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Secondary Kinetic Deuterium Isotope Effects in the Reaction of MeI with Organoplatinum(II) Complexes

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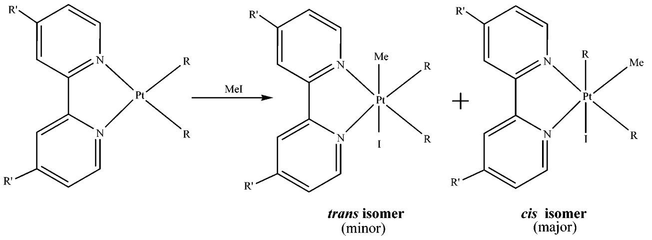
Secondary α-deuterium (α-D) kinetic isotope effects (KIEs) have been determined for the reactions of the (diimine)diarylplatinum(II) complexes [Pt(p-MeC$_6$H$_4$)$_2$(NN)] (NN = bipyridine (bpy), **1a**; NN = 4,4′-dimethyl-2,2′-bipyridine (Me$_2$bpy), **1b**; NN = 4,4′-di-*tert*-butyl-2,2′-bipyridine (^{t}Bu$_2$bpy), **1c**) with MeI in acetone solvent at different temperatures. Consistent with an S$_N$2-type mechanism, very small normal secondary deuterium isotope effects (k_H/k_D) values of 1.00−1.11 are obtained for the reactions studied. The trends in KIEs and activation parameter values are discussed in terms of recent experimental and theoretical investigations. The platinum(IV) products have been fully characterized using ^{1}H and ^{13}C NMR spectroscopy.

Introduction

There has been considerable effort to use equilibrium or kinetic isotope effects to study reactions.[1−5] In particular, secondary α-deuterium (α-D) kinetic isotope effects (KIEs) have been used to study Menschutkin-type reactions[6] and Stang et al.[7] have used KIEs to confirm an S$_N$2 type mechanism for the oxidative addition reaction of Vaska's compound, (Ph$_3$P)$_2$Ir(CO)-Cl, with MeI. The oxidative addition reaction of alkyl halides with transition-metal complexes is a key step in many industrially important catalytic processes.[8] Reactions using d^8 square-planar (diimine)organoplatinum(II) complexes have been extensively studied during the past three decades.[9−11] In these reactions, the electron-rich platinum center attacks alkyl halides usually by a classical S$_N$2 type mechanism. However, sometimes the reactions are proceeded by a radical mechanism. The concerted three-center mechanism is also a possibility, and although it has been proposed for some reactions, it has never been demonstrated by experimental evidence.[9] The last mechanism is usually proposed in the oxidative addition of C−H and C−C bonds, and also we have recently proposed it in the oxidative addition of some peroxides, including H$_2$O$_2$, to (diimine)diarylplatinum(II) complexes.[12]

Scheme 1



	R'	R		R'	R
1a	H	p-MeC$_6$H$_4$	**2a**	H	p-MeC$_6$H$_4$
1b	Me	p-MeC$_6$H$_4$	**2b**	Me	p-MeC$_6$H$_4$
1c	^{t}Bu	p-MeC$_6$H$_4$	**2c**	^{t}Bu	p-MeC$_6$H$_4$
1d	^{t}Bu	Me	**2d**	^{t}Bu	Me

In the present work, we have studied the kinetics of reactions of CH$_3$I/CD$_3$I with some (diimine)diarylplatinum(II) complexes[9,13] (Scheme 1); the KIE results have confirmed the operation of an S$_N$2 type mechanism in this important type of oxidative addition reaction. The complexes used were reacted at rates that could easily be monitored by UV−vis spectroscopy by conventional methods, and thus careful measurements were possible. The results are discussed in terms of recent theoretical and experimental studies. The platinum(IV) products have been fully characterized using ^{1}H and ^{13}C NMR spectroscopy.

Experimental Section

The ^{1}H and ^{13}C NMR spectra of the complexes were recorded as CDCl$_3$ solutions on a Bruker Avance DPX 250 MHz spectrometer, and TMS (0.00) was used as an external reference. All the chemical shifts and coupling constants are given in units of ppm and Hz, respectively. Kinetic studies were carried out by using a Perkin-Elmer Lambda 25 spectropho-

