Supporting Information for:

On the Involvement of NHC Carbenes in Catalytic Reactions by Iridium Complexes, Nanoparticle and Bulk Metal Dispersed in Imidazolium Ionic Liquids

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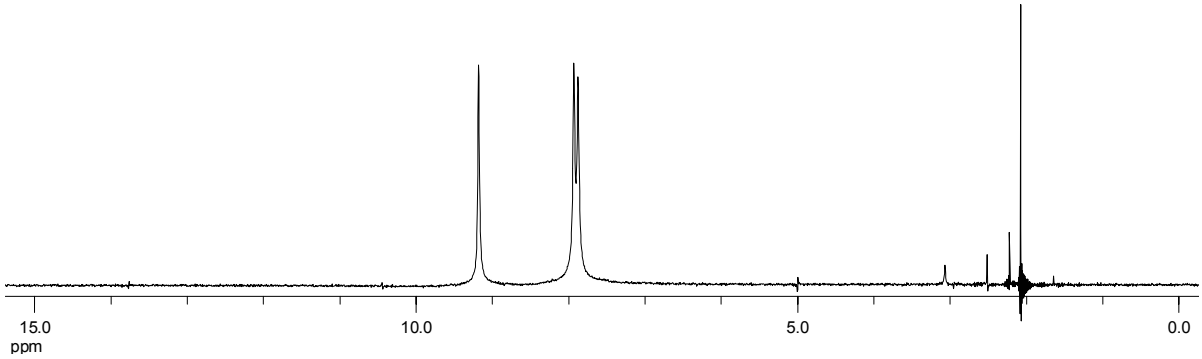

Fig. S1 ^{2}H NMR (46 MHz) [BMI]-d_3.NTf_2 in acetone at room temperature (the signal at around 3 ppm is probably HDO) .

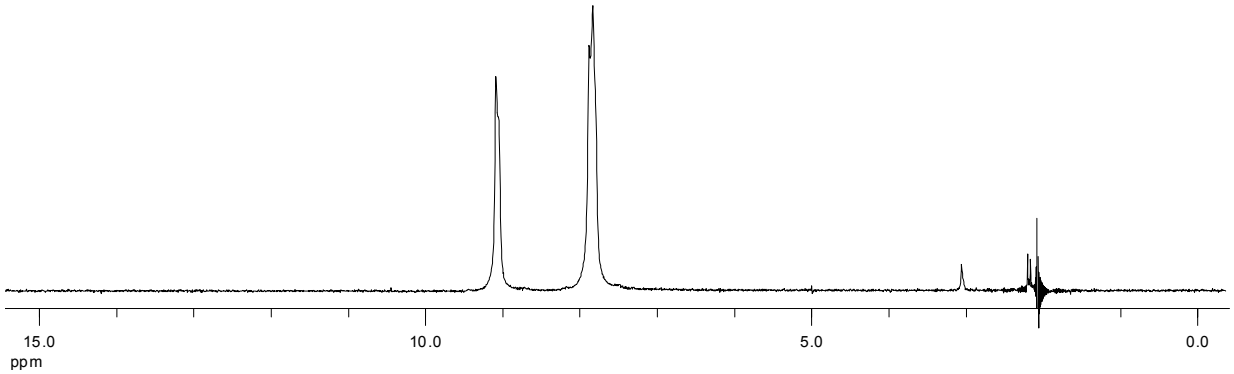

Fig. S2 ^{2}H NMR (46 MHz) [BMI]-d_3.PF_6 in acetone at room temperature (the signal at around 3 ppm is probably HDO).

