Mechanism and Energetics of Reductive Elimination of Ethane from Some Tetramethylplatinum(IV) Complexes

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The new complexes *cis*-[$PtMe_4L_2$], L = MeNC or 2,6-$Me_2C_6H_3NC$, decompose cleanly in the solid state or in solution to give ethane and *cis*-[$PtMe_2L_2$]. Studies using differential scanning calorimetry give a value of $\bar{D}$(PtMe) = 133 ± 5 kJ mol^{-1} for the mutually *trans* PtMe groups, and deuterium-labelling studies show that the reductive elimination step is intramolecular. Kinetic studies show that the reaction occurs very largely after ligand dissociation and gives a value of $k(PtCH_3)/k(PtCD_3)$ = 1.30 ± 0.04. It is suggested that an agostic interaction of one CH_3Pt group in the five-co-ordinate intermediate precedes the reductive elimination step and reasons for this proposal are advanced.

The mechanism of reductive elimination with carbon–carbon bond formation has been of great interest, primarily because of its relevance to homogeneous catalysis by transition element complexes with d^6 or d^8 electron configurations.[1] Of particular relevance to the present work are mechanistic studies of reductive elimination from palladium(II),[2,3] palladium(IV),[4] platinum(II),[5] and platinum(IV),[6] but important studies have also been made of gold(III)[7] and rhodium(III)[8] alkyl or aryl complexes. Reductive elimination from octahedral complexes with the d^6 electron configuraton always appears to be accelerated by ligand dissociation though, if there is no easily dissociated ligand, direct reductive elimination may occur.[4,6,8,9]

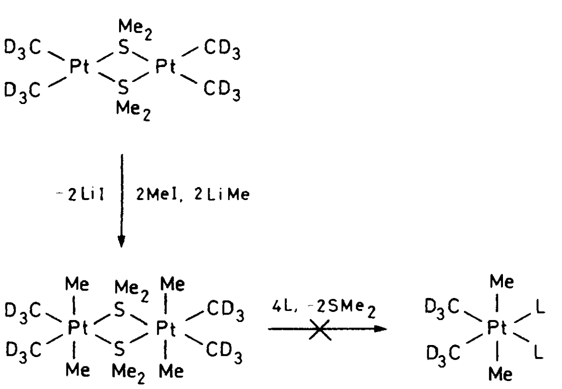
Some tetramethylplatinum(IV) complexes undergo clean reductive elimination of ethane, but no mechanistic studies of such reactions have been reported.[10–13] Most known derivatives decompose at temperatures over 100 °C[10,11] but the new complexes *cis*-[$PtMe_4L_2$], with L = an alkyl or aryl isocyanide ligand, decompose cleanly to ethane and *cis*-[$PtMe_2L_2$] at temperatures suitable for mechanistic studies. In the solid state the thermolysis occurs well below the melting point, in contrast to tertiary phosphine derivatives which often decompose only at the melting point.[10–13] The complex with L = MeNC is a useful precursor to chemical vapour deposition of platinum thin films[14] and this gives an added reason for wishing to understand the mechanism and energetics of the thermolysis of such compounds. This article reports the thermolysis of the complexes *cis*-[$PtMe_4L_2$] [L = MeNC (**1a**); or 2,6-$Me_2C_6H_3NC$ (**1b**)] and a study of the kinetics and energetics of the reactions.

Results

Synthesis of Tetramethylplatinum(IV) *Complexes*.—The new complexes (**1a**) and (**1b**) were prepared by the reaction (1).[12]

$$cis,cis\text{-}[Me_4Pt(\mu\text{-}SMe_2)_2PtMe_4] \xrightarrow[-2SMe_2]{4L} 2\ cis\text{-}[PtMe_4L_2] \quad (1)$$

