Rapid Reversible Oxidative Addition of Group 14−Halide Bonds to Platinum(II): Rates, Equilibria, and Bond Energies

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Abstract: The reversible oxidative addition reactions of methyl(halogeno)tin and methyl(halogeno)germanium compounds to electron-rich platinum(II) complexes of the type [PtMe$_2$(diimine)] have been studied. Complete kinetic and thermodynamic parameters have been obtained by VT ^{1}H NMR for the reversible oxidative addition of Me$_3$EX (E = Sn, X = Cl, Br, I) to [PtMe$_2$(bpy-^{t}bu$_2$)] (bpy-^{t}bu$_2$ = 4,4′-di-*tert*-butyl-2,2′-bipyridyl) and related compounds, while partial data have been obtained for the reductive elimination of Me$_2$SnCl$_2$ from [PtClMe$_2$(Me$_2$SnCl)-(bpy-^{t}bu$_2$)] and for the oxidative addition of Me$_3$GeCl to [PtMe$_2$(bpy-^{t}bu$_2$)]. UV−visible spectroscopic studies have also yielded equilibrium constants and $\Delta G°$ for the reversible oxidative addition reactions of Me$_3$SnX (X = Cl, Br, I) to [PtMe$_2$(diimine)]. Thermodynamic studies quantitatively establish the halogen effect on the oxidative addition reactions studied according to the favorability series I > Br > Cl. Kinetic studies clearly point to an S$_N$2 mechanism for the reactions studied, and this is further supported by the observation of the cationic complex [PtMe$_2$(Me$_3$Sn)-(bpy-^{t}bu$_2$){OC(CD$_3$)$_2$}]$^+$ at low temperature in acetone-d_6. Extremely large second-order rate constants are observed for the oxidative addition of Sn−X bonds to dimethylplatinum(II) complexes, some being greater than 10^8 M^{-1} s^{-1}, and it is established that rates follow the series Sn > Ge > Si > C and I > Br > Cl. Estimates have been made of the Pt−MMe$_3$ bond dissociation energies for [PtXMe$_2$(MMe$_3$)(bpy-^{t}bu$_2$)], X = halide, and these are 233, 182, and 172 kJ mol^{-1} for M = Si, Ge, and Sn, respectively; the values are useful in rationalizing the chemistry of the Pt−M bonds.

Introduction

The oxidative addition of M−X bonds (M = group 14 element; X = H, Me, halogen, etc.) to transition metal centers and the reverse reductive elimination reactions may be important in many catalytic reactions, but there has been little research on the mechanisms or energetics of such reactions, especially when compared to the much studied reactions of alkyl halides.[1] Such knowledge is important in understanding and predicting chemical reactivity. For example, there is a delicate balance between reductive elimination of methyl halide or ethane from trimethyl(halogeno)platinum(IV) complexes, and this can only be understood in terms of both mechanism and thermochemistry.[2,3] To obtain a complete picture of the energetics, it is desirable to study reversible oxidative addition/reductive elimination, but such reactions at platinum centers are relatively rare. Goldberg and co-workers[3] have reported the reversible oxidative addition of MeI to [PtMe$_2$(dppe)], dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$, while the competitive reductive elimination of ethane was found to be thermodynamically favored. There have also been recent reports of reversible tin−halide oxidative addition to platinum-(0) complexes of the general formula [Pt(N−N)(olefin)].[4] None of these studies appears to have focussed on reversibility of the oxidative addition as a function of the halide in R−X or R$_3$M−X, though it is well-known that many oxidative addition

reactions of alkyl or aryl halides R−X become more facile for the heavier halides X.[1] For example the reactivity series C−Br > C−Cl > C−H > C−F for the oxidative addition of Ar−X bonds to platinum(II) has been established,[5] but because the reactions were not easily reversible, it was not possible to determine if thermodynamic effects would follow the same series.

This paper reports both kinetic and thermodynamic data for the reversible oxidative addition reactions of Sn−X and Ge−X (X = halide) bonds to a number of complexes of the formula [PtMe$_2$(diimine)], including the first quantitative data on both the thermodynamics and kinetics of the "halogen effect" in oxidative addition of group 14 halides to platinum(II). In particular, it is shown that the thermodynamics are more favorable and the rates are faster for the heavier halides. A preliminary report of some of this work has been published,[6] and details of the synthesis and characterization of the platinum-(IV) complexes have been reported elsewhere.[7]

Results

VT-NMR Spectroscopic Studies of the Reversible Oxidative Addition Reactions. Variable temperature ^{1}H NMR spectra were obtained for the reversible oxidative addition of Me$_3$SnCl to [PtMe$_2$(bpy-^{t}bu$_2$)] in CD$_2$Cl$_2$ and yielded information on both the kinetics and thermodynamics. Figure 1 shows the NMR spectral series for the Me−Pt and Me−Sn regions

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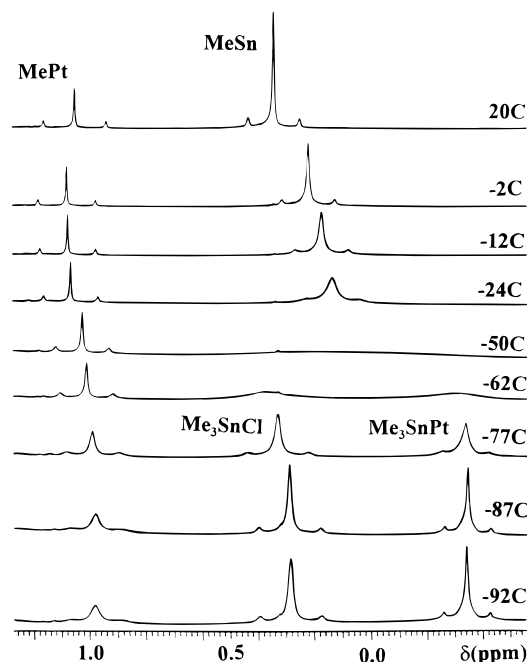
Figure 1. VT ^{1}H NMR spectra (-0.5 to 1.2 ppm) for a solution of [PtClMe$_2$(SnMe$_3$)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in CD$_2$Cl$_2$.

obtained for a solution of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in CD$_2$Cl$_2$. Due to the rapid equilibrium process, this can be considered a 1:2 solution of [PtMe$_2$(bpy-^{t}bu$_2$)]:Me$_3$SnCl (eq 1).
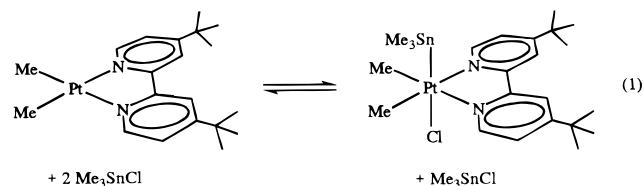
All signals in the spectra shown in Figure 1, except for the trimethyltin signals in low-temperature spectra, are averaged signals arising from a mixture of starting materials and products, and the chemical shifts and J(PtH) values are temperature dependent. The largest change in coupling constant with temperature is seen for ^2J(PtH) associated with the Me–Pt signal. At 20 °C, the value of ^2J(PtH) is 68.1 Hz, and since the coupling constants in both platinum(II) and platinum(IV) complexes are known,[8] it is easily shown that approximately half (58%) of the total platinum exists as [PtMe$_2$(bpy-^{t}bu$_2$)] at this temperature. The magnitude of ^2J(PtH) becomes smaller as the temperature is lowered, and the proportion of [PtMe$_2$-(bpy-^{t}bu$_2$)] decreases. At -50 °C the magnitude of ^2J(PtH) is 56.6 Hz, indicating that the majority of the platinum is in the form of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]. Changes in other coupling constants are smaller and so give a less accurate determination of the equilibrium position.

Figure 1 also shows that the chemical shifts of signals in the ^{1}H NMR spectrum of a solution of [PtClMe$_2$(Me$_3$Sn)-(bpy-^{t}bu$_2$)]·Me$_3$SnCl change with temperature, and the Me–Sn resonance shows the most significant change in chemical shift. At 20 °C, the chemical shift is 0.347 ppm, *ca.* 0.3 ppm smaller than the chemical shift of free Me$_3$SnCl. As the temperature is lowered, the Me–Sn signal moves to lower frequency as a result of the increasing proportion of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] (δ(Me–Sn) = -0.340). At -50 °C the Me–Sn signal is at the coalescence temperature, below

(8) ^2J(PtH) is 85.6 Hz for [PtMe$_2$(bpy-^{t}bu$_2$)] and 55.5 Hz for [PtClMe$_2$(Me$_3$-Sn)(bpy-^{t}bu$_2$)].

which it splits to give separate signals for Me$_3$SnCl and [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)].

