Supplementary Material

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Influence of anionic components of ionic liquid solvents on oxidative addition reactions of organoplatinum(II) complexes with MeI

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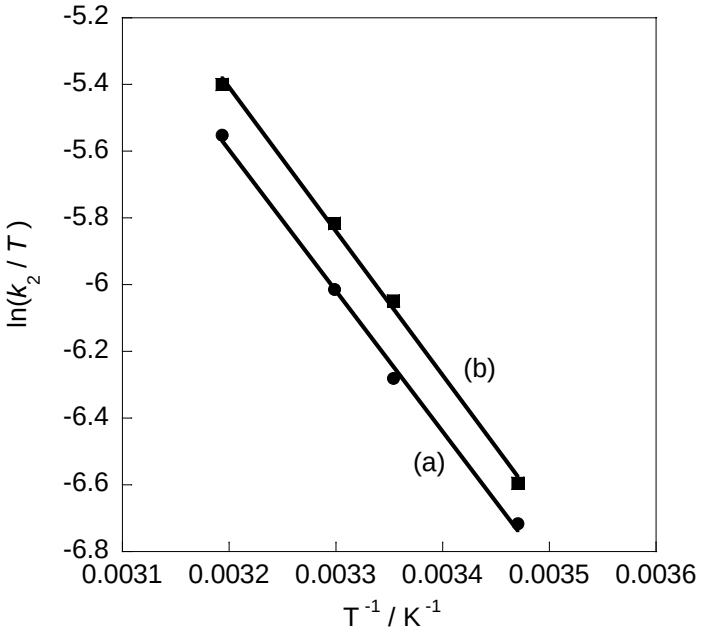

Fig. 1S Plots of $\ln(k_2/T)$ versus (1/T) for the reaction of MeI with (a) [Pt(*p*-$MeC_6H_4)_2(^tBu_2bpy)$], **1b**, and (b) [Pt(*p*-$MeC_6H_4)_2$(phen)], **1a**, in [bmim][$(CN)_2N$].

Errors for pseudo first order conditions (reaction of MeI with diaryl Pt(II) complexes):

The books "**Quantitative Chemical Analysis**" [by Daniel C. Harris, 5th ed. W. H. Freeman and Company, New York, 1999] and "**Fundamentals of Analytical Chemistry**" [by D. A. Skoog, D. M. West and F. J. Holler, 5th ed. Saunders College Publishing, New York, 1988] give rules for propagation of experimental uncertainty in calculations. They suggest that 2 methods are possible for the estimate of uncertainty, standard deviation and a confidence interval (such as 95%). We have used standard deviation to report our experimental errors.

The *regression analysis* technique provides the mean to derive a best straight line from the points [MeI]-k_{obs}. We have considered the simplest regression procedure, i.e. the *method of least squares* for specifying the uncertainties associated with its subsequent use. The line generated by the least-squares method is the one that minimizes the squares of residual from that line. Three quantities have been defined as follows:

$$S_{xx} = \sum (x_i - \bar{x})^2$$

$$S_{yy} = \sum (y_i - \bar{y})^2$$

$$S_{xy} = \sum (x_i - \bar{x})(y_i - \bar{y})$$

Here, x_i and y_i are individual pairs of data for [EtI] and k_{obs} , and $\bar{x}$ and $\bar{y}$ are the average values for the variables, that is, $\bar{x} = \frac{\sum x_i}{N}$ and $\bar{y} = \frac{\sum y_i}{N}$.

N is the number of pairs of data used in preparation of calibration curve. Three quantities can be obtained from S_{xx} , S_{yy} and S_{xy} :

A) the slope of the line, $k_2 = S_{xy} / S_{xx}$

B) the standard deviation about regression, $s_r = \sqrt{\frac{S_{yy} - b^2 S_{xx}}{N-1}}$

C) the standard deviation of the slope, $s_{k_2} = \sqrt{s_r^2 / S_{xx}}$

We have reported the values of k_2 and s_{k_2} in our manuscript.

Estimated errors of activation parameters:

The activation parameters were calculated from a nonlinear least square procedure contained in the program KaleidaGraph version 3.6, which is available from Synergy Software. The errors in the activation parameters were computed from the error propagation formula suggested by Girolami, *et. al*. , see; Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

Tables S1 – S10: The observed first order rate constants for the reactions.