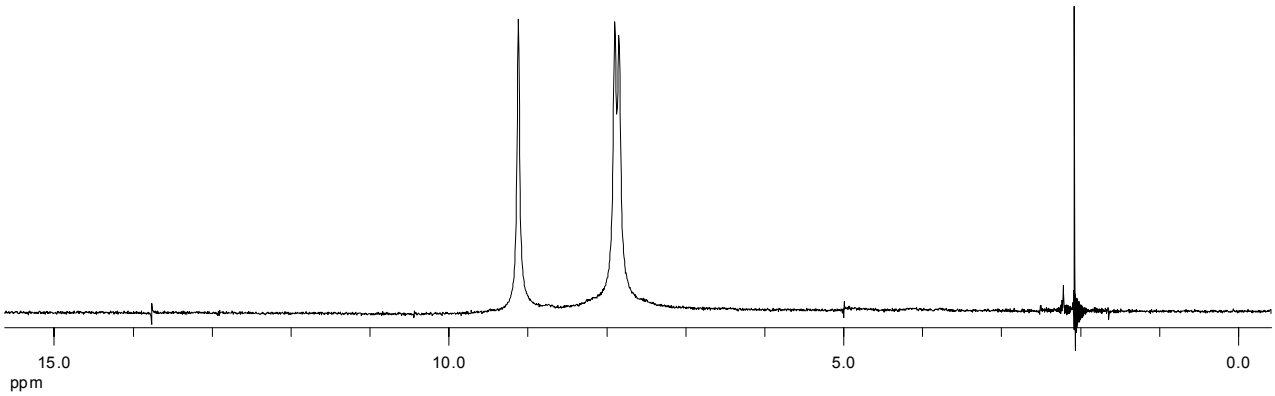

Fig. S3 ^{2}H NMR (46 MHz) [BMI]-d_3.BF_4 in acetone at room temperature.

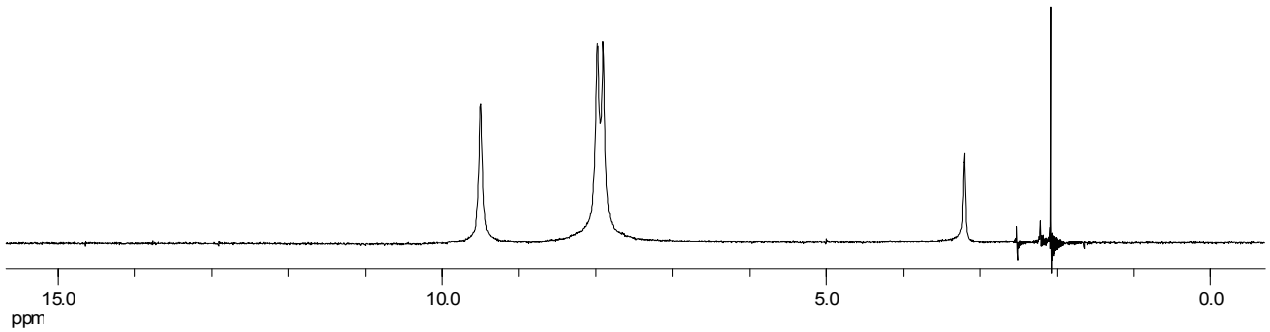

Fig. S4 ^{2}H NMR (46 MHz) [EMI]-d_3.$EtSO_4$ in acetone at room temperature (the signal at around 3 ppm is probably HDO).

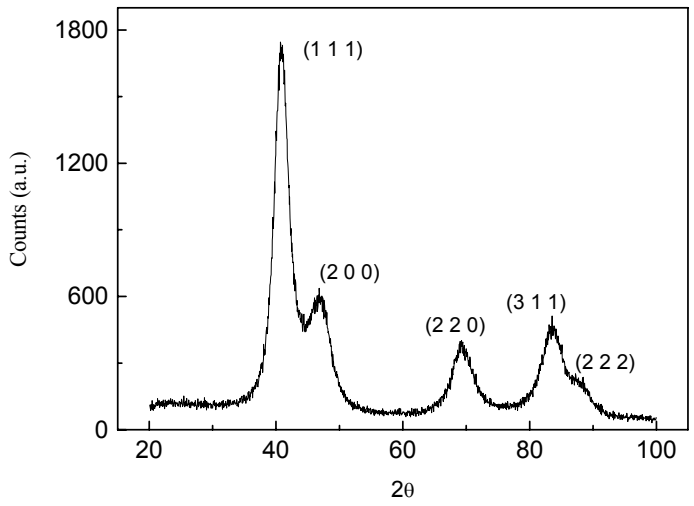

Fig. S5 XRD (X-ray Diffraction) analysis of the Ir(0) bulk metal.