The spectra shown in Figure 1 display changes in peak widths with temperature arising, for example, from the large chemical shift difference ($\delta\nu$ = 227 Hz at 300 MHz) between the Me$_3$Sn signals in Me$_3$SnCl and [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] which are in rapid equilibrium. At 20 °C, the averaged Me$_3$Sn signal is fairly sharp (W^* = 1.72 Hz), but as the temperature is lowered the signal begins to broaden until W^* reaches a maximum at the coalescence temperature (-50 °C). Below the coalescence temperature, the Me$_3$Sn signals due to Me$_3$SnCl and [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] begin to sharpen as the temperature is decreased. The peak width of the Me$_3$SnCl signal reaches a minimum at -82 °C and then increases slightly on going to the lowest temperature (-92 °C). Similarly, the averaged Me–Pt resonance shown in Figure 1 shows significant broadening below -50 °C as a result of the same exchange process, namely the chemical equilibrium due to reversible oxidative addition. The effect on the Me–Pt signal is much less pronounced due to the much smaller chemical shift difference (0.266 ppm, 79.9 Hz) between the Me–Pt resonances in [PtMe$_2$-(bpy-^{t}bu$_2$)] and [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] than that between the Me–Sn signals in Me$_3$SnCl and [PtClMe$_2$(Me$_3$Sn)-(bpy-^{t}bu$_2$)] (227 Hz). Therefore, significant broadening of the Me–Pt signal is only seen for slow exchange rates, and hence low temperatures.

The VT ^{1}H-NMR spectral series for CD$_2$Cl$_2$ solutions of [PtBrMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnBr and [PtIMe$_2$(Me$_3$Sn)-(bpy-^{t}bu$_2$)]·Me$_3$SnI are similar to that shown for [PtClMe$_2$-(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in Figure 1. One significant difference between the systems is the position of the equilibria. For the [PtBrMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnBr and [PtIMe$_2$(Me$_3$Sn)-(bpy-^{t}bu$_2$)]·Me$_3$SnI solutions there is never a large fraction of platinum(II) species in solution as evidenced by ^2J(PtMe) values close to those of the platinum(IV) complexes at all temperatures.

The VT-NMR spectral series for a solution of [PtClMe$_2$-(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in toluene-d_8 shows the same general features as for this complex in CD$_2$Cl$_2$ (Figure 1), but with some significantly different features at low temperatures (Figure S1, Supporting Information). The line width of the signal due to free Me$_3$SnCl reaches a minimum at -67 °C, and then gradually increases as the temperature is lowered. At -85 °C the signal is very broad, as are other signals in the spectrum. Accompanying this broadening is an increase in the frequency of the free Me$_3$SnCl signal with decreasing temperature. At -40 °C the free Me$_3$SnCl signal appears at 0.57 ppm, and at -92 °C, its chemical shift has increased to 0.90 ppm. A variable temperature study of pure Me$_3$SnCl in toluene-d_8 indicated that the chemical shift of the Me$_3$SnCl signal in toluene-d_8 does change with temperature, but to a much lesser degree and in the opposite direction to that seen for the Me$_3$SnCl signal of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in toluene-d_8. These features are due to formation of a complex involving a weak PtCl···Me$_3$SnCl bond (see below).

The VT-NMR spectra of a solution of [PtClMe$_2$(Me$_3$Sn)-(bpy-^{t}bu$_2$)]·Me$_3$SnCl in acetone-d_6 also show extra features (Figure S2, Supporting Information). Coalescence of the Me–Sn signal occurs close to -30 °C, and above the coalescence temperature, the spectra are similar to those for the same complex in CD$_2$Cl$_2$ (Figure 1), except that a considerably smaller proportion of oxidative addition product is present. However, as the temperature is lowered below the coalescence point, the Me–Pt signal broadens and splits into two broad signals (coalescence near -62 °C), due to [PtMe$_2$(bpy-^{t}bu$_2$)] (0.98 ppm) and [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] (1.14 ppm). As

the temperature is lowered further the Me−Pt^{IV} signal broadens and splits into two signals (1.14 and 1.08 ppm) as can be seen in the −92 °C spectrum. There is a corresponding splitting of the Me$_3$Sn−Pt^{IV} signal with coalescence near −72 °C and two signals with tin satellites are clearly present at −92 °C. These observations clearly point to two equilibrating Me$_3$Sn−Pt^{IV} species in solution at low temperature. The signal due to free Me$_3$SnCl is sharp at low temperature and does not show any broadening or splitting as the temperature is lowered, indicating that it is not involved in the equilibrium between the two platinum(IV) species. The two Me$_3$Sn−Pt^{IV} signals can be assigned to [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] (1.14 ppm) and [PtMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$){OC(CD$_3$)$_2$}]$^+$ (1.08 ppm) (see below). The low-temperature spectra of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]· Me$_3$SnCl in acetone-d_6 provide information that allows the determination of the free energy of reaction (−1.0 kJ mol^{-1}) as well as the free energy of activation (43 kJ mol^{-1}) on going from the cationic intermediate to the neutral product.

The VT ^{1}H-NMR spectra for a solution of [PtClMe$_2$-(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in CD$_3$CN were also obtained, but due to the higher melting point of CD$_3$CN, the reaction can only be observed above the coalescence temperature. VT ^{1}H-NMR spectral series for both [PtBrMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] and [PtIMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnI in CD$_3$CN were also obtained, and the [PtIMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnI study is the only example of a VT-NMR experiment in CD$_3$CN where both the fast and slow exchange regions are clearly evident. Qualitatively, this indicates that the reductive elimination process is slower for [PtIMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] in CD$_3$CN than for the chloro and bromo analogs. The position of the equilibrium in the [PtIMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnI spectral series does not allow thermodynamic analysis, and so a dilute solution of 1:1 [PtMe$_2$(bpy-^{t}bu$_2$)]:Me$_3$SnI was used.

The VT-^{1}H NMR spectral series obtained for a 1:2 CD$_2$Cl$_2$ solution of [PtMe$_2$(bpy-^{t}bu$_2$)]:Me$_2$SnCl$_2$ shows two distinct Me$_2$SnCl signals (slow exchange region) throughout the available temperature range, with significant broadening due to the oxidative addition/reductive elimination processes above −24 °C. The chemical shift of the Me$_2$SnCl$_2$ signal is relatively constant (δ = ~1.14) at the higher temperatures studied, but below −25 °C there is a pronounced movement to lower frequency (δ = 0.953 at −87 °C). There is a corresponding increase in the ^2J(SnH)$_{ave}$ value associated with the signal [−25 °C, ^2J(SnH)$_{ave}$ = 74.7 Hz; −67 °C, ^2J(SnH)$_{ave}$ = 80.0 Hz]. A similar study in CD$_3$CN revealed exchange broadening over the available temperature range. At low temperature, the Me$_2$SnCl$_2$ signal has large ^2J($^{119/117}$SnH) values of 90.4 and 86.5 Hz, 20 Hz larger than for Me$_2$SnCl$_2$ in benzene, due to PtCl···Me$_2$SnCl$_2$ complex formation.

A VT ^{1}H-NMR study was carried out on a CD$_2$Cl$_2$ solution of [PtClMe$_2$(Me$_3$Ge)(bpy-^{t}bu$_2$)], and Figure 2 shows the Me−Pt and Me−Ge regions at different temperatures. The varying intensities of the two Me−Ge signals show clearly that there is an equilibrium due to a reversible oxidative addition. There is a corresponding decrease in the intensity of the Me−Pt^{II} signal relative to the Me−Pt^{IV} signal with decreasing temperature. There is very little variation in the line widths of the signals with temperature, indicating that the exchange process is slow on the ^{1}H NMR time scale. The full spectrum of the solution at all temperatures clearly shows separate signals for [PtClMe$_2$(Me$_3$Ge)(bpy-^{t}bu$_2$)] and [PtMe$_2$(bpy-^{t}bu$_2$)], also consistent with a slow exchange process. There is little change in the chemical shift of the Me$_3$GeCl signal, indicating that coordination to give [PtClMe$_2$(Me$_3$Ge)(bpy-^{t}bu$_2$)]·Me$_3$GeCl is not occurring to any significant extent. The spectral series is
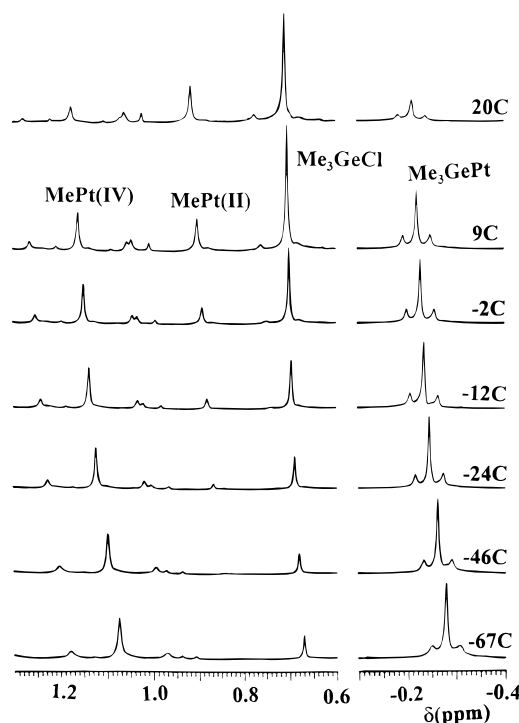
Figure 2. VT ^{1}H NMR spectra (−0.5 to −0.1; 0.6 to 1.3 ppm) for a solution of [PtClMe$_2$(GeMe$_3$)(bpy-^{t}bu$_2$)] in CD$_2$Cl$_2$.

useful for thermodynamic studies by use of integral regions, but the oxidative addition/reductive elimination processes are too slow to allow kinetic analysis.

