# Energy Profile of a Rapid, Reversible Oxidative Addition Reaction

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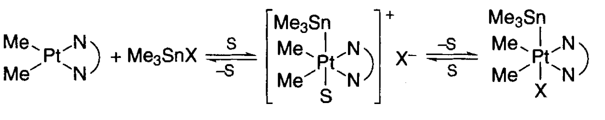
The trimethyltin halides undergo a very fast, reversible oxidative addition reaction with [PtMe$_2$(Bu$_2$bipy)], Bu$_2$bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, to give [PtXMe$_2$(SnMe$_3$)(Bu$_2$bipy)] for which a complete energy profile can be obtained by using variable-temperature NMR methods; the reaction with X = I is the fastest known oxidative addition and activation energies when X = Cl suggest a detailed structure for the transition state.

Oxidative addition and reductive elimination reactions are central to many transition metal catalysed reactions but it has proved difficult to find reactions for which a complete energy profile can be obtained.[1] This article reports that the reaction of Scheme 1, NN = 4,4′-*tert*-butyl-2,2′-bipyridine (Bu$_2$bipy),[2] provides an ideal system because the oxidative addition occurs easily and reversibly such that both kinetic and thermodynamic data are readily obtained. The proposed mechanism is shown in Scheme 1, S = solvent.

The exchange between [PtMe$_2$(Bu$_2$bipy)], **1**, and Me$_3$SnX (X = Cl, Br or I) and [PtXMe$_2$(SnMe$_3$)(Bu$_2$bipy)], **2**, occurs rapidly at room temperature in several solvents such that only averaged singals for the methylplatinum groups of **1** and **2** or of the methyltin groups of Me$_3$SnX and **2** are observed in the $^1$H NMR spectra. However, in most cases, the reactions are slowed sufficiently at low temperature to allow resolution of separate signals (Fig. 1). It is very unusual for oxidative addition reactions to occur so rapidly and this feature is extremely useful as outlined below. The equilibrium constants can be obtained in the fast-exchange region from the average values of NMR parameters such as the coupling constants $^2J_{PtMe}$ for the methylplatinum groups[†] and, in the slow-exchange region, by integration of the spectra, thus yielding values over a large temperature range. In addition, rate constants for the reductive elimination can be obtained by analysis of the NMR linewidths both above and below the coalescence temperature, thus yielding rate constants over a range of temperatures.[3] The rates of oxidative addition can then be calculated and an energy profile obtained (Table 1). The fastest second-order rate constant for oxidative addition measured was $k_2$ = (2.2 ± 0.2) × 10$^8$ dm$^3$ mol$^{-1}$ s$^{-1}$, for Me$_3$Sn–I and [PtMe$_2$(Bu$_2$bipy)] in CD$_3$CN at 20 °C, close to the limit of diffusion control and, as far as we are aware, the fastest such rate yet measured.

An important additional feature is observed for the reaction of Me$_3$SnCl with **1** in acetone solution as illustrated in Fig. 2.[‡] At low temperature, two platinum(IV) complexes are present in equilibrium and, from the NMR parameters,[4] are identified as [PtClMe$_2$(SnMe$_3$)(Bu$_2$bipy)], **2a**, and the cationic [PtMe$_2$(Sn-



