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

S. Masoud Nabavizadeh,* Hajar Sepehrpour, Hamid R. Shahsavari and Mehdi Rashidi*

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The effects of several imidazolium-based ionic liquids on the rate of the oxidative addition reactions of organoplatinum(II) complexes [Pt(p-MeC₆H₄)₂(NN)], in which NN is either 1,10-phenanthroline (phen), **1a**, or 4,4'-di-*tert*-butyl-2,2'-bipyridine (^{*t*}Bu₂bpy), **1b**, with MeI to give the organoplatinum(IV) products [Pt(p-MeC₆H₄)₂MeI(NN)] were investigated as a function of the ionic liquid (as solvent) using UV-vis spectroscopy techniques. The obtained rate constants and activation parameters showed a dependence on the nature of the anionic component of the ionic liquid as related to the polarity/polarizability parameter, π^* , of the ionic liquids.

Introduction

The wide applicability of ionic liquids (ILs) as useful and environmentally friendly solvents has recently led to great interest and research on this subject. Thus, due to their unique properties, ionic liquids are being investigated as suitable alternatives for volatile organic solvents. They are good solvents for a wide range of applications, such as organic synthesis, transition metal two-phase catalysis, biocatalysis and nanotechnology.^{1–9}

Oxidative addition reactions are one of the most fundamental processes in transition metal chemistry, and play an important role in many synthetic and catalytic reactions, particularly in organic synthesis.¹⁰ Square planar platinum(II) complexes can easily take part in this kind of reactions and are of interest for several reasons, for example as products or intermediates in catalytic reactions.¹¹ As such, reactivity of square planar platinum(II) complexes containing bidentate nitrogen donor ligands (NN), such as 2,2'-bipyridine and 1,10-phenanthroline, in oxidative addition reactions with alkyl halides have been studied with regards to the effect of NN ligands, the electronic effect of different substituents, and the solvent polarity effects.^{12,13} Solvent effect on the rates of oxidative addition reactions of MeI with $[PtR_2(NN)]$, in which R could be alkyl or aryl, indicate the involvement of a polar transition, such as is expected for the S_N2 mechanism,¹⁴ given the platinum atom acts as a nucleophilic centre during the process. Therefore it is clear that solvent should play an important role in the rate of oxidative addition reactions. Besides, we have recently investigated the kinetic and mechanism

of these reactions using [bmim][Tf₂N] ionic liquid as solvent and found that the reaction rates in different solvents followed the order acetone > [bmim][Tf₂N] > benzene,¹⁵ although no attempts were made to investigate the influence of the nature of the anionic component of the ionic liquid solvents on the related reaction rates. Kinetics and mechanism of many reactions including substitution reactions using ionic liquids as solvent have been studied,¹⁶ even though only two oxidative addition reactions involving organometallic complexes have been reported in the literature.^{15,17}

In this work the oxidative addition reactions of organoplatinum(II) complexes $[Pt(p-MeC_6H_4)_2(NN)]$ (1a: NN = 1,10-phenanthroline (phen); 1b: NN = 4,4'-di-*tert*-butyl-2,2'bipyridine ('Bu₂bpy)) with MeI in different IL solvents were carried out in attempts to further study the effects of the nature of the ionic liquid on related reaction rates; the solvents used were ionic liquids containing 1-butyl-3-methylimidazolium (bmim) as cation and bis(trifluoromethanesulfonyl)imide ([Tf₂N]⁻), tetrafluoroborate ([BF₄]⁻), dicyanimide ([(CN)₂N]⁻), trifluoroacetate ([CF₃CO₂]⁻) or hexafluorophosphate ([PF₆]⁻) as anions (see Fig. 1).

