# Oxidative addition reaction of diarylplatinum(II) complexes with MeI in ionic liquid media: a kinetic study<sup>†</sup>

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A kinetic study of the oxidative addition reaction of diarylplatinum(II) complexes [Pt(p-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(NN)] (1a: NN = 1,10-phenanthroline (phen) and 1b: NN = 4,4'-di-*tert*-butyl-2,2'-bipyridine ('Bu<sub>2</sub>bpy)) with MeI in ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([bmim][bta]) or 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]) is described. The reactions were investigated as a function of MeI concentration and temperature under pseudo-first-order conditions using UV-vis spectroscopy techniques. In general, the oxidative addition reactions in ionic liquids followed an S<sub>N</sub>2 mechanism, similar to that reported for the related reactions in conventional solvents, *e.g.* benzene or acetone. The reaction rates in different solvents followed the order acetone > ionic liquids > benzene. The trend in the values of  $k_2$  clearly indicated that ionic liquids behave like conventional solvents and that no particular 'ionic liquid effect' was detected in this kind of reaction. The effect of solvent on the reactions was examined using a linear solvation energy relationship (LSER) based on the Kamlet–Taft solvent scale. The activation parameters,  $\Delta H^{\dagger}$  and  $\Delta S^{\dagger}$ , were obtained for the reactions in each solvent and the investigation of enthalpy-entropy compensation confirmed that the mechanism operated in all solvents is similar.

## Introduction

Oxidative addition reactions of square planar complexes of d<sup>8</sup> metal ions such as Pt(II), Pd(II) and Ir(I) play a fundamental role in many chemical processes, for instance, in biochemistry and homogeneous catalysis.1 Detailed mechanistic studies have demonstrated that such complexes usually proceed by an S<sub>N</sub>2 mechanism, however, sometimes the concerted three-centre mechanism is also a possibility.<sup>2</sup> The concerted three-centre mechanism is usually proposed in the oxidative addition of C-H and C-C bonds,<sup>2b,2c</sup> and also we have proposed it in the oxidative addition of the O-O bonds in  $R_2O_2$  (R = H or C(=O)Ph) to some diarylplatinum(II) complexes [PtAr<sub>2</sub>(NN)] (in which Ar is Ph or some simple substituted Ph groups and NN is a chelating bidentate ligand such as bipyridine).<sup>3</sup> The transition state has a fivecoordinate cationic character in the case of an associative  $(S_N 2)$ mechanism, or forms a concerted three-centred six-coordinate intermediate in the case of a concerted three-centre mechanism. Another possibility for the mechanism of oxidative addition is a radical pathway, although it has been rarely observed.<sup>2a</sup> The kinetics of reaction of some alkyl halides with different mono and binuclear organoplatinum(II) complexes, including those bearing a bridging biphosphine ligand or having a chelating N,N or P,N

ligand, have extensively been studied.<sup>2,4</sup> The inner-sphere electrontransfer/caged radical-pair mechanism becomes possible when a formal two electron oxidation is available. This pathway can lead to the  $S_N 2$  product *via* cage collapse, but escape of the radical pair gives free radicals which can form byproducts.<sup>2a</sup> Such a mechanism has been suggested for the oxidative addition of AuCl<sub>4</sub><sup>-</sup> to [PtCl<sub>2</sub>(phen)].<sup>2d</sup>