**1** **3**, X = Cl, S = acetone **2a**, X = Cl
**b**, X = Br
**c**, X = I

**Scheme 1**

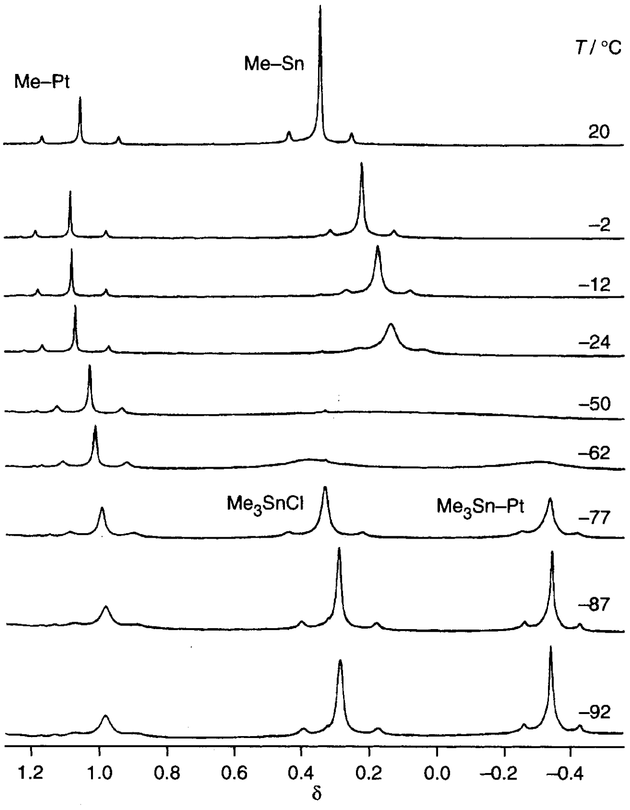


**Fig. 1** Variable-temperature $^1$H NMR spectra (300 MHz) of the equilibrium mixture of [PtMe$_2$(Bu$_2$bipy)], Me$_3$SnCl and [PtClMe$_2$(SnMe$_3$)(Bu$_2$bipy)] in CD$_2$Cl$_2$. The ratio Sn : Pt is 2 : 1.

**Table 1** Thermodynamic and kinetic data for the reaction of Me$_3$Sn–X with [PtMe$_2$(Bu$_2$bipy)] at 25 °C[a]

| | X = Cl<br>CD$_2$Cl$_2$ | X = Br<br>CD$_2$Cl$_2$ | X = I<br>CD$_2$Cl$_2$ | X = Cl<br>(CD$_3$)$_2$CO | X = Cl<br>CD$_3$CN |
|---|---|---|---|---|---|
| ΔH° (ox) | −33 ± 2 | −35 ± 2 | −45 ± 3 | −25 ± 1 | −23 ± 2 |
| ΔS° (ox) | −84 ± 9 | −66 ± 6 | −70 ± 10 | −70 ± 4 | −52 ± 6 |
| ΔG° (ox) | −7.9 ± 0.1 | −14.7 ± 0. | 225.4 ± 0.5 | −3.5 ± 0.3[b] | −7.2 ± 0.1 |
| ΔH‡ (red) | 38.3 ± 0.8 | 33.6 ± 0.8 | 48 ± 3 | 45 ± 2 | 37 ± 2 |
| ΔS‡ (red) | −23 ± 3 | −58 ± 3 | −20 ± 10 | 8 ± 7 | −25 ± 8 |
| ΔG‡ (red) | 45.1 ± 0.2 | 50.7 ± 0.2 | 53.3 ± 0.2 | 42 ± 1 | 44.3 ± 0.3 |
| ΔH‡ (ox) | 5 ± 3 | 0 ± 2 | 3 ± 4 | 20 ± 2 | 15 ± 3 |
| ΔS‡ (ox) | −110 ± 10 | −124 ± 7 | −80 ± 20 | −62 ± 8 | −77 ± 9 |
| ΔG‡ (ox) | 37.2 ± 0.3 | 36.0 ± 0.3 | 29.7 ± 0.6 | 39 ± 1 | 37.1 ± 0.3 |
| K (ox) | 24 ± 1 | 380 ± 20 | 29 000 ± 2000 | 4.2 ± 0.9[c] | 18.1 ± 0.8[c] |
| 10$^{-6}$ $k_2$ (ox) | 1.86 ± 0.04 | 3.10 ± 0.08 | 39 ± 2 | 0.94 ± 0.07 | 1.96 ± 0.05 |

[a] Units: ΔH, ΔG in kJ mol$^{-1}$; ΔS in J mol$^{-1}$ K$^{-1}$; K(ox) in dm$^3$ mol$^{-1}$; $k_2$ in dm$^3$ mol$^{-1}$ s$^{-1}$. Error limits are at the 95% probability level. (ox) = parameter for oxidative addition; (red) = parameter for reductive elimination. [b] The value given in Fig. 3 is at low temperature and so differs from this. [c] These are for total platinum(IV) complexes, including the ionic and neutral forms of Scheme 1.

