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Secondary Kinetic Isotope Effects in Oxidative Addition of Benzyl Bromide to Dimethylplatinum(II) Complexes

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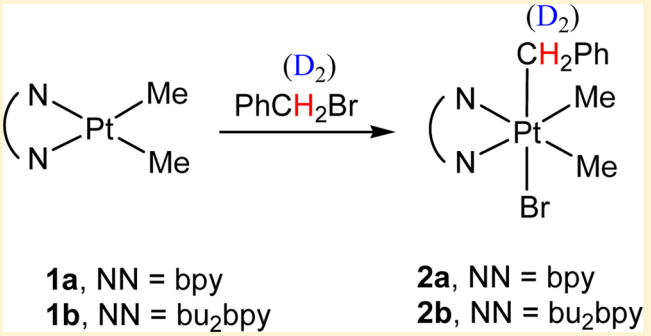
ABSTRACT: The secondary α-deuterium kinetic isotope effects (KIEs), $(k_H/k_D)_\alpha$, have been determined, at different temperatures and in solvents having different polarities, for reaction of $PhCH_2Br/PhCD_2Br$ with the dimethylplatinum(II) complexes $[PtMe_2(NN)]$, in which the bidentate NN ligand is bpy (=2,2′-bipyridine) or bu_2bpy (=4,4′-di-*tert*-butyl-2,2′-bipyridine). The values obtained for the secondary α-deuterium KIEs in acetone solution are close to 1 and may be normal or inverse, but much larger values are found for the reactions in benzene. An explanation is presented on the basis of solvent dependence of the degree of looseness of the transition state in the S_N2 mechanism.



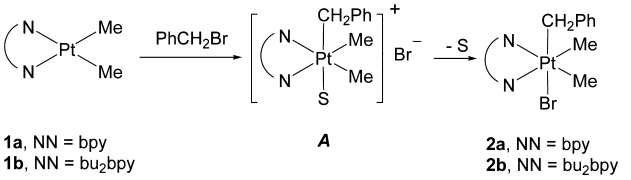
INTRODUCTION

The oxidative addition of alkyl halides with d^8 square-planar complexes is often a key step in catalytic reactions that are of importance to the petrochemical industry,[1] and studies of oxidative addition to platinum(II) complexes have provided much of the information needed to understand the reactivity and mechanism in these reactions.[2] The secondary deuterium kinetic isotope effect (KIE) can give information about the reaction mechanism and the structure of the transition state,[3] and it has previously been applied to studies of oxidative addition of methyl or ethyl iodide to square-planar complexes.[4] Benzyl halides are known to be very reactive in oxidative addition reactions.[2j,5] These reactions can find significant applications in cross-coupling reactions of benzyl halides[5m] and in the synthesis of functional organoplatinum(IV) complexes, ranging from dendrimers to building blocks for self-assembly of polymers, polyrotaxanes, and nanotubes.[1d,2a,l,6] Nevertheless, there have been no studies of kinetic isotope effects in these reactions, and this paper provides the first information on this topic, using oxidative addition of $PhCH_2Br$ or $PhCD_2Br$ to the complexes $[PtMe_2(NN)]$, where NN is bpy (=2,2′-bipyridine) or its derivative bu_2bpy (=4,4′-di-*tert*-butyl-2,2′-bipyridine).

RESULTS AND DISCUSSION

The oxidative addition reactions of benzyl bromide to dimethylplatinum(II) complexes of general formula $[PtMe_2(NN)]$ (**1**) are thought to occur according to the mechanism shown in Scheme 1, to give the products of trans oxidative addition, **2**, by the polar S_N2 mechanism, by way of the ionic intermediate ***A***.[1d,2i] For the reactions with NN = bpy, bu_2bpy, the products were **2a**,**b** (Scheme 1). For example, the stereochemistry of **2b** was readily shown by the presence of single resonances in the ^1H NMR spectrum for the methylplatinum groups at δ 1.52 (s, 6H, ^2J(PtH) = 70 Hz) and for the methylene protons of the benzylplatinum group at δ 2.84 (s, 2H, ^2J(PtH) = 95 Hz). None of the alternative product of cis oxidative addition, which would give two MePt resonances and two resonances for diastereotopic $PtCH^AH^BPh$ protons, was observed.

Scheme 1. Proposed Mechanism of Oxidative Addition (S = Solvent)



The kinetics of the oxidative addition reactions were studied in benzene and acetone solution. The reactions were rapid and were most conveniently followed by using equimolar concentrations of **1a** or **1b** and $PhCH_2Br$, in a way similar to that used previously in reactions with methyl iodide.[4c] A typical set of UV−visible spectra taken during a kinetic run is shown in Figure 1, using the decay of the MLCT band of complex **1a** to monitor the reaction.

Under these conditions, the reactions followed good second-order kinetics, and the resulting rate constants are given in Table 1. It should also be noted that the rates of the reactions were not affected by the addition of the radical scavenger *p*-benzoquinone.