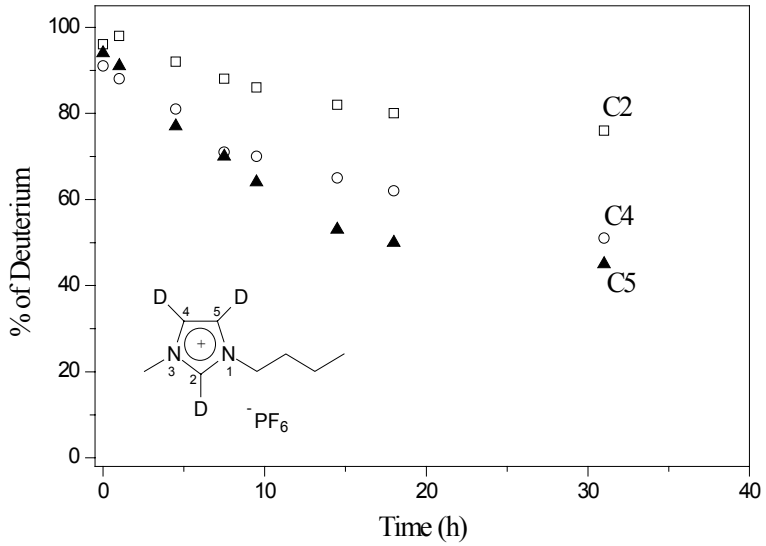

Fig. S6 D/H exchange observed in the experiment involving the cyclohexene (1.06 g) hydrogenation by $[Ir(COD)Cl]_2$ (0.0174 g) dispersed in [BMI]-d_3.PF_6 (1.0 mL, 96% D at C2 and 93% D at C4+C5) at 75°C under 5 atm (constant pressure).

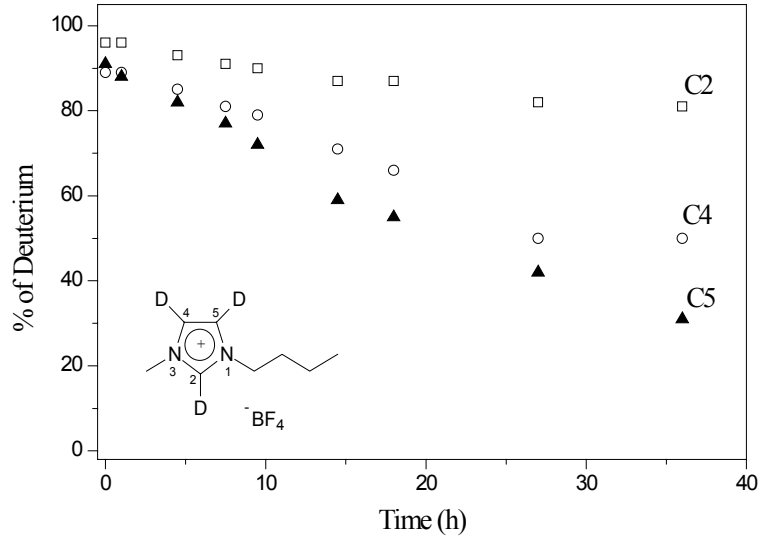

Fig. S7 D/H exchange observed in the experiment involving the cyclohexene (1.06 g) hydrogenation by $[Ir(COD)Cl]_2$ (0.0174 g) dispersed in [BMI]-d_3.BF_4 (1.0 mL, 96% D at C2 and 90% D at C4+C5) at 75°C under 5 atm (constant pressure).