Estimated errors in k_{obs} values are ±4%.

Table S1. k_{obs} (s^{-1}) values for the reaction of complex [Pt(*p*-MeC_6H_4)$_2$(phen)], **1a** at varying [MeI] and *T* in [bmim][Tf_2N]

[MeI] / M	T=15 ºC	T=20 ºC	T=25 ºC	T=30 ºC	T=40 ºC
0.011429				0.0034376	0.0051640
0.017143		0.0020181	0.0027391	0.0037297	0.0065214
0.022857	0.0020190	0.0026333	0.0042573		0.0090748
0.028571	0.0031251			0.0075242	
0.034286	0.0038412	0.0043760	0.0077223	0.0086630	0.014585
0.045714	0.0046285	0.0067293	0.0087948	0.013094	0.0195186
0.057143		0.0084002	0.012980		
0.068571	0.0066643				
k_2 ($dm^3mol^{-1}s^{-1}$)	0.10	0.14	0.21	0.27	0.42

Table S2. k_{obs} (s^{-1}) values for the reaction of complex [Pt(*p*-MeC_6H_4)$_2$(^{t}Bu_2bpy)], **1b**, at varying [MeI] and *T* in [bmim][Tf_2N]

[MeI] / M	T=10 ºC	T=15 ºC	T=25 ºC	T=30 ºC	T=40 ºC
0.011429					0.0056198
0.017143				0.0059292	0.0076442
0.022857		0.0025467	0.0041403	0.0093073	0.012388
0.028571		0.0040217		0.0094667	
0.034286			0.0087383		0.017943
0.045714	0.00319543	0.0058423	0.012296	0.016497	0.0241147
0.057143	0.0043945	0.0078920	0.014217	0.020753	
0.068571	0.0058795		0.021947		
0.091429	0.007995	0.012947			
0.11443	0.0110116				
k_2 ($dm^3mol^{-1}s^{-1}$)	0.09	0.14	0.28	0.36	0.52

Table S3. k_{obs} (s^{-1}) values[a] for the reaction of complex [Pt(*p*-MeC_6H_4)$_2$(phen)], **1a** at varying [MeI] and *T* in [bmim][BF_4]

[MeI] / M	T=15 ºC	T=20 ºC	T=25 ºC	T=30 ºC
0.017143				0.012071
0.022857	0.0083198	0.010285	0.012719	0.015094
0.028571	0.01008174	0.0130713	0.016542	0.022065
0.034286	0.01299	0.016121	0.019465	0.023488
0.045714	0.016643	0.020547	0.029277	0.032957
0.068571	0.024017	0.032085	0.042184	
k_2 ($dm^3mol^{-1}s^{-1}$)	0.36	0.46	0.61	0.71

Table S4. k_{obs} (s^{-1}) values for the reaction of complex [Pt(*p*-MeC_6H_4)$_2$(^{t}Bu_2bpy)], **1b**, at varying [MeI] and *T* in [bmim][BF_4]

[MeI] / M	T=15 ºC	T=25 ºC	T=30 ºC	T=40 ºC
0.011429				0.014139
0.017143		0.009849	0.010498	
0.022857	0.0052447	0.011576	0.015319	0.025997
0.028571			0.017997	0.0314965
0.034286	0.007874	0.018073	0.0210332	0.037753
0.045714	0.014555	0.025030	0.029863	0.051004
0.057143	0.016550	0.031091		
0.091429	0.026430			
k_2 ($dm^3mol^{-1}s^{-1}$)	0.29	0.54	0.64	1.12

Table S5. k_{obs} (s^{-1}) values[a] for the reaction of complex [Pt(*p*-MeC_6H_4)$_2$(phen)], **1a** at varying [MeI] and *T* in [bmim][PF_6]

[MeI] / M	T=15 ºC	T=25 ºC	T=30 ºC	T=40 ºC
0.011429				0.014533
0.022857		0.0097822	0.0133299	0.026220
0.034286	0.0098752	0.015378	0.0223628	0.037657
0.045714	0.0143109	0.022065	0.02901287	
0.048000	0.0162083			0.058079
0.080000	0.0264219	0.0385412	0.0542351	0.0879545
0.12800	0.0430901	0.0576411	0.0846204	
k_2 ($dm^3mol^{-1}s^{-1}$)	0.33	0.46	0.66	1.13