On the other hand, ionic liquids (ILs) are ionic media resulting from the combination of organic cations and various anions. These materials have attracted much attention recently in many areas of science, particularly in green synthesis,<sup>5</sup> mainly due to the absence of any vapour pressure and interesting physical characteristics. Many applications have already been developed and new ones are added every day.6 They are non-flammable, have high thermal stability<sup>7a</sup> and are emerging as novel replacements for volatile organic compounds traditionally used as solvents in many industrial processes. They are also used as catalysts in organic reactions.76 In addition, ionic liquids can be recycled after clean up and this offers great advantages. Despite these developments, not much research has been carried out on the details of the mechanisms of the reactions occurring in these media, and possible changes that are involved in comparison with usual organic solvents. Due to the unique properties of ionic liquids, changes in reaction mechanisms could occur and may account for some of the observed effects such as the acceleration of reactions or a higher catalyst lifetime.8 In addition, some of the ionic liquids can even act as co-catalysts and thus change the reaction mechanism.8 Fig. 1 shows the chemical structures of the most commonly used organic cations and anions that make up the more popular ILs investigated. Amongst these, 1-butyl-3-methylimidazolium (bmim) salts have been studied extensively

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and the one with bis(trifluormethylsulfonyl)-amide, bta, as anion, *i.e.* [bmim][bta], is a well-described ionic liquid with a relatively low viscosity (as compared to other ionic liquids) and having a melting point below 0 °C. Thus, the latter seems to be suitable for kinetic investigations once obtained in colorless form.<sup>9</sup>



The present investigation deals with the use of [bmim][bta] or [bmim][BF<sub>4</sub>] ionic liquids as solvent for a typical oxidative addition reaction of a metal complex [PtAr<sub>2</sub>(NN)] with MeI that has been studied extensively during the past several decades using more conventional aprotic solvents, such as benzene or acetone. Substitution reactions in ionic liquid media have previously been studied<sup>10</sup> and in some cases a special ionic liquid effect has been observed. van Eldick et al. have reported<sup>10b</sup> that the substitution reaction of [Pt(terpyridine)Cl]+ with thiocyanate has the same mechanism as found for molecular solvents, but the observed rate constants showed a significant dependence on the nature of ionic liquids. For example, the latter reaction in methanol is about 100 times faster than in [emim][OTf].<sup>10b</sup> Besides, Shaughnessy and co-workers have reported the kinetic data for oxidative addition reactions or ligand substitution reactions involving Vaska's complex in ionic liquids.11 However, to the best of our knowledge, this work presents for the first time a systematic temperature-dependence study involving oxidative addition reaction in ionic liquid media. The data indicate that there is not any special 'ionic liquid effect' in the reactions under study in contrast with such effects which have been previously reported for substitution reactions.<sup>10b</sup>

### Experimental

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([bmim][bta]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]) were purchased from Solvent Innovation, and the precursor complexes [Pt(p-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(phen)], **1a**,<sup>3,4g</sup> (phen = 1,10-phenanthroile) and [Pt(p-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>('Bu<sub>2</sub>bpy)], **1b**,<sup>4f,4g</sup> ('Bu<sub>2</sub>bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) were made by the known methods. The Pt(IV) complexes were made using the appropriate platinum(II) complex and CH<sub>3</sub>I in ionic liquid media and the isolated compounds were characterized by comparing their NMR and UV-Vis spectra with those of the previously prepared materials.<sup>4f,4g</sup> Kinetic studies were carried out by using a Perkin-Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath.

#### Kinetic studies of the oxidative addition reactions

In a typical experiment, a solution of  $[Pt(p-MeC_6H_4)_2(phen)]$ , **1a**, in [bmim][bta] (1.4 ml,  $3 \times 10^{-4}$  M) in a cuvette was thermostated at 25 °C and a known excess of MeI was added using a microsyringe. Concentration range used for MeI was 0.01–0.1 M. After rapid stirring, the absorbance at  $\lambda = 430$  nm was collected with time (Fig. 2 and 1S<sup>†</sup>). The absorbance time curves were analyzed by pseudo-first-order methods. The pseudo first-order rate constants  $(k_{obs})$  were evaluated by nonlinear least-squares fitting of the absorbance-time profiles to a first-order equation (eqn (1)). A plot of  $k_{obs}$  versus [MeI] was linear (Fig. 3), and the slope gave the second-order rate constant  $(k_2)$ .

$$A_t = A_{\infty} + (A_0 - A_{\infty})[\exp(-k_{\text{obs}}t)]$$
<sup>(1)</sup>



**Fig. 2** Changes in the UV-vis spectrum during the reaction of complex [Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(phen)], **1a**,  $(3 \times 10^{-4} \text{ M})$  and MeI in [bmim][bta] at T = 25 °C: (a) initial spectrum (before adding MeI) and (b) spectrum at t = 30 s; successive spectra were recorded at intervals of 45 s.