The complexes were colourless, crystalline solids which were readily characterized by elemental analysis and by their spectroscopic properties (Table 1). The corresponding complex *cis*-[$Pt(CD_3)_4(MeNC)_2$], (**1a′**), was prepared in a similar way from *cis,cis*-[$Pt_2(CD_3)_8(\mu\text{-}SMe_2)_2$]. An attempt was made to prepare specifically labelled complexes, but this was not successful. For example, the products from equation (2), L = MeNC, contained a mixture of *cis*-[$PtMe_4(MeNC)_2$], *cis*-[$PtMe_3(CD_3)(MeNC)_2$], and *cis*-[$PtMe_2(CD_3)_2(MeNC)_2$] as determined by mass spectrometric (m.s.) analysis, and the methyl and CD_3 groups were scrambled between equatorial and axial positions as determined by n.m.r. analysis.



(2)

The platinum(II) complexes *cis*-[$PtMe_2L_2$] [L = MeNC (**2a**); or 2,6-$Me_2C_6H_3NC$ (**2b**)] were prepared by reaction of the appropriate ligand L with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$], and were readily characterized by spectroscopic methods.

Thermolysis of the Complexes.—Both complexes (**1a**) and (**1b**) decomposed cleanly in the solid state to give ethane, which was analyzed by gas chromatography (g.c.)–m.s., and (**2a**) and (**2b**) respectively, which were shown to be pure by ^1H n.m.r. spectroscopy. The decompositions were monitored quantitatively by thermal gravimetric analysis (t.g.a.) and differential scanning calorimetry (d.s.c.). The d.s.c. scans are shown in Figure 1. The weight loss after the first exotherm corresponded well to the loss of ethane. The peak in the d.s.c. scan was at 123 ± 2 for (**1a**) and at 111 ± 1 °C for (**1b**), and the platinum product was pure *cis*-[$PtMe_2L_2$], (**2a**) or (**2b**), at this stage. Further complex reactions then occurred at and above the melting points of (**2a**) and (**2b**) and metallic platinum was eventually formed (t.g.a.). The remainder of this paper is concerned with the initial reductive elimination step, which occurred at a suitable rate for kinetic studies over the temperature range 50—70 °C in benzene solution. The thermolysis of an equimolar mixture of complexes (**1a**) and (**1a′**) in

Table 1. Spectroscopic data for compounds of Pt^{II} and Pt^{IV}

Complex	^{1}H N.m.r. [$CDCl_3$, δ, J Hz]	I.r. [ν(C≡N)/cm^{-1}]^a	Mass spectrum (m/z^+)^b
cis-[$PtMe_2(MeNC)_2$]	0.41 [s, 6 H, ^2J(PtH) 74, CH_3Pt] 3.20 [s, 6 H, ^2J(NH) 6, CH_3NC]	2 188, 2 216	307
cis-[$PtMe_2(2,6\text{-}Me_2C_6H_3NC)_2$]	0.76 [s, 6 H, ^2J(PtH) 74, CH_3Pt] 2.41 [s, 12 H, 2,6-($CH_3)_2C_6H_3$] 7.06, 7.10, 7.17 (6 H, C_6H_3)	2 105, 2 135	487
cis-[$PtMe_4(MeNC)_2$]	0.41 [s, 6 H, ^2J(PtH) 64, *cis*-$(CH_3)_2Pt$] −0.11 [s, 6 H, ^2J(PtH) 46, *trans*-$(CH_3)_2Pt$] 3.39 [s, 6 H, ^2J(NH) 5, CH_3NC]	2 218	337, 322, 298
cis-[$Pt(CD_3)_4(MeNC)_2$]	3.38 [s, 6 H, ^2J(NH) 5, CH_3NC]	2 216	349, 331, 313
cis-[$PtMe_4(2,6\text{-}Me_2C_6H_3NC)_2$]	0.65 [s, 6 H, ^2J(PtH) 63, *cis*-$(CH_3)_2Pt$] 0.17 [s, 6 H, ^2J(PtH) 46, *trans*-$(CH_3)_2Pt$] 2.41 [s, 12 H, 2,6-($CH_3)_2C_6H_3$] 7.09, 7.12, 7.19 (6 H, C_6H_3)	2 156	502, 472, 324

[a] Nujol mull on NaCl plates. [b] The (m/z) values refer to ions containing the ^{195}Pt isotope.