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tometer with temperature control using an EYELA NCB-3100 constant-temperature bath. The diimine ligand 4,4′-di-*tert*-butyl-2,2′-bipyridine (^{t}Bu$_2$bpy)[14] and the starting complex *cis*-[Pt(p-MeC$_6$H$_4$)$_2$(SMe$_2$)$_2$][15] were made by literature methods. The complex [PtMe$_2$(^{t}Bu$_2$bpy)] was prepared as reported.[16] ^{13}C{^{1}H} NMR: δ −17.5 (s, ^1J(PtC) = 801 Hz, MePt), 29.8 (s, terminal C atoms of ^{t}Bu groups), 35.4 (s, central C atoms of ^{t}Bu groups); aromatic C atoms of ^{t}Bu$_2$bpy ligand 146.5 (s, ^2J(PtC) = 34 Hz, C^6), 123.8 (s, ^3J(PtC) = 19 Hz, C^5), 156.3 (s, ^4J(PtC) = 9 Hz, C^4), 118.6 (s, ^3J(PtC) = 11 Hz, C^3), 160.7 (s, C^2).

[Pt(p-MeC$_6$H$_4$)$_2$(^{t}Bu$_2$bpy)] (1c). To a solution of *cis*-[Pt(p-MeC$_6$H$_4$)$_2$(SMe$_2$)$_2$] (500 mg, 1 mmol) in ether (100 mL) was added ^{t}Bu$_2$bpy (270 mg, 1 mmol). A red solution was formed. This was stirred for 30 min, and then the solvent was removed. The resulting red needles were washed with ether (2 × 2 mL) and dried under vacuum; yield 87%, mp 226 °C dec. Anal. Calcd for $C_{32}H_{38}N_2Pt$: C, 59.5; H, 5.9; N, 4.3. Found: C, 60.0; H, 6.2; N, 4.4. UV−vis (λ_{max}/nm): in acetone, 434, in benzene, 475 (shoulder 450); in n-hexane, 510 (shoulder 478). ^{13}C{^{1}H} NMR: δ 20.0 (s, Me groups on aryl ligands), 29.8 (s, terminal C atoms of ^{t}Bu groups), 35.2 (s, central C atoms of ^{t}Bu groups); aromatic C atoms of ^{t}Bu$_2$bpy ligand 149.5 (s, ^2J(PtC) = 40 Hz, C^6), 123.6 (s, ^3J(PtC) = 20 Hz, C^5), 155.8 (s, C^4), 118.1(s, C^3), 161.5 (s, C^2); aromatic C atoms of p-tolyl ligands 140.9 (s, ^1J(PtC) = 1070 Hz, C atoms directly attached to platinum), 127.6 (s, ^2J(PtC) = 83 Hz, 2 C^o), 137.6 (s, ^3J(PtC) = 35 Hz, 2 C^m), 135.7(s, ^4J(PtC) = 38 Hz, C^p). ^{1}H NMR: δ 2.26 (s, 6H, Me groups on p-tolyl ligands), 1.41(s, 18 H, ^{t}Bu); aromatic protons of ^{t}Bu$_2$bpy ligand 8.55 (d, ^3J(PtH) = 23.5 Hz, ^3J(H^{5}H^6) = 5.8 Hz, 2H, H^6), 7.27 (d, ^3J(H^{6}H^5) = 5.0 Hz, 2H, H^5), 7.97 (s, 2H, H^3); aromatic protons of p-tolyl ligands 7.38 (d, ^3J(PtH) = 68.8 Hz, ^3J(H^{m}H^o) = 7.5 Hz, 4H, H^o), 6.88 (d, ^3J(H^{o}H^m) = 7.0 Hz, 4H, H^m).

[Pt(p-MeC$_6$H$_4$)$_2$(Me$_2$bpy)] (1b). This was made similarly using Me$_2$bpy in CH$_2$Cl$_2$, and the final product was washed with n-hexane; yield 90%, mp 225 °C dec. Anal. Calcd for $C_{26}H_{26}N_2Pt$: C, 55.6; H, 4.6; N, 5.0. Found: C, 55.7; H, 4.7; N, 4.9. UV−vis (λ_{max}/nm): in acetone, 435. ^{1}H NMR: δ 2.23 (s, 6H, Me groups on p-tolyl ligands), 2.41(s, 6H, Me groups on Me$_2$bpy); aromatic protons of Me$_2$bpy ligand 8.51 (d, ^3J(PtH) = 18.4 Hz, ^3J(H^{5}H^6) = 5.5 Hz, 2H, H^6), 7.19 (d, ^3J(H^{6}H^5) = 5.5 Hz, 2H, H^5), 7.86 (s, 2H, H^3); aromatic protons of p-tolyl ligands 7.37 (d, ^3J(PtH) = 62.5 Hz, ^3J(H^{m}H^o) = 6.7 Hz, 4H, H^o), 6.88 (d, ^3J(H^{o}H^m) = 6.7 Hz, 4H, H^m).