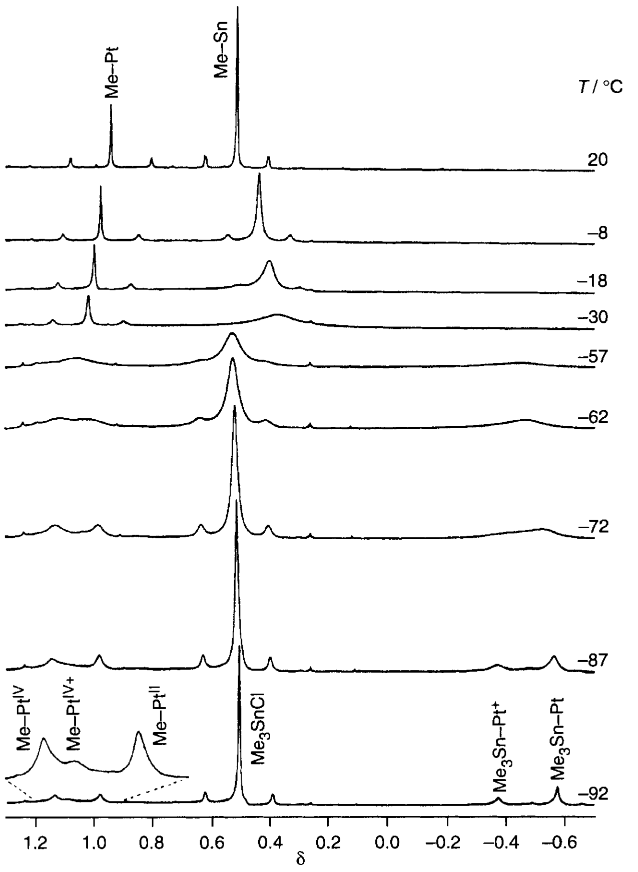


**Fig. 2** Variable-temperature $^1H$ NMR spectra (300 MHz) of the equilibrium mixture of $[PtMe_2(Bu_2bipy)]$, $Me_3SnCl$, $[PtClMe_2(SnMe_3)(Bu_2bipy)]$ and $[PtMe_2(SnMe_3)\{(CD_3)_2CO\}(Bu_2bipy)]Cl$ in $[^2H_6]$acetone. The ratio Sn : Pt is 2 : 1.

$Me_3)(Me_2CO)(Bu_2bipy)]^+Cl^-$, **3**. At −90 °C, integration gives the equilibrium constant **2a**/**3** = 2 ($\Delta G$ = 1 kJ $mol^{-1}$) and, at the coalescence temperature of −70 °C, the activation energy for their interconversion is 43 kJ $mol^{-1}$. A complete free energy profile for the oxidative addition/reductive elimination reaction of $Me_3SnCl$ in acetone solution is given in Fig. 3.

It is immediately apparent from Fig. 3 that the energies of the transition state species in both the oxidative addition step and the chloride for acetone exchange step are identical within experimental error. This could be a coincidence, but it is considered more likely that the transition state complexes have similar energies because they have similar structures. Now, it is known that ligand substitution at platinum(IV) occurs by a dissociative mechanism and so the transition state in the present case is expected to be close to $[PtMe_2(SnMe_3)(Bu_2bipy)]^+$.§ It is therefore proposed that the transition state for the oxidative addition/reductive elimination step has a similar structure. This will be the case if the oxidative addition occurs by the $S_N2$ mechanism, with formation of the Pt–Sn bond and dissociation of the Sn–Cl bond almost complete in the transition state but with the coordination of solvent *trans* to the $Me_3Sn$ group not yet significantly developed (Fig. 3). The activation parameters given in Table 1 are fully consistent with this hypothesis. Thus, these very fast, reversible oxidative additions have allowed a particularly detailed picture of the nature and energy of the transition state to be determined.

