Supplementary Information for:

N-Heterocyclic Carbene-Stabilized Gold Nanoparticles

Eleanor C. Hurst, Karen Wilson, Ian J. S. Fairlamb* and Victor Chechik*

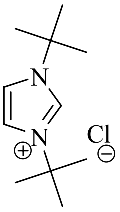
Contents:

1. General details

All reactions were conducted under N_2, using Schlenk or dry-box techniques, unless otherwise stated. Mass spectrometry was carried out using a Waters Micromass instrument. Thermal MS analysis was carried out by slowly heating the sample on the MS probe to 350 °C under vacuum. TGA was carried out on a Stanton Redcroft STA-780 Series ^{1}H NMR and ^{13}C NMR were recorded in the deuterated solvent indicated, at 400MHz using JEOL ECX400 spectrometer unless otherwise stated. Chemical shifts are reported in parts per million using the internal deuterated solvent as reference. Coupling constants (J values) are reported in hertz (Hz) and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sx (sextet), sept (septet), m (multiplet), br (broad). XPS was acquired using a Kratos Axis HSi Instrument, using Mg K_α X-Ray source (1253.4 eV) operating at 169 W with an analyzer pass energy of 40 eV. Spectra were acquired at normal emission employing a charge neutraliser to eliminate sample charging. Two point energy referencing was employed using the C 1s at 285 eV and valence band regions. Peak analysis was performed using Casa-XPS Version 2.1.9 with all spectra Shirley-background subtracted prior to fitting. The elemental composition was calculated from the respective atomic sensitivity factors for Au 4f (6.846), S 2p (0.723), C 1s (0.318), O (0.736) and N (0.505). Deconvolution of N 1s spectra was performed by fitting components with a Gaussian-Lorentzian mix of 70:30 with a FWHM of 1.9 eV. Elemental analysis was carried out on CE-440 Exeter Analytical Inc. C, H, N, S machine. Standard for calibration used was acetanilide and internal standard check is S-benzyl thiouronium chloride. Atomic absorption spectroscopy was carried out on Hitachi Z-5300 Polarised Zeeman Atomic absorption spectrometer using Gold or Palladium atomic absorption standard solutions (purchased from Aldrich) as calibrants.

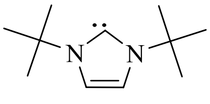
THF and toluene were distilled over sodium wire and benzophenone prior to use. DCM and Benzene were distilled over CaH. *Tert*-butyl amine was distilled before use. NaH without stabilizing oil and KO^{t}Bu were purchased from Aldrich, stored in a glove box and used as received. GPC was in either toluene or DCM using 200-400 mesh Biobeads-S-X1, purchased from BioRad Laboratories. Unless otherwise stated, all products were in good comparison with literature data and following literature procedures.

2. Synthesis of 1, 3-Di-tert-butlyimidazolium chloride



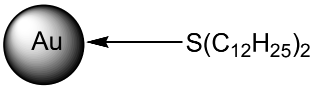
A total of 300 mg of paraformaldehyde (10 mmol) was dissolved in 10 mL toluene in a dry Schlenk flask. 1.06 mL of tert-butylamine (731 mg, 10 mmol) was added dropwise *via* syringe under N_2. The mixture was stirred and heated (40 °C) until a clear solution is formed. After cooling to 0 °C, another aliquot of tert-butylamine (1.06 mL) was added dropwise. A total of 3.33 mL of 4N aqueous HCl was added dropwise and after removal of the cooling, 1.14 mL glyoxal (40 % water, 10 mmol) were added dropwise. The reaction mixture was stirred at 40 °C for 18 h. After dilution with $NaHCO_3$(aq), the aqueous phase was washed with Et_2O. The water was removed in vacuo to give a white residue. CH_2Cl_2 was used to extract the product and after removal of the volatiles, a white solid was obtained. (Yield = 78.1 %). ^{1}H NMR (DMSO-d_6): δ 9.22 (t, J_{HH}=1.6Hz, 1H, C^2-H), 8.10 (s, 2H, NHC=CHN), 1.59 (s, 18H, CH_3). ^{13}C NMR: δ 135.5 (NCN), 118.2 (NCH=CHN), 61.2 (C-CH_3), 30.3 (CH_3). m/z (ESI) 181 (M^+, 100).