[PtIMe$_3$(^{t}Bu$_2$bpy)] (2d). An excess of MeI (1 mL) was added to a solution of [PtMe$_2$(^{t}Bu$_2$bpy)] (100 mg) in CH$_2$Cl$_2$ (15 mL). The reaction mixture was stirred for 30 min, after which time an orange-yellow solution had developed. The solvent was removed at reduced pressure, leaving a yellow solid. This was washed with n-hexane (4 mL) and dried under vacuum; yield 95%, mp 236 °C dec. Anal. Calcd for $C_{21}H_{33}N_2IPt$: C, 39.7; H, 5.2; N, 4.4. Found: C, 40.0; H, 5.4; N, 4.3. ^{13}C{^{1}H} NMR: δ −5.3 (s, ^1J(PtC) = 666 Hz, Me groups trans to N), 9.2 (s, ^1J(PtC) = 682 Hz, Me group trans to I), 31.7 (s, terminal C atoms of ^{t}Bu groups), 36.7 (s, central C atoms of ^{t}Bu groups); aromatic C atoms of ^{t}Bu$_2$bpy ligands 148.1 (s, ^2J(PtC) = 16 Hz, C^6), 125.2 (s, ^3J(PtC) = 14 Hz, C^5), 155.9 (s, C^4), 121.2 (s, ^3J(PtC) = 8 Hz, C^3), 164.4 (s, C^2). ^{1}H NMR: δ 0.55 (s, ^2J(PtH) = 73.5 Hz, 3H, Me group trans to I), 1.45 (s, ^2J(PtH) = 70.3 Hz, 6H, Me groups trans to N), 1.38 (s, 18 H, ^{t}Bu); aromatic protons of ^{t}Bu$_2$bpy ligand 8.80 (d, ^3J(PtH) = 13.4 Hz, ^3J(H^{5}H^6) = 6.0 Hz, 2H, H^6), 7.52 (d, ^3J(H^{6}H^5) = 5.7 Hz, 2H, H^5), 8.05 (s, 2H, H^3).

The following complexes were made similarly using the appropriate platinum(II) complex and CH$_3$I or CD$_3$I.

[PtIMe(p-MeC$_6$H$_4$)$_2$(^{t}Bu$_2$bpy)] (2c). Yield: 90%. Mp: 188 °C dec. Anal. Calcd for $C_{33}H_{41}N_2IPt$: C, 50.3; H, 5.3; N, 3.6. Found: C, 51.0; H, 5.5; N, 3.8. ^{13}C{^{1}H} NMR (trans isomer): δ 20.2 (s, ^1J(PtC) = 670 Hz, MePt), 32.0 (s, terminal C atoms of ^{t}Bu groups), 37.1 (s, central C atoms of ^{t}Bu groups); aromatic C atoms of ^{t}Bu$_2$bpy ligand 151.0 (s, ^2J(PtC) = 16 Hz, C^6), 125.9 (s, C^5), 156.8 (s, C^4), 121.6 (s, C^3), 165.2 (s, C^2); aromatic C atoms of p-tolyl ligands 134.0 (s, ^1J(PtC) = 716 Hz, C atoms directly attached to platinum), 133.3 (s, C^o atoms), 128.3−131.0 (C^m and C^p atoms). ^{13}C{^{1}H} NMR (cis isomer): δ 5.2 (s, ^1J(PtC) = 657 Hz, MePt), 32.0 (s, terminal C atoms of ^{t}Bu groups), 37.0 (s, central C atoms of ^{t}Bu groups); aromatic C atoms of ^{t}Bu$_2$bpy ligand 148.4 (s, ^2J(PtC) = 13 Hz, C^6), 149.9 (s, ^2J(PtC) = 14 Hz, C^6), 125.5 and 125.6 (s, C^5), 156.2 (s, C^4), 121.7 and 121.9 (s, C^3), 165.2 (s, C^2); aromatic C atoms of p-tolyl ligands 134.5 and 136.0 (s, ^1J(PtC) obscured, C atoms directly attached to platinum), 133.3 (s, C^o atoms), 128.3−131.0 (C^m and C^p atoms). ^{1}H NMR (trans isomer): δ 1.3 (s, ^2J(PtH) obscured, 3H, MePt), 1.38 (s, 18 H, ^{t}Bu); aromatic protons of ^{t}Bu$_2$bpy ligand 8.85 (d, ^3J(PtH) = 12.4 Hz, ^3J(H^{5}H^6) = 6.0 Hz, 2H, H^6), 6.7 (H^5), 8.09 (s, 2H, H^3), 2.22 (s, 6H, Me groups on p-tolyl ligands); aromatic protons of p-tolyl ligands 7.2−7.6 (4H, H^o), 6.2−6.6 (4H, H^m). ^{1}H NMR (cis isomer): δ 2.06 (s, ^2J(PtH) = 71.1 Hz, 3H, MePt), 1.34 (s, 9 H, ^{t}Bu), 1.37 (s, 9 H, ^{t}Bu); aromatic protons of ^{t}Bu$_2$bpy ligand 8.98 (d, ^3J(PtH) = 11.6 Hz, ^3J(H^{5}H^6) = 5.9 Hz, 2H, H^6), 6.7 (H^5), 8.02 and 8.04 (s, 2H, H^3), 2.23 (s, 6H, Me groups on p-tolyl ligands); aromatic protons of p-tolyl ligands 7.2−7.6 (4H, H^o), 6.2−6.6 (4H, H^m).