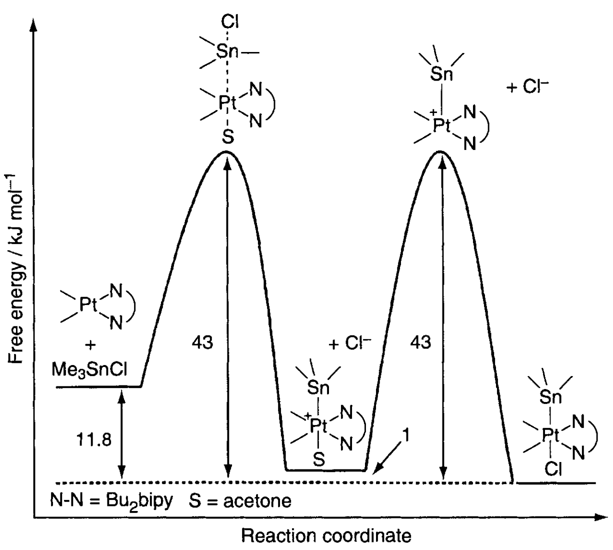


**Fig. 3** A plot of free energy *vs.* reaction coordinate for the reaction of $[PtMe_2(Bu_2bipy)]$ with $Me_3SnCl$. Note, that it was not possible to determine all parameters at a fixed temperature, but values quoted are obtained over the narrowest possible temperature range of −70 to −90 °C.

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## Footnotes

† The limiting values of $^2J_{PtH}$ are 85.6 Hz for $[PtMe_2(Bu_2bipy)]$ **1**, and 55.5 Hz for $[PtClMe_2(SnMe_3)(Bu_2bipy)]$, **2a**, in $CD_2Cl_2$. In a typical experiment, the observed average values $^2J_{PtH}$ were 68.1 Hz at 20 °C and 56.6 Hz at −50 °C, clearly indicating an increase in $K_{eq}$ at lower temperature.

‡ The cationic intermediate is not detected in the solvents $CH_2Cl_2$ or toluene, presumably because these solvents cannot stabilise it by coordination to platinum. We presume that the cation is formed in $CD_3CN$ solution but the freezing point of the solvent is higher than the coalescence temperature. Hence, acetone is unique as a solvent in allowing identification of the cation and hence the complete energy profile.

§ The high rate of reaction is attributed to the high *trans* influence of the $Me_3Sn$ group. Ligand substitution at platinum(IV) in classical coordination complexes is slow.

## References

1 For example, see J. J. Garcia, B. E. Mann, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Am. Chem. Soc.*, 1995, **117**, 2179; K. I. Goldberg, J. Y. Yan and E. L. Winter, *J. Am. Chem. Soc.*, 1994, **116**, 1573; C. Duckerbenfer, R. van Eldik and A. J. Canty, *Organometallics*, 1994, **13**, 2412; A. Panunzi, F. Ruffo, B. Akermark and V. De Felice, *Acta Chem. Scand.*, 1992, **46**, 499.
2 C. J. Levy, R. J. Puddephatt and J. J. Vittal, *Organometallics*, 1994, **13**, 1559.
3 J. Sandström, *Dynamic NMR Spectroscopy*, Academic, Toronto, 1982.
4 M. Crespo and R. J. Puddephatt, *Organometallics*, 1987, **6**, 2548; P. K. Byers, A. J. Canty, B. W. Skelton, P. R. Traill, A. A. Watson and A. H. White, *Organometallics*, 1992, **11**, 3085.