Reaction of *trans*-Dichloro(ethylene)pyridineplatinum(II) Complexes with Substituted Pyridines and Ethylene: Mechanism of Ligand Exchange and Attack of Free Base on the Co-ordinated Olefin. Preparation of Two Zwitterionic Complexes containing Platinum–Carbon σ-Bonds

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Two complexes of formula *trans*-[Pt(CH₂CH₂L)Cl₂L] (L = 4-methylpyridine or 3,5-dimethylpyridine) have been prepared by nucleophilic attack of the free amine on the co-ordinated ethylene of *trans*-[Pt(C₂H₄)Cl₂L]. Such a reaction occurs only with the more basic and less hindered pyridines. The free pyridines also exhibit nucleophilic attack on the metal centre leading to a pyridine-exchange reaction. The free energy of activation for the exchange process is <42 kJ mol⁻¹ for all the pyridines with the exception of 2,4,6-trimethylpyridine for which the free energy of activation is >80 kJ mol⁻¹. In the presence of free ethylene, exchange between free and complexed olefin occurs. Also in this case the exchange process takes place through attack of the free ethylene on the metal centre and formation of a five-co-ordinate bis(ethylene) transition state. The free energy of activation for this process is <43 kJ mol⁻¹ for unhindered pyridines and >76 kJ mol⁻¹ for pyridines with two methyl substituents in the *ortho* positions.

NUCLEOPHILIC attack of amines on co-ordinated ethylene and consequent π ⟶ σ rearrangement of the metal–olefin bond has been observed in platinum(II) complexes either in solution by n.m.r.[1,2] or in the solid by chemical analysis of the products.[2,3] With aliphatic amines at room temperature, only secondary amines of high basicity and relative freedom from steric hindrance are able to add to ethylene in *trans*-[Pt(C₂H₄)Cl₂L] complexes (L = base); primary amines (even the most basic ones) and triethylamine do not react.[2] In the case of heterocyclic aromatic amines the only report concerns the formation in solution at low temperature (−50 °C) and in the presence of a four-fold excess of free pyridine (py) of *trans*-[Pt(CH₂CH₂NC₅H₅)Cl₂(py)] in 1 : 1 equilibrium with *trans*-[Pt(C₂H₄)Cl₂(py)].[1] The effect of the basicity and steric hindrance of substituted pyridines was not investigated.

A free amine could also react with the *trans*-[Pt(C₂H₄)Cl₂L] substrate to give a five-co-ordinate complex of type [Pt(C₂H₄)Cl₂L₂] analogous to those recently synthesized by us with bidentate amines.[4] In this study we have investigated whether such a five-co-ordinate species is formed at least as an activated reaction intermediate. A broadening of the ethylene resonance and loss of coupling with platinum has been observed for the *trans*-[Pt(C₂H₄)Cl₂L] complexes on increasing the temperature above 30 °C. The origin of this phenomenon has also been investigated.

EXPERIMENTAL

Starting Materials.—Commercial pyridines were purified by distillation over K[OH] in a nitrogen atmosphere. Zeise's salt was prepared according to the method of Cramer *et al.*[5] from potassium platinite and ethylene gas.

Preparation of Complexes.—The complexes *trans*-[Pt-

(C₂H₄)Cl₂L] [L = 2,4,6-trimethylpyridine (2,4,6Me₃-py), 2,5-dimethylpyridine (2,5Me₂-py), 2-methylpyridine (2Me-py), 2-chloropyridine (2Cl-py), 3,5-dimethylpyridine (3,5-Me₂-py), 4-methylpyridine (4Me-py), 4-chloropyridine (4Cl-py), and pyridine (py)] were prepared by the method of Schmidt and Orchin,[6] adding the appropriate pyridine to an aqueous solution of Zeise's salt; the product is formed instantaneously and precipitates out from the solution; it was recrystallized from chloroform–pentane.

The complexes *trans*-[Pt(CH₂CH₂L)Cl₂L] (L = 3,5Me₂-py or 4Me-py) were prepared by treating a suspension of *trans*-[Pt(C₂H₄)Cl₂L] in methanol (1 mmol in 5 cm³ of solvent) at 0 °C with a two-fold excess of ligand and stirring the solution for no more than 30 min.† In the case of 4Me-py the solid was recovered by filtration of the mother liquor, washed with cold ethanol and once with cold diethyl ether, and dried {Found: C, 34.7; H, 3.5; Cl, 14.7; N, 5.6. [Pt(CH₂CH₂NC₅H₄Me-4)Cl₂(4Me-py)] requires C, 35.0; H, 3.8; Cl, 14.8; N, 5.8%}. In the case of (3,5Me₂-py) since the freshly prepared complex is quite soluble both in alcohol and diethyl ether, the solid, after filtration of the mother liquor, was pumped *in vacuo* to remove trace amounts of solvent and unchanged pyridine and it was shown to be sufficiently pure {Found: C, 37.5; H, 4.1; Cl, 13.8; N, 5.4. [Pt(CH₂CH₂NC₅H₃Me₂-3,5)Cl₂(3,5Me₂-py)] requires C, 37.8; H, 4.4; Cl, 14.0; N, 5.5%}.

Kinetic Data.—Variable-temperature n.m.r. studies were carried out on a Varian N.V.-14 spectrometer. The probe temperature was adjusted with a variable-temperature probe accessory. Values for the free energy of activation were calculated using the expression $\Delta G^{\ddagger} = -RT\ln(\pi\Delta\nu h/2^{\frac{1}{2}}kT)$ where $\Delta\nu$ is the chemical shift of the coalescing peaks under the conditions of slow exchange, T is the coalescence temperature, and R, k, and h have their normal meaning.