[PtI(CD$_3$)(p-MeC$_6$H$_4$)$_2$(^{t}Bu$_2$bpy)]. This compound had ^{1}H NMR data similar to data obtained for **2c**, except for MePt peaks that were missed.

[PtIMe(p-MeC$_6$H$_4$)$_2$(Me$_2$bpy)] (2b). Yield: 78%. Mp: 190 °C dec. Anal. Calcd for $C_{27}H_{29}N_2IPt$: C, 46.1; H, 4.2; N, 4.0. Found: C, 45.3; H, 4.3; N, 4.1. ^{1}H NMR (trans isomer): δ 1.89 (s, ^2J(PtH) = 69.7, 3H, MePt), 2.55 (s, 6H, Me groups on Me$_2$bpy ligand); aromatic protons of Me$_2$bpy ligand 8.87 (d, ^3J(PtH) = 13.0 Hz, ^3J(H^{5}H^6) = 5.8 Hz, 2H, H^6), 6.87 (H^5), 8.14 (s, 2H, H^3), 2.32 (s, 6H, Me groups on p-tolyl ligands); aromatic protons of p-tolyl ligands 7.28−7.5 (4H, H^o), 6.28−6.7 (4H, H^m). ^{1}H NMR (cis isomer): δ 1.45 (s, ^2J(PtH) = 70.9 Hz, 3H, MePt), 2.21, 2.15 (s, 6H, Me groups on Me$_2$bpy ligand); aromatic protons of Me$_2$bpy ligand, 9 (d, ^3J(PtH) = 11.1 Hz, ^3J(H^{5}H^6) = 5.4 Hz, 2H, H^6), 6.89 (H^5), 8.04 and 8.06 (s, 2H, H^3), 2.33 (s, 6H, Me groups on p-tolyl ligands); aromatic protons of p-tolyl ligands 7.28−7.5 (4H, H^o), 6.28−6.7 (4H, H^m).

[PtI(CD$_3$)(p-MeC$_6$H$_4$)$_2$(Me$_2$bpy)]. This compound had ^{1}H NMR data similar to data obtained for **2b**, except for MePt peaks that were missed.

Kinetic Studies of the Reaction of [Pt(p-MeC$_6$H$_4$)$_2$(Me$_2$bpy)] with MeI. A solution of [Pt(p-MeC$_6$H$_4$)$_2$(Me$_2$bpy)] (**1b**) in acetone (3 mL, 2.64 × 10^{-4} M) in a cuvette was thermostated at 25 °C, and a known excess of MeI was added using a syringe. After rapid stirring, the absorbance at λ 435 nm was collected with time (Figures 1 and 2). 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 (eq 1). A plot of k_{obs} versus [MeI] was linear (Figure 3), and the slope gave the second-order rate constant. The same method was used at other temperatures (see Table 1), and activation parameters were obtained from the Eyring equation (eq 2 and Figure 4).

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_0 - \mathrm{Abs}_\infty)\exp(-k_{\mathrm{obs}}t) \qquad (1)$$

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

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Similar methods were used to study the other reactions at the corresponding λ_{max} values, and the data are collected in Table 1.