The VT ^{1}H-NMR spectral series discussed above yield data which allowed the calculation of the thermodynamic and kinetic parameters of the reactions under study. Table 1 contains selected thermodynamic parameters obtained for the oxidative addition reactions studied, Table 2 contains the rate constants and activation parameters for reductive elimination reactions (rate constants at −2.1 °C were selected because errors in the rates are smaller at intermediate temperatures near the coalescence point), and Table 3 contains the activation parameters and rate constants for oxidative addition reactions. An Eyring plot obtained from the VT-NMR study of the reductive elimination of Me$_3$SnCl from [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] in CD$_2$Cl$_2$ shows excellent linearity (r^2 = 0.9985) over a wide temperature range (Figure S3, Supporting Information), though not all systems studied were so well-behaved and so gave larger standard deviations (Tables 1−3).

Results of UV−Visible Spectroscopic Studies. UV−visible spectroscopic studies were conducted in toluene solution since, at the very low concentrations used, side reactions were observed in the solvents dichloromethane and acetone. All the dimethylplatinum(II) complexes employed in this work have intense Pt(5d) to ligand (π^*) MLCT bands in the visible region (503−546 nm in toluene), allowing for straightforward determination of their concentrations in solution.

In the presence of excess Me$_3$SnX (X = Cl, Br), the oxidative addition products resulting from the addition of Me$_3$SnX to [PtMe$_2$(diimine)] are light yellow in solution, and the electronic spectra show no absorbance at λ_{max} of the parent platinum(II) complexes, allowing for a straightforward determination of platinum(II) concentrations in the titration studies. Solutions of the complexes [PtIMe$_2$(Me$_3$Sn)(diimine)] are bright yellow, and the MLCT maxima remain in the visible region and bands have significant overlap with the MLCT bands of the parent platinum(II) complexes. It was thus necessary to obtain the

Table 1. 1H VT-NMR-Derived Thermodynamic Parameters for the Oxidative Addition of Group 14−Halide Bonds to [PtMe$_2$(diimine)] Complexes

group 14 reagent	diimine ligand	solvent	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})	K_{eq}(25 °C (mol^{-1} L)
Me$_3$SnCl	bpy-^{t}bu$_2$	toluene-d_8	−49 ± 2	−151 ± 6	−4.7 ± 0.4*	7 ± 1*
Me$_3$SnCl	bpy-^{t}bu$_2$	CD$_2$Cl$_2$	−33 ± 2	−84 ± 9	−7.9 ± 0.1	24 ± 1
Me$_3$SnCl	py-n-pr	CD$_2$Cl$_2$	−36 ± 1	−110 ± 4	−2.8 ± 0.2*	3.2 ± 0.7*
Me$_3$SnCl	paen-me$_2$	CD$_2$Cl$_2$	−35.0 ± 0.9	105 ± 4	−4.2 ± 0.2*	5.6 ± 0.6*
Me$_3$SnCl	bpy-^{t}bu$_2$	acetone-d_6	−25 ± 1	−70 ± 4	−3.5 ± 0.3	4.2 ± 0.9
Me$_3$SnCl	bpy-^{t}bu$_2$	CD$_3$CN	−23 ± 2	−52 ± 6	−7.2 ± 0.1	18.1 ± 0.8
Me$_3$SnBr	bpy-^{t}bu$_2$	CD$_2$Cl$_2$	−35 ± 2	−66 ± 6	−14.7 ± 0.2	380 ± 20
Me$_2$SnBr	bpy-^{t}bu$_2$	CD$_3$CN	−30 ± 2	−49 ± 7	−15.9 ± 0.3	620 ± 30
Me$_3$SnI	bpy-^{t}bu$_2$	CD$_2$Cl$_2$	−45 ± 3	−70 ± 10	−25.4 ± 0.5	29000 ± 2000
Me$_3$SnI	bpy-^{t}bu$_2$	CD$_3$CN	−49 ± 6	−80 ± 20	−26.9 ± 0.7	52000 ± 4000
Me$_3$GeCl	bpy-^{t}bu$_2$	CD$_3$Cl$_2$	−38 ± 4	−100 ± 20	−7.4 ± 0.2*	20 ± 2^a

^{a} T = 20 °C.

Table 2. Rate Constants and Activation Parameters for Reductive Elimination Reactions of Tin−Halide Bonds from Pt(IV) Complexes

group 14 reagent	diimine ligand	solvent	k_{red}(−2.1 °C) (s^{-1})	$\Delta H^{\ddagger}_{red}$ (kJ mol^{-1})	$\Delta S^{\ddagger}_{red}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}_{red}$(25 °C)^a (kJ mol^{-1})
Me$_3$SnCl	bpy-^{t}bu$_2$	toluene-d_8	2100 ± 300	47 ± 6	−9 ± 20	49 ± 1^b
Me$_3$SnCl	bpy-^{t}bu$_2$	CD$_2$Cl$_2$	16000 ± 2000	38.3 ± 0.8	−23 ± 3	45.1 ± 0.2
Me$_3$SnCl	py-n-pr	CD$_2$Cl$_2$	23000 ± 3000	34 ± 2	−37 ± 7	44 ± 1^b
Me$_3$SnCl	paen-me$_2$	CD$_2$Cl$_2$	12000 ± 1000	35 ± 1	−38 ± 5	45.9 ± 0.6^b
Me$_3$SnCl	bpy-^{t}bu$_2$	acetone-d_6	42000 ± 5000	45 ± 2	8 ± 7	42 ± 1
Me$_3$SnCl	bpy-^{t}bu$_2$	CD$_3$CN	18000 ± 1000	37 ± 2	−25 ± 8	44.3 ± 0.3^b
Me$_3$SnBr	bpy-^{t}bu$_2$	CD$_2$Cl$_2$	1850 ± 120	33.6 ± 0.8	−58 ± 3	50.7 ± 0.2
Me$_2$SnBr	bpy-^{t}bu$_2$	CD$_3$CN	4100 ± 400^c	32 ± 1	−55 ± 4	48.3 ± 0.3
Me$_3$SnI	bpy-^{t}bu$_2$	CD$_2$Cl$_2$	584 ± 36	48 ± 3	−20 ± 10	53.3 ± 0.2
Me$_3$SnI	bpy-^{t}bu$_2$	CD$_3$CN	600 ± 30	55 ± 2	10 ± 8	51.9 ± 0.2
Me$_3$GeCl	bpy-^{t}bu$_2$	CD$_3$Cl$_2$	12 ± 1	58 ± 5	−10 ± 20	61.1* ± 0.3

^{a} Calculated directly from k_{red}. ^{b} T = 20 °C. ^{c} T = −7.5 °C.

Table 3. Calculated Activation Parameters for Oxidative Addition Reactions of Trimethyltin−Halide Bonds to [PtMe$_2$(diimine)] Complexes

group 14 reagent	diimine ligand	solvent	k_{ox}(25 °C) (L mol^{-1} s^{-1})	$\Delta H^{\ddagger}_{ox}$ (kJ mol^{-1})	$\Delta S^{\ddagger}_{ox}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}_{ox}$(25 °C) (kJ mol^{-1})
Me$_3$SnCl	bpy-^{t}bu$_2$	toluene-d_8	(6.0 ± 0.4) × 10^4 ^{a}	0 ± 6	−160 ± 20	45 ± 1^a
Me$_3$SnCl	bpy-^{t}bu$_2$	CD$_2$Cl$_2$	(1.86 ± 0.04) × 10^6	5 ± 3	−110 ± 10	37.2 ± 0.3
Me$_3$SnCl	py-n-pr	CD$_2$Cl$_2$	(2.5 ± 0.2) × 10^5	0 ± 2	−148 ± 8	41 ± 1^a
Me$_3$SnCl	paen-me$_2$	CD$_2$Cl$_2$	(2.3 ± 0.1) × 10^5 ^{a}	0 ± 2	−142 ± 6	41.6 ± 0.7^a
Me$_3$SnCl	bpy-^{t}bu$_2$	acetone-d_6	(9.4 ± 0.7) × 10^5	20 ± 2	−62 ± 8	39 ± 1
Me$_3$SnCl	bpy-^{t}bu$_2$	CD$_3$CN	(1.96 ± 0.05) × 10^6	15 ± 3	−77 ± 9	37.1 ± 0.3
Me$_3$SnBr	bpy-^{t}bu$_2$	CD$_2$Cl$_2$	(3.10 ± 0.08) × 10^6	0 ± 2	−124 ± 7	36.0 ± 0.3
Me$_2$SnBr	bpy-^{t}bu$_2$	CD$_3$CN	(1.30 ± 0.05) × 10^7	2 ± 2	−103 ± 8	32.4 ± 0.4
Me$_3$SnI	bpy-^{t}bu$_2$	CD$_2$Cl$_2$	(3.9 ± 0.2) × 10^7	3 ± 4	−80 ± 20	29.7 ± 0.6
Me$_3$SnI	bpy-^{t}bu$_2$	CD$_3$CN	(2.2 ± 0.2) × 10^8 ^{a}	6 ± 7	−60 ± 20	25.0 ± 0.7^a

^{a} T = 20 °C.