3. Synthesis of 1,3-Di-tert-butylimidazol-2-ylidene **1**



1, 3-Di-tert-butlyimidazolium chloride (1.50 g, 6.9 mmol) and KO^{t}Bu (1.01 g, 9.0 mmol) were added to a Schlenk flask in a dry-box. After removal from the dry-box, the solids were evacuated on a Schlenk line for one hour whilst stirring. THF (17.5 mL) was added at -78 ºC (using dry ice/EtOAc bath), and stirred for 20 min. The mixture was allowed to warm to room temperature over 30 min. The volatiles were removed in vacuo and the residue was extracted with toluene (35 mL) and filtered by cannula over celite. The toluene is removed in vacuo to give a white solid. (Yield = 65 %). ^{1}H NMR (C_6D_6): δ 6.75 (s, 2H, NCH=CHN), 1.50 (s, 18H, CH_3). ^{13}C NMR: δ 213.2 (br.s. NCN), 115.8 (s, NC=CN), 56.5 (s, C-CH_3), 32.1 (s, CH_3). m/z (CI) 181 (M^+, 100), 132 (42), 125 (47).

4. Thioether protected Au nanoparticles **2**



3.25 mL of 10 % $HAuCl_4$ solution was stirred with 109.4 mg of TOABr in 2 mL of toluene for 15 m to ensure complete transfer of $AuCl_4^-$ into the toluene layer. The aqueous phase turned colourless quickly whilst the organic phase turned orange. 111 mg of dodecyl sulfide was added in 7.5 mL of toluene. Immediately, a fresh solution of 45.4 mg of $NaBH_4$ in 12 mL of H_2O was added and the organic layer turned black which signified the synthesis of the nanoparticles. After 20 min the organic layer was washed with water and dried over Na_2SO_4. The volatiles were removed to a minimum amount of solvent and 70 mL of EtOH was added. The particles were left to precipitate overnight at -20 °C and were then centrifuged and washed with 30 mL of EtOH, three times. The particles were then dried using a Schlenk line. ^1H NMR (400 MHz, C_6D_6): δ 2.43 (t, 1H), 1.57 (q, 1H), 1.29 (br.s, 10H), 0.92 (t, 2H), 0.39 (s, 3H), 0.29 (s, 3H). AAS found Au 45.4 %. Excess thioether cannot be removed from the nanoparticles due to irreversible aggregation.

5. NHC-protected gold nanoparticles **3.**

Under an inert atmosphere, 30 mg (0.54 μmol assuming 1 ligand per Au atom in a 148 atom cluster) of nanoparticles **2** was dissolved in 5 mL of benzene and 200 times excess (0.11 mmol) of bis(1,3-*tert*-butyl)imidazol-2-ylidene **1** was added in a solid portion. The particles were left to crash out overnight, with no stirring. They were then centrifuged (4000 rpm, 3 m) and washed with 3 x 5 mL of benzene. The particles were then dried by Schlenk line techniques. ^1H NMR (MeCN-d_3) δ 6.71 (CH=CH), 1.81 ($C(CH_3)_3$). TGA showed loss of ligand at 230 °C which gave 68 % remaining Au (Fig. S1). AAS gave ~ 66.6 % Au. Elemental analysis found C- 22.24 %, H- 3.18 % and N- 3.89 %. (Theoretical values: C- 22.0 %, H- 3.33 %, N- 4.67 % based on 30 % ligand).