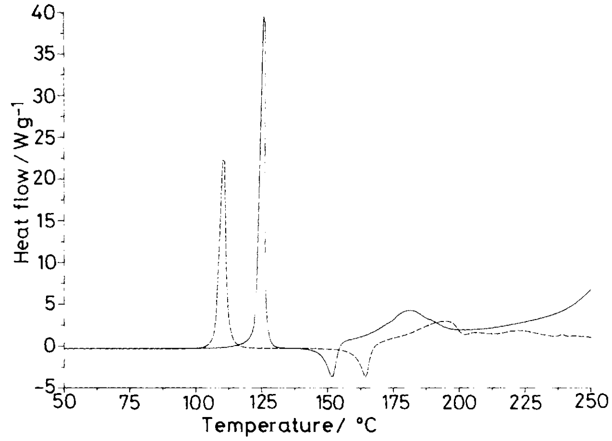


Figure 1. Differential scanning calorimetry for the thermolysis of *cis*-[$PtMe_4(MeNC)_2$] (——) and *cis*-[$PtMe_4(2,6\text{-}Me_2C_6H_3NC)_2$] (- - - -)

Table 2. Differential scanning calorimetry and estimated mean Pt–Me bond dissociation energy

Complex	T_1^{a}/ °C	T_2^{b} °C	$-\Delta H^c$/ kJ mol^{-1}	D_{Pt-C} kJ mol^{-1}
[$PtMe_4(MeNC)_2$]	123 ± 2	148	94 ± 2	137 ± 1
[$Pt(CD_3)_4(MeNC)_2$]	125 ± 2	149	93 ± 2	138 ± 1
[$PtMe_4(2,6\text{-}Me_2C_6H_3NC)_2$]	111 ± 1	164	110 ± 2	129 ± 1

[a] Mean value of decomposition temperature. [b] M.p. of corresponding dialkylplatinum(II) complex. [c] Average value from six independent runs.

Table 3. U.v. spectral data for compounds of Pt^{II} and Pt^{IV}

Compound	Solvent	λ nm (log ε)
[$PtMe_4(MeNC)_2$]	MeOH	213 (4.15), 244 (3.88)
	C_6H_6	311 (2.05)
[$PtMe_4(XYNC)_2$]*	MeOH	212 (4.60), 238 (4.56), 294 (3.60)
	C_6H_6	287 (3.66), 302 (3.60)
[$PtMe_2(MeNC)_2$]	MeOH	216 (4.18), 230 (4.06), 277 (3.96)
	C_6H_6	284 (3.92), 312 (2.99)
[$PtMe_2(XYNC)_2$]*	MeOH	209 (4.68), 252 (4.37), 296 (4.16)
	C_6H_6	303 (4.21), 330 (3.46)

* XY = 2,6-$Me_2C_6H_3$

benzene solution gave mostly C_2D_6 and C_2H_6, with 8% of CD_3CH_3 as determined by m.s., indicating that the reductive elimination is very largely an intramolecular reaction.

Table 4. First-order rate constants for reductive elimination of [$PtMe_4(MeNC)_2$] and [$Pt(CD_3)_4(MeNC)_2$] in benzene solution

Complex	T/°C	10^4 $k_{obs.}$/s^{-1}
[$PtMe_4(MeNC)_2$]	50	7.3 ± 0.4
	55	11.6 ± 0.2
	60	17.2 ± 1.3
	65	25.2 ± 1.5
	70	35.9 ± 1.6[a,b]
[$Pt(CD_3)_4(MeNC)_2$]	70	27.7 ± 0.3[a,c]

[a] Average value from three independent runs. [b] $E_a = 71 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger}$ (20 °C) = -86 ± 12 J K^{-1} mol^{-1}. [c] $k_H/k_D = 1.30 \pm 0.04$.