Experimental

Ionic liquids, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim][Tf₂N]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), 1-butyl-3-methylimidazolium dicyanamide ([bmim][(CN)₂N]), 1-butyl-3-methylimidazolium trifluoroacetate ([bmim][CF₃CO₂]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) used as solvent for kinetic studies were purchased from Solvent Innovation. The commercially available ionic liquids were analyzed for halide ions and water content. The halide ions and water content of these ionic liquids were determined and found to be

Department of Chemistry, College of Sciences, Shiraz University, Shiraz, 71454, Iran. E-mail: nabavi@chem.susc.ac.ir, rashidi@chem.susc.ac.ir; Fax: +98 711 228 6008; Tel: +98 711 228 4822

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less than 30 and 80 ppm, respectively, which had no effect on

the kinetic measurements. The Pt(II) complexes [Pt(p-MeC₆H₄)₂(phen)] (phen = 1,10phenanthroline), **1a**,¹⁸ and [Pt(p-MeC₆H₄)₂('Bu₂bpy)] ('Bu₂bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine), **1b**,¹² were prepared as reported in the literature. The related Pt(IV) compounds [Pt(p-MeC₆H₄)₂-MeI(NN)], **2**, obtained from reactions of the appropriate platinum(II) complexes with CH₃I in ionic liquid media followed by simple isolation of the products, were characterized by comparing their ¹H NMR spectra with those of the authentic samples.^{12,19}

Kinetic measurements

Kinetic studies were carried out by using a Perkin-Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. The oxidative addition reactions were followed on UV-vis by monitoring the change in absorbance at the indicated wavelength. Stock solutions of the Pt(π) complexes (*ca.* 3 × 10⁻⁴ mol L⁻¹) were prepared in ionic liquids for the kinetic studies. Experiments were performed at the appropriate temperatures by mixing required volumes of the thermostatted MeI and transferring the mixture to the absorption cell (with 1.0 cm length). The concentration range used for MeI was 0.01–0.13 M. The solution of the platinum(II) complexes 1 in ionic liquids turned colourless on addition of MeI. The kinetic measurements have been done 3 times or more (in some cases). The influence of the addition of MeI on the spectra of $[(Pt(p-MeC_6H_4)_2(NN)]$ is shown in the Fig. 2. The decrease in absorbance of the reaction mixture was recorded automatically at the indicated wavelength as a function of time. All kinetic measurements were monitored under pseudo-first-order conditions with excess MeI with respect to the concentration of the complexes 1 in the specified solution.

Calculations

All kinetic mathematical fits were done utilizing the fitting program KaleidaGraph.²⁰ Observed pseudo-first-order rate constants, k_{obs} , were obtained from the fitting of kinetic data to the first-order equation (see Table 1S, ESI†). The k_{obs} values were reproducible to within ±4%. The determined pseudo-first-order rate constants were converted to second order rate constants, k_2 , by determining the slope of the linear plots of k_{obs} against the concentration of the incoming MeI reagent. Zero intercepts under all conditions imply a firstorder dependence of the rate on the concentration of MeI, $k_{obs} = k_2$ [MeI]. The activation parameters ΔH^{\ddagger} (activation enthalpy) and ΔS^{\ddagger} (activation entropy) for the oxidative addition reactions were determined from least-squares fits of the reaction rate constants *versus* temperature data according to the Eyring equation (see Fig. 1S (ESI†) and Table 1).

Results and discussion

The complexes [Pt(*p*-MeC₆H₄)₂(NN)], in which NN is either 1,10-phenanthroline (phen), **1a**, or 4,4'-di-*tert*-butyl-2,2'-bipyridine ('Bu₂bpy), **1b**, were reacted with MeI in different ionic liquids solvents to give platinum(IV) complexes [Pt(*p*-MeC₆H₄)₂-MeI(NN)], **2** (Scheme 1). The resulting complexes were characterized by comparing their NMR spectra with those of the authentic samples.^{12,19}

Kinetics of oxidative addition reactions of the complexes $[Pt(p-MeC_6H_4)_2(NN)]$, **1**, with MeI in five different ionic liquid solvents, all containing the same cation but differing in anionic components, were examined spectrophotometrically with the



Fig. 2 Spectra of a reaction mixture of (a) $[Pt(p-MeC_6H_4)_2(^{t}Bu_2bpy)]$, **1b**, and MeI in $[bmim][PF_6]$ and (b) $[Pt(p-MeC_6H_4)_2(phen)]$, **1a**, and MeI in $[bmim][(CN)_2N]$ at time intervals of 45 s at 25 °C. The arrows indicate decrease band intensities as the reactions proceed.

