

## Supplementary Information

### Structure and reactivity of polymer supported carbonylation catalysts

Anthony Haynes,<sup>\*a</sup> Peter M. Maitlis,<sup>a</sup> Ruhksana Quyoum,<sup>a</sup> Claire Pulling<sup>a</sup> Harry Adams,<sup>a</sup> Sharon E. Spey<sup>a</sup> and Richard W. Strange<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK

<sup>b</sup> Synchrotron Radiation Department, Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD, UK.

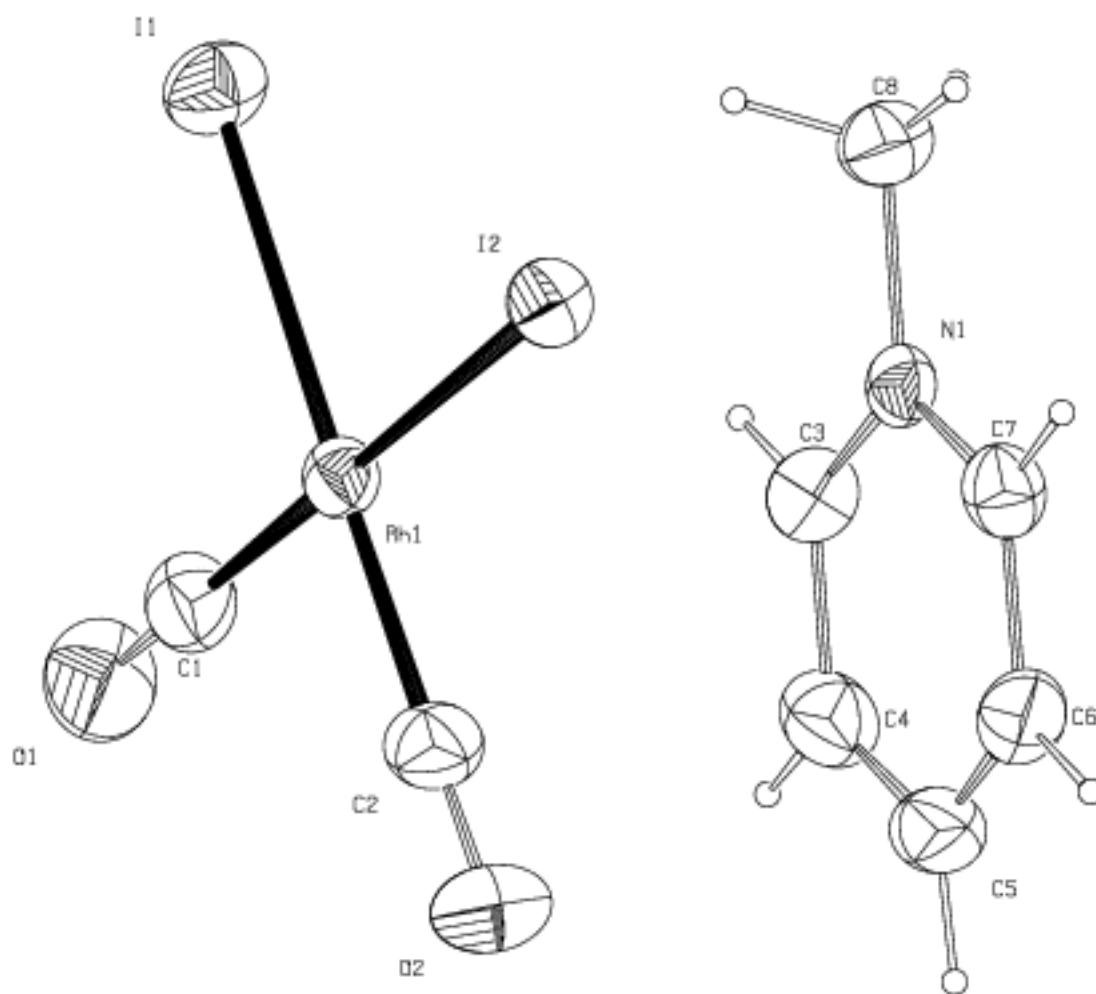
#### Kinetic data

**Table S1.** Observed pseudo first order rate constants,  $k_{\text{obs}}$ , for oxidative addition of MeI to  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  with polymeric and monomeric counterions in  $\text{CH}_2\text{Cl}_2$  or neat MeI.