Table 4. K_{eq} and $\Delta G°$ for Oxidative Addition of Me$_3$SnX (X = Cl, Br, I) to [PtMe$_2$(diimine)] at 25 °C

	Me$_3$SnCl		Me$_3$SnBr		Me$_3$SnI	
	K_{eq} (L mol^{-1})	$\Delta G°$ (kJ mol^{-1})	K_{eq} (L mol^{-1})	$\Delta G°$ (kJ mol^{-1})	K_{eq} (L mol^{-1})	$\Delta G°$ (kJ mol^{-1})
[PtMe$_2$(bpy)]	114.9 ± 0.5	−11.75 ± 0.04	145.0 ± 0.7	−12.33 ± 0.04	34300 ± 400	−25.87 ± 0.09
[PtMe$_2$(bpy-^{t}bu$_2$)]	46.5 ± 0.2	−9.51 ± 0.03	145.0 ± 0.7	−12.33 ± 0.04	40800 ± 500	−26.30 ± 0.09
[PtMe$_2$(py-n-pr)]	123.5 ± 0.6	−11.9 ± 0.04	190 ± 1	−13.00 ± 0.05	14100 ± 300	−23.7 ± 0.1
[PtMe$_2$(paen-me$_2$)]	80.3 ± 0.4	−10.87 ± 0.04	150.3 ± 0.8	−12.42 ± 0.04	37800 ± 600	−26.1 ± 0.1

extinction coefficients of these complexes at the wavelength at which measurements were taken for the equilibrium study. The platinum(IV) complexes resulting from the oxidative addition of Me$_3$SiX (X = Br, I) to [PtMe$_2$(diimine)] were sparingly soluble in toluene, thus making the determination of electronic spectra difficult. Therefore, dichloromethane was used for these determinations.

Toluene solutions of $1-3 \times 10^{-4}$ M [PtMe$_2$(diimine)] were titrated with 0.1, 0.08, and 0.002 M toluene solutions of Me$_3$SnCl, Me$_3$SnBr, and Me$_3$SnI, respectively. Addition of tin reagent resulted in a lightening in the color of the solutions, and a corresponding decrease in the intensity of the lowest energy MLCT band attributed to the [PtMe$_2$(diimine)]

species. Table 4 presents the equilibrium constants and standard free energies obtained for the oxidative addition reactions of Me$_3$SnX (X = Cl, Br, I) to [PtMe$_2$(diimine)]. The oxidative addition reactions of Me$_3$SnX to [PtMe$_2$(diimine)] show equilibrium constants of 46.5 to 123.8 L mol^{-1}, 145.2 to 191.3 L mol^{-1}, and 14600 to 40800 L mol^{-1} for X = Cl, Br, and I, respectively. There is a decrease in $\Delta G°_{ox}$ of 1.1 to 2.8 kJ/mol on going from X = Cl to Br and of 10.7 to 14.0 kJ/mol on going from X = Br to I.

There is some disagreement between thermodynamic data obtained by UV−visible spectroscopy (Table 4) and by NMR (Table 1) for toluene solutions. It is likely that the UV−visible data are more accurate since they are obtained at lower

concentrations, where complications due to secondary complexation will not occur.

Discussion

Interpretation of the Spectral Data. The VT ^{1}H-NMR studies of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl clearly show that oxidative addition of Me$_3$SnCl to [PtMe$_2$(bpy-^{t}bu$_2$)] is rapid and reversible. The system behaves in a relatively straightforward manner in CD$_2$Cl$_2$, but some different features are seen in other solvents. In toluene-d_8 there is a broadening of the Me$_3$SnCl signal at low temperatures, indicating that there is another equilibrium process involving PtCl···Me$_3$SnCl complex formation (eq 2). This arises since toluene-d_8 has very poor

(N−N = bpy-^{t}bu$_2$)
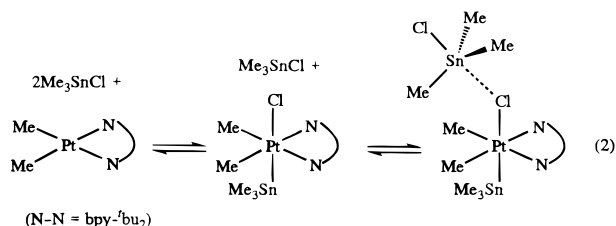
coordination ability. In solvents such as acetone and acetonitrile, the solvents S coordinate to give a five-coordinate tin complex Me$_3$SnCl(S), but noncoordinating solvents such as toluene do not.[9] In the absence of solvent coordination, the polar Pt−X group (*trans* to Me$_3$Sn which has a strong *trans* influence) of the platinum(IV) complex coordinates to give a solution structure analogous to that observed in the solid state for [PtMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnI.[7]

Support for this conclusion is provided by the increases in the ^{1}H chemical shift and $^2J(^{117/119}$SnH) of the Me$_3$SnCl signal with decreasing temperature in toluene-d_8, indicating an increase in concentration of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl (Figure S1, Supporting Information).[10] Further evidence of coordination to Me$_3$SnCl by the platinum(IV) complex at low temperatures is provided by the large value of $^2J(\text{SnH})_{ave}$ for the Me$_3$SnCl signal; at −72 °C, the value of $^2J(\text{SnH})_{ave}$ is 66.6 Hz, considerably larger than the 57.2 Hz observed for pure Me$_3$SnCl in toluene-d_8 at −60 °C, and indicative of 5-coordinate tin.[9]

There is evidence for the coordination of tin reagent to the platinum(IV) complex in solution, such as in eq 2, in CD$_2$Cl$_2$ solution also. For example, we note that the value of $^1J(\text{SnH})_{ave}$ is 66.1 Hz for the Me$_3$SnCl signal in a solution of [PtClMe$_2$-(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl at −87 °C in CD$_2$Cl$_2$ (Figure 1), and only 57.2 Hz for pure Me$_3$SnCl in CD$_2$Cl$_2$. In the case of [PtBrMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnBr, a broadening in the Me$_3$SnBr signal occurs on going from −77 °C to −87 °C, and the $^2J(\text{SnMe})_{ave}$ value is 62.4 Hz at −87 °C compared to 56.8 Hz for Me$_3$SnBr in CD$_2$Cl$_2$ at room temperature.[11] However, the low temperature (−57 °C) ^{1}H-NMR spectrum of [PtIMe$_2$-(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnI in CD$_2$Cl$_2$ shows $^2J(^{119}$SnH) = 58.2 Hz for the Me$_3$SnI signal, close to the value of 57.7 Hz observed for Me$_3$SnI at room temperature in CD$_2$Cl$_2$, indicating that little [PtIMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnI is formed.[10,11] These findings are consistent with the established relative Lewis acid strengths: Me$_3$SnCl > Me$_3$SnBr > Me$_3$SnI.[12,13]

The VT ^{1}H-NMR spectral series of a 1:2 solution of [PtMe$_2$(bpy-^{t}bu$_2$)]:Me$_2$SnCl$_2$ shows a pronounced increase in $^2J(\text{SnH})_{ave}$ as well as a substantial decrease in chemical shift for the Me−Sn signal of Me$_2$SnCl$_2$, and this is again attributed to increased complex formation PtCl···Me$_2$SnCl$_2$ at lower temperatures.

The NMR parameters for the platinum(IV) complexes formed from Me$_3$SnCl and [PtMe$_2$(bpy-^{t}bu$_2$)] in acetone-d_6 are not consistent with the above type of complex formation, and this is not surprising since the Me$_3$SnCl in solution will already be present as the acetone complex.[9] One might consider the possibility that the two platinum(IV) species are simply *cis* and *trans* isomers, but again the NMR data are not consistent with this hypothesis.[14] The most likely identity of the second platinum(IV) species at low temperatures in acetone-d_6 is a platinum(IV) cation, [PtMe$_2$(Me$_3$Sn)(Me$_2$CO)(bpy-^{t}bu$_2$)]$^+$, with solvent acetone occupying the coordination site *trans* to Me$_3$Sn. The relative populations of the two species at −92 °C indicate a free energy change of only −1.0 kJ mol^{-1} on going from the cation to the neutral platinum(IV) species. The remarkable ease of ionization of the platinum(IV)−halide bond can be rationalized in terms of the extremely long Pt−I bond [2.881(4) Å] in the crystal structure of [PtIMe$_2$(Me$_3$Sn)-(bpy-^{t}bu$_2$)],[7] indicating the powerful *trans* influence exerted by the trimethyltin ligand. A similar situation is expected for [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)], and since the Pt^{IV}−Cl bond is very weak and polar, it is reasonable to expect only a small energy difference between this complex and the cation. The coexistence of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)] and [PtMe$_2$(Me$_3$Sn)-(bpy-^{t}bu$_2$)(OC(CD$_3$)$_2$)]$^+$ is thus reasonable in thermodynamic terms. Recent work by Elsevier *et al.*[15] shows similar equilibria for complexes of the type [PtMe$_3$(SO$_3$CF$_3$)(N−N)] where N−N is a rigid diimine ligand. Although chloride is a much better ligand than SO$_3$CF$_3$−, the Me$_3$Sn group has a considerably higher *trans* influence than methyl, and hence the systems are roughly analogous. Precedence for the stability of platinum−acetone complexes has been established by the structure of [PtMe(Me$_2$CO)(PMe$_2$Ph)$_2$]PF$_6$.[16]