6. Characterisation

i)

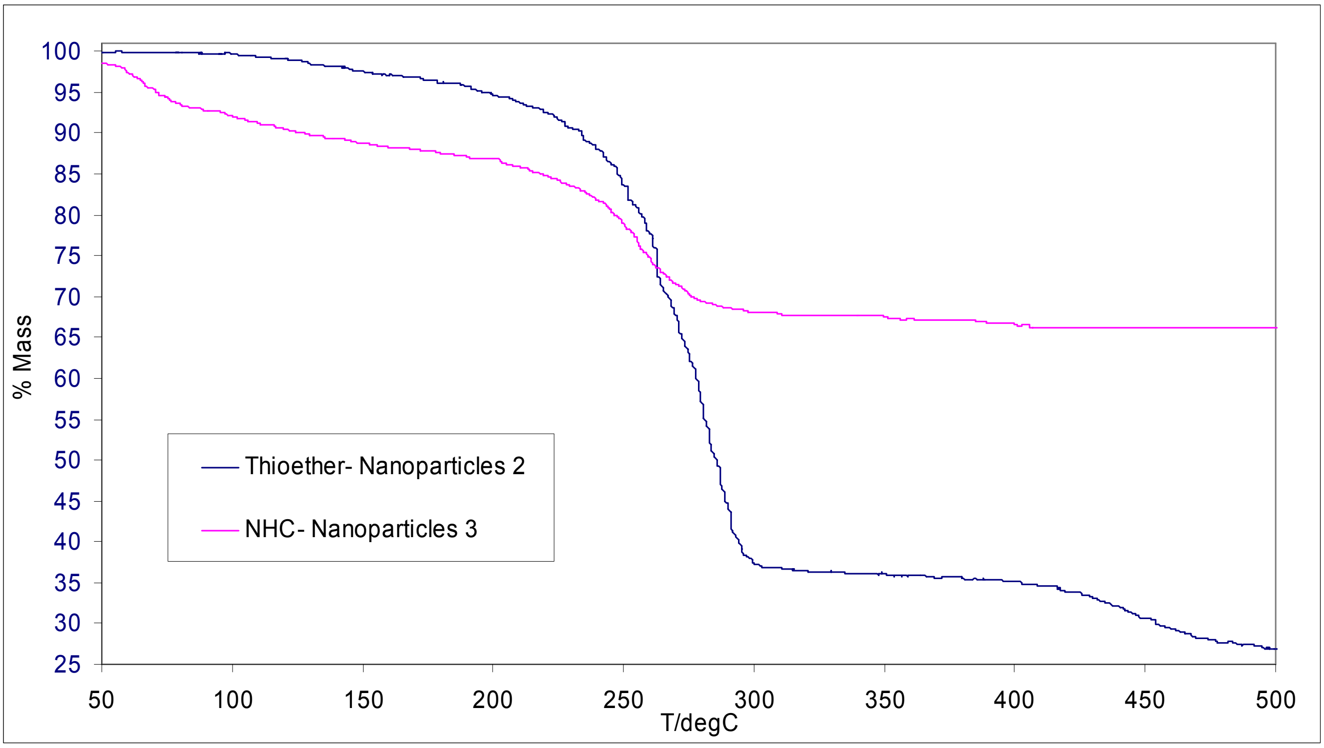


Figure S1. TGA comparison of thioether- and NHC-protected Au nanoparticles.

ii) Table S1. XPS quantification of Au nanoparticles and free NHC ligand.

Compound Number	Compound	Atomic ratio	
		N:Au	S:Au
2	Nanoparticles **2**	0.0	7.0
3	Nanoparticles **3**	0.7	0.0