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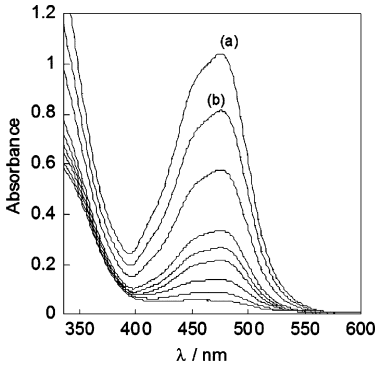

Figure 1. Changes in the UV−visible spectrum during the reaction of $[PtMe_2(bpy)]$ (**1a**; 3 mL of 3×10^{-4} M solution), with $PhCH_2Br$, under second-order 1:1 stoichiometric conditions, in acetone at 25 °C: (a) initial spectrum (before adding $PhCH_2Br$); (b) spectrum at $t = 0$; successive spectra recorded at intervals of 30 s.

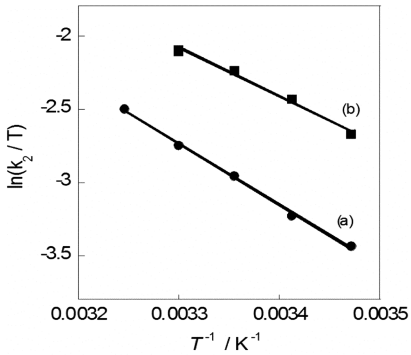

Figure 2. Eyring plots for the reactions with $PhCH_2Br$ in acetone: (a) for complex **1a**; (b) for complex **1b**.

Eyring plots for the reactions in acetone solution are given in Figure 2, from which the activation parameters were calculated (Table 1). The large negative entropies of activation are typical values for oxidative addition by the S_N2 mechanism. For example, in reactions of **1a** in acetone, benzyl bromide gives $\Delta H^{\ddagger} = 34.7 \pm 3.0$ kJ mol^{-1} and $\Delta S^{\ddagger} = -105 \pm 9$ J K^{-1} mol^{-1} while methyl iodide gives $\Delta H^{\ddagger} = 22.0 \pm 1.2$ (1) kJ mol^{-1} and $\Delta S^{\ddagger} = -138 \pm 4$ J K^{-1} mol^{-1}.[4d]

We also measured the KIE using ^{1}H NMR spectroscopy, typically for the reaction of $PhCH_2Br/PhCD_2Br$ (50%/50% mixture) with complex **1a** in either acetone or benzene solvent. Thus, after the reaction is carried out at 20 °C, the final solid products $[PtBr(CH_2Ph)Me_2(bpy)]/[PtBr(CD_2Ph)Me_2(bpy)]$ (**2a**/**2a***) were obtained and the KIEs were determined from the ^{1}H NMR spectrum in $CDCl_3$ by proper integration (see the description in the Experimental Section), and the data are collected in Table 1. The results are in agreement with those obtained from UV−visible spectroscopy.

A comparison of the secondary α-deuterium kinetic isotope effects for some related oxidative addition reactions is given in Table 2, using the more accurate data from kinetic studies. The reactions in acetone give only a small secondary α-deuterium KIE, which is inverse at lower temperatures and normal at

Table 2. Secondary α-Deuterium Kinetic Isotope Effects for the Reaction of Complex $[PtMe_2(bpy)]$ (1a) in Acetone or Benzene

solvent	reagent	T/ °C	$(k_H/k_D)_\alpha$
acetone	$PhCH_2Br$	25	0.97 ± 0.01
		30	0.98 ± 0.01
benzene	$PhCH_2Br$	25	1.25 ± 0.01
		30	1.33 ± 0.01
acetone	MeI[a]	25	1.02 ± 0.02
benzene	MeI[a]	25	0.93 ± 0.04
acetone	EtI[b]	25	1.24 ± 0.01
benzene	EtI[b]	25	1.28 ± 0.06

[a]From ref 4d, using CH_3I/CD_3I. [b]From ref 4e, using CH_3CH_2I/CH_3CD_2I.

Table 1. Rate Constants, Kinetic α-Deuterium Isotope Effects, and Activation Parameters for the Reaction of Complexes $[PtMe_2(bpy)]$ (1a) and $[PtMe_2(bu_2bpy)]$ (1b) with $PhCH_2Br/PhCD_2Br$ in Acetone or Benzene