Table 1 Second-order rate constants and activation parameters for reaction of $[Pt(p-MeC_6H_4)_2(NN)]$ (NN = phen (1a) or 'Bu₂bpy (1b)) with MeI in different ionic liquids

				k_2^c/L m	$ol^{-1} s^{-1} at$	different t				
Complex	Solvent	λ^d/nm	$\epsilon^{e}/M^{-1} \mathrm{~cm}^{-1}$	15 °C	20 °C	25 °C	30 °C	40 °C	$\Delta H^{\ddagger}/\mathrm{kJ}~\mathrm{mol}^{-1}$	$\Delta S^{\ddagger}/J \ \mathrm{K}^{-1} \ \mathrm{mol}^{-1}$
1a 1a	$[\text{bmim}][\text{Tf}_2\text{N}]^a$	433	2166	0.10	0.14	0.21	0.27	0.42	41.6 ± 0.4	-119 ± 1
1a 1a	$[\text{bmim}][\text{PF}_6]$	428	2620	0.30	0.40	0.46	0.66	1.13	35.0 ± 1.7 35.5 ± 1.0	-139 ± 6 -133 ± 3
1a 1a	[bmim][(CN) ₂ N] [bmim][CF ₃ CO ₂]	432 433	1670 3330	0.39 0.22	0.16^{b}	0.70 0.42	0.90	1.41 0.91	$36.0 \pm 0.2 \\ 39.7 \pm 0.8$	-129 ± 1 -121 ± 3
1b 1b	$[bmim][Tf_2N]^a$ $[bmim][BF_4]^a$	418 417	3100 3120	0.14 0.29	0.09^{b}	0.28 0.54	0.36 0.64	0.52	42.5 ± 0.5 37.9 ± 1.9	-114 ± 2 -123 ± 6
1b	$[\text{bmim}][\text{PF}_6]$	416	2570	0.20		0.40	0.49	0.81	39.5 ± 0.5	-122 ± 2
1b 1b	$[bmim][(CIN)_2IN]$ $[bmim][CF_3CO_2]$	421 418	2670	0.35		0.56	0.74	1.21	35.1 ± 0.2 35.2 ± 0.1	-132 ± 1 -133 ± 1

^{*a*} From ref. 15. ^{*b*} At 10 °C. ^{*c*} Estimated errors in k_2 values are ±4%. ^{*d*} λ specifies the wavelength used for fitting data from kinetics studies. ^{*e*} Extinction coefficient.



Scheme 1 The reactions studied in the present work.

aim of studying solvent dependence of the reaction. The linearity of plots of k_{obs} versus [MeI] comply with the reactions being first order with respect to MeI, with the slope of each plot showing the second-order rate constant of the related reaction (k_2) , as are reported in Table 1.

The reaction rate increases with the rise in the temperature as expected from the Eyring equation. Activation parameters, enthalpy (ΔH^{\ddagger}) and entropy (ΔS^{\ddagger}) of activation, were calculated from Eyring plots (Fig. 1S⁺) and are collected in Table 1. The negative values of ΔS^{\ddagger} support that the reactions in ionic liquids proceed through an associative mechanism, typical of oxidative addition reactions by a common S_N2 mechanism involving nucleophilic attack of the metallic centre at the methyl group of MeI and formation of the cationic intermediate $[(p-MeC_6H_4)_2 (NN)PtMe]^{+}I^{-}$; the formation of this cationic intermediate is the rate-determining step. The $\Delta S^{\ddagger}/\Delta H^{\ddagger}$ compensation plot (Fig. 3) suggests the operation of similar mechanism for the oxidative addition reactions of $[Pt(p-MeC_6H_4)_2(NN)]$, 1, with MeI in all the studied ionic liquid solvents. These results are similar to those reported for the same reactions involving addition of different alkyl halides to organoplatinum(II) complexes in organic solvents, such as acetone and benzene, for which the operation of S_N2 mechanism have been well established.^{12,13,19,21}