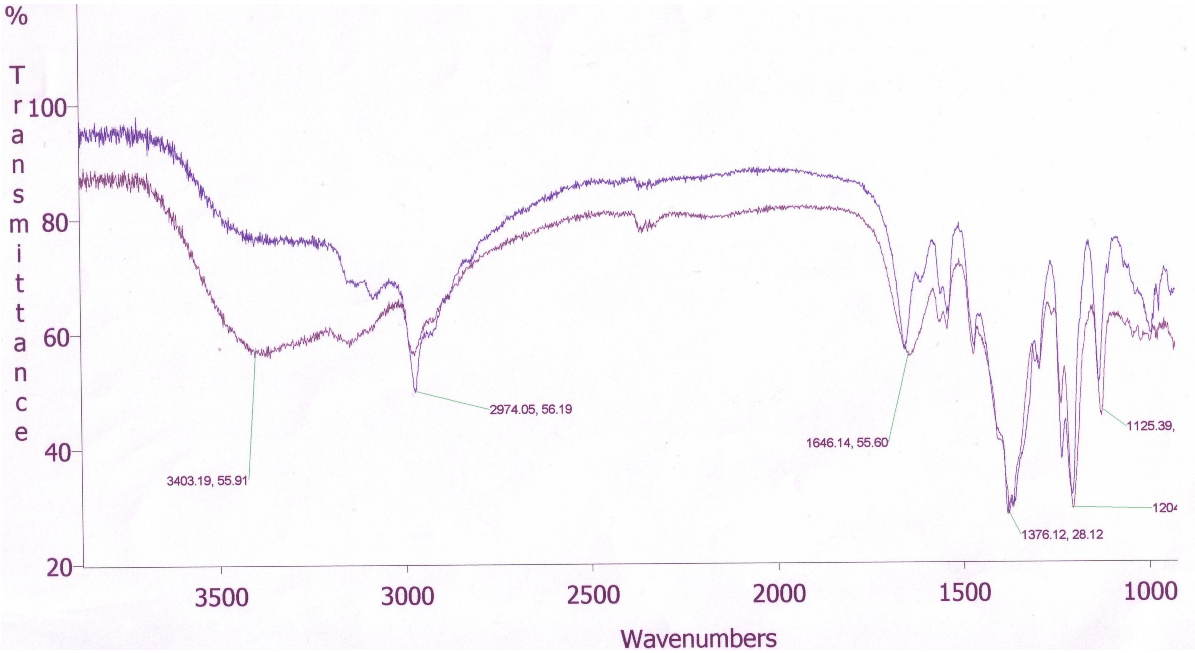


Figure S2. FT-IR spectra of ligand **1** (blue) and NHC-Au nanoparticles **3** (purple).

8) Synthesis of trioctylphosphine-protected Pd nanoparticles (TOP-Pd)

0.33 mmol of Pd(acac)$_2$ and 7 mL of trioctylphosphine was heated to 300 °C for 2 days (by means of a graphite bath) under N$_2$. The nanoparticles were left to cool to room temperature and centrifuged. The resulting particles were washed with MeOH to remove any remaining TOP. AAS gave 40 % Pd. IR: 2918.2, 1653.9, 1464.5, 1379.6 cm^{-1}.