**Fig. 3** Plots of first-order rate constants for the reaction of complex  $[Pt(p-MeC_6H_4)_2(phen)]$ , **1a**, with MeI at different temperatures (a, 15 °C; b, 20 °C; c, 25 °C; d, 30 °C, e, 40 °C) *versus* the concentration of MeI in [bmim][bta].

The same method was used at other temperatures (see Table 1), and activation parameters were obtained from the Eyring equation (eqn (2) and Figure 2S).

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}$$
(2)

Table 1 Second-order rate constants<sup>*a*</sup> and activation parameters<sup>*b*</sup> for reaction of  $[Pt(p-MeC_6H_4)_2(NN)]$ , 1, with MeI in different solvents

Complex	NN	Solvent	$k_2/L$ mol	<sup>-1</sup> s <sup>-1</sup> at differ						
			10 °C	15 °C	20 °C	25 °C	30 °C	40 °C	$\Delta H^{\ddagger}/\mathrm{kJ}~\mathrm{mol}^{-1}$	$\Delta S^{*}/\mathrm{J}~\mathrm{K}^{-1}~\mathrm{mol}^{-1}$
1a	phen	acetone	0.45	0.56	0.71	0.87	1.07		$28.9 \pm 2.0$	$-149 \pm 7$
1a	phen	benzene <sup>c</sup>	0.05	0.06	0.08	0.10	0.13		$32.2 \pm 2.2$	$-156 \pm 7$
1a	phen	[bmim][bta]		0.10	0.14	0.21	0.27	0.42	$41.6 \pm 0.4$	$-119 \pm 1$
1a	phen	[bmim][BF <sub>4</sub> ]		0.36	0.46	0.61	0.71		$33.0 \pm 1.7$	$-139 \pm 6$
1b	<sup>7</sup> Bu <sub>2</sub> bpy	acetoned	0.64	0.84	1.08	1.43	1.84		$35.3 \pm 0.4$	$-123 \pm 1$
1b	'Bu <sub>2</sub> bpy	benzene <sup>d</sup>	0.10	0.12	0.16	0.19	0.23		$29.2 \pm 0.8$	$-161 \pm 3$
1b	'Bu <sub>2</sub> bpy	[bmim][bta]	0.09	0.14		0.28	0.36	0.52	$42.5 \pm 0.5$	$-114 \pm 2$
1b	<sup><i>t</i></sup> Bu <sub>2</sub> bpy	[bmim][BF <sub>4</sub> ]		0.29		0.54	0.64	1.12	$37.9 \pm 1.9$	$-123 \pm 6$

<sup>*a*</sup> Estimated errors in  $k_2$  values are ±5%. <sup>*b*</sup> Activation parameters were calculated from the temperature dependence of the second order rate constant in the usual way using Eyring equation. <sup>*c*</sup> From ref. 4g. <sup>*d*</sup> From ref. 4f.

#### **Results and discussion**

The kinetic study of the oxidative addition reaction of  $[Pt(p-MeC_6H_4)_2(NN)]$  (NN = 1,10-phenanthroline, phen, or 4,4'-di-*tert*butyl-2,2'-bipyridine, 'Bu<sub>2</sub>bpy) with MeI was performed in ionic liquids [bmim][bta] or [bmim][BF<sub>4</sub>] and also in molecular solvents (acetone and benzene), in order to study the solvent dependence of the reaction. The reactions are described in Scheme 1.