In the *trans* oxidative addition of MeI to [PtMe$_2$(bpy)], the cationic intermediate [PtMe$_3$(bpy)(NCMe)]$^+$ has been observed in CD$_3$CN solution at low temperature.[17] The chemical shift of the equatorial Me−Pt^{IV} resonance in the intermediate cation was found to be 0.22 ppm lower than for the thermodynamic product, [PtIMe$_3$(bpy)]. Similarly, the Me−Pt^{IV} resonance of the cation is expected to have a lower chemical shift than the neutral platinum^{IV} complex. Thus, it is reasonable to assign the Me$_3$Sn−Pt^{IV} signal at higher frequency to the cationic species, [PtMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$){OC(CD$_3$)$_2$}]$^+$, and the Me$_3$Sn−Pt^{IV} at lower frequency to the neutral complex, [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]. Since CD$_3$CN is a better coordinating solvent than acetone-d_6,[18] it is expected that a solution of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in CD$_3$CN will contain the cation [PtMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)(N≡CCD$_3$)]$^+$ analogous to

(9) Bolles, T. F.; Drago, R. S. *J. Am. Chem. Soc.* **1966**, *88*, 5730.

(10) We have measured the room temperature chemical shifts of Me$_3$SnCl in acetone-d_6 and CD$_3$CN as 0.61 and 0.59 ppm respectively, compared to a chemical shift of 0.25 ppm in toluene-d_8. Me$_3$SnCl has been shown to exist largely as five-coordinate solvated species in the first two solvents and as discrete molecules in toluene-d_8 (ref 9).

(11) Since CD$_2$Cl$_2$ has poor coordination ability, the magnitude of $^2J(\text{SnMe})_{ave}$ is not expected to change appreciably on going to lower temperatures.

(12) Van Der Kelen, G. P.; Van Den Berghe, E. V.; Verdonck, L. *Organotin Compounds*; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1971; Vol. 1, pp 118−9.

(13) Van Den Berghe, E. V.; Van Der Kelen, G. P. *J. Organomet. Chem.* **1966**, *6*, 515.

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(17) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548.

(18) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science Publishers Ltd.: London, 1973; pp 307−8.

that formed in acetone-d_6. However, since we do not observe the slow exchange region for the Me$-$Sn or Me$-$Pt signals in CD$_3$CN, there is no direct evidence for the existence or absence of a cationic species.

Titrations of [PtMe$_2$(diimine)] complexes with Me$_3$SiX (X = Cl, Br, I) in toluene resulted in UV$-$visible spectra consistent with [PtMeX(diimine)] and not the oxidative addition product. One explanation for this is the oxidative addition of Me$_3$SiX (X = Br, I) to [PtMe$_2$(diimine)], followed by the reductive elimination of tetramethylsilane to give [PtXMe(bpy)]; since methane was detected by GC, it is likely that the silane reacts with traces of water to give Me$_3$SiOH and HX, which then undergoes oxidative addition to the dimethylplatinum(II) complex. This is followed by the rapid reductive elimination of methane to give [PtMeX(diimine)]. Similar behavior was observed for attempted titrations of Me$_3$GeCl to [PtMe$_2$(bpy-^{t}bu$_2$)]. It is very difficult to avoid these problems at the low concentrations required for the UV$-$visible studies.

Thermodynamics

Effect of Solvent on Thermodynamic Parameters. As a model system for the discussion of solvent effects we will consider the oxidative addition of Me$_3$SnCl to [PtMe$_2$(bpy-^{t}bu$_2$)] to give [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]. The relative solvent effects on the starting materials and products determine the overall effect of a change in solvent on the thermodynamics of the reaction. One important factor is the bimolecular nature of the reaction: there are two neutral starting materials and one neutral product, and hence solvation of the starting materials should be greater than that for the product. Since solvation decreases with diffusion of charge,[19] Me$_3$SnCl, which is relatively small and polar, will be more strongly solvated than other species in solution.

Solvation affects both the enthalpy and entropy of a reaction. The solvation of a species has a stabilizing effect, and so the ΔH of a reaction will increase if the starting materials are better solvated than the products, thereby disfavoring the reaction. This is the case for the oxidative addition reactions discussed here. On changing to a more polar solvent the solvation of all species in solution is increased, but the effect is greater for the starting materials since the reaction is bimolecular and the starting materials are more polar than the product. The result is a stabilization of the starting materials with respect to the product, and an increase in ΔH is expected for the reaction on going to more polar solvents. A further consideration is the added stabilization of Me$_3$SnCl resulting from adduct formation with the solvent. This is not expected in toluene-d_8 and CD$_2$Cl$_2$; however, both acetone-d_6 and CD$_3$CN are known to coordinate to Me$_3$SnCl, with ΔH values of -23.8 and -20.1 kJ mol^{-1}, respectively.[9] The invariance of the ^2J(SnH) value associated with the Me$_3$Sn$-$Pt^{IV} signal indicates that coordination of this type is not significant in the platinum(IV) species, and coordination of solvent to Me$_3$SnCl is expected to disfavor the oxidative addition reaction on enthalpic grounds. It is clear from the thermodynamic parameters for the oxidative addition of Me$_3$SnCl to [PtMe$_2$(bpy-^{t}bu$_2$)] in various solvents (Table 1) that there is a pronounced increase in ΔH with increasing solvent polarity.

The bimolecular nature of the oxidative addition reactions is expected to result in a decrease in entropy. However, the total effect of both reagents and solvent must be considered to determine the overall entropy change for the reaction. It is expected that the degree of solvation (and hence ordering) of the solvent

Table 5. Free Energy Change in Oxidative Addition to Platinum(II) with Halide Change in Me$_3$SnX

method (solvent)	$\Delta G^\circ_{Cl} - \Delta G^\circ_{Br}$	$\Delta G^\circ_{Br} - \Delta G^\circ_{I}$
electronic spec. (toluene)[a]	1.1$-$2.8	10.7$-$14.0
VT-NMR (CD$_2$Cl$_2$)[b]	6.8 $\pm$ 0.3	10.7 $\pm$ 0.5
VT-NMR (CD$_3$CN)[b]	8.8 $\pm$ 0.3	11.0 $\pm$ 0.7
calcd[6a]	4.5	10.5

[a] Range for all reactions studied. [b] Reaction with [PtMe$_2$(bpy-^{t}bu$_2$)].

will be greater for the starting materials. The result is an expected increase in solvent entropy upon oxidative addition. Table 1 shows that the values of ΔS become less negative with increasing solvent polarity, consistent with an increase in solvent order for the starting materials relative to the product with increasing solvent polarity.

The free energy for the oxidative addition of Me$_3$SnCl to [PtMe$_2$(bpy-^{t}bu$_2$)] is small and negative in all solvents, leading to a small driving force for the reaction. There is no clear trend to link ΔG to solvent polarity because of the counteracting effects in the ΔH and ΔS terms as a function of polarity.

Effect of Diimine Ligand. Little effect on thermodynamic parameters of the oxidative addition reaction is seen upon changing the nature of the diimine ligand. The reactions involving ligands with dangling groups [py-n-pr = 2-(C$_5$H$_4$N)CH=NCH$_2$-CH$_2$CH$_3$ and paen-me$_2$ = 2-(C$_5$H$_4$N)CH=NCH$_2$CH$_2$NMe$_2$] are somewhat less favored than those involving bpy-^{t}bu$_2$, largely due to an entropy effect. This is probably the result of the restricted movement of the dangling group in the platinum(IV) complex compared to the platinum(II) complex as a result of the axial ligands in the former.

Effect of the Group 14 Reagent. There is a pronounced decrease in the free energy of oxidative addition in the order Cl > Br > I in toluene-d_8, CD$_2$Cl$_2$, and CD$_3$CN (Table 5). The decrease in free energy on going from Me$_3$SnCl to Me$_3$SnBr in CD$_2$Cl$_2$ and CD$_3$CN (VT ^{1}H NMR) is somewhat larger than those found in toluene (UV$-$vis). The decrease in free energy on going from Me$_3$SnBr to Me$_3$SnI is essentially identical, within experimental error, in all solvents studied. An inspection of the ΔH and ΔS values in Table 1 indicates that, in most cases, the change in free energy upon a change in halide is the result of an enthalpy change. However, in some cases there are substantial variations in ΔS, which have a significant impact on the free energy difference between reactions. For example, the entropy term is the dominant factor affecting the free energy difference between the oxidative addition of Me$_3$SnCl and Me$_3$SnBr to [PtMe$_2$(bpy-^{t}bu$_2$)].

