A Novel Stabilisation Model for Ruthenium Nanoparticles in Imidazolium Ionic Liquids: *In situ* Spectroscopic and Labelling Evidence

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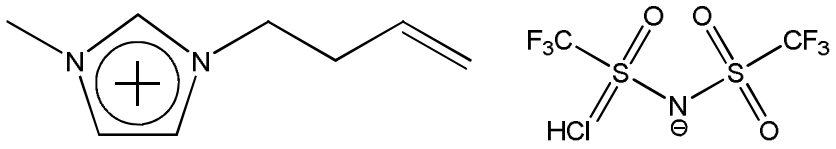
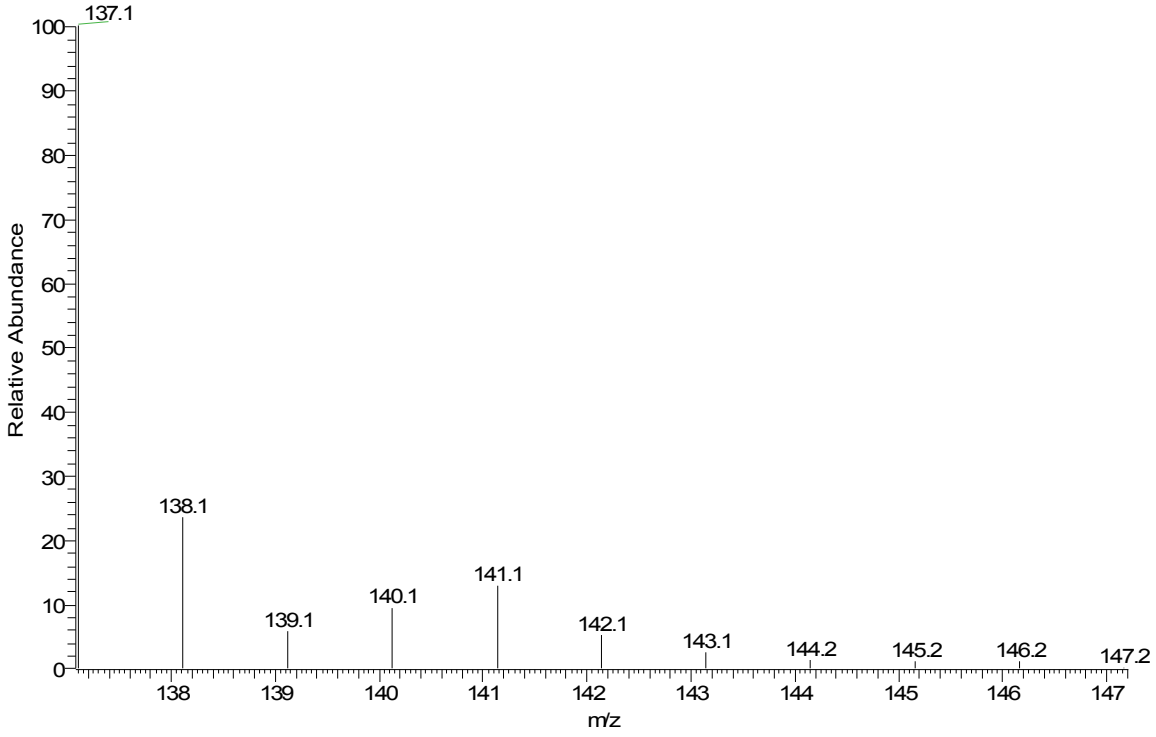
Electronic supplementary information

1) ESI^+ mass spectrum for IL_2 after deuterium incorporation.

IL_2 :