complex	solvent	T (°C)	$k_2(H)$[a] (L mol^{-1}s^{-1})	$k_2(D)$[b] (L mol^{-1}s^{-1})	$(k_H/k_D)_\alpha$	$(k_H/k_D)_\alpha$ NMR[c]
1a	acetone	15	9.30 ± 0.01	10.07 ± 0.01	0.92 ± 0.01	
		20	11.61 ± 0.01	12.30 ± 0.03	0.94 ± 0.01	0.94
		25	15.60 ± 0.01	15.98 ± 0.04	0.97 ± 0.01	
		30	19.55 ± 0.01	19.85 ± 0.05	0.98 ± 0.01	
		35	25.30 ± 0.14	24.02 ± 0.10	1.05 ± 0.01	
1a	benzene	15	0.81 ± 0.01	0.66 ± 0.01	1.22 ± 0.01	
		20	1.05 ± 0.01	0.85 ± 0.01	1.23 ± 0.01	1.26
		25	1.38 ± 0.01	1.10 ± 0.01	1.25 ± 0.01	
		30	1.82 ± 0.01	1.36 ± 0.01	1.33 ± 0.01	
		35	2.22 ± 0.01	1.73 ± 0.01	1.28 ± 0.01	
1b	acetone	15	20.06 ± 0.02	23.51 ± 0.01	0.85 ± 0.01	
		20	25.70 ± 0.02	27.88 ± 0.01	0.92 ± 0.01	
		25	31.82 ± 0.01	31.77 ± 0.01	1.00 ± 0.01	
		30	37.16 ± 0.01	35.89 ± 0.02	1.05 ± 0.01	
1b	benzene	30	3.85 ± 0.01	2.78 ± 0.01	1.38 ± 0.01	

[a]Values for $PhCH_2Br$. Activation parameters in acetone: for **1a**, $\Delta H^{\ddagger} = 34.7 \pm 3.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -105 \pm 9$ J K^{-1} mol^{-1}; for **1b**, $\Delta H^{\ddagger} = 27.5 \pm 3.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -124 \pm 9$ J K^{-1} mol^{-1}. Activation parameters in benzene: for **1a**, $\Delta H^{\ddagger} = 35.3 \pm 3.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -123 \pm 9$ J K^{-1} mol^{-1}. [b]Values for $PhCD_2Br$. Activation parameters in acetone: for **1a**, $\Delta H^{\ddagger} = 30.2 \pm 2.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -120 \pm 8$ J K^{-1} mol^{-1}; **1b**, $\Delta H^{\ddagger} = 17.9 \pm 2.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -156 \pm 6$ J K^{-1} mol^{-1}. Activation parameters in benzene: for **1a**, $\Delta H^{\ddagger} = 33.0 \pm 2.0$ kJ mol^{-1}, $\Delta S^{\ddagger} = -133 \pm 8$ J K^{-1} mol^{-1}. Error bars were estimated by Girolami's method.[3c] [c]KIE from NMR product analysis at 20 °C.

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higher temperatures (Table 1). These are typical values for an S_N2 reaction.[3a,7] However, in benzene solution the value of $(k_H/k_D)_\alpha$ is 1.33, which is the highest value yet observed for an oxidative addition reaction.[4e]

Table 3 gives values of the secondary α-deuterium KIE for nucleophilic substitution reactions of benzyl derivatives. Many

Table 3. Secondary α-Deuterium Kinetic Isotope Effects for Nucleophilic Substitution Reactions of Benzyl Derivatives

reagent	nucleophile	solvent	T/°C	k_H/k_D	ref
$PhCH_2Cl$	Cl^-	dmf	40	1.05	7a
$PhCH_2Cl$	Cl^-	dmso	35	1.08	7b
$PhCH_2Br$	Et_3N	*a*	25	0.99	7c
$PhCH_2Br$	N_3^-	*a*	25	1.01	7c
$PhCH_2Cl$	CN^-	*b*	40	1.02	7d
$4\text{-}MeC_6H_4CH_2Cl$	CN^-	*b*	40	1.26	7d
$PhCH_2NMe_2Ph^+$	Br^-	$CHCl_3$	30	1.25	7e
$PhCH_2NMe_2Ph^+$	Br^-	acetone	30	1.19	7e
$PhCH_2NMe_2Ph^+$	PhS^-	dmf	0	1.48	7f

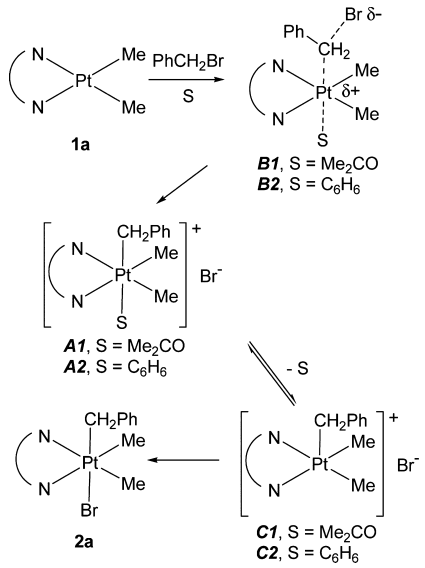
[a]Solvent 80/20 dioxane/water. [b]Solvent 55/45 water/2-methoxyethanol.

of these reactions give values of $(k_H/k_D)_\alpha$ in the range 0.99–1.08, which are typical values for the S_N2 mechanism.[7a−d] The magnitude of these KIEs depends on the changes in zero point energy on going to the transition state, and this in turn is determined by changes in the C_α–H(D) vibrations on going from reactants to the transition state. As described by Westaway,[3a] changes in C–H(D) stretching vibrations would typically give a small inverse KIE, but this may be balanced by changes in the C–H(D) out-of-plane bending vibration, which may contribute to a normal KIE. The net effect is that there is usually a small KIE, which may be inverse or normal. However, some much larger values of $(k_H/k_D)_\alpha$ in the range 1.19–1.48 have been observed.[3a,7d−f] In some cases these have been interpreted in terms of an S_N1 mechanism, sometimes within tight ion pairs, but it has also been argued that these large values are consistent with an S_N2 mechanism with an unsymmetrical or very loose transition state.[3a,7f] The easier out-of-plane bending vibration is the main contributor to these larger KIE values.