Results and Discussion

Synthesis and Characterization of the Complexes. The (*p*-tolyl)platinum(II) precursors [Pt(*p*-$MeC_6H_4)_2$(NN)] (NN = bipyridine (bpy), **1a**; NN = 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), **1b**; NN = 4,4′-di-*tert*-butyl-2,2′-bipyridine (^{t}Bu_2bpy), **1c**) were made by the reaction of *cis*-[Pt(*p*-$MeC_6H_4)_2(SMe_2)_2$] with an equimolar amount of the corresponding NN, by displacement of SMe_2 ligands. As shown in Scheme 1, the platinum(II) complexes **1** reacted cleanly with MeI to give the organoplatinum(IV) complexes [PtIMeR_2(NN)] (**2**), in each case as an approximately 2:1 mixture of cis and trans isomers which could not be separated. The complexes were fully characterized by NMR spectroscopy. The analogous methylplatinum(II) complex **1d** and the corresponding platinum(IV) complex **2d** were made similarly, and their more straightforward NMR results were used to ascertain the assignments for the aryl analogues. Full data are collected in the Experimental Section. The platinum(II) and platinum(IV) complexes with ^{t}Bu_2bpy as ligand show characteristic ^{1}H NMR signals which are based on that of free ^{t}Bu_2bpy and that of the dimethyl complexes **1d** and **2d**. Particularly useful are H^6 protons, which are shifted downfield upon coordination and are coupled to platinum with a typical value of ^3J(PtH) = 23.5 Hz for the platinum(II) complex [Pt(*p*-$MeC_6H_4)_2$(^{t}Bu_2bpy)] (**1c**), which as expected is considerably reduced in the corresponding platinum(IV) complex [PtIMe(*p*-$MeC_6H_4)_2$(^{t}Bu_2bpy)] (**2c**) (^3J(PtH) = 11.6 Hz in the cis isomer and ^3J(PtH) = 12.4 Hz in the trans isomer). Integration of these peaks is used to estimate the isomer ratios. The remaining signals in the aromatic region are assigned to H^m and H^o protons of *p*-tolyl ligands. Similarly the other diimine complexes were characterized. The ^{t}Bu_2bpy complexes were more soluble and gave good ^{13}C NMR spectra. In particular, the signal for aryl carbon directly attached to platinum in the platinum(II) complex **1c** gave a PtC coupling value of ^1J(PtC) = 1070 Hz, which appeared further upfield with a considerably reduced coupling value of ^1J(PtC) = 716 Hz in the platinum(IV) complex **2c**. Similarly, the ^2J(PtC) value for the C^6 of the ^{t}Bu_2bpy ligand was ^2J(PtC) = 40 Hz in the platinum(II) complex **1c**, which was reduced to ^2J(PtC) = 16 Hz in the platinum(IV) complex **2c**.

Kinetic Study. The kinetics of oxidative addition of MeI or CD_3I to [Pt(*p*-$MeC_6H_4)_2$(^{t}Bu_2bpy)] (**1c**) in acetone were studied by using UV−vis spectroscopy. In each case, excess halide reagent was used and the disappearance of the MLCT band at λ = 435 nm was used to monitor the reaction. For minimization of errors, the rates of addition of MeI and CD_3I were measured in parallel with the identical stock solution of the platinum(II) complex. The reactions followed good first-order kinetics (Figures 1 and 2). Graphs of these first-order rate constants against the concentration of the halide gave good straight-line plots passing through the origin, showing a first-order dependence of the rate on the concentration of the halide (Figure 3). Thus, the overall second-order rate constants were determined. The activation parameters were also determined from measurement at different temperatures (Figure 4), and the data are given in Table 1. These reactions followed good second-order kinetics, first order in both platinum(II) and halide reagent, with remarkable reproducibility (±2%), and the rates were not affected by the addition of *p*-benzoquinone as radical scavenger. The rates of the reaction with MeI in benzene at different temperatures were slower than the rates of similar reactions in acetone by a factor of around 7. The kinetics of other platinum(II) complexes were studied similarly, and the data are collected in Table 1. The reaction of MeI with the methyl analogue [PtMe_2(^{t}Bu_2bpy)] (**1d**) was very fast and could not be measured easily. These observations suggest an S_N2 mechanism of oxidative addition of methyl iodide to the platinum(II) complex.[17] Also, the large negative values of $\Delta S^‡$ are typical of oxidative addition by a common S_N2 mechanism which involves

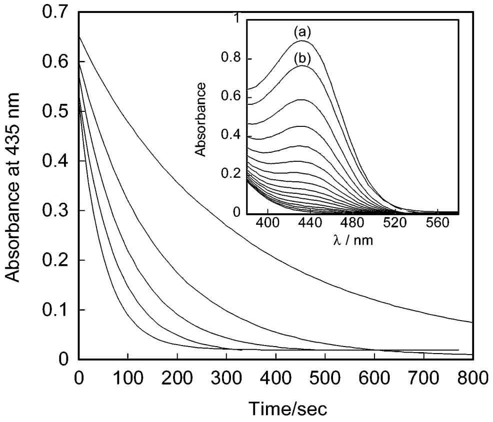

Figure 1. Absorbance−time curves for the reaction of [Pt(*p*-$MeC_6H_4)_2(Me_2$bpy)] with MeI (2.65−15.9 mM with [MeI] increases reading downward) in acetone at 25 °C. The inset shows the changes in the UV−vis spectrum during the reaction of [Pt(*p*-$MeC_6H_4)_2$(^{t}Bu_2bpy)] (2.64×10^{-4} M) and MeI (15.9 mM) in acetone at T = 20 °C: (a) initial spectrum (before adding MeI); (b) spectrum at t = 0; successive spectra recorded at intervals of 16 s.