The anion effect on the kinetics

Oxidative addition reactions of organoplatinum(π) complexes [Pt(*p*-MeC₆H₄)₂(NN)], **1**, with MeI were examined in five ionic

liquid solvents all having $[bmim]^+$ cationic components but with variable anions differing in size, symmetry, and coordination ability. The related reactivities of complexes **1a** and **1b** as a function of the nature of ionic liquids are shown in Fig. 4. The data appearing in Tables 1 and 2 and Fig. 4 show that the reactivity increases along the series as follows:

For complex 1a:

$$[bmim][Tf_2N] < [bmim][CF_3CO_2] < [bmim][PF_6] < [bmim][BF_4] < [bmim][(CN)_2N].$$

For complex 1b:

$$[\text{bmim}][\text{Tf}_2\text{N}] < [\text{bmim}][\text{PF}_6] < [\text{bmim}][\text{BF}_4]$$

< $[\text{bmim}][(\text{CN})_2\text{N}] \text{T} \approx [\text{bmim}][\text{CF}_3\text{CO}_2].$

The detected orders are completely different from those determined on the basis of solvent parameter α values (the hydrogen bond donation (HBD) ability; $\alpha = 0.55$, 0.52, 0.54, 0.44 and 0.43 for [bmim][Tf₂N], [bmim][BF₄], [bmim][PF₆], [bmim][(CN)₂N] and [bmim][CF₃CO₂], respectively). Also the observed reactivity trends could not be explained only on the basis of parameters such as dielectric constant (ϵ_r) and polarity parameter, E_T^N ($\epsilon_r = 11.6$, 11.7 and 11.4 for [bmim][Tf₂N], [bmim][BF₄] and [bmim][PF₆], respectively; $E_T^N = 0.642$, 0.673, 0.667 and 0.620 for [bmim][Tf₂N], [bmim][BF₄], [bmim][PF₆] and [bmim][CF₃CO₂], respectively). Likewise, the reactivity trends are different from



Fig. 3 $\Delta S^{\dagger} vs. \Delta H^{\dagger}$ compensation plot for the oxidative addition reactions of MeI with complexes **1a** and **1b** in different ionic liquids.



Fig. 4 Plot of second-order rate constant values (k_2) for oxidative addition of MeI to complexes **1a** and **1b** in ionic liquid solvents at 25 °C.

Table 2 The property parameters of solvents and the second-order rate constants $(k_2/L \text{ mol}^{-1} \text{ s}^{-1})$ for the reactions of $[Pt(p-MeC_6H_4)_2(NN)]$, **1**, with MeI in different ionic liquid solvents at 25 °C

Solvent	$\varepsilon_{\mathrm{r}}^{a,b}$	$E_{\mathrm{T}}{}^{\mathrm{N}b,c}$	$\alpha^{d,e}$	$\beta^{d,e}$	$\pi^{*d,f}$	$k_2 \\ (NN = phen; 1a)$	k_2 (NN = 'Bu ₂ bpy; 1b)
[bmim][Tf ₂ N]	11.6	0.642	0.55	0.42	0.984	0.21	0.28
[bmim][BF ₄]	11.7	0.673	0.52	0.55	1.047	0.61	0.54
[bmim][PF ₆]	11.4	0.667	0.54	0.44	1.032	0.46	0.40
[bmim][(CN) ₂ N]			0.44	0.64	1.052	0.70	0.56
[bmim][CF ₃ CO ₂]		0.620	0.43	0.74		0.42	0.57
^a Dielectric constant. ^b From ref. 22. ^c Polarity. ^d Kamlet-Taft para-							
meters. ^e Data from ref. 23. ^f Data from ref. 24.							