The oxidative addition of benzyl bromide in benzene clearly does not occur by an S_N1 mechanism; therefore, the large value of $(k_H/k_D)_\alpha$ must be attributed to one of the other effects. A radical mechanism, with intermediate formation of free benzyl radicals, might give a high value of $(k_H/k_D)_\alpha$, but no evidence for radical intermediates was found.[2j,4e]

In order to understand the observed differences in kinetic isotope effects when S = acetone, benzene, DFT calculations were carried out on the complexes and potential intermediates. Because polar intermediates are invoked and the solvent effect is critically important in this context, it was necessary to incorporate both general solvation effects and, for intermediates, individual solvent molecules. The conductor-like screening model (COSMO) was used to model general solvation effects by acetone or benzene.[8] The likely mechanism of reaction of benzyl bromide with the complex $[PtMe_2(bpy)]$ (**1a**) is shown in Scheme 2.[1d,2d,i] The reaction is initiated by nucleophilic attack by the $5d_{z^2}$ HOMO of $[PtMe_2(bpy)]$ on the σ^* LUMO of benzyl bromide (Figure 3). For the reaction in acetone solution, the cationic intermediate ***A1*** has been detected by NMR at low temperature[2i] and is probably formed via the

Scheme 2. Proposed Mechanism of the Reaction (NN = bpy)



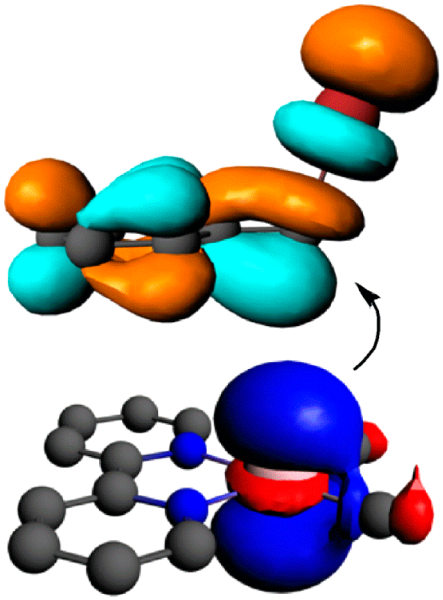


Figure 3. Proposed initiation of the S_N2 oxidative addition.

transition state ***B1***. The displacement of acetone from ***A1*** by the bromide ion, formed in the S_N2 oxidative addition step, must occur by a dissociative mechanism by way of a five-coordinate intermediate or transition state ***C***,[9] to finally give the product **2a**.

Figure 4 shows the calculated structures and energies for the compounds shown in Scheme 2 in acetone solution. The calculation indicates an easy reaction to give the cationic acetone complex ***A1***, followed by a slower reaction to give **2a**, consistent with the experimental observations.[2i] Note that, in the kinetics experiments, the loss of complex **1a** is measured so that the rates refer to formation of ***A1***. The calculation of the energy of the transition state ***B1*** (+24 kJ mol^{-1}) is in reasonable agreement with the observed value of $\Delta H^\ddagger$ = 34.7(1) kJ mol^{-1}. The calculated activation energy is higher in benzene solution, partially due to the low polarity, which does not stabilize the polar intermediates, and partially because it is a poor ligand and so cannot stabilize the platinum(IV) oxidation

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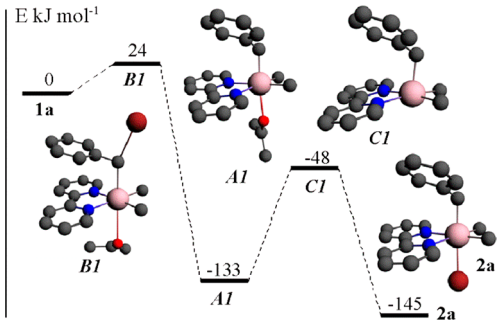


Figure 4. Calculated structures and relative energies (kJ mol^{-1}) for product **2a**, intermediate ***A1***, and transition states ***B1*** and ***C1***, arising from the reaction of **1a** + $PhCH_2Br$ + acetone (E = 0) in acetone solution.

state by coordination. The ionic intermediate ***A2*** will be formed only transiently.