The solvent dependence of the oxidative addition reactions was studied by dissolving the complexes 1 in the selected solvents followed by rapid mixing with a known excess of MeI. Typical examples of the observed spectral changes and kinetic traces (Abstime curves) are shown in Fig. 2 and 1S (ESI<sup>†</sup>), respectively. The kinetic traces recorded for the reactions in the ILs (Fig. 1S) as well as in molecular solvents, benzene or acetone, showed excellent fits to a single-exponential function (eqn (1)); this confirms the pseudo-first-order behavior of the reactions as shown in Scheme 1.

It is well established that the oxidative addition reactions of organoplatinum(II) complexes with MeI usually proceed by an  $S_N 2$  mechanism and follows the well known second order rate law:<sup>2,4</sup>

 $Rate = -d[Pt(p-MeC_6H_4)_2(NN)]/dt = k_2[complex][MeI]$ (3)

Under pseudo-first order condition,  $[MeI]_0 \gg [complex]_0$ , eqn (3) is simplified to:

$$Rate = k_{obs}[complex]$$
(4)

The plots of calculated pseudo first order rate constants,  $k_{obs}$ , against the concentration of MeI, are linear with a zero intercept under all conditions showing a first-order dependence of the rate on the concentration of MeI (Fig. 3).

The rate constant  $k_{obs}$  can be expressed as a function of [MeI], namely,  $k_{obs} = k_2$ [MeI], in which  $k_2$  is the second-order rate constant.

The activation parameters were determined from the effect of temperature on  $k_2$ . The enthalpy and entropy of activation,  $\Delta H^{\ddagger}$ and  $\Delta S^{\ddagger}$ , were obtained from Eyring plots (see Fig. 2S<sup>†</sup>). Table 1 summarizes the values of  $k_2$ ,  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  for the studied reactions of complexes 1a and 1b in the selected solvents. It should be noted that the reactions in the ionic liquid showed the same behavior as that found for other more conventional solvents as a function of the experimental variables. The large negative values of  $\Delta S^{\ddagger}$ obtained for the reaction in all solvents including [bmim][bta] are typical of oxidative addition by a common S<sub>N</sub>2 mechanism which involves nucleophilic attack of the metallic centre at the methyl group of MeI and formation of the cationic intermediate [(p-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(NN)Pt-Me]<sup>+</sup> I<sup>-</sup>. Although an inner-sphere electrontransfer/caged radical-pair mechanism is a possibility, MeI addition is thought to be an  $S_N 2$  reaction on the basis of its clean second-order kinetics and the failure of radical traps to inhibit it. Also no byproduct has been detected by the reaction of complexes 1 with MeI in ionic liquids, thus further supporting the  $S_N 2$ mechanism. Also the  $\Delta H^{\ddagger}/\Delta S^{\ddagger}$  compensation plots obtained for reactions of complexes 1a and 1b with MeI in different solvents (see Fig. 5) give a good straight line. It may be taken as an evidence for operation of a common (associative, second-order) mechanism in this series of reactions. The reactions of organoplatinum(II) complexes [PtR<sub>2</sub>(NN)], in which R = Me or Ar and NN is various diimine ligands such as 2,2'-bipyridine and 1,10-phenanthroline, with MeI have been extensively investigated.<sup>2a,2b,4g,4h</sup> In all cases, an  $S_N 2$  mechanism has been suggested. A secondary  $\alpha$ -deuterium KIE study involving the reaction of MeI/CD<sub>3</sub>I with some organoplatinum(II) complexes has also been reported to confirm the operation of the  $S_N 2$  mechanism in the oxidative addition of MeI to some organoplatinum(II) complexes.4f,4g So it is well established that these reactions proceed by an  $S_N 2$  mechanism.