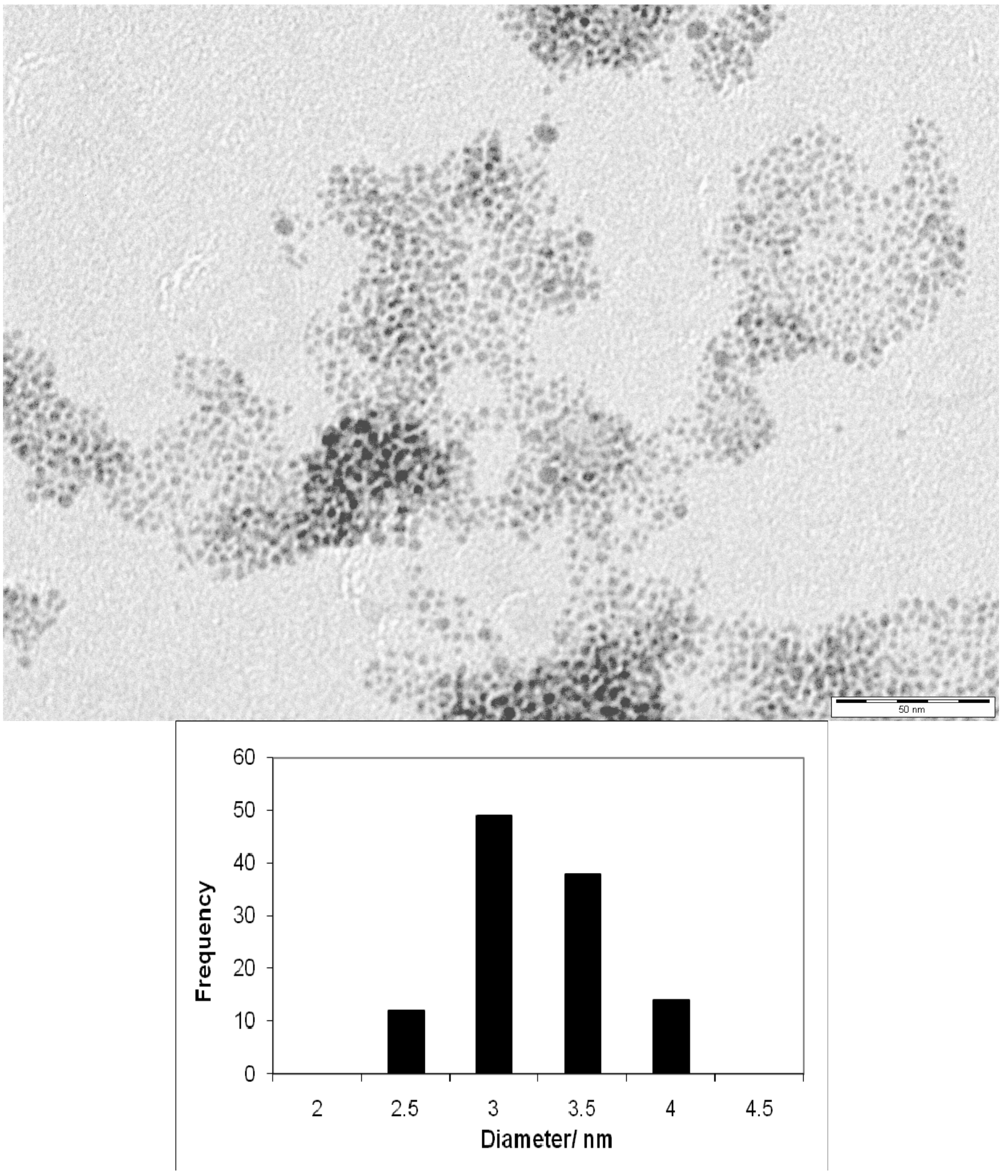


Figure S3. TEM image of TOP-Pd nanoparticles. Average diameter 3.04 nm, standard deviation 0.60 nm.

9) Synthesis of NHC-protected Pd nanoparticles (NHC-Pd)

10 mg (0.11 mmol, 200 equiv.) of bis-*tert*-butylimidazoylidene **1** was dissolved in 5 mL of benzene and added to 20 mg of TOP-Pd nanoparticles and left to precipitate overnight, with no stirring. The resulting particles were washed with benzene. Elemental analysis: 61 % Pd. TGA showed loss of ligand at 235 °C and left 65 % Pd remaining. IR: 3125.6, 2927.3, 1664.3, 1535.0, 1466.1, 1384.2 cm^{-1}.