The d.s.c. results are summarized in Table 2. The estimated average platinum–methyl bond dissociation energies are calculated from the observed enthalpy of reaction by assuming that the only contributions are from cleavage of two Pt–CH_3 bonds and formation of the CH_3–CH_3 bond.[15] The values of D(Pt–C) are 137 ± 1 kJ mol^{-1} for complex (**1a**) and 129 ± 1 kJ mol^{-1} for (**1b**) (the error bars refer to the precision of the measurement of ΔH, and do not include systematic errors due to the assumptions made).[15,16] These can be compared with similar values of D(Pt–C) = 144 kJ mol^{-1} in *fac*-[$PtIMe_3(PMe_2Ph)_2$][6] and D(Pd–C) = 131 kJ mol^{-1} in *fac*-[$PdIMe_3$(bipy)] (bipy = 2,2′-bipyridine).[4] In (**1a**) and (**1b**) the thermochemistry refers to cleavage of the two mutually *trans* methylplatinum bonds. It is therefore not surprising that the bond energy is lower than that in *fac*-[$PtIMe_3(PMe_2Ph)_2$], since the antisymbiosis effect weakens mutually *trans* alkyl–platinum bonds.[13] Independent evidence for this is seen in lower ν(Pt–C) stretching frequencies in the i.r. spectra, lower ^2J(PtH) couplings in the ^{1}H n.m.r. spectra, and high chemical reactivity for such groups.[10–13] The lower value of D(Pt–C) for complex (**1b**) compared with (**1a**) is probably a steric effect of the bulky 2,6-$Me_2C_6H_3NC$ ligand.

Kinetic Studies.—The kinetics of the reductive elimination was monitored in benzene solution by u.v.–visible spectrophotometry. Spectral data are given in Table 3, and the strong solvent dependence of the absorption maxima strongly suggests that the absorptions are due to metal-to-ligand charge-transfer bands.[13] Kinetic results are given in Tables 4 and 5. Qualitative experiments using ^{1}H n.m.r. spectroscopy to monitor the reactions were in good agreement.

In the absence of added isocyanide ligand, the reactions followed first-order kinetics and the data are given in Table 4. Since traces of free isocyanide ligand have a great retarding effect on the reactions, it was essential to have the complexes very pure and this was achieved by multiple recrystallizations.

Table 5. First-order rate constants for the reductive elimination of [PtMe$_4$(MeNC)$_2$] and [PtMe$_4$(2,6-Me$_2$C$_6$H$_3$NC)$_2$] in benzene solution at 60 °C in the presence of isocyanides

[PtMe$_4$(MeNC)$_2$]		[PtMe$_4$(2,6-Me$_2$C$_6$H$_3$NC)$_2$]	
10^5 [MeNC]/mol dm^{-3}	10^5 $k_{obs.}$/s^{-1}	10^5 [2,6-Me$_2$(C$_6$H$_3$NC)$_2$]/mol dm^{-3}	10^5 $k_{obs.}$/s^{-1}
0	172.0 ± 13.0	0	91.9 ± 4.0
0.67	48.2 ± 1.5	3.5	5.78 ± 0.08
1.35	14.8 ± 0.6	7.0	4.38 ± 0.14
2.0	6.01 ± 0.10	9.9	3.79 ± 0.08
2.7	4.44 ± 0.20	11.7	3.40 ± 0.15
6.7	3.19 ± 0.20	13.5	3.11 ± 0.05
10.1	2.59 ± 0.10		
13.5	2.06 ± 0.04		

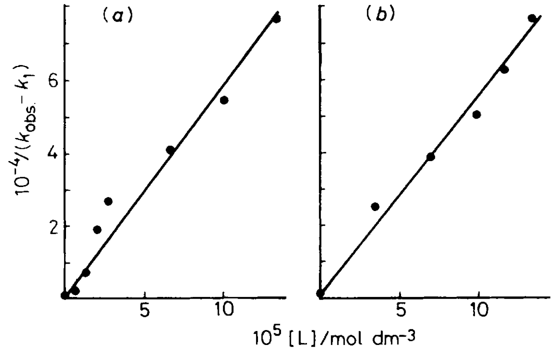


Figure 2. Plots of ($1/k_{obs.} - k_1$) *vs.* [L] for the thermolysis of *cis*-[PtMe$_4$L$_2$] in benzene at 60 °C: (*a*) L = MeNC, $k_1 = 7.5 \times 10^{-6}$ s^{-1}; (*b*) L = 2,6-Me$_2$C$_6$H$_3$NC, $k_1 = 1.8 \times 10^{-5}$ s^{-1}