The reaction rates of MeI with complex 1b is slightly greater than that with complex 1a for the studied solvents (with the exception of [bmim][BF<sub>4</sub>]). A slight increase in the rate is observed on going from phen to 'Bu<sub>2</sub>bpy in the arylplatinum(II) complexes

Solvent	$\mathcal{E}_r^{\ b}$	$E_T{}^{N c}$	$lpha^d$	$eta^{d}$	$\pi^{*d}$	$k_2$ (NN = 'Bu <sub>2</sub> bpy)	$k_2$ (NN = phen)
Acetone	20.7	0.355	0.08	0.43	0.71	1.43	0.87
Benzene	2.30	0.111	0.00	0.10	0.55	0.19	0.10
[bmim][bta]	11.6	0.642	0.62	0.24	0.98	0.28	0.21
[bmim][BF <sub>4</sub> ]	11.7	0.673	0.73	0.73	1.09	0.54	0.61
<sup>a</sup> Data from ref. 12	and 14. <sup>b</sup> Dieleo	ctric constant. <sup>e</sup> P	olarity. <sup>d</sup> Kamle	t–Taft paramete	ers.		

**Table 2** The property parameters of solvents<sup>*a*</sup> and the second-order rate constants  $(k_2/L \text{ mol}^{-1} \text{ s}^{-1})$  for the reaction of [Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(NN)], 1, with MeI in different solvents at 25 °C

(by a factor of about 1.3 from phen to 'Bu<sub>2</sub>bpy) probably due to more electron releasing character of 'Bu<sub>2</sub>bpy ligand as compared to that of phen ligand, which makes the platinum centre in the [Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>('Bu<sub>2</sub>bpy)] complex more electron rich than the platinum centre in [Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(phen)] complex, towards oxidative addition reactions. This has recently been confirmed using density functional calculations, based on the charge on nitrogen atoms of the 'Bu<sub>2</sub>bpy ligand (-0.438) and phen (-0.429).<sup>4g</sup> The same behavior has been reported for the reaction of MeI with [Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(4,4'-R<sub>2</sub>-bpy)] (where R = H, Me or 'Bu) complexes.<sup>4f</sup>

As is clear from Tables 1 and 2, the reaction rate order obtained for oxidative addition reaction of complexes 1 with MeI in different solvents is:  $k_2$  (acetone) >  $k_2$  ([bmim][BF<sub>4</sub>]) >  $k_2$  ([bmim][bta]) >  $k_2$  (benzene). Our goal is to find a correlation between  $k_2$  values and solvent parameters.

Different solvent parameters have been proposed over the years to give various solvent properties.<sup>12</sup> They have been used to explain discrepancies observed between various properties of a given solute as the solvents are changed. In many cases, it has been demonstrated that solute properties are dependent on more than one solvent parameter.<sup>13</sup>

A method was applied for the treatment of the experimental results in which the rate constant of the oxidative addition reaction of complexes 1 with MeI in different solvents was first correlated separately with each one of the solvent parameters to evaluate them for their ability to provide a reasonable explanation (the solvents used and their parameters are given in Table 2). Then, to give an independent interpretation of the kinetic results in different solvents, the linear solvation energy relationship (LSER)

multi-parameter method, based on that of Kamlet *et al.*,<sup>15</sup> was performed using two solvent parameters. Good multi-parametric correlations were obtained when more than one solvent parameter were considered. The general relationship can be expressed by:

$$\ln k_2 = (\ln k_2)^\circ + aX_1 + bX_2$$

where  $(\ln k_2)^{\circ}$  is the value of  $\ln k_2$  in a solvent for which the properties  $X_i$  are zero for all *i* values,  $X_1$  and  $X_2$  are different solvent parameters, and *a* and *b* are the coefficients of  $X_1$  and  $X_2$ , respectively, which can be obtained by multiple linear regression analysis.<sup>15</sup>