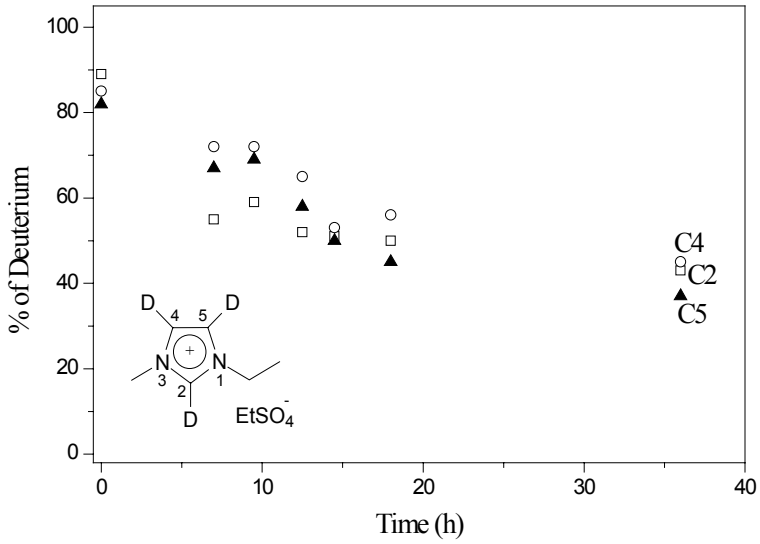

Fig. S8 D/H exchange observed in the experiment involving the cyclohexene (1.06 g) hydrogenation by $[Ir(COD)Cl]_2$ (0.0174 g) dispersed in [EMI]-d_3.$EtSO_4$ (1.0 mL, 89% D at C2 and 84% D at C4+C5) at 75°C under 5 atm (constant pressure).

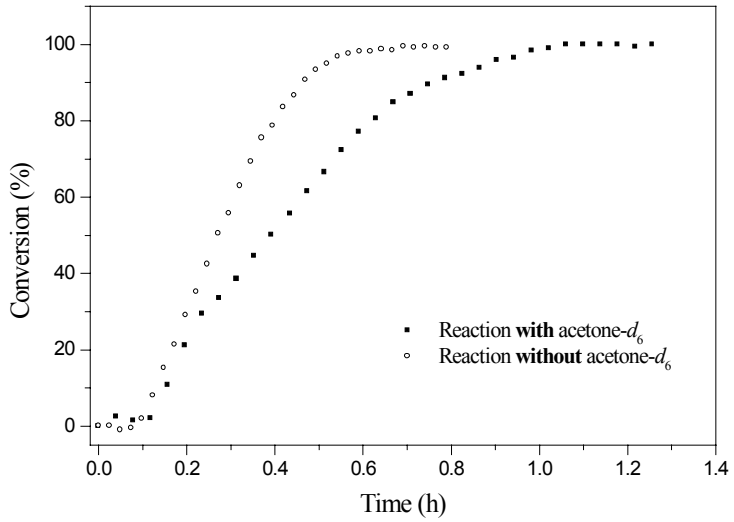

Fig. S9 Cyclohexene (1.06 g) hydrogenation by $[Ir(COD)Cl]_2$ (0.0174 g) dispersed in [BMI]-d_3.NTf_2 (1.0 mL) and in [BMI]-d_3.NTf_2 (1.0 mL) plus acetone-d_6 (1.5 mL) at 75°C under 5 atm (constant pressure).

Table S1 D/H exchange observed in the experiment **without** cyclohexene with $[Ir(0)]_n$ nanoparticles (0.004 g) re-dispersed in [BMI]-d_3.NTf_2 (0.4 mL) at 75°C under 5 atm (constant pressure).