The activation parameters when L = MeNC were $E_a = 71 \pm 3$ kJ mol^{-1} and $\Delta S^\ddagger = -86 \pm 12$ J K^{-1} mol^{-1}, and the secondary isotope effect for thermolysis of complexes (**1a**) and (**1a′**) was $k_H/k_D = 1.30 \pm 0.04$.

The kinetics were also studied in the presence of free isocyanide ligand (Table 5). These experiments were particularly difficult since very low concentrations of free isocyanide ligands (0—1.3 × 10^{-4} mol dm^{-3}) were required to give measurable rates of reductive elimination from (**1a**) or (**1b**), whose concentrations were 2.7 × 10^{-4} mol dm^{-3} for the kinetic experiments. At higher isocyanide concentrations the rates were too slow to be measured conveniently. Under the conditions used the reactions did not follow good first-order kinetics but the rates increased with time. A number of causes were considered. The possibility of autocatalysis was rejected because the initial rates were not affected by addition of the product *cis*-[PtMe$_2$L$_2$]. Loss of the free retarding ligand MeNC by evaporation was rejected by carrying out the reactions in a sealed cuvette and by showing that the decomposition of complex (**1b**) in the presence of the involatile ligand 2,6-Me$_2$C$_6$H$_3$NC followed the same kinetic behaviour. Finally it was established that the free isocyanides were decomposing, presumably by reaction with traces of water in the solvent, by monitoring this decay separately in the absence of (**1a**) or (**1b**) and showing that the rate of disappearance of the free ligand correlated with the apparent increase in rate of thermolysis. The data in Table 5 are therefore first-order rate constants for the early part of the reaction only. The error estimates are the standard deviations calculated for this first linear part of the first-order plots and probably underestimate the real error. Despite these experimental difficulties, the data in Table 5 clearly show the retardation by free ligand, and are most easily rationalized in terms of the mechanism in equations (3)—(6). This mechanism gives the

$$[\mathrm{PtMe_4L_2}] \xrightarrow{k_1} [\mathrm{PtMe_2L_2}] + \mathrm{C_2H_6} \qquad (3)$$

$$[\mathrm{PtMe_4L_2}] \underset{k_3}{\overset{k_2}{\rightleftharpoons}} [\mathrm{PtMe_4L}] + \mathrm{L} \qquad (4)$$

$$[\mathrm{PtMe_4L}] \xrightarrow{k_4} [\mathrm{PtMe_2L}] + \mathrm{C_2H_6} \qquad (5)$$

$$[\mathrm{PtMe_4L}] + \mathrm{L} \xrightarrow{\text{fast}} [\mathrm{PtMe_2L_2}] \qquad (6)$$

rate law (7) and hence expressions (8) and (9).

$$-d[\mathrm{PtMe_4L_2}]/dt = \{k_1 + k_2k_4/(k_3[\mathrm{L}] + k_4)\}[\mathrm{PtMe_4L_2}] \qquad (7)$$