The change of the  $k_2$  values for complex **1a** was correlated at first with each of the solvent parameters as follows:  $\varepsilon_r$ , dielectric constant of the solvent;  $E_T^N$ , its polarity;  $\alpha$ , the hydrogen bond donation (HBD) ability;  $\beta$ , its hydrogen bond acceptance (HBA) or electron pair donation ability to form a coordinative bond;  $\pi^*$  is its polarity/polarizability parameter. The correlations were found to be unsatisfactory (correlation coefficients were  $R^2 = 0.80$ , 0.21, 0.06, 0.67 and 0.18 for  $\varepsilon_r$ ,  $E_T^N$ ,  $\alpha$ ,  $\beta$  and  $\pi^*$ , respectively). Correlations of rate constants of complex **1a** with the solvent parameters of Kamlet *et al.* are given in Table 3 with multiple correlation coefficients  $R^2$  in the range 0.44–0.98. As is clear from Table 3, multi-parameter correlations using two parameters gave further improvement, with the following most useful form:

$$\ln k_2 = (\ln k_2)^\circ + a\varepsilon_r + b\beta$$

which includes  $\varepsilon_r$  and  $\beta$  parameters ( $R^2 = 0.98$ ). The fitting results are shown in Fig. 4. These results suggest that the influence of  $E_T^N$ ,  $\alpha$  and  $\pi^*$  terms on the  $k_2$  values may be considered negligible.

**Table 3** Parametric solvent coefficients of the reaction of  $[Pt(p-MeC_6H_4)_2(NN)]$ , **1**, with MeI obtained from the different multi-parametric equations  $(LSER)^a$ 

	Complex [Pt()	p-MeC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> (phe	en)], <b>1a</b>	Complex [Pt(p-MeC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> ('Bu <sub>2</sub> bpy)], 1b				
LSER equation	$(\ln k_2)^\circ$	а	b	$R^2$	$(\ln k_2)^\circ$	а	b	$R^2$
$\ln k_2 = (\ln k_2)^\circ + a\varepsilon_r$	-2.49(0.55)	0.12(0.04)		0.80	-2.07(0.40)	0.11(0.03)		0.87
$\ln k_2 = (\ln k_2)^\circ + a E_T^N$	-1.89(1.18)	1.72(2.35)		0.21	-1.08(1.16)	0.63(2.32)		0.04
$\ln k_2 = (\ln k_2)^\circ + a\alpha$	-1.36(0.88)	0.65(1.83)		0.06	-0.74(0.81)	-0.17(1.68)		0.01
$\ln k_2 = (\ln k_2)^\circ + a\beta$	-2.25(0.65)	3.03(1.49)		0.67	-1.54(0.82)	1.98(1.86)		0.36
$\ln k_2 = (\ln k_2)^\circ + a\pi^*$	-2.52(2.21)	1.68(2.57)		0.18	-1.15(2.15)	0.42(2.50)		0.01
$\ln k_2 = (\ln k_2)^\circ + a\varepsilon_r + bE_T^N$	-2.64(0.90)	0.11(0.06)	0.50(1.74)	0.82	-1.87(0.58)	0.12(0.04)	-0.68(1.12)	0.90
$\ln k_2 = (\ln k_2)^\circ + a\varepsilon_r + b\alpha$	-2.62(0.81)	0.12(0.06)	0.41(1.12)	0.83	-1.95(0.55)	0.12(0.04)	-0.39(0.77)	0.89
$\ln k_2 = (\ln k_2)^\circ + a\varepsilon_r + b\beta$	-2.78(0.27)	0.09(0.02)	1.82(0.62)	0.98	-2.16(0.55)	0.10(0.04)	0.56(1.26)	0.90
$\ln k_2 = (\ln k_2)^\circ + a\varepsilon_r + b\pi^*$	-3.03(1.43)	0.11(0.06)	0.75(1.70)	0.83	-1.68(1.03)	0.12(0.04)	-0.54(1.22)	0.89
$\ln k_2 = (\ln k_2)^\circ + a\beta + bE_T^N$	-2.15(1.07)	3.34(2.74)	-0.49(2.77)	0.68	-1.29(1.28)	2.74(3.26)	-1.18(3.31)	0.44
$\ln k_2 = (\ln k_2)^\circ + a\beta + b\alpha$	-2.20(0.79)	3.84(2.23)	-0.99(1.61)	0.76	-1.45(0.87)	3.25(2.45)	-1.56(1.77)	0.64
$\ln k_2 = (\ln k_2)^\circ + a\beta + b\pi^*$	-1.53(1.95)	3.81(2.73)	-1.21(2.96)	0.72	-0.28(2.22)	3.35(3.11)	-2.12(3.37)	0.54

<sup>a</sup> Values in parentheses are standard deviations.