A summary of some calculated properties of the compounds of Scheme 2 is given in Table 4. The charge on platinum is

Table 4. Calculated Hirshfeld Atomic Charges and Selected Distances (Å) for the Compounds of Scheme 2

	Q(Pt)[c]	Q(Br)[c]	Q(C)[c]	Pt−Br	Pt−CH_2	C−Br	Pt−S[d]
$BnBr^a$		−0.13	−0.03			2.06	
$BnBr^b$		−0.11	−0.04			2.04	
1a[a]	0.11						
1a[b]	0.12						
2a[a]	0.39	−0.48	−0.12	2.71	2.12		
2a[b]	0.39	−0.42	−0.13	2.67	2.13		
A1	0.44	−1	−0.11		2.09		2.32
A2	0.44	−1	−0.07		2.12		3.67
B1	0.44	−0.84	−0.09	5.27	2.13	3.35	2.83
B2	0.33	−0.54	−0.05	5.06	2.47	2.74	3.97
C1	0.46	−1	−0.07		2.11		
C2	0.45	−1	−0.06		2.12		

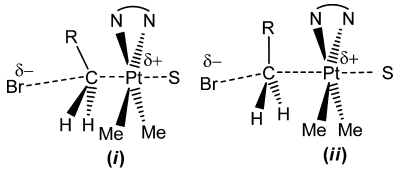
[a]Solvent acetone. [b]Solvent benzene. [c]Hirshfeld charge. [d]O or C atom when S = acetone, benzene.

significantly lower in the platinum(II) complex **1a** than in the other compounds, supporting the view that **1a** acts as the nucleophile in the reaction with benzyl bromide (Figure 3). The S_N2 reactions can occur with a single or double energy maximum, but only one transition state could be found for each reaction. The major difference is that the transition state in acetone solution was calculated to be productlike, with Pt−C = 2.13 Å and C−Br = 3.35 Å, whereas in benzene solution it was more symmetrical, with Pt−C = 2.47 Å and C−Br = 2.74 Å. The charge on the bromine atom was calculated to be −0.84e and −0.54e in the transition states ***B1*** and ***B2***, respectively. The Pt−C−Br unit was nonlinear in both cases, the angles being 150 and 152° in acetone and benzene, respectively. In benzene solution, the benzyl group in ***B2*** is calculated to be essentially flat, and the long distances to both the platinum and bromine atoms may allow it to vibrate in a way similar to that for a benzyl radical. This calculated transition state can be considered to be very loose and corresponds to those in some of the rare cases in which S_N2 reactions are found to give large normal isotope effects.[3a,7f] The difference in the kinetic isotope effects for the reaction of complex **1a** with benzyl bromide in acetone or benzene can therefore be attributed to the lower ability of benzene to stabilize the polar transition state.

CONCLUSIONS

In the present study, we have observed that although $(k_H/k_D)_\alpha$ for the reaction of $PhCH_2Br/PhCD_2Br$ with the dimethylplatinum(II) complexes $[PtMe_2(bpy)]$ (**1**) in the polar solvent acetone are close to unity, much larger values of around 1.3 are found for the reactions in the nonpolar solvent benzene. Our calculations (vide supra) suggest that the transition state of the reaction in benzene solvent is looser than that of the related reaction in acetone solvent. This looser transition state for the reaction in benzene solvent will give more room for the C_α−H(D) out-of-plane bending vibration, which is believed to play a major role in determining the magnitude of $(k_H/k_D)_\alpha$ for S_N2 reactions in which there is a combination of bulkier alkyl halides and heavier nucleophiles.[3a] In the present case, the C_α−H(D) bond in the transition state involving the nonpolar solvent benzene (Scheme 3; R = Ph,

Scheme 3. Proposed Transition State Structures



structure *ii*) has an almost planar carbon center, with long Pt−C and Br−C distances, giving room for the C−H (or C−D) bending vibration. This can be compared to the transition state in acetone (Scheme 3; R = Ph, structure *i*), in which the polar solvent molecule is coordinated more tightly to the platinum center, bringing the geometry close to octahedral at platinum and in which there is a shorter Pt−C bond and more tetrahedral carbon center, with less room for the C−H bending vibration. In the analogous reaction of CH_3CH_2I/CH_3CD_2I with the dimethylplatinum(II) complex $[PtMe_2(bpy)]$ at 25 °C, the kinetic isotope effect $(k_H/k_D)_\alpha$ was found to be high for both acetone and benzene solvents (being 1.24 in acetone and slightly higher, 1.28, in benzene).[4e] Here, the donor ability of R = Me (as compared to the withdrawing ability of R = phenyl) is expected to make the nucleophilic attack by platinum(II) more difficult, so that the transition state in both acetone and benzene is closer to the structure type *ii* (Scheme 3), making $(k_H/k_D)_\alpha$ values similar and large in both solvents.