$$k_{obs.} = k_1 + k_2k_4/(k_3[\mathrm{L}] + k_4) \qquad (8)$$

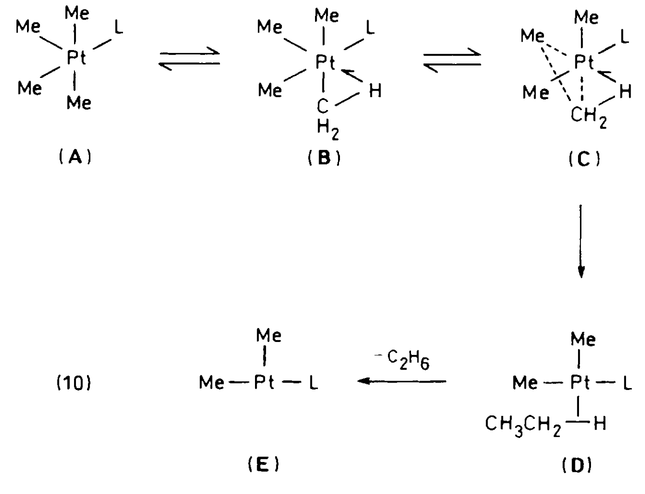
$$1/(k_{obs.} - k_1) = k_3[\mathrm{L}]/k_2k_4 + 1/k_2 \qquad (9)$$

The data were fit by equation (9) using an iterative procedure in which k_1 was varied to give the best straight line plot of $1/(k_{obs.} - k_1)$ *vs.* [L], and the results are shown in Figure 2. Despite the scatter, due to the experimental problems discussed above, the data are fully consistent with the above rate law and mechanism. Graphs of $1/k_{obs.}$ *vs.* [L] were not linear and the k_1 term was therefore clearly necessary. Analysis of the data, for reactions at 60 °C in benzene solution, gave for *cis*-[PtMe$_4$(MeNC)$_2$], $k_1 = 7.5 \times 10^{-6}$ s^{-1}, $k_2 = (1.71 \pm 0.1) \times 10^{-3}$ s^{-1}, and $k_3/k_4 = (9.8 \pm 0.6) \times 10^5$ dm^3 mol^{-1}, and for *cis*-[PtMe$_4$(2,6-Me$_2$C$_6$H$_3$NC)$_2$], $k_1 = (1.8 \pm 0.4) \times 10^{-5}$ s^{-1}, $k_2 = (9.0 \pm 0.5) \times 10^{-4}$ s^{-1}, and $k_3/k_4 = (4.9 \pm 0.2) \times 10^5$ dm^3 mol^{-1}. The very high values of k_3/k_4 clearly reflect the great sensitivity of the reaction rates to the presence of free isocyanide ligand. It is clear that, in the mechanism of equations (4)—(6), the step (5) is rate determining in the presence of free ligand. In the absence of added free ligand, this is less obvious but the low equilibrium concentration of free ligand formed in equation (4) is probably still sufficient to make the k_3 step of (4) competitive with the step (5).

Discussion

This is one of the cleanest and simplest examples of reductive elimination involving carbon–carbon bond formation and could be studied both in the solid state and in solution.

The d.s.c. results give an average value for complexes (**1a**) and (**1b**) of $\bar{D}$(Pt–Me) = 133 kJ mol^{-1} which happens to be in exact agreement with the bond energy calculated by generalized valence bond (g.v.b.) theory for the model compound [PtCl$_2$Me$_2$(PH$_3$)$_2$].[17] These same calculations predict the activation energy for reductive elimination of ethane from [PtCl$_2$Me$_2$(PH$_3$)$_2$] to be 146 kJ mol^{-1}, whereas the observed activation energy was only 86 kJ mol^{-1} for reductive elimination from *cis*-[PtMe$_4$(MeNC)$_2$]. The observation of an activation energy much less than the Pt–Me bond dissociation energy clearly suggests a concerted (rather than free radical) mechanism of reductive elimination. The value of E_a calculated by g.v.b. theory was for reductive elimination from the octahedral complex, whereas our results clearly show that the major reaction route involves ligand dissociation and reductive elimination from a five-co-ordinate species [equations (4)—(6)]. From the kinetic data in benzene solution at 60 °C in the absence of free ligand, over 99% of the reaction occurs by the ligand dissociation route when L = MeNC and over 98% when L = 2,6-Me$_2$C$_6$H$_3$NC. Clearly then, the activation energy for reductive elimination must be much lower for the five-co-ordinate intermediate than for the octahedral precursor complex.