One other group 14 reagent whose oxidative addition reaction to [PtMe$_2$(bpy-^{t}bu$_2$)] proved amenable to thermodynamic analysis was Me$_3$GeCl. This reagent showed thermodynamic parameters similar to those for the reaction involving Me$_3$SnCl (Table 1).

Activation Parameters and Mechanism of Reaction

The reversible nature of the oxidative addition of group 14$-$halogen bonds to [PtMe$_2$(diimine)] rules out free radical mechanisms and thus suggests a two-electron mechanism, i.e. three-center *cis* addition or S$_N$2 oxidative addition. It is well-known that methylhalotin compounds can readily accept a Lewis base to give five-coordinate (and higher) species.[20] The structure of the adduct [PtIMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnI shows a five-coordinate tin species,[7] and the variable-temperature ^{1}H-NMR study of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in toluene-d_8 suggests a similar structure in solution at low

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(20) For example, see: Omae, I. *Organotin Chemistry*; Elsevier: New York, 1989; pp 241$-$248.
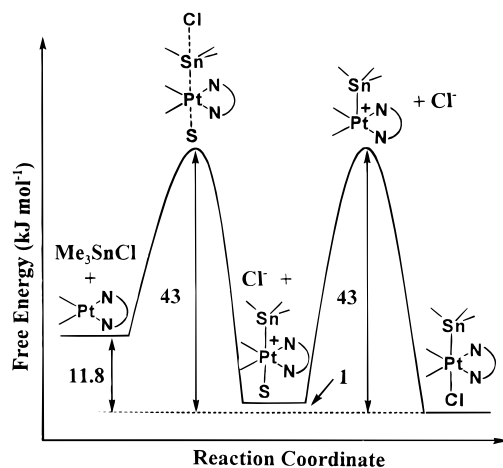
Figure 3. Proposed reaction coordinate for the reversible oxidative addition of Me$_3$SnCl to [PtMe$_2$(bpy-^{t}bu$_2$)] in acetone-d_6.

temperature. Thus, it seems evident that methylhalotin reagents are well-suited to react by an S$_N$2 pathway, which would require a five-coordinate tin species in the transition state.

All platinum(IV) products reported here are formed by *trans* oxidative addition. Though not conclusive evidence, this strongly favors an S$_N$2 over a concerted pathway. In a concerted pathway, the initial oxidative addition product would be that resulting from *cis* addition, and an exclusively *trans* addition product would only be observed if there was a rapid isomerization following initial *cis* oxidative addition. The principle of microscopic reversibility would require isomerization in the opposite direction prior to reductive elimination, suggesting a low-energy barrier and rapid isomerization. Under these conditions the observation of both isomers would be expected, but this never occurs.

One strong piece of evidence for the S$_N$2 mechanism is provided by the low-temperature ^{1}H NMR spectra of [PtClMe$_2$-(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in acetone-d_6 (Figure S2, Supporting Information). This shows the cationic complex [PtMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)(OC(CD$_3$)$_2$)]$^+$ to be in equilibrium with [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]. A cationic species is the expected intermediate of an S$_N$2 oxidative addition reaction.[21] The spectral series of [PtClMe$_2$(Me$_3$Sn)(bpy-^{t}bu$_2$)]·Me$_3$SnCl in acetone-d_6 shows the coalescence point (both MePt and Me−Sn signals) for the equilibrium between the cation and the neutral platinum(IV) product. The coalescence temperature along with the relative proportions of the two species can be used to calculate the free energy of activation for the process (43.0 ± 0.6 kJ mol^{-1}).[22] The free energy of activation for the oxidative addition of Me$_3$SnCl to [PtMe$_2$(bpy-^{t}bu$_2$)] at −70 °C can be calculated as 43 ± 1 kJ mol^{-1}. This represents an averaged free energy since both the cation and the neutral platinum(IV) complex are present in solution over the range of measurements. However, because the two species are very close in energy (1 kJ mol^{-1}), the free energy can be considered as that for the reaction of Me$_3$SnCl with [PtMe$_2$(bpy-^{t}bu$_2$)] to form the cationic intermediate. The result is that we can construct a complete reaction coordinate for the reaction (Figure 3). This is the first example of a fully elucidated reaction coordinate, including the cationic intermediate, for an oxidative addition reaction of a metal complex. It is perhaps surprising that the free energy of activation on going from the starting materials to the intermediate is essentially the same as that on going from the cation to the neutral platinum(IV) complex. The similarity in the energies of the two activated complexes suggests the possibility that they

may be very similar in structure. By this reasoning, the activated complex formed by initial attack of Me$_3$SnCl on [PtMe$_2$(bpy-^{t}bu$_2$)] has, to a large degree, completed Pt−Sn bond formation and Sn−Cl bond cleavage. As well, there is likely an insignificant degree of solvent coordination to the activated complex. For the more weakly coordinating solvent used in this work (CD$_2$Cl$_2$ and toluene-d_8) we can expect the cationic intermediate to be significantly higher in energy due to much poorer solvation than in acetone-d_6. However, in CD$_3$CN we expect a very similar reaction coordinate as that in acetone-d_6 due to the strong coordinating ability of this solvent.

With the above discussion in mind, the activation parameters obtained by our variable-temperature ^{1}H-NMR studies can be interpreted. One of the most striking features of the reversible oxidative addition/reductive elimination reactions is the extremely rapid rate of the processes. For the oxidative addition reaction of Me$_3$SnI to [PtMe$_2$(bpy-^{t}bu$_2$)] in CD$_3$CN at 25 °C, the rate constant is 3 × 10^8 M^{-1} s^{-1}, close to the diffusion-controlled process (*ca.* 10^9 M^{-1} s^{-1}).[23] This is several orders of magnitude faster than is seen for the oxidative addition of MeI to organoplatinum(II) complexes. For example, a rate constant of 47 M^{-1} s^{-1} was found for the oxidative addition of MeI to [PtPh$_2$(bpy)] in acetone at 30 °C,[24] and a rate constant of 69 M^{-1} s^{-1} was found for the oxidative addition of MeI to [PtMe$_2$(bpy)] in acetone at 25 °C.[25] The very rapid reactions involving tin reagents can be ascribed to the ease with which these compounds achieve a five-coordinate geometry, as would be required in the activated complex of a reaction proceeding by the S$_N$2 mechanism. Stable five-coordinate tin complexes are quite common and are formed even with weak Lewis bases such as acetone.[9] Alkyl halides only form five-coordinate species with great difficulty, and hence the activation barrier is much higher than that for a S$_N$2 reaction involving a methylhalotin compound.

Effect of Solvent. Consider the reversible oxidative addition of Me$_3$SnCl to [PtMe$_2$(bpy-^{t}bu$_2$)] as a typical example. There is a pronounced increase in the rate of reductive elimination in the series toluene-d_8 < CD$_2$Cl$_2$ < acetone-d_6 (Table 3). Such a trend is generally accepted as being characteristic of a transition state that is more polar than the starting materials.[26] One would expect the dipolar activated complex to be stabilized by an increase in the polarity of the solvent, whereas the neutral reactants would hardly be affected. This implies that the enthalpy of activation, $\Delta H^{\ddagger}$, should decrease on going to solvents of higher polarity, and indeed, this is consistent with our results in toluene-d_8, CD$_2$Cl$_2$, and acetone-d_6.

For reactions where neutral reagents proceed *via* a highly polar transition state, it has been observed that $\Delta S^{\ddagger}$ increases in more polar solvents, indicating decreasing order in the transition state relative to the ground state.[26] Examples of this include the oxidative addition of MeI to [PtPh$_2$(bpy)][24] and [IrCl-(CO)(PPh$_3$)$_2$].[27,28] For the oxidative addition reaction, it is clear that $\Delta S^{\ddagger}$ becomes less negative with more polar solvents; values of −160, −106, and −61.8 J mol^{-1} K^{-1} are seen for reactions in toluene-d_8, CD$_2$Cl$_2$, and acetone-d_6, respectively.[29] It has been found that solvent effects on the rate of an oxidative

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(23) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 314.

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(28) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.

addition reaction are usually dominated by the $\Delta S^{\ddagger}$ term, and this is typical of reactions proceeding through a highly polar transition state.[30] Our results are consistent with this proposal. The decrease in $\Delta G^{\ddagger}$ on going from toluene-d_8 to CD_2Cl_2 is largely due to the entropy change. Both enthalpy and entropy changes have a significant effect on the change in $\Delta G^{\ddagger}$ on going from CD_2Cl_2 to acetone-d_6, but the large influence of the $\Delta H^{\ddagger}$ term is easily explained as resulting from acetone-d_6 coordination to Me_3SnCl. These results indicate a highly polar transition state and provide further evidence for the S_N2 pathway.