Finally, it is noted that the observed higher isotope effect in the less polar solvent contrasts with data from the solvolysis of benzyl derivatives, in which the isotope effect increases in more polar solvents as the transition state moves closer to the S_N1 limiting case.[7h,j]

EXPERIMENTAL SECTION

The benzyl halides $PhCH_2Br$ (99%) and $PhCD_2Br$ (98 atom % D) were purchased from Aldrich Chemical. The ^1H and ^{13}C NMR spectra of the complexes were recorded as $CDCl_3$ solutions on a Bruker Avance DPX 250 (or 300 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 spectrophotometer. Temperature was carefully controlled by a EYELA NCB-3100 low-temperature thermoregulation bath. The starting organoplatinum(II) complexes $[PtMe_2(bpy)]$ (**1a**)[10] and

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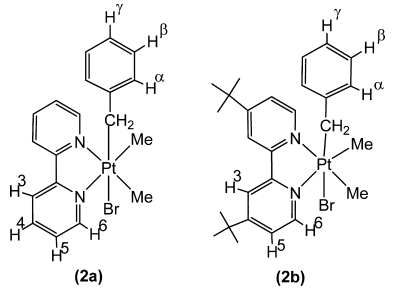
[$PtMe_2$(^{t}Bu$_2$bpy)] (**1b**)[11] were synthesized and characterized as reported elsewhere. The ^{1}H NMR labeling is depicted in Scheme 4.

Scheme 4. ^{1}H NMR Labeling of Complexes 2



***trans*-[PtBr(CH$_2$Ph)Me$_2$(bpy)] (2a).** [$PtMe_2$(bpy)] (**1a**; 100 mg, 0.26 mmol), was dissolved in acetone (15 mL), and benzyl bromide (31 μL, 0.26 mmol) was added to it. The mixture was stirred at room temperature over a period of 3 h. The solvent was evaporated from the resulting white solution, and the residue was washed with ether. The product as a white solid was dried under vacuum. Yield: 91%. Mp: 220 °C dec. Anal. Calcd for $C_{19}H_{21}BrN_2Pt$: C, 41.31; H, 3.96; N, 5.07. Found: C, 41.66; H, 3.75; N, 5.11. ^{1}H NMR data (in $CDCl_3$): δ(^{1}H) 1.55 (s, 6H, ^2J(PtH) = 69.9 Hz, Pt*Me*), 2.83 (s, 2H, ^2J(PtH) = 93.3 Hz, Pt*CH*$_2$Ph), 6.28 (d, 2H, $^3J(H^\alpha H^\beta)$ = 7.0 Hz, $^4J(PtH^\alpha)$ = 12.5 Hz, H$^\alpha$ of Ph), 6.56 (t, 2H, $^3J(H^\alpha H^\beta) = {}^3J(H^\beta H^\gamma)$ = 7.0 Hz, H$^\beta$ of Ph), 6.67 (m, 1H, H$^\gamma$ of Ph), 7.45 (m, 2H, H^5 of bpy), 7.87 (dt, 2H, $^3J(H^4H^3) = {}^3J(H^4H^5) \approx$ 7.8 Hz, $^4J(H^4H^6)$ = 1.2 Hz, H^4 of bpy), 7.96 (d, 2H, $^3J(H^3H^4)$ = 8.1 Hz, H^3 of bpy), 8.70 (d, 2H, $^3J(H^6H^5)$ = 6.3 Hz, $^3J(PtH^6)$ = 12.0 Hz, H^6 of bpy); ^{13}C NMR data: δ(^{13}C) −3.0 (s, 2C, ^1J(PtC) = 678 Hz, Pt*Me*), 23.4 (s, 1C, ^1J(PtC) = 641 Hz, Pt*CH*$_2$Ph); aromatic carbons 123.0 (s, J(PtC) = 9 Hz), 124.0 (s, J(PtC) = 17 Hz), 126.3 (s, J(PtC) = 14 Hz), 127.3 (s, J(PtC) = 23 Hz), 127.6 (s, J(PtC) = 16 Hz), 138.2 (s), 144.9 (s), 146.9 (s, J(PtC) = 14 Hz), 154.8 (s).