those obtained considering the β parameter (the hydrogen bond acceptance (HBA) or electron pair donation ability; $\beta =$ 0.42, 0.55, 0.44, 0.64 and 0.74 for [bmim][Tf₂N], [bmim][BF₄], [bmim][PF₆], [bmim][(CN)₂N] and [bmim][CF₃CO₂], respectively). Upon fixing the cation, the reaction seems to be favored by anions having a higher polarity/polarizability parameter, π^* ($\pi^* = 0.984$, 1.047, 1.032 and 1.052 for [bmim][Tf₂N], [bmim][BF₄], [bmim][PF₆], and [bmim][(CN)₂N], respectively). A good linear correlation between π^* and k_2 values for the oxidative addition reactions has been found according to equation $\ln k_2 = a + b\pi^*$ (see Fig. 5; a = -18.4 and b = 17.1 for complex 1a, and a =-11.3 and b = 10.1 for complex **1b**). Indeed reactivity decreases on going from $[BF_4^-]$ and $[PF_6^-]$ ILs up to $[Tf_2N^-]$ IL. A higher π^* value results in a stronger interaction with the cationic intermediate $[(p-MeC_6H_4)_2(NN)PtMe]^+$ by which it is stabilized. This means that a higher π^* value correlates with stabilization of the cationic intermediate and destabilization of the neutral reactants and products. There is a difference in the triflate salt position for complex 1b as compared with complex 1a, which may be a result of presence of tert-butyl group in complex 1b and stronger interaction of $CF_3CO_2^-$ anion with cationic intermediate. As shown in Table 2, it seems that the oxidative addition reaction of MeI with Pt(II) complexes is faster for ionic liquid solvent containing nonflourinated anion ([(CN)₂N]) than fluorinated one, although more detailed experiments will be needed to provide a full comparing.

Activation parameters

The oxidative addition reactions of Pt(II) complexes 1 with MeI in ionic liquid media were carried out at different temperatures going from 283 to 313 K and an excellent linear correlation of $\ln(k_2/T)$ versus 1/T was obtained in each case. As is indicated in Table 1, the calculated activation parameters span a narrow range and thus, the enthalpy and entropy values in ionic liquid solutions range from 33.0 kJ mol⁻¹ up to 42.5 kJ mol⁻¹, and from -114 J K⁻¹ mol⁻¹ up to -139 J K⁻¹ mol⁻¹, respectively. For [bmim][X] ILs, the changes in both enthalpy and entropy values can be rationalized on the grounds of different cation-anion interactions and, consequently, on the grounds of different IL anion ability to stabilize the cationic intermediate $[(p-MeC_6H_4)_2(NN)PtMe]^+$. An acceptable linear correlation of the enthalpy of activation versus the π^* value of ionic liquids for complex 1b (Fig. 6) confirms the influence on the activation barrier of the reaction and the higher the π^* value: lower related activation enthalpy in turn causes an increase in the rate of the reaction. The cationic intermediate is better stabilized by the anion of the IL as compared with the reactants and final products, and as the energy of the intermediate is reduced the activation barrier is decreased. Thus, the activation enthalpy can be readily correlated with the π^* value. The same behaviour has been observed



Fig. 5 Linear correlation of $\ln k_2$ for the reactions of complexes 1a and 1b with the π^* values of ionic liquids.



Fig. 6 Correlation of the enthalpy of activation (top) and the activation entropy (bottom) *versus* the π^* value.

for the activation entropy when it is plotted against the polarity parameter, π^* (Fig. 6). A similar linear correlation, although poor, was also observed using complex **1a** (Fig. 6).

Conclusion

The oxidative addition reaction of organoplatinum(II) complexes with MeI was chosen as a simple, single-step reaction (with no reverse, subsequent, or parallel reactions) for investigating the effect of the anionic part of the ionic liquids (as solvent) on the reaction rate. The results of the present work showed the reaction rates in different ILs were dependent on the nature of the anionic component of the IL. It is likely that the anionic component of the IL stabilizes the cationic intermediate Pt complex by interacting with it. By fixing the cation, the reaction seems to be favored by anions having a higher polarity/polarizability parameter, π^* . A good linear correlation between π^* and k_2 values for the oxidative addition reactions were found according to equation $\ln k_2 = a + b\pi^*$.

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