The major questions remaining are why ligand dissociation has such a dramatic effect on the rate of reductive elimination and what is the detailed mechanism of the reaction (5). We note that the reverse of equation (5) would involve the activation of the C–C bond of ethane and it has been argued convincingly that such activation must occur after C–H activation.[18–20] It follows, from microscopic reversibility, that C–C coupling can be expected to be preceded by C–H activation of a methyl group, and such α-elimination or agostic interactions are known to be facile in co-ordinatively unsaturated complexes,[21,22] including alkylplatinum(IV) complexes.[23] Theoretical work on the reductive elimination of ethane from a hypothetical $PtMe_2$ fragment also predicts strongly tilted methyl groups, equivalent to agostic interactions, in the transition state.[17] Together these data suggest a mechanism of the type shown in equation (10).

This shows a probable reaction pathway for the kinetic step (5). If species (**A**) is initially formed in the ligand-dissociation step the equilibration with (**B**) would be very rapid; the data are also consistent with ligand dissociation being assisted by simultaneous formation of (**B**), in which case species (**A**) is not necessary. The transition state is expected to be associated with the reductive elimination step and so should resemble species (**C**); loss of ethane from (**D**) would be rapid. The mechanism in which species (**B**) is formed directly on ligand dissociation is most consistent with the value of k_H/k_D of 1.30 ± 0.04, a high value for a simple secondary isotope effect but reasonable if C–H activation is involved. The highly ordered transition state is consistent with the observed negative value of $\Delta S^\ddagger$, which is not expected for a dissociative reaction (recall that preliminary ligand dissociation should give a positive contribution to $\Delta S^\ddagger$). There is, of course, some speculation involved but this mechanism appears to be most consistent with the experimental data, with theoretical predictions[17] and with organometallic precedents.[18–23] The need for the agostic interaction in C–C coupling is probably greatest for alkyl–alkyl coupling, due to steric factors, and differences from aryl–aryl coupling results are not unexpected.[5]

Experimental

All the reactions involving organolithium reagents were carried out using standard Schlenk techniques. Diethyl ether was dried by refluxing over sodium under nitrogen and then distilled.

Proton n.m.r. spectra were recorded on a Varian XL-200 instrument, i.r. spectra on a Bruker-IFS32/IBM-9000 FT-IR spectrometer, and m.s. and g.c.–m.s. spectra on a Varian MAT 311A instrument. Analyses were performed by Guelph Chemical Laboratories Ltd. Kinetic studies were carried out by using a Varian CARY 2290 spectrophotometer, with temperature control within 0.5 °C, using a Polyscience series 900 constant-temperature bath. Differential scanning calorimetry (d.s.c.) was carried out by using a DuPont Instruments 912 DSC in conjunction with the 9900 computer/thermal analyser. The experimental methods used in the d.s.c. experiments were as described earlier.[4] T.g.a. analysis was performed using a DuPont 951 thermogravimetric analyser.

Syntheses.—The complexes $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, *cis,cis*-$[Pt_2Me_8(\mu\text{-}SMe_2)_2]$, and the corresponding deuteriomethyl analogues were prepared by literature methods.[12,24]

cis-$[PtMe_2(MeNC)_2]$. To a stirred solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.13 g, 0.23 mmol) in diethyl ether at 0 °C and under nitrogen was added MeNC (0.03 cm^3, 0.55 mmol). After stirring for a further 6 h, the solution was concentrated under vacuum and n-hexane (10 cm^3) was added. The precipitated solid was filtered off, washed with hexane, and dried *in vacuo*. The yield of $[PtMe_2(MeNC)_2]$ was 0.12 g (85%). The complex *cis*-$[PtMe_2(2,6\text{-}Me_2C_6H_3NC)_2]$ was prepared in a similar way and isolated in 92% yield.

cis-$[PtMe_4(MeNC)_2]$. Methyl isocyanide (0.11 cm^3, 2.02 mmol) was added to a solution of $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ (0.16 g, 0.253 mmol) in ether (10 cm^3) and the mixture was left at 0 °C overnight. The precipitated crystals were isolated by filtration, washed with cold ether, and dried *in vacuo*. The yield of $[PtMe_4(MeNC)_2]$ was 0.15 g (88%) (Found: C, 28.2; H, 5.5; N, 8.6. Calc. for $C_8H_{18}N_2Pt$: C, 28.5; H, 5.4; N, 8.3%).