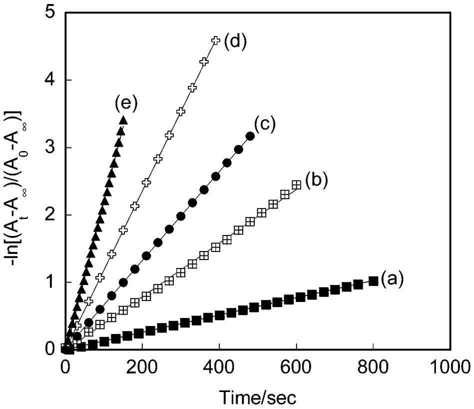

Figure 2. First-order plots for the reaction of [Pt(*p*-$MeC_6H_4)_2$(NN)] with methyl iodide at different temperatures in acetone: (a) CD_3I (2.65 mM), T = 10 °C, NN = Me_2bpy; (b) MeI (5.3 mM), T = 10 °C, NN = ^{t}Bu_2bpy; (c) CD_3I (7.95 mM), T = 25 °C; NN = bpy; (d) MeI (10.6 mM), T = 25 °C, NN = ^{t}Bu_2bpy; (e) CD_3I (13.25 mM), T = 25 °C, NN = ^{t}Bu_2bpy.

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Table 1. Second-Order Rate Constants and Activation Parameters[a] for Reaction of [Pt(p-MeC$_6$H$_4$)$_2$(NN)] (1) with MeI and CD$_3$I in Acetone (or Benzene)[b]

			k_2/L mol^{-1} s^{-1}						
compd no.	NN	reagent	5 °C	10 °C	15 °C	25 °C	k_H/k_D (25 °C)	$\Delta H^{\ddagger c}$/ kJ mol^{-1}	$\Delta S^{\ddagger c}$/ J K^{-1} mol^{-1}
1a	bpy	MeI	0.21 ± 0.01	0.28 ± 0.01	0.37 ± 0.02	0.62 ± 0.01	1.03 ± 0.02	34.9 ± 0.4	−132 ± 2
1a	bpy	CD$_3$I	0.21 ± 0.02	0.27 ± 0.01	0.36 ± 0.04	0.60 ± 0.01		34.1 ± 0.7	−135 ± 2
1b	Me$_2$bpy	MeI	0.43 ± 0.01	0.57 ± 0.02	0.77 ± 0.01	1.29 ± 0.01	1.04 ± 0.03	35.6 ± 0.3	−123 ± 1
1b	Me$_2$bpy	CD$_3$I	0.42 ± 0.04	0.57 ± 0.01	0.76 ± 0.01	1.24 ± 0.03		34.8 ± 0.3	−126 ± 2
1c[d]	^{t}Bu$_2$bpy	MeI		0.64 ± 0.03	0.84 ± 0.02	1.43 ± 0.05	1.11 ± 0.05	35.3 ± 0.4	−123 ± 1
				(0.10 ± 0.01)	(0.12 ± 0.02)	(0.19 ± 0.03)		(29.2 ± 0.8)	(−161 ± 3)
1c	^{t}Bu$_2$bpy	CD$_3$I	0.44 ± 0.02	0.60 ± 0.02	0.77 ± 0.03	1.30 ± 0.04		34.7 ± 0.4	−126 ± 1

[a] Values given on the basis of 95% confidence limits from least-squares regression analysis. [b] Values in parentheses are in benzene. [c] Obtained from the Eyring equation. The errors were computed from the Girolami formula.[18] [d] The values for k_2/L mol^{-1} s^{-1}: at 20 °C, 1.08 ± 0.04 in acetone (0.16 ± 0.02 in benzene); at 30 °C, 1.84 ± 0.03 in acetone (0.23 ± 0.07 in benzene).