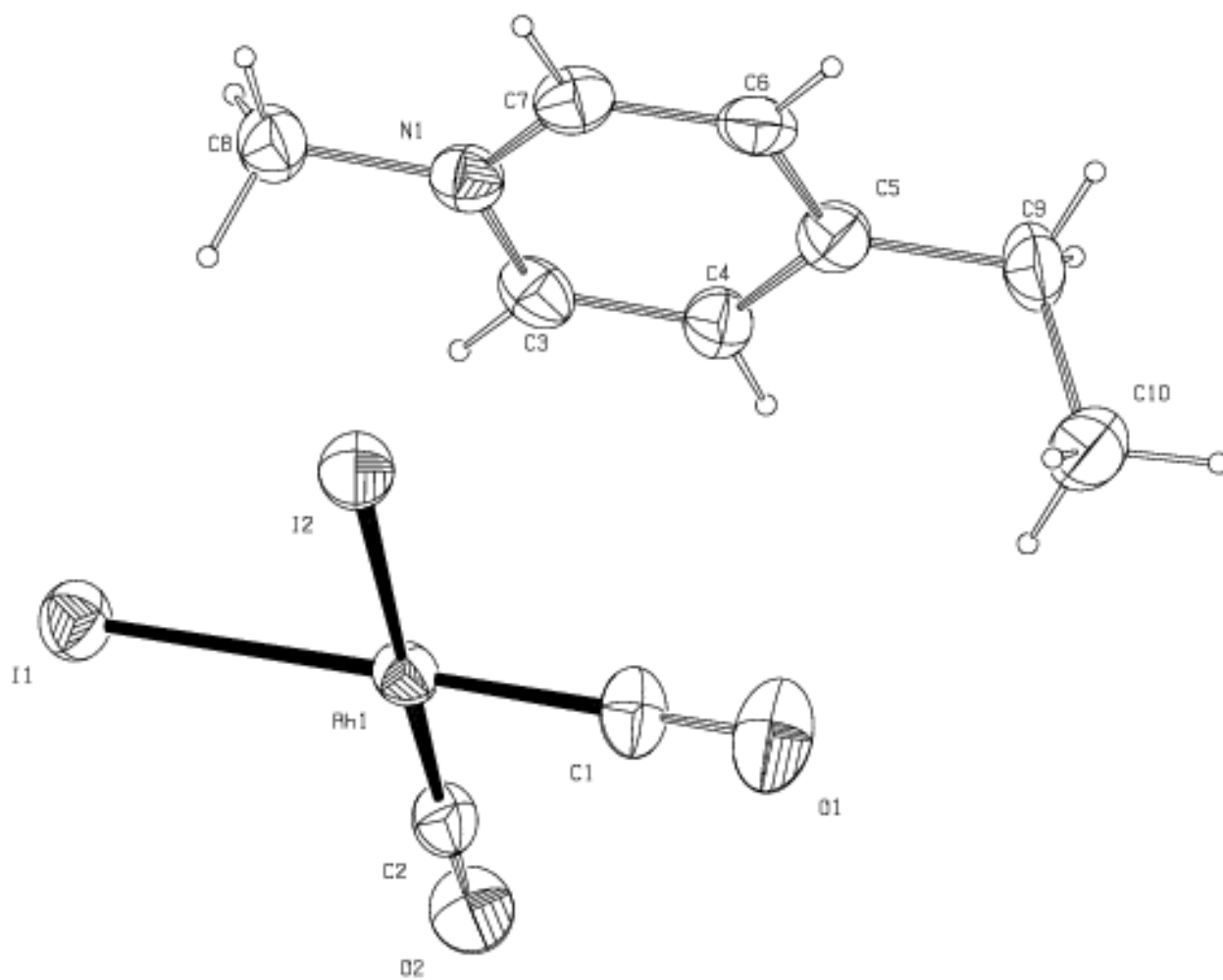
Temp °C	[MeI] M	Cross- linking %	4-VP content mmol g <sup>-1</sup>	Film thickness µm	R	10 <sup>4</sup> $k_{\text{obs}}$ s <sup>-1</sup>				
						Polym <sup>+</sup>	Bu <sub>4</sub> N <sup>+</sup>	PyMe <sup>+</sup>	EtPyMe <sup>+</sup>	BzPyMe <sup>+</sup>
25	2.0	22	1	96	Me	0.4	0.6			
25	4.0	22	1	96	Me	0.9	1.1			
25	8.0	22	1	96	Me	1.7	1.9			
10	16	22	1	96	Me	1.1	1.3	2.5	2.8	2.2
15	16	22	1	96	Me	1.7	2.0	3.1	3.5	2.9
20	16	22	1	96	Me	2.5	2.8	4.7	5.5	5.2
25	16	22	1	96	Me	4.0	4.4	7.1	9.2	7.9
30	16	22	1	96	Me	5.3	5.8	11.0	11.6	9.6
35	16	22	1	96	Me	11.4	9.6	17.0	19.1	16.4
40	16						12.9	28.0	23.6	22.0
25	16	22	1	59	Me	4.8				
25	16	22	0.5	51	Me	4.4				
25	16	22	1.3	51	Me	4.3				
25	16	22	8.7	43	Me	3.6				
25	16	11	2	96	Me	4.9				
25	16	11	2	96	<sup>n</sup> Pr	4.8				
25	16	11	2	96	<sup>t</sup> Bu	5.1				

**Table S2.** Observed pseudo first order rate constants,  $k_{\text{obs}}$ , for oxidative addition of MeI to  $[\text{Ir}(\text{CO})_2\text{I}_2]^-$  with polymeric and monomeric counterions in  $\text{CH}_2\text{Cl}_2$ .

Temp °C	[MeI] M	Cross- linking %	4-VP content mmol g <sup>-1</sup>	Film thickness μm	R	10 <sup>4</sup> $k_{\text{obs}}$ s <sup>-1</sup>	
						Polymer <sup>+</sup>	Ph <sub>4</sub> As <sup>+</sup>
25	0.08	22	1	96	Me	0.7	2.4
25	0.16	22	1	96	Me	1.7	5.0
25	0.24	22	1	96	Me	2.2	7.5
5	0.32						1.9
15	0.32	22	1	96	Me	0.5	4.7
20	0.32	22	1	96	Me	1.2	
25	0.32	22	1	96	Me	3.1	10.3, 9.9
30	0.32	22	1	96	Me	3.8	
35	0.32	22	1	96	Me	3.8	20.5
25	0.32	22	1	96	<sup>n</sup> Pr	2.9	



**Figure S1.** ORTEP plot for  $[C_5H_5NMe][Rh(CO)_2I_2]$  **1**. Thermal ellipsoids are shown at the 50% probability level.



**Figure S2.** ORTEP plot for [4-Et-C<sub>5</sub>H<sub>4</sub>NMe][Rh(CO)<sub>2</sub>I<sub>2</sub>] **2**. Thermal ellipsoids are shown at the 50% probability level.