Ugo and co-workers[31] have noted that substantial negative $\Delta S^{\ddagger}$ values are not inconsistent with a concerted mechanism since considerable distortion of the complex is required at the transition state. However, studies have established large negative $\Delta S^{\ddagger}$ values for oxidative addition reaction proceeding by the S_N2 mechanism, and considerably less negative $\Delta S^{\ddagger}$ values for reactions proceeding by a concerted mechanism.[26,32] The concerted pathway for oxidative addition does not lead to a highly polar species and hence there is not as large a decrease in solvent entropy on approaching the transition state. $\Delta S^{\ddagger}$ values of -156 and -114 J mol^{-1} K^{-1} in benzene and acetone, respectively, were found for the oxidative addition of MeI to $[PtPh_2(bpy)]$ by an S_N2 type mechanism.[24] Our values for the oxidative addition of Me_3SnCl to $[PtMe_2(bpy\text{-}^tbu_2)]$ are comparable to those of these studies, and are consistent with a similar mechanism. The rate constants for the reductive elimination of Me_3SnCl from $[PtClMe_2(Me_3Sn)(bpy\text{-}^tbu_2)]$ at -2.1 °C show a pronounced rate increase with increasing solvent polarity: toluene-d_8 < CD_2Cl_2 < acetone-d_6. There is a correspondingly large increase in the rate of oxidative addition on moving from toluene-d_8 to the more polar solvents, as evidenced by the $\Delta G^{\ddagger}_{ox}$ values. Such rate increases are often taken as evidence of a polar transition state for reactions involving neutral reagents.[33]

The rate of the reductive elimination reaction in CD_3CN is anomalously slow. According to the above arguments, the rate would be expected to be faster than in acetone-d_6, but this is not the case. In examining the $\Delta S^{\ddagger}_{red}$ and $\Delta H^{\ddagger}_{red}$ values for the reaction in the two solvents it appears that the change in $\Delta G^{\ddagger}_{red}$ is largely an entropy effect. This may be the result of substantial amounts of low-energy cationic intermediate $[PtMe_2(Me_3Sn)(bpy\text{-}^tbu_2)(NCCD_3)]^+$ in solution which results in a high degree of solvent ordering.

Effect of Diimine Ligand. Kinetic data were determined for the reactions between Me_3SnCl and $[PtMe_2(N\text{-}N)]$ ($N\text{-}N$ = bpy-$^tbu_2$, py-n-py, paen-me$_2$) to determine if the dangling amino group had any effect on the reaction. Oxidative addition reactions involving the dangling ligands were somewhat slower than those for $[PtMe_2(bpy\text{-}^tbu_2)]$, perhaps indicating that the dangling ligand must be positioned in such a way as not to interfere with the incoming electrophile. There is no evidence

to imply that the dangling dimethylamino group of paen-me$_2$ participates in the reaction.

Effect of Group 14 Reagent. Changing the nature of the tin reagent has a dramatic effect on the rates of Sn$-$X oxidative addition and reductive elimination. In both CD_2Cl_2 and CD_3CN there is a substantial decrease in the rate of reductive elimination in the following order: Me_3SnCl > Me_3SnBr > Me_3SnI. This rate decrease is directly reflected in the increased $\Delta G^{\ddagger}$ values (Table 2), and there is a strong correlation with the corresponding ΔG values (Table 1, $\Delta G_{re} = -\Delta G_{ox}$; Figure S4, Supporting Information). The opposite effect is expected for the oxidative addition reaction and, for reactions carried out in both CD_2Cl_2 and CD_3CN, there is a significant decrease in $\Delta G^{\ddagger}$ following the order Me_3SnCl > Me_3SnBr > Me_3SnI. This same reactivity order, I > Br > Cl, follows the classic pattern established for the rates of S_N2 oxidative addition.[35] A plot of $\Delta G^{\ddagger}$ vs ΔG for the reactions of Me_3SnX (X = Cl, Br, I) to $[PtMe_2(bpy\text{-}^tbu_2)]$ shows a reasonable correlation in both CD_2Cl_2 and CD_3CN, indicating a linear free-energy relationship for the reaction.

The rate constant for the reductive elimination of Me_2SnCl_2 from $[PtClMe_2(Me_2SnCl)(bpy\text{-}^tbu_2)]$ is much smaller than that for any of the corresponding Me_3SnX eliminations, and the ΔG for the reductive elimination reaction must be significantly more positive than that for all other reactions studied. It is therefore reasonable to expect that the oxidative addition reaction is the fastest of all those studied. These results are consistent with the increasing ability of methylhalotin compounds to form species with coordination numbers greater than four when the number of halide atoms surrounding the tin center is increased.[20]

The VT-NMR spectral series for the reaction between Me_3GeCl and $[PtMe_2(bpy\text{-}^tbu_2)]$ in CD_2Cl_2 shows distinct signals for all ^1H nuclei in both the platinum(II) and platinum-(IV) complexes. The reaction was too slow for any rate determination by this method. The reason for the substantial rate decrease on going from tin to germanium may be at least partly due to the reduced ability of Me_3GeX to form a five-coordinate intermediate, as would be found in the transition state of a reaction following the S_N2 pathway. The rate decrease on going from tin to germanium may also be partly due to a size effect; germanium is smaller than tin and hence must get closer to the platinum center for reaction to occur. This means that steric effects are more important for germanium as opposed to tin reagents. Despite the similar ΔH values for the two reactions, the one involving Me_3GeCl is much slower. The ^1H NMR spectra of platinum(IV)$-$silicon complexes did not show any evidence of a reversible oxidative addition process, and hence we conclude this process proceeds at a rate too slow to be detected on the ^1H NMR time scale. Clearly, there is a group 14 rate dependence for the oxidative addition reactions which follows the series Sn > Ge > Si.

Conclusions

The oxidative addition of trimethyltin halides to complexes $[PtMe_2(diimine)]$ is shown to be very fast and easily reversible. This is important because it allows direct study of both the rates and thermodynamics of the reactions by variable temperature ^1H NMR spectroscopy, and the thermodynamics can be studied independently by UV$-$visible spectroscopy. In the products $[PtXMe_2(SnMe_3)(diimine)]$, the Pt$-$X bond is polarized and weakened by the very strong *trans* influence of the trimethyltin

(29) The entropy of activation values for the reductive elimination of Me_3SnCl from $[PtClMe_2(Me_3Sn)(bpy\text{-}^tbu_2)]$ in various solvents is fairly small (-25 to $+9$ J mol^{-1} K^{-1}) and the large relative errors associated with the values do not allow for a meaningful discussion. The small magnitude of $\Delta S^{\ddagger}$ is not unreasonable since reductive elimination is a dissociative process and this counteracts the negative entropy of solvation on approaching a polar transition state. The calculated $\Delta S^{\ddagger}$ values for the oxidative addition process have considerably larger magnitudes.

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group, and this has two effects. In nonpolar solvents such as toluene, the Pt−X group is polar and can form a bridge to a second molecule of Me_3SnX. Such compounds have been isolated previously and are now detected directly in solution by low-temperature ^{1}H NMR. In polar solvents such as acetone or CH_3CN, the halide can be displaced very easily to give an equilibrium with the cations $[PtMe_2(SnMe_3)(S)(diimine)]^+$, S = solvent, and these too can be detected by low-temperature ^{1}H NMR. A reaction coordinate diagram has been obtained for the first time for such reactions, and provides powerful evidence for the S_N2 mechanism of oxidative addition in which the transition state is close to the 5-coordinate platinum(IV) species $[PtMe_2(SnMe_3)(diimine)]^+X^-$. It is perhaps surprising that there is no evidence for solvent coordination to platinum at this stage, but this can be rationalized in the following way. In the starting complex $[PtMe_2(diimine)]$, the platinum is electron rich and will orient to the positive dipole of the solvent, and since the reaction with Me_3SnX is very fast to give a much more electron-deficient platinum center, solvent coordination probably occurs subsequent to the transition state. The rates of reaction $Me_3Sn−X > Me_3Ge−X > Me_3Si−X > Me_3C−X$ correlate with the size of the central atom.

The "halogen effect" on the thermodynamics of the oxidative addition of Me_3SnX (X = Cl, Br, I) to $[PtMe_2(bpy-^tbu_2)]$ in CD_2Cl_2 and CD_3CN has been established quantitatively. The oxidative addition reaction is thermodynamically favored by heavier halides, largely due to a change in enthalpy. The values obtained are comparable to the calculated values, based on literature bond energies. The thermodynamic basis of this "halogen effect" is the greater decrease in M−X bond energies for the harder metal (group 14 element) compared to the softer metal (platinum). The nature of the halide also has a pronounced effect on the rates of oxidative addition and reductive elimination. The reductive elimination reactions become slower as the halide becomes larger, but the oxidative addition reactions become much faster. The difference in rate for the two processes is tied directly to the position of the equilibrium, with the heavier halides favoring the oxidative addition product. There is good evidence for a linear relationship between the free energy of reaction and the free energy of activation for the reductive elimination (as well as for the oxidative addition) process. The increase in the rate of oxidative addition for the series Cl < Br < I is fully consistent with an S_N2 reaction mechanism. These results quantitatively establish, for the first time, the magnitude of the halide effect on oxidative addition reactions. This should prove of great value in predictions of halide effects on other element−halogen bond oxidative addition metal centers.