**Fig. 4** Plot showing a correlation between the experimental rate constants  $(\ln k_2)$  for the reaction of (a) complex **1a** and (b) complex **1b** with MeI at 25 °C in different solvents and calculated rate constants based on Kamlet–Taft LSER fit;  $\ln k_2 = (\ln k_2)^\circ + a\epsilon_r + b\beta$  equation.



**Fig. 5** Plot of  $\Delta S^{\dagger}$  vs.  $\Delta H^{\dagger}$  for the oxidative addition of MeI with (a) complex **1a** and (b) complex **1b** in different solvents.

From the results presented in Table 3, it can be concluded that the dielectric constant of the solvent is the most important parameter in this system ( $R^2 = 0.80$  for  $\ln k_2$  versus  $\varepsilon_r$  plot). Acetone, with the highest dielectric constant, shows the largest value for  $k_2$ . The oxidative addition reaction of complex 1a with MeI is nearly 7 times faster in acetone than in benzene. This, of course, strongly supports the operation of the  $S_N$ 2-type mechanism in the reactions because in the latter mechanism, in which after each MeI attack a polar transition state is expected, the rate should be faster in a more polar acetone solvent than in benzene with a significantly lower dielectric constant. Solvents that are strong hydrogen bond donors (larger  $\beta$ ) accelerate the reaction. This effect becomes evident when comparing the pair [bmim][bta]/[bmim][BF<sub>4</sub>]. For both ionic liquids the values of  $\varepsilon_r, E_T^N, \alpha$  and  $\pi^*$  barely differ but the higher value of  $\beta$  for [bmim][BF<sub>4</sub>] leads to a significant increase (nearly 2 times) of the  $k_2$  value. It should be noted that the reactions in the ionic liquid showed the same behavior as that found for other more conventional solvents as a function of the experimental variables. The trend in the values of  $k_2$  clearly indicates that the ionic liquid behaves like acetone and that no drastic acceleration or deceleration of the oxidative addition of MeI can be observed.

#### Enthalpy-entropy compensation effect

Table 1 presents the values obtained for the activation enthalpy  $(\Delta H^{\ddagger})$  and entropy  $(\Delta S^{\ddagger})$  in all the solvents. The  $\Delta H^{\ddagger}/\Delta S^{\ddagger}$  compensation plots for reactions of complexes **1a** and **1b** with MeI in different solvents are shown in Fig. 5. For each complex a good straight line is obtained and although the number of the points is not ample, as it is it may be taken as an evidence for operation of a common (associative, second-order) mechanism in this series of reactions.<sup>16</sup>

#### Conclusions

The oxidative addition reaction of diarylplatinum(II) complexes with MeI was chosen as an experimental system for investigating the effect of ionic liquids (as solvent) on the reaction mechanism. We have observed that the studied reactions proceeded according to an  $S_N 2$  mechanism in ionic liquids. The results here show that ionic liquids are solvents with a range of different properties that can be described using the Kamlet–Taft approach in the studied reactions. The application of the Kamlet–Taft approach in LSERs showed that there is no any significant "ionic liquid effect", since the same correlation was obtained considering all solvents, including common organic solvents (benzene and acetone) and ionic liquids and no strong acceleration or deceleration of the oxidative addition of MeI can be observed. The determined thermodynamic parameters also indicate that mechanism of the reactions is the same in all the related solvents.

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