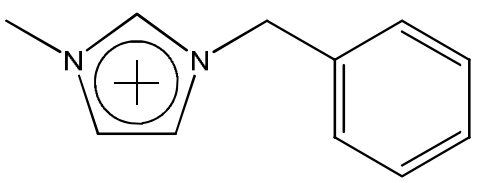


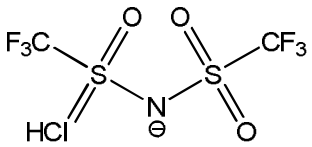


Relative peak intensities from above spectrum

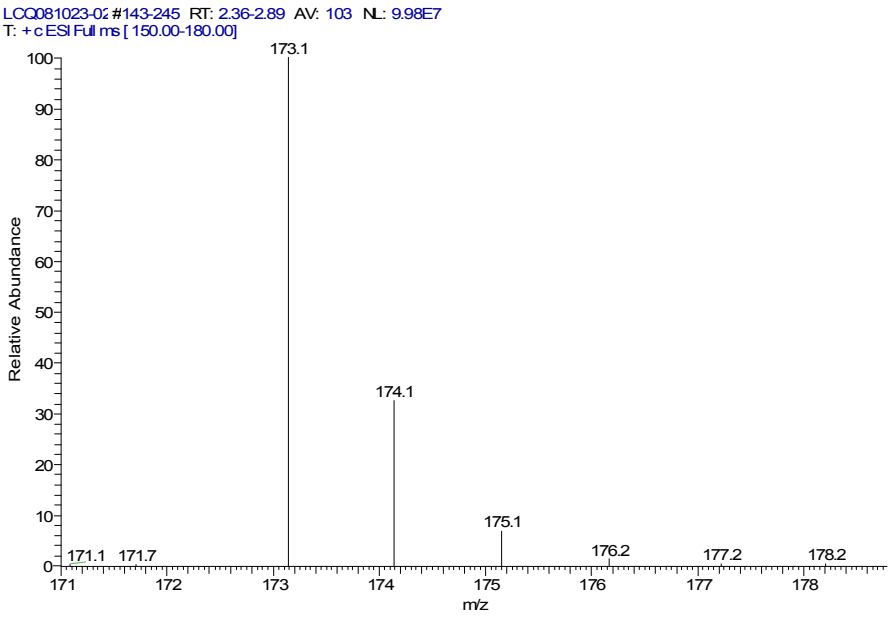
m/z	Intensity	Relative
137.1	7750906.9	100.00
138.1	1824751.6	23.54
139.1	445068.6	5.74
140.1	732534.6	9.45
141.1	998252.5	12.88
142.1	401417.5	5.18
143.1	188360.9	2.43
144.2	93604.7	1.21
145.2	85572.5	1.10
146.2	85245.4	1.10
147.2	7639.2	0.10
148.2	315.9	0.00
149.2	7.7	0.00
150.2	0.1	0.00

2) ESI^+ mass spectrum for IL_3 after deuterium incorporation





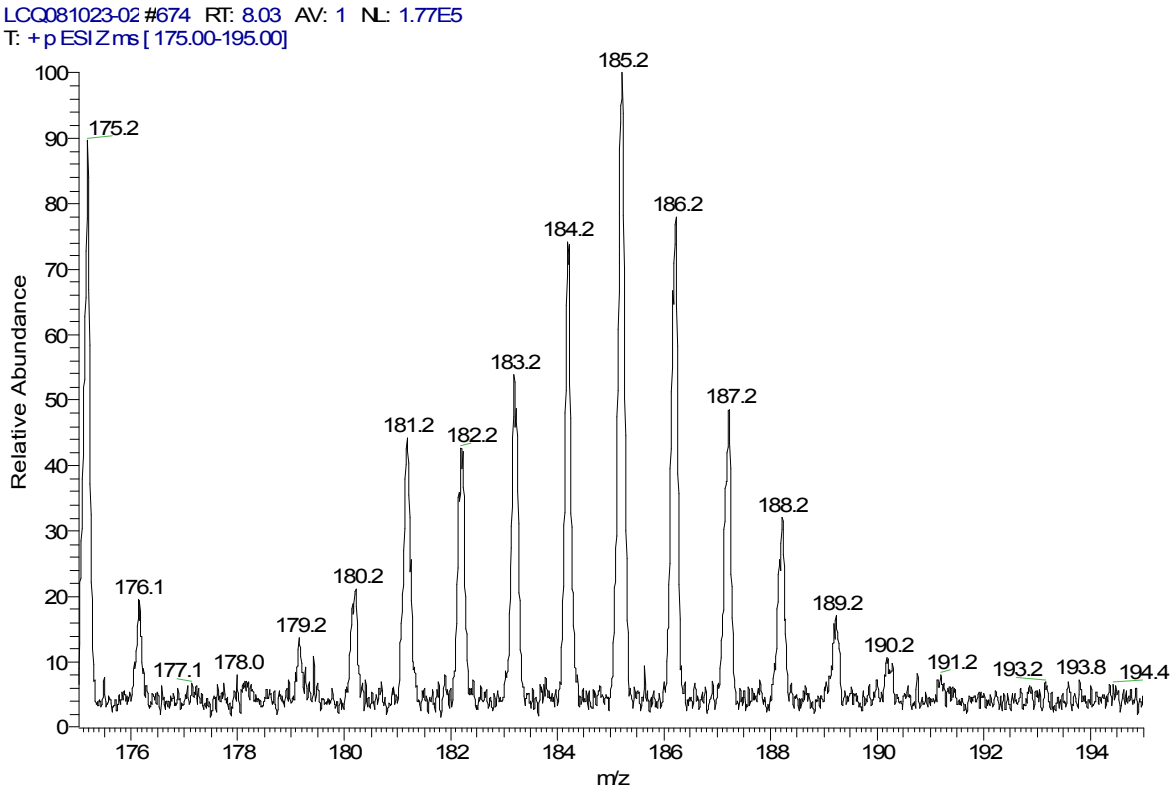
IL_3:



Relative intensities of the above spectrum

m/z	Intensity	Relative
173.1	7504755.5	100.00
174.1	2460646.9	32.79
175.1	473357.1	6.31
176.1	117093.6	1.56
177.1	11710.2	0.16
178.1	631.7	0.01
179.1	21.6	0.00
180.1	0.5	0.00
181.1	0.0	0.00

