic bath before use. $Na_2PtCl_6 \cdot 2H_2O$ (Johnson Matthey PLC, Precious metals division) was of analytical reagent grade quality and was dried in vacuo and stored in a desiccator prior to use.

ICP-OES

Determination of the samples Pt, Cl^- and Br^- concentrations was accomplished with a SPECTRO *Arcos* ICP-OES spectrometer operating with a RF power set to 1400 W using a Burgener T2002 nebulizer and cyclonic spray chamber. The nebulizer flow rate was set at 0.8 $mLmin^{-1}$, auxiliary gas flow rate was set to 1 $L.min^{-1}$ and coolant flow rate to 13 $L.min^{-1}$. Pt standard solutions were prepared from a 1000 ppm ± 3 ppm stock solution in a 500 mL 10% HCl matrix obtained from De Bruyn Spectroscopy (Ultraspec). Cl^- and Br^- standard solutions were prepared from NaCl and NaBr (puriss; 99 %) obtained from Sigma-Aldrich, respectively. NaCl and NaBr was dried at 60ºC for 1 day and cooled in a vacuo desiccator prior to preparation of the relevant standard solutions. Matrix matching was strictly upheld throughout the preparation of all the standard solutions (Pt, Cl and Br). The Pt, Cl^- and Br^- concentrations obtained by means of ICP-OES for the samples 1, 2 and 3 used to obtain Figures 1a, b and c respectively, shown in Table S1.

IP-RP-HPLC-ICP-OES

The column used throughout this study was a Gemini C_{18}, 250 mm x 4.6 mm i.d., 5 µm particles. Column conditioning comprised of mobile phase passage through the column for 45 minutes prior to analysis followed by a 45 minute post-analysis wash with pure acetonitrile. Platinum samples, Table S1, were prepared in an HCl matrix. The bromido Pt^{IV} species was obtained by the addition of appropriate amounts of NaBr, Table S1. Prior to injection each Pt sample was diluted 3 times and injected as a 40µl aliquot onto the C_{18} reversed phase column unless stated otherwise. The HPLC hyphenated ICP-OES setup comprised of a Varian *Prostar* liquid chromatograph equipped with a binary 210 solvent delivery module and a 410 auto-sampler operating at an optimized flow rate of mobile phase of 0.8 $mL.min^{-1}$ connected the same SPECTRO *Arcos* ICP-OES spectrometer mentioned above, operating with a RF power set to 1600 W using a Burgener

T2002 nebulizer and cyclonic spray chamber. The nebulizer flow rate was set to 0.6 $mLmin^{-1}$, auxiliary gas flow to 2 $L.min^{-1}$, and coolant flow rate to 17 $L.min^{-1}$. The aliquot was transferred directly from the column to the nebulizer *via* PEEK tubing with internal diameter equal to 0.12 mm.

Table S1. Total experimental Pt, Cl^- and Br^- concentrations as determined by means of ICP-OES directly for the 3 samples used in this study. Samples were prepared by the addition of 2.0 M stock solutions containing appropriate quantities of HCl and NaBr to weighed amounts of Na_2PtCl_6 to give a known [Pt] ~ 10 mM in 5 ml. These samples were dilute three times with the relevant mobile phase before injection.

Sample	Experimental concentration ($mol\ L^{-1}$)		
	Pt	Cl	Br
1	0.0127 ± 0.0002	0.1550 ± 0.0053	–
2	0.0125 ± 0.0002	0.1580 ± 0.0054	0.0246 ± 0.0002
3	0.0160 ± 0.0002	0.0840 ± 0.0033	0.2362 ± 0.0021