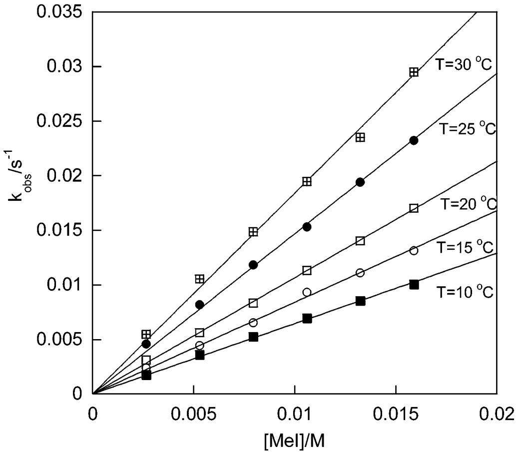

Figure 3. Plots of first-order rate constants (k_{obs}/s^{-1}) for the reaction of [Pt(p-MeC$_6$H$_4$)$_2$(^{t}Bu$_2$bpy)] with MeI in acetone at different temperatures versus concentration of MeI.

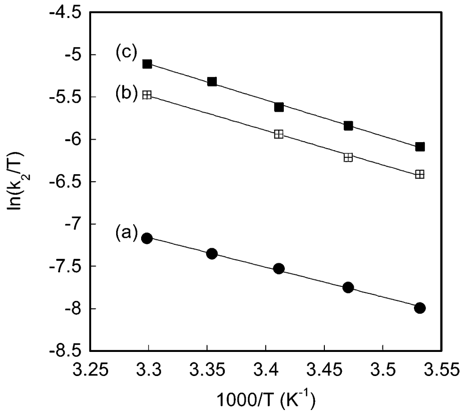

Figure 4. Eyring plots for the reaction of (a) [Pt(p-MeC$_6$H$_4$)$_2$(^{t}Bu$_2$bpy)] + MeI in benzene, (b) [Pt(p-MeC$_6$H$_4$)$_2$(Me$_2$bpy)] + CD$_3$I in acetone, and (c) [Pt(p-MeC$_6$H$_4$)$_2$(^{t}Bu$_2$bpy)] + MeI in acetone.

nucleophilic attack of the metallic center at the methyl group of MeI and formation of the cationic intermediate [(p-MeC$_6$H$_4$)$_2$(^{t}Bu$_2$bpy)Pt-Me]$^+$ I$^-$.

When the 4- and 4′-positions of the bpy ligand are substituted with alkyl groups (whether Me or ^{t}Bu), the reaction rates of the corresponding complexes are increased slightly more than twice compared to the case where the bpy complex is used. This is consistent with the proposed mechanism, as the alkyl substitutions render more basic character to the diimine nitrogen donor atoms, which in turn increase the nucleophilicity of the platinum center. The (^{t}Bu$_2$bpy)Pt^{II} complex **1c** reacted slightly faster than did the (Me$_2$bpy)Pt^{II} complex **1b**, but the rate increase is not significant at all. Also, note that, as expected, the complexes studied in the present work reacted with MeI much faster than did Vaska's complex, [IrCl(CO)(PPh$_3$)$_2$], in a related reaction.[7] For example, for [Pt(p-MeC$_6$H$_4$)$_2$(^{t}Bu$_2$bpy)] (**1c**) k_2 at 25 °C in acetone is 1.43 L mol^{-1} s^{-1}, while for Vaska's complex, the rate at 25 °C in acetonitrile is 0.0229 L mol^{-1} s^{-1}, even though acetonitrile is more polar than acetone.[7]

As shown in Table 1, consistent with the proposed S$_N$2 mechanism, the small normal KIEs (k_H/k_D = 1.03−1.11 at 25 °C) were observed for the three systems studied. This is also consistent with the previous results obtained for the Menschutkin-type reactions of methyl halides with different nucleophiles,[6] for the reduction of MeI with hydride ion,[19] and for the oxidative addition reaction of Vaska's compound, (Ph$_3$P)$_2$Ir(CO)Cl, with MeI;[7] an S$_N$2 mechanism has been suggested in each case with small inverse to small normal KIEs of 0.93−1.11, 0.98−1.056, and 0.94−1.00, respectively. Also, small normal KIEs of 1.06−1.16 have recently been reported for the reaction of *cis*-[M(CO)$_2$I$_2$]$^-$ (M = Rh, Ir) with MeI, which are in excellent agreement with the theoretical values of 1.09−1.15 obtained for the reactions having a classical S$_N$2 type intermediate.[20] Haynes et al. in the latter reference have also reported ab initio molecular orbital calculations for the reaction of the Rh complex, with MeI approaching the complex from the carbon end, but in a side-on manner as compared to the linear approach in the S$_N$2 type; a much larger computed KIE value of 1.92 is obtained for the bent transition state. Although they emphasize that the bent TS does not correspond to a three-center concerted addition of MeI to the metal center, it probably eliminates the possibility of such a mechanism. As mentioned before, we have recently studied the kinetics of addition of some peroxides, R$_2$O$_2$, to (diimine)diarylplatinum(II) complexes[12] and suggested a concerted three-center intermediate. We found that, probably because the intermediate is not ionic as in a classical S$_N$2 type one, reactions were not sensitive to the solvent polarity and in fact the rates were slightly faster in the nonpolar benzene solvent than in the polar acetone solvent. In

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(18) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

(19) Holm, T. *J. Am. Chem. Soc.* **1999**, *121*, 515.