ESI^+ spectrum – deuterated methylenecyclohexyl region



3) Ethylene Hydrogenation Calculations

$pV = nRT$

$V_{reactor} = 125.8\ cm^3 = 1.258 \times 10^{-4}\ m^3$

$p_r = 129\ mbar = 1.29 \times 10^4\ Pa$

$R = 8.314\ m^3\ Pa\ K^{-1}\ mol^{-1}$

$T = 298\ K$

$n = (1.29 \times 10^4 \times 1.258 \times 10^{-4}) / (8.314 \times 298)\ m^3\ Pa\ m^{-3}\ Pa^{-1}\ K\ mol\ K^{-1} =$
6.54×10^{-5} mol ethylene introduced

GC calibration results: $2.3\times10^{-12} \times A$ = *no. moles of C*
300µL injections = 3×10^{-7} m^3

Table 1: GC results following treatment under ethylene

Species	*Ret time/ mins*	*Peak Area*	*No. Moles of C*	*No. of Moles (in 300 µL)*	*No. of Moles (in reactor)*
ethane	4.816	2.31×10^{4}	5.3×10^{-8}	2.7×10^{-8}	1.1×10^{-5}
ethylene	5.094	6.57×10^{4}	1.5×10^{-7}	7.6×10^{-8}	3.2×10^{-5}
isobutane	8.322	367	8.4×10^{-10}	2.1×10^{-10}	8.8×10^{-8}
butenes	10.5	805	1.9×10^{-9}	4.6×10^{-10}	1.9×10^{-7}

$C_2H_4 + H_2 \rightarrow C_2H_6$:
1 mole ethane produced = 1 mole H_2 consumed, i.e. 2 moles of surface hydrides
$2C_2H_4 + H_2 \rightarrow C_4H_{10}$:
1 mole isobutane produced = 1 mole H_2 consumed, i.e. 2 moles of surface hydrides
$2C_2H_4 \rightarrow C_2H_8$
1 mole butene produced = No H_2 consumed

Table 2: GC results following treatment under H_2 liberating surface alkyls

Species	*Ret time/ mins*	*Peak Area*	*No. Moles of C*	*No. of Moles (in 300 µL)*	*No. of Moles (in reactor)*
methane	4.501	4.79×10^{3}	1.1×10^{-8}	1.1×10^{-8}	4.6×10^{-6}
ethane	4.826	1.69×10^{4}	3.9×10^{-8}	1.9×10^{-8}	8.1×10^{-6}
n-propane	5.871	8.47×10^{3}	1.9×10^{-8}	6.5×10^{-9}	2.7×10^{-6}
n-butane	8.753	4.04×10^{3}	9.2×10^{-9}	2.3×10^{-9}	9.7×10^{-7}
n-pentane	12.434	463	1.1×10^{-9}	2.1×10^{-10}	8.9×10^{-8}

$\frac{1}{2} C_2H_4 + \frac{1}{2} H_2 \rightarrow -CH_3$
1 mole methyl produced = ½ mole H_2 consumed, i.e. 1 mole of surface hydrides
$C_2H_4 + \frac{1}{2} H_2 \rightarrow -C_2H_5$
1 mole ethyl produced = ½ mole H_2 consumed, i.e. 1 mole of surface hydrides
$1\frac{1}{2} C_2H_4 + \frac{1}{2} H_2 \rightarrow -C_3H_7$
1 mole propyl produced = ½ mole H_2 consumed, i.e. 1 mole of surface hydrides
$2C_2H_4 + \frac{1}{2} H_2 \rightarrow -C_4H_9$
1 mole butyl produced = ½ mole H_2 consumed, i.e. 1 mole of surface hydrides
$2\frac{1}{2} C_2H_4 + \frac{1}{2} H_2 \rightarrow -C_5H_{11}$
1 mole pentyl produced = ½ mole H_2 consumed, i.e. 1 mole of surface hydrides

Total surface hydrides counted = **38 µmol**

Ethylene Mass balance
6.54×10^{-5} mol (introduced) - 6.02×10^{-5} mol (detected by GC) = 5.2 µmol ~ 8% error

4) TON calculations

Butenyl IL → butyl IL

Ru(COT)(COD) – 2.2×10^{-4} moles
RuNPs, 1.1 ± 0.2 nm, dispersion ~75%
Ru_s – 1.7×10^{-4} moles
Butenyl IL 7.5g/ 417g mol^{-1} = 1.8×10^{-2} moles
15 % converted → 2.7×10^{-3} moles
TON → 2.7×10^{-3} moles/ 1.7×10^{-4} moles = **16**

Benzyl IL → methylenecyclohexyl IL

Ru(COT)(COD) – 2.2×10^{-4} moles
RuNPs, 3.2 ± 0.7 nm, dispersion ~35%
Ru_s – 7.7×10^{-5} moles
Benzyl IL 7.5g/ 453g mol^{-1} = 1.7×10^{-2} moles
30% converted → 4.9×10^{-3} moles
TON → 4.9×10^{-3} moles/7.7×10^{-5} moles = **64**