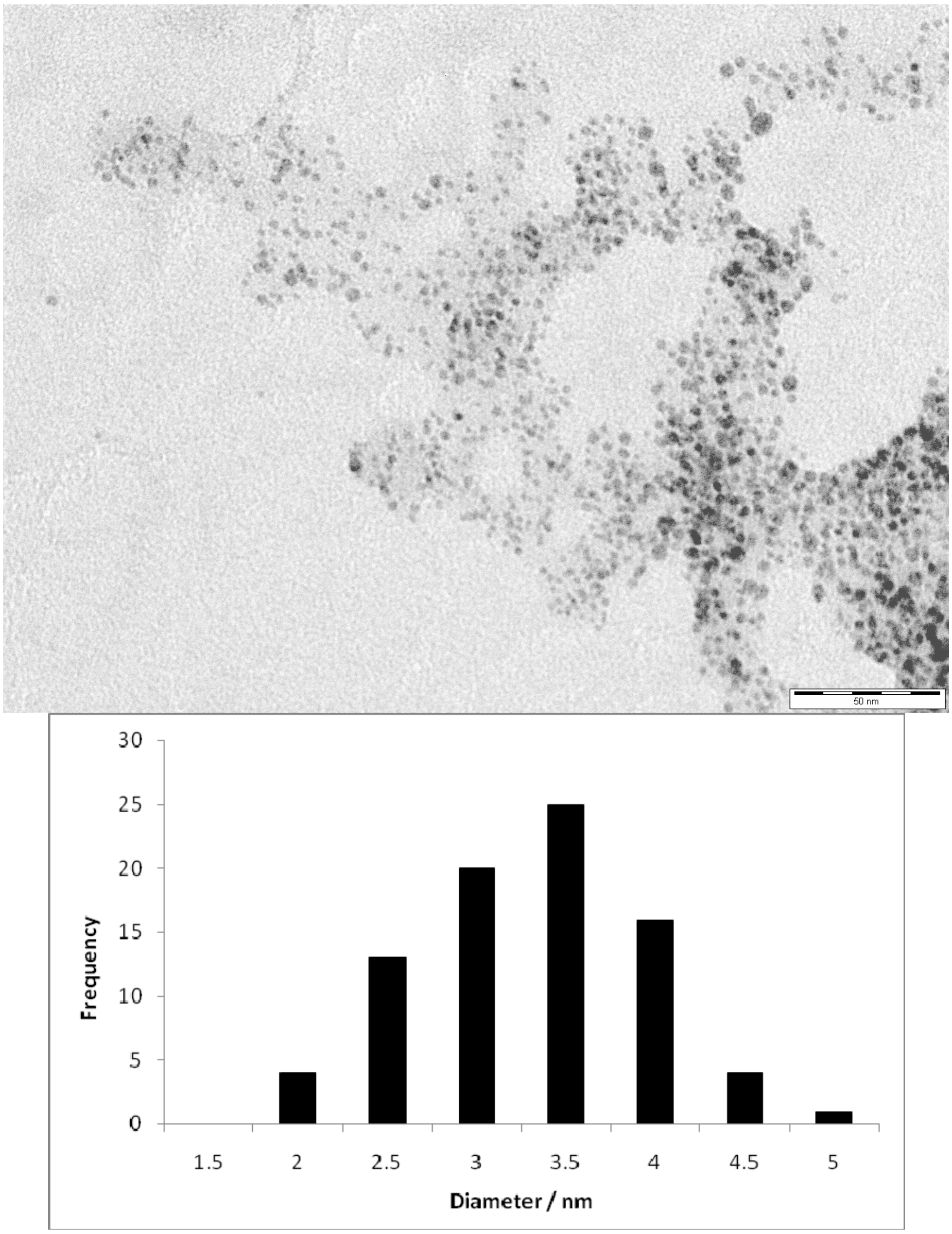


Figure S4. TEM image of NHC-Pd nanoparticles.Average size 3.04 nm, standard deviation 0.63 nm.

10)