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the present study, the complex **1c** reacted nearly 7 times faster in acetone than in benzene, which further supports the operation of a classical S_N2 type mechanism. Our results also eliminate the possibility of the radical mechanism in the systems studied, as higher KIE values are normally expected for this kind of mechanism. Holm in his recent study[19] addresses KIEs in radical mechanisms for reactions between metals and MeI, and he has reported for example a value of $k_H/k_D = 1.68$ for electron transfer to MeI from a platinum cathode.

Truhlar[4] has shown that, in determining the total KIE, the picture based on changes in zero point energies upon deuteration (vibrations) is incomplete and translations and rotations must also be considered. Using ab initio calculations, Bierbaum[5] has investigated the factors influencing the total KIE (η) in terms of the contributions (η_{trans}, translational; η_{rot}, rotational; η_{vib}, vibrational) as $\eta = \eta_{trans}\eta_{rot}\eta_{vib}$. He has shown that the translational contribution does not change appreciably for the reactions he studied, but η_{rot} clearly shows large variations among the different reactions. He then has related the rotational partition function to the moments of inertia, involving the heaviness of the nucleophile. He concludes that "the final η_{rot} becomes larger for *heavier* nucleophiles reacting with the same neutral". Our results in the present study seem to be consistent with Bierbaum's studies. First, as Table 1 shows, for the reaction of the (^{t}Bu$_2$bpy)Pt^{II} complex **1c**, $k_H/k_D = 1.11$, which is rather significantly larger than the values of $k_H/k_D = 1.03$ and 1.04 for the (bpy)Pt^{II} complex **1a** and the (Me$_2$bpy)Pt^{II} complex **1b**, respectively. The three systems we studied are very closely related; especially the environments around the reacting areas (crowdedness, which is an important factor[5]) in different complexes are very similar. The higher k_H/k_D value observed for the reaction of a significantly heavier nucleophile, the (^{t}Bu$_2$bpy)Pt^{II} complex **1c**, is thus understandable. Second, as the temperature rises, the value of k_H/k_D also increases in the reaction of the (^{t}Bu$_2$bpy)Pt^{II} complex **1c**; $k_H/k_D = 1.07$, 1.09, and 1.11 at 10, 15, and 25 °C, respectively. This might be due to the effect of temperature on the η_{rot} factor.

Finally, an interesting result from Table 1, which has not been discussed in the previous studies, is that in all reactions both $\Delta\Delta H^\ddagger = 0.8$ kJ mol^{-1} ($\Delta\Delta H^\ddagger = \Delta H^\ddagger_{MeI} - \Delta H^\ddagger_{CD_3I}$) and $\Delta\Delta S^\ddagger = +3$ J K mol^{-1} ($\Delta\Delta S^\ddagger = \Delta S^\ddagger_{MeI} - \Delta S^\ddagger_{CD_3I}$) are very close to zero within experimental error. On the basis of Halpern's discussion[21] it is not possible to rule out artifactual as opposed to real compensation effects. The small KIE could actually be a result of the different vibrational modes having opposite contributions.

Conclusions

Very small normal secondary deuterium kinetic isotope effects of 1.00−1.11 were observed for the reactions of (diimine)organoplatinum(II) complexes with MeI at different temperatures, which presents further support for the operation of an S_N2-type mechanism in these important oxidative addition reactions. The results are discussed in terms of recent experimental and theoretical studies.[4,5,19,20] The KIE for the reaction of the (^{t}Bu$_2$bpy)Pt^{II} complex **1c** (1.11) is rather larger than those of the other nucleophiles (**1a**, 1.03; **1b**, 1.04). This is attributed to complex **1c** being a heavier nucleophile than the others. For the reaction of the (^{t}Bu$_2$bpy)Pt^{II} complex **1c**, k_H/k_D values increase as the temperature is raised. This is attributed to the effect of temperature on the η_{rot} factor (rotational contribution to the total KIE, η). In all the reactions studied, the $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ values are very close to zero and thus the small KIE is attributed to different vibrational modes having opposite contributions.

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