Table S6. k_{obs} (s^{-1}) values for the reaction of complex [Pt(*p*-$MeC_6H_4)_2$($^tBu_2$bpy)], **1b**, at varying [MeI] and *T* in [bmim][PF_6]

[MeI] / M	T=15 ºC	T=25 ºC	T=30 ºC	T=40 ºC
0.011429				0.0082952
0.022857	0.0040185	0.0078652	0.0104	0.018070
0.034286	0.0068452	0.014139	0.0168202	0.028400
0.045714	0.0085852	0.018543	0.0214808	0.03793
0.057143	0.010697	0.0251569	0.0291614	0.045465
0.091429	0.018542	0.03585655	0.0450655	
k_2 ($dm^3mol^{-1}s^{-1}$)	0.20	0.40	0.49	0.81

Table S7. k_{obs} (s^{-1}) values[a] for the reaction of complex [Pt(*p*-$MeC_6H_4)_2$(phen)], **1a** at varying [MeI] and *T* in [bmim][$(CN)_2N$]

[MeI] / M	T=15 ºC	T=25 ºC	T=30 ºC	T=40 ºC
0.011429				0.015309
0.017143		0.0123084	0.015658	0.0239820
0.022857	0.0087737	0.016712	0.0214196	0.029805
0.028571	0.0102553		0.024423	0.040091
0.034286	0.01457	0.023993	0.0313025	0.050450
0.045714	0.019592	0.031962	0.042030	
0.068571	0.026007	0.0476535		
k_2 ($dm^3mol^{-1}s^{-1}$)	0.39	0.70	0.90	1.41

Table S8. k_{obs} (s^{-1}) values for the reaction of complex [Pt(*p*-$MeC_6H_4)_2$($^tBu_2$bpy)], **1b**, at varying [MeI] and *T* in [bmim][$(CN)_2N$]

[MeI] / M	T=15 ºC	T=25 ºC	T=30 ºC	T=40 ºC
0.011429				0.015761
0.017143			0.011890	
0.022857	0.0069313	0.010639	0.016638	0.033660
0.028571			0.021888	
0.034286	0.011941	0.019363		0.043963
0.045714	0.015907	0.028382	0.034525	0.050370
0.057143	0.018800	0.030260	0.0419029	0.0690477
0.091429	0.032883	0.051249		
k_2 ($dm^3mol^{-1}s^{-1}$)	0.35	0.56	0.74	1.21

Table S9. k_{obs} (s^{-1}) values[a] for the reaction of complex [Pt(*p*-$MeC_6H_4)_2$(phen)], **1a** at varying [MeI] and *T* in [bmim][CF_3CO_2]

[MeI] / M	T=10 ºC	T=15 ºC	T=25 ºC	T=40 ºC
0.016000	0.0021185	0.00245	0.0066396	0.018960
0.032000	0.00450456	0.00685258	0.014308	0.029363
0.048000	0.0074996	0.01104708	0.021705	0.043963
0.064000	0.0110276	0.015160822	0.024947	0.058193
0.096000	0.0151367	0.020230815	0.039904	0.086763
k_2 ($dm^3mol^{-1}s^{-1}$)	0.16	0.22	0.42	0.91

Table S10. k_{obs} (s^{-1}) values for the reaction of complex [Pt(*p*-MeC_6H_4)$_2$(^{t}Bu_2bpy)], **1b**, at varying [MeI] and *T* in [bmim][CF_3CO_2]

[MeI] / M	T=15 ºC	T=25 ºC	T=40 ºC
0.016000			0.019715
0.032000	0.0085853	0.016840	0.032747
0.048000	0.014393	0.024773	0.0574016
0.064000	0.0241602	0.039425	0.076801
0.080000	0.025888	0.045063	0.1010998
0.12800	0.047057	0.0731069	
k_2 ($dm^3mol^{-1}s^{-1}$)	0.35	0.57	1.22