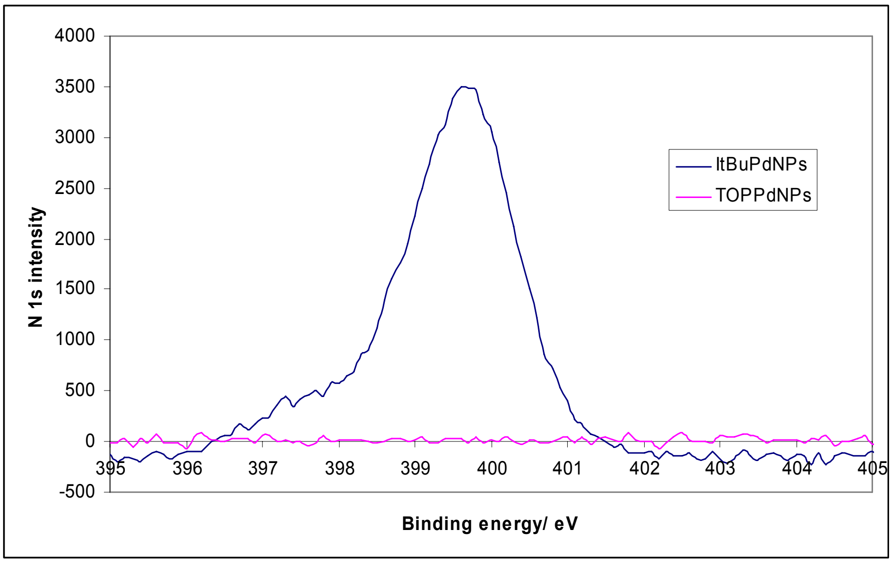
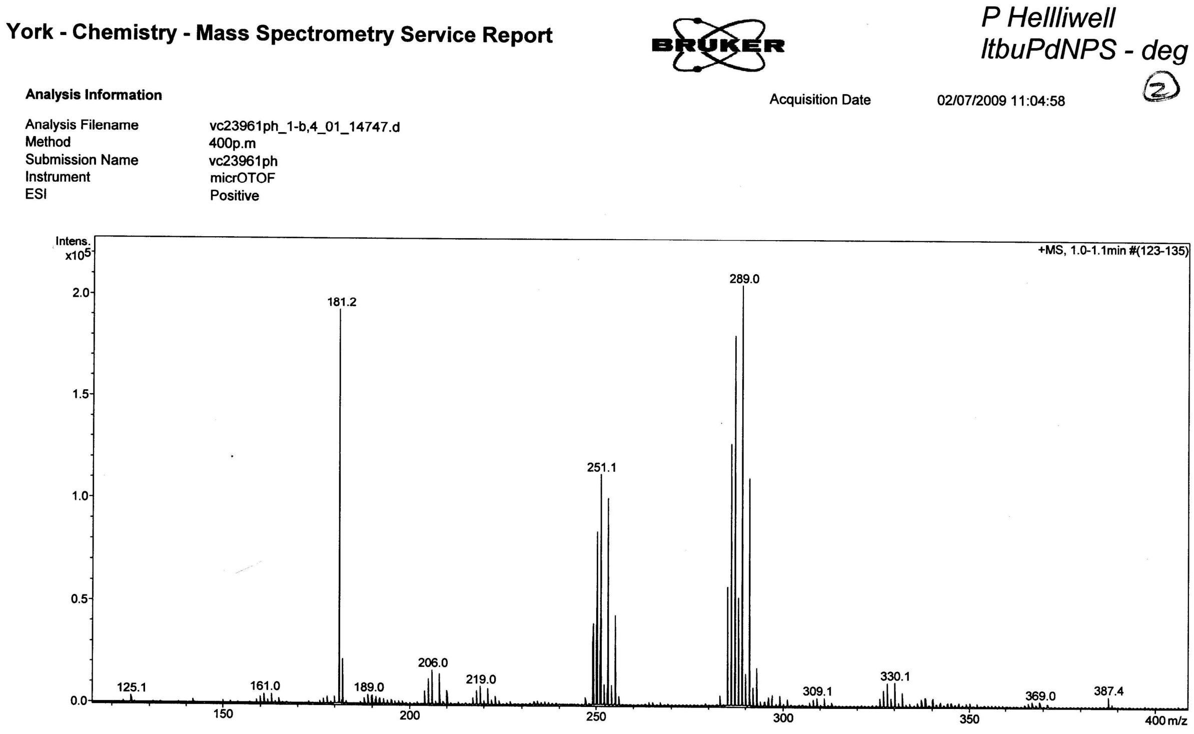


Figure S5. XPS N data for NHC-Pd and TOP-Pd nanoparticles.

11)



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ItbuPdNPS - deg
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Analysis Information

Acquisition Date 02/07/2009 11:04:58

Analysis Filename vc23961ph_1-b,4_01_14747.d
Method 400p.m
Submission Name vc23961ph
Instrument micrOTOF
ESI Positive

Figure S6. ESI-MS spectrum of mother liquor after aggregation of NHC-Pd nanoparticles.