If enthalpic effects due to differential solvation of starting materials and products can be ignored, the overall enthalpy of the oxidative addition reaction of $Me_3M−X$ may be given by eq 3.

$$\Delta H = (Me_3Me−X) − D(Pt−MMe_3) − D(Pt−X) \quad (3)$$

It is then possible to estimate the platinum−tin or platinum−germanium bond dissociation energies if values of $D(Me_3M−X)$ and $D(Pt−X)$ are known (eq 4).

$$D(Pt−MMe_3) = D(Me_3M−X) − D(Pt−X) − \Delta H \quad (4)$$

The value of $D(Pt−Cl)$ is taken to be 215 kJ mol^{-1} (the value obtained by calorimetry for $[PtCl_6]^{2-}$),[36] and, based on the known differences in Pt−X bond energies,[6] the values of $D(Pt−$

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Table 6. Calculated Enthalpies of Oxidative Addition of Me₃M-X to $[PtMe_2(bpy)]$ To Give $[PtXMe_2(MMe_3)(bpy)]^a$

M	X					
	H	Me	MMe₃	Cl	Br	I
C	37	73	23	−15	−43	−131
Si	−68	6	−129	24	−10	−45
Ge	−52	−1	−59	−38	−100	
Sn	−71	−37	−110	−31	−34	−46

^{a} Based on the values of bond dissociation energies (kJ mol^{-1})[6,7,36−39]: C−H 385; C−Me, 343; C−CMe₃ 293; C−Cl 335; C−Br 268; C−I 213; Si−H 378; Si−Me 374; Si−SiMe₃ 337; Si−Cl, 472; Si−Br 402; Si−I 321; Ge−H 343; Ge−Me 316; Ge−GeMe₃ 305; Ge−Cl 359; Ge−Br 261; Sn−H 314; Sn−Me 270; Sn−SnMe₃ 234; Sn−Cl 356; Sn−Br 318; Sn−I 259; Pt−H, 213; Pt−C 135; Pt−Si 233; Pt−Ge 182; Pt−Sn 172.

Br) and $D(Pt−I)$ are then estimated as 182 and 133 kJ mol^{-1}, respectively. The values of $D(Me_3Sn−X)$ are taken to be 356 (X = Cl), 318 (X = Br), and 259 (X = I) kJ mol^{-1},[37] while from a number of divergent values quoted for $D(Me_3Ge−Cl)$,[38] the most recent value of 359 kJ mol^{-1} is used.[39] The values of $D(Pt−MMe_3)$ calculated in this way (using the ΔH values obtained by ^{1}H NMR in the relatively noncoordinating solvent CD_2Cl_2) are 174, 171, and 171 kJ mol^{-1} for $D(Pt−Sn)$ when X = Cl, Br, and I, respectively, and 182 kJ mol^{-1} for $D(Pt−Ge)$ when X = Cl.

These should be considered as rough estimates only, since although the values of ΔH are precise, the values of $D(Pt−X)$ and $D(Ge-X)$ are not.[36−39] It is significant, however, that the three independent values of $D(Pt−Sn)$ are remarkably self-consistent at 172 ± 2 kJ mol^{-1}, though the accuracy is likely to be lower. Coupled with the values of $D(Pt−SiMe_3) = 233$ kJ mol^{-1} and $D(Pt−CH_3) = 135$ kJ mol^{-1} estimated previously, the series $D(Pt−C) < D(Pt−Si) > D(Pt−Ge) > D(Pt−Sn)$ is obtained and is consistent with trends of $D(Pt−X)$ for bonds to group 15−17 elements, for which the second-row element usually gives the strongest bond.[40]

Although these values should be viewed with caution, it is interesting to examine predictions of the enthalpies of oxidative addition of $Me_3M−X$ to platinum(II) based on their values and on eq 3. The predicted enthalpy changes are listed in Table 6, and some trends are as follows. For all M, the oxidative addition of $Me_3M−I$ is clearly favored over $Me_3M−Cl$ and the enthalpy difference decreases on descending group 14, that is for M = C > Si > Sn, and so the "halogen effect" decreases on descending the group. Of all the compounds $Me_3M−X$ with X = halogen, only the oxidative addition of $Me_3Si−Cl$ is predicted to be unfavorable and this is consistent with the experimental observations. The oxidative addition of $Me_3M−MMe_3$ is predicted to be unfavorable, for carbon but very favorable for all the heavier group 14 elements. The oxidative addition of $Me_3M−Me$ is likely to be favorable only for M = Sn, since the unfavorable entropy term will dominate for the cases with M = Si and Ge for which the predicted enthalpy change (Table 6) is small. Finally, $Me_3M−H$ oxidative addition is predicted to be unfavorable for M = C, but highly favorable for M = Si, Ge, and Sn.

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The values given in Table 6 can rationalize some known chemical reactions. For example, in platinum complex catalyzed hydrosilation of alkenes it is proposed that oxidative addition of R_3Si-H gives the $PtH(SiR_3)$ group, followed by insertion of alkene into the $Pt-H$ bond to give $PtR'(SiR_3)$ and then reductive elimination of R_3Si-R'.[41] It is important that oxidative addition of $Si-H$ and reductive elimination of $Si-C$ both be favorable reactions which occur easily.[42] While the thermochemistry cannot predict the ease of reaction, it does at least predict that each of these reactions is thermodynamically favorable.

Experimental Section

General. The NMR spectra were recorded with a Varian Gemini 300 spectrometer. The temperature of the probe was calibrated by using a MeOH sample and the Varian instrumental calibration routine. ^{1}H-NMR spectra were referenced to TMS by use of the residual solvent protons. All platinum complexes were prepared as described previously.[6,7] All samples were prepared in dry 5-mm NMR tubes under a nitrogen atmosphere.

UV−visible spectra were recorded with a Varian Cary 2290 spectrometer with a temperature-controlled sample chamber maintained at 25 °C and the sample and reference solvent contained in quartz cells (1 cm). Solvents were dried and distilled immediately prior to use. For spectroscopic titrations, cells were loaded with freshly-prepared solutions of the platinum(II) complexes in a nitrogen atmosphere by use of a Vacuum Atmospheres Mo-40-1 dry lab. The sample cell was fitted with a PTFE-lined septum to allow for additions of the group 14 reagent under an inert atmosphere. Titrations were conducted by the addition of solutions of group 14 reagent to the sample cell with use of a 50 μL air-tight syringe with a PTFE plunger. The titration of [PtMe$_2$(bpy)] with Me$_3$SnCl which follows represents a typical procedure.

The thermodynamic parameters in this study were determined by two different methods, UV−visible and variable-temperature (VT) [1]H-

NMR spectroscopies. For the UV−visible spectroscopic studies Scatchard-type plots were used to find the free energies of the reactions. To obtain the thermodynamic data from VT-NMR studies, the mole fractions of platinum complexes in solution were determined by the magnitude of the averaged $^3J(\mathbf{Pt}-\mathbf{C}-\mathbf{H})$ coupling constants associated with the Me−Pt signal. The Pt:Sn ratios as well as initial concentrations were known, allowing equilibrium constants to be calculated. For the equilibrium involving Me$_3$GeCl the averaged Me−Pt signals were not seen in the ^{1}H NMR spectra, and integration was used to determine concentration in solution. In all cases the equilibrium constants were determined over a range of temperatures allowing for the determinations of ΔG, ΔH, and ΔS with standard thermodynamic relationships.

Kinetics data were determined from the line widths of Me−Sn VT-NMR signals.[43−45] Once the kinetic parameters for the reductive elimination reaction and the thermodynamic parameters of the reaction are known, the kinetic parameters for the oxidative addition reaction can be easily calculated by using standard relationships.

The enthalpy and entropy of oxidative addition for each VT-NMR study were determined from a plot of $\ln K_{eq}$ *vs* T^{-1}, and errors were determined by using standard regression analyses. Activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for reductive elimination were determined from Eyring plots ($\ln k_{red}/T$ *vs* T^{-1}). The confidence level of 95% was used.[37]

Background NMR and UV−vis data needed for the calculations are included in the Supporting Information.

Visible Spectroscopic Titration of [PtMe$_2$(bpy)] with Me$_3$SnCl. Toluene solutions of [PtMe$_2$(bpy)] ($2.648 \pm 0.0009 \times 10^{-4}$ M) and Me$_3$SnCl (0.1020 ± 0.0008 M) were prepared. The sample cell was charged with the [PtMe$_2$(bpy)] solution (3.000 mL), and the visible spectrum was recorded. Aliquots (25.0 ± 0.5 μL) of Me$_3$SnCl solution were added to the sample cell, and the spectrum was run after each addition. The color of the solution lightened immediately on addition of the tin reagent.

Supporting Information Available: Figures S1−S4, NMR and UV−vis spectroscopic data, calculation details, as well as data and plots for visible and VT ^{1}H NMR studies (92 pages). See any current masthead page for ordering and Internet access instructions.

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