Time (h)	% of D/H exchange at C2	% of D/H exchange at C4+C5
1.0	-----	12
2.5	1	15
5.5	2	24
20.5	7	42

Table S2 D/H exchange observed in the experiment involving the cyclohexene (1.06 g) hydrogenation by $[Ir(COD)Cl]_2$ (0.0174 g) dispersed in [BDMI]-d_5.NTf_2 (1.0 mL) at 75°C under 5 atm (constant pressure).

Time (h)	% of D/H exchange at C2-CD_3	% of D/H exchange at C4+C5
1.0[a]	-----	-----
4.5	-----	7
7.5	-----	10
23.5	-----	19

[a] Time for total substrate conversion.

Table S3 Mercury poisoning test using $[Ir(COD)(PCy_3)(py)]PF_6$ as catalytic precursor in cyclohexene hydrogenation. Reaction conditions: $[Ir(COD)(PCy_3)(py)]PF_6$ (0.010 g; 0.013 mmol), [BMI]-d_3.NTf_2 (0.25 mL), cyclohexene (0.27 g; 3.25 mmol), 75ºC and molecular hydrogen (5 atm, constant pressure). After around 59% of cyclohexene conversion, Hg(0) (0.78 g; 3.9 mmol) was added.

Time (h)	D/H exchange at C2 position (%)	D/H exchange at C4+C5 positions (%)
0.3[a]	-----	-----
2.5[b]	4	1
4.4	10	2
7.3	16	5
18.3	23	11

[a] Conversion of 59%; [b] Total conversion was observed.

Table S4 D/H exchange observed in the experiment involving the cyclohexene (1.06 g) hydrogenation by $[Ir(COD)Cl]_2$ (0.0174 g) dispersed in [BMI]-d_3.NTf_2 (1.0 mL) and acetone-d_6 (1.5 mL) at 75°C under 5 atm (constant pressure).

Time (h)	% of D/H exchange at C2	% of D/H exchange at C4+C5
1.3[a]	-----	1
3.0	5	13
5.5	12	22
44.5[b]	44	56

[a] Time for total cyclohexene conversion. [b] Total conversion of acetone-d_6 was observed.

Table S5 D/H exchange observed in the experiment involving the cyclohexene (1.0 mL) hydrogenation by $[Ir(COD)Cl]_2$ (0.007 g) dispersed in [BMI]-d_3.NTf_2 (0.3 mL) at 30°C under 5 atm (constant pressure).

Time (h)	% of D/H exchange at C2	% of D/H exchange at C4+C5
22.0	6	19

Time for total substrate conversion: 4.4 h

Table S6 D/H exchange observed in the experiment involving the cyclohexene (1.0 mL) hydrogenation by $[Ir(0)]_n$ nanoparticles (0.004 g) re-dispersed in [BMI]-d_3.NTf_2 (0.3 mL) at 30°C under 5 atm (constant pressure).

Time (h)	% of D/H exchange at C2	% of D/H exchange at C4+C5
22.0	5	9

Time for total substrate conversion: 12.4 h

Table S7 D/H exchange observed in the experiment involving the cyclohexene (1.0 mL) hydrogenation by $[Ir(COD)Cl]_2$ (0.007 g) dispersed in [BMI]-d_3.NTf_2 (0.3 mL), PS^{TM}(0.002 g) and acetone-d_6 (1.5 mL) at 30°C under 5 atm (constant pressure).

Time (h)	% of D/H exchange at C2	% of D/H exchange at C4+C5
22.0	12	-----

Time for total substrate conversion: 6.4 h

Table S8 D/H exchange observed in the experiment involving the cyclohexene (1.0 mL) hydrogenation by $[Ir(COD)Cl]_2$ (0.007 g) dispersed in [BMI]-d_3.NTf_2 (0.3 mL) and PS^{TM} (0.002 g) at 30°C under 5 atm (constant pressure).

Time (h)	% of D/H exchange at C2	% of D/H exchange at C4+C5
22.0	9	7

Time for total substrate conversion: 8.2 h