***trans*-[PtBr(CH$_2$Ph)Me$_2$(^{t}Bu$_2$bpy)] (2b).** [$PtMe_2$(^{t}Bu$_2$bpy)] (**1b**; 100 mg, 0.20 mmol) was dissolved in acetone (15 mL), and benzyl bromide (24 μL, 0.20 mmol) was added to it. The mixture was stirred at room temperature over a period of 3 h. The solvent was evaporated from the resulting white solution, and the residue was washed with ether. The product as a white solid was dried under vacuum. Yield: 98%. Mp: 244 °C dec. Anal. Calcd for $C_{27}H_{37}BrN_2Pt$: C, 48.79; H, 5.61; N, 4.21. Found: C, 48.35; H, 5.42; N, 4.19. ^{1}H NMR data: δ(^{1}H) 1.42 (s, 18H, Me groups of 2 ^{t}Bu), 1.53 (s, 6H, ^2J(PtH) = 69.6 Hz, Pt*Me*), 2.84 (s, 2H, ^2J(PtH) = 94.8 Hz, Pt*CH*$_2$Ph), 6.29 (d, 2H, $^3J(H^\alpha H^\beta)$ = 7.2 Hz, $^4J(PtH^\alpha)$ =12.8 Hz, H$^\alpha$ of Ph), 6.56 (t, 2H, $^3J(H^\alpha H^\beta) = {}^3J(H^\beta H^\gamma)$ = 7.2 Hz, H$^\beta$ of Ph), 6.70 (m, 1H, H$^\gamma$ of Ph), 7.44 (d, 2H, $^3J(H^6H^5)$ = 5.7 Hz, H^5 of ^{t}Bu$_2$bpy), 7.88 (s, 2H, H^3 of ^{t}Bu$_2$bpy), 8.60 (d, 2H, $^3J(H^5H^6)$ = 6.0 Hz, $^3J(PtH^6)$ = 12.5 Hz, H^6 of ^{t}Bu$_2$bpy). ^{13}C NMR data: δ(^{13}C) −3.3 (s, 2C, ^1J(PtC) = 675 Hz, Pt*Me*), 22.8 (s, 1C, ^1J(PtC) = 645 Hz, Pt*CH*$_2$Ph), 30.4 (s, 6C, Me carbon atoms of ^{t}Bu groups), 35.4 (s, 2C, central carbon atoms of ^{t}Bu groups); aromatic carbons 119.4 (s, J(PtC) = 9 Hz), 123.6 (s, J(PtC) = 14 Hz), 123.7 (s, J(PtC) = 17 Hz), 127.4 (s, J(PtC) = 16 Hz), 127.5 (s, J(PtC) = 24 Hz), 145.1 (s, J(PtC) = 56 Hz), 146.4 (s, J(PtC) = 14 Hz), 154.8 (s), 162.8 (s, J(PtC) = 59 Hz).

Kinetic Study. A solution of complex **1a** or **1b** in acetone or benzene (3 mL, 3.0 × 10^{-4} M) in a cuvette was thermostated at 25 °C, and benzyl bromide with a known concentration was added using a microsyringe. After rapid stirring, the absorbance at λ 475 nm for complex **1a** in acetone and at λ 508 nm in benzene and for complex **1b** at λ 465 nm in acetone and at λ 550 nm in benzene decreased with time. The absorbance−time curves were analyzed by 1:1 stoichiometric techniques. The rate of the reaction was not affected by addition of the radical scavenger *p*-benzoquinone. The data at other temperatures were obtained similarly.

KIEs by Competition Experiments. To a solution of [$PtMe_2$(bpy)] (**1a**; 5 mg) in acetone (4 mL) was added a mixture containing 15 μL of each of the reagents $PhCH_2Br$ and $PhCD_2Br$ (overall 10 times excess). The solution was stirred at 20 °C for 1 h, and then the solvent was removed and the residue was dried under vacuum. The kinetic isotope effects (KIEs) was obtained from the ^{1}H NMR spectrum of the product mixture [PtBr(CH$_2$Ph)Me$_2$(bpy)]/[PtBr(CD$_2$Ph)Me$_2$(bpy)] (**2a**/**2a***) in $CDCl_3$. A sufficiently long delay time was used to ensure that minor differences in relaxation times T1, arising from the ^{2}H isotope effect in **2a***, did not affect the integration. Thus, integration of the left satellite of Pt−CH_2 protons was used to determine the relative concentration of **2a**. The relative integration of the left satellite of Pt−CH_3 protons due to Me ligands of **2a** + **2a*** was used to determine the relative concentration for the total of **2a** + **2a***; note that these two satellites, used to determine the relative concentrations, were the most clear peaks in the spectrum. Subtraction of concentration of **2a** from this total gave the relative concentration of **2a***. Dividing the relative concentration of **2a** by the relative concentration of **2a*** gives the KIE. Similarly, the KIE for the same reaction in benzene solvent was determined.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Collman, J.; Hegedus, L.; Norton, J.; Finke, R. *Principles and Applications of Organometallic Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: Hoboken, NJ, 2009. (c) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735.

(2) (a) Canty, A. *Comprehensive Organometallic Chemistry III*: Elsevier: Amsterdam, 2007; Vol *8* (Compounds of Group 10). (b) Capapé, A.; Crespo, M.; Granell, J.; Font-Bardía, M.; Solans, X. *Dalton Trans.* **2007**, 2030. (c) Canty, A. J.; Watson, R. P.; Karpiniec, S. S.; Rodemann, T.; Gardiner, M. G.; Jones, R. C. *Organometallics* **2008**, *27*, 3203. (d) Nabavizadeh, S. M.; Shahsavari, H. R.; Sepehrpour, H.; Hosseini, F. N.; Jamali, S.; Rashidi, M. *Dalton Trans.* **2010**, *39*, 7800. (e) Nabavizadeh, S. M.; Hoseini, S. J.; Momeni, B. Z.; Shahabadi, N.; Rashidi, M.; Pakiari, A. H.; Eskandari, K. *Dalton Trans.* **2008**, 2414. (f) Niroomand Hosseini, F.; Ariafard, A.; Rashidi, M.; Azimi, G.; Nabavizadeh, S. M. *J. Organomet. Chem.* **2011**, *696*, 3351. (g) Nabavizadeh, S. M.; Amini, H.; Jame, F.; Khosraviolya, S.; Shahsavari, H. R.; Hosseini, F. N.; Rashidi, M. *J. Organomet. Chem.* **2011**, *698*, 53. (h) Hoseini, S. J.; Nasrabadi, H.; Nabavizadeh, S. M.; Rashidi, M.; Puddephatt, R. J. *Organometallics* **2012**, *31*, 2357. (i) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548. (j) Hill, R. H.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1218. (k) Monaghan, P. K.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1988**, 595. (l) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1538.