The complexes *cis*-$[PtMe_4(2,6\text{-}Me_2C_6H_3NC)_2]$ and *cis*-$[Pt(CD_3)_4(MeNC)_2]$ were prepared in a similar way and were isolated in 82 and 77% yields respectively (Found: C, 50.7; H, 6.1; N, 5.6. Calc. for $C_{22}H_{30}N_2Pt$: C, 51.0; H, 5.8; N, 5.4%).

Attempted preparation of $[PtMe_2(CD_3)_2(MeNC)_2]$. A solution of LiMe (0.8 cm^3 of 1.2 mol dm^{-3} in ether) was added dropwise with stirring to a mixture containing $[Pt_2(CD_3)_4(\mu\text{-}SMe_2)_2]$ (0.08 g, 0.137 mmol) and MeI (0.02 cm^3, 0.32 mmol) in ether (20 cm^3) at 0 °C under nitrogen. After 1 h, excess of LiMe was destroyed by careful addition of saturated aqueous NH_4Cl. The organic layer was separated, washed with water (2×5 cm^3), dried over anhydrous magnesium sulphate, and the solution was concentrated *in vacuo* to *ca.* 10 cm^3. After addition of MeNC (0.04 cm^3, 0.74 mmol), the mixture was left at 0 °C overnight. The precipitated crystals were filtered off, washed with cold ether, and dried *in vacuo*. Yield 0.06 g; ^1H N.m.r. [$CDCl_3$, δ, J(Hz)]: 0.128 [s, ^2J(PtH) 46], 0.132 [s, ^2J(PtH) 46], 0.136 [s, ^2J(PtH) 46], 0.374 [s, ^2J(PtH) 64], 0.378 [s, ^2J(PtH) 64], 3.381 [s, ^2J(NH) 5], and 0.382 [s, ^2J(PtH) 64]. I.r. [Nujol, ν(CN) (cm^{-1})]: 2 062, 2 109, 2 218, and 2 232. Mass spectrum (m/z^+): 343, 340, 337, 328, 325, and 322.

Kinetic Studies.—A freshly prepared solution of $[PtMe_4(MeNC)_2]$ in benzene (3 cm^3, 2.7×10^{-4} mol dm^{-3}) was transferred to a cuvette, and placed in the cell compartment, thermostatted at a specified temperature. Absorbance values at λ = 290 and 300 nm were collected at 1—5 min intervals over a period of 1—3 h. Computer treatment of the data showed good first-order kinetics from which the first-order rate constant was calculated. In the studies with $[PtMe_4(2,6\text{-}Me_2C_6H_3NC)_2]$, absorbance values were collected at λ = 293 and 303 nm.

For the kinetic measurements in the presence of isocyanide, a competing reaction of isocyanide with trace amounts of water in the solution over an extended period of time was observed. The rate constants, therefore, were calculated taking data points over 0.5—1 h.

Gas Analysis.—Decomposition of $[PtMe_4(MeNC)_2]$ *and* $[Pt(CD_3)_4(MeNC)_2]$ *in benzene at* 60 °C. A mixture of $[PtMe_4(MeNC)_2]$ and $[Pt(CD_3)_4(MeNC)_2]$ (0.1 mmol each) in benzene (5 cm^3) was heated in a closed reaction flask at 60 °C and under nitrogen for 1 h. The flask was cooled to −80 °C and the gaseous products were directly analysed by m.s.

Acknowledgements

We thank the Ontario Centre for Materials Research (Ontario Centre of Excellence Program) for financial support.

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Received 14*th November* 1988; *Paper* 8/04514C