(3) (a) Westaway, K. C. *J. Label. Comp. Radiopharm.* **2007**, *50*, 989. (b) Parkin, G. *Acc. Chem. Res.* **2009**, *42*, 315. (c) Morse, P. M.; Spencer, M. D.; Wilsom, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

(4) (a) Stang, P. J.; Schiavelli, M. D.; Chenault, H. K.; Breidegam, J. L. *Organometallics* **1984**, *3*, 1133. (b) Griffin, T. R.; Cook, D. B.; Haynes, A.; Pearson, J. M.; Monti, D.; Morris, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 3029. (c) Rashidi, M.; Nabavizadeh, S. M.; Akbari, A.; Habibzadeh, S. *Organometallics* **2005**, *24*, 2528. (d) Habibzadeh, S.; Rashidi, M.; Nabavizadeh, S. M.; Mahmoodi, L.; Hosseini, F. N.; Puddephatt, R. J. *Organometallics* **2010**, *29*, 82. (e) Nabavizadeh, S. M.;

Habibzadeh, S.; Rashidi, M.; Puddephatt, R. J. *Organometallics* **2010**, *29*, 6359.
(5) (a) Thoonen, S. H. L.; Lutz, M.; Spek, A. L.; Deelman, B. J.; van Koten, G. *Organometallics* **2003**, *22*, 1156. (b) Kuyper, J.; Laan, R. v. d.; Jeanneaus, F.; Vrieze, K. *Transition Met. Chem.* **1976**, *1*, 199. (c) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Lavington, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613. (d) De Graaf, W.; Boersma, J.; Van Koten, G. *Organometallics* **1990**, *9*, 1479. (e) Scott, J. D.; Crespo, M.; Anderson, C. M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 1772. (f) Werner, M.; Bruhn, C.; Steinborn, D. *Transition Met. Chem.* **2009**, *34*, 61. (g) Tejel, C.; Ciriano, M. A.; Edwards, A. J.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2000**, *19*, 4968. (h) Canty, A. J.; Jin, H.; Roberts, A. S.; Skelton, B. W.; Traill, P. R.; White, A. H. *Organometallics* **1995**, *14*, 199. (i) Baar, C. R.; Jenkins, H. A.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 2805. (j) von Zelewsky, A.; Suckling, A. P.; Stoeckli-Evans, H. *Inorg. Chem.* **1993**, *32*, 4585. (k) Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *Organometallics* **1994**, *13*, 2053. (l) Amatore, C.; Catellani, M.; Deledda, S.; Jutand, A.; Motti, E. *Organometallics* **2008**, *27*, 4549. (m) Kambe, N.; Iwasaki, T.; Terao, J. *Chem. Soc. Rev.* **2011**, *40*, 4937.
(6) (a) Achar, S.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1895. (b) Achar, S.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **1994**, *33*, 867. (c) Fraser, C. S. A.; Jennings, M. C.; Puddephatt, R. J. *Chem. Commun.* **2001**, 1310. (d) Au, R. H. W.; Jennings, M. C.; Puddephatt, R. J. *Dalton Trans.* **2009**, 3519.
(7) (a) Östman, B. *J. Am. Chem. Soc.* **1965**, *87*, 3163. (b) Strecker, H.; Elias, H. *Chem. Ber.* **1969**, *102*, 1270. (c) Vitullo, V.; Grabowski, J.; Sridharan, S. *J. Am. Chem. Soc.* **1980**, *102*, 6463. (d) Willi, A. V.; Ho, C. K.; Ghanbarpour, A. *J. Org. Chem.* **1972**, *37*, 1185. (e) Ko, E.; Leffek, K. *Can. J. Chem.* **1971**, *49*, 129. (f) Westaway, K. C.; Van Pham, T.; Fang, Y. *J. Am. Chem. Soc.* **1997**, *119*, 3670. (g) Islam, M. N.; Leffek, K. T. *J. Chem. Soc., Perkin Trans. 2* **1977**, 958. (h) Shiner, V. J., Jr.; Rapp, M. W.; Pinnick, H. R., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 232. (i) Lee, I.; Koh, H. J.; Lee, B. S.; Sohn, D. S.; Lee, B. C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1741. (j) Shiner, V. J., Jr; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakovsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838.
(8) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.
(9) (a) Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 261. (b) Grice, K. A.; Scheuermann, M. L.; Goldberg, K. I. *Top. Organomet. Chem.* **2011**, *35*, 1.
(10) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444.
(11) Achar, S.; Scott, J. D.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 4592.