(i) *Pyridine exchange.* The complex *trans*-[Pt(C₂H₄)-Cl₂L] (*ca.* 50 mg) and a stoicheiometric amount of free L were dissolved in CDCl₃ (0.3 cm³) and placed in an n.m.r.

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† The reaction time is critical since longer periods also lead to formation of the bis adduct *trans*-[PtCl₂L₂].

[1] P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Amer. Chem. Soc.*, 1968, **90**, 4175.

[2] D. Hollings, M. Green, and D. V. Claridge, *J. Organometallic Chem.*, 1973, **54**, 399.

[3] R. Palumbo, A. De Renzi, A. Panunzi, and G. Paiaro, *J. Amer. Chem. Soc.*, 1969, **91**, 3879.

[4] L. Cattalini, F. Gasparrini, L. Maresca, and G. Natile, *J.C.S. Chem. Comm.*, 1973, 369; L. Maresca, G. Natile, and L. Cattalini, *Inorg. Chim. Acta*, 1975, **14**, 79; M. Calligaris, P. Delise, L. Maresca, G. Natile, and L. Randaccio, *J.C.S. Dalton*, 1976, 2386.

[5] R. D. Cramer, E. L. Jenner, R. V. Lindsey, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1963, **85**, 1961.

[6] P. Schmidt and M. Orchin, *Inorg. Chem.*, 1967, **6**, 1260.

tube. The tube was sealed and the n.m.r. spectrum was recorded at intervals over the range -65 to 90 °C.

(ii) *Ethylene exchange.* A solution of *trans*-[Pt(C$_2$H$_4$)Cl$_2$L] (*ca.* 50 mg) in CDCl$_3$ (0.3 cm^3) was pipetted into the n.m.r. tube. The tube was cooled to 0 °C and ethylene gas was bubbled through the solution. After a preliminary n.m.r. run had shown that the complex and ethylene were present in approximately equimolar amounts, the tube was sealed and the n.m.r. spectrum was recorded at intervals over the range -65 to 90 °C.

RESULTS AND DISCUSSION

Two complexes, *trans*-[Pt(CH$_2$CH$_2$NC$_5$H$_4$Me-4)Cl$_2$(4-Me-py)] (1) and *trans*-[Pt(CH$_2$CH$_2$NC$_5$H$_3$Me$_2$-3,5)Cl$_2$-(3,5Me$_2$-py)] (2), were prepared by treating a suspension of [Pt(C$_2$H$_4$)Cl$_2$L] (L = 4Me-py or 3,5Me$_2$-py) at 0 °C with a two-fold excess of free ligand. The complexes were obtained as solids by filtration of the reaction mixture. The experimental conditions (temperature and solvent) are similar to those used for the preparation of the five-co-ordinate complexes [Pt(C$_2$H$_4$)Cl$_2$(L–L)] (L–L = bidentate nitrogen-donor ligand) starting from Zeise's salt, K[Pt(C$_2$H$_4$)Cl$_3$], and bidentate amines, however, complexes (1) and (2) cannot be formulated as five-co-ordinate platinum(II) adducts (A), but as four-co-ordinate platinum(II) zwitterions (B) on the basis of their i.r. and n.m.r. spectra.

(A)   (B)
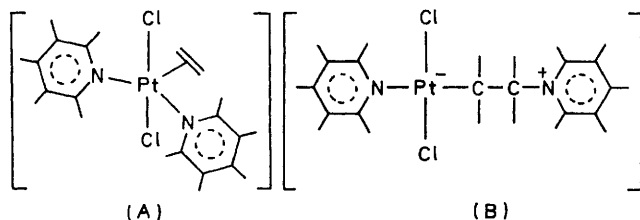
I.r. Data.—The i.r. spectra of both complexes showed absorptions at $2\,800$ cm^{-1} in the ν(C–H) region (near $3\,000$ cm^{-1}), while the starting substrates, *trans*-[Pt-(C$_2$H$_4$)Cl$_2$L], and the free pyridines do not have absorption bands lower than $2\,870$ cm^{-1}; this is an indication of the presence of a CH$_2$ group in complexes (1) and (2). In the $1\,400$—$1\,500$ cm^{-1} region the ring-breathing vibrations of the pyridine ligands and δ_{asym}(CH$_3$), δ_{sym}(–CH$_2$–), and δ_{asym}(=CH$_2$) occurred. The i.r. spectra of the *trans*-[Pt(C$_2$H$_4$)Cl$_2$L] complexes showed absorption bands at *ca.* $1\,430$ cm^{-1} assignable to pyridine breathing and to δ_{asym}(=CH$_2$) of the ethylene ligand. However, complexes (1) and (2) showed a broad absorption band with maxima at $1\,460$ and $1\,490$ cm^{-1}, respectively, which can be assigned to δ_{asym}(–CH$_2$–) of the methylene group bonded to the amino-nitrogen in (B); the other methylene group, σ-bonded to platinum, should have the corresponding δ_{asym}(–CH$_2$–) at lower frequency and thus it overlaps with the other absorptions of the pyridine ligand. In the spectrum of *trans*-[Pt(C$_2$H$_4$)Cl$_2$(3,5Me$_2$-py)] we can confidently assign the medium-strong band at $1\,010$ cm^{-1} to the asymmetric wagging of the π-bonded ethylene; this band is missing in the spectrum

of (2). An analogous conclusion is not possible for the 4Me-py derivatives since in this case the amine has a vibration close to $1\,000$ cm^{-1}. All metal–ligand vibrations occurred in the <500 cm^{-1} region. For the *trans*-[Pt(C$_2$H$_4$)Cl$_2$L] complexes we can assign the bands at 385 and 390 cm^{-1} observed for the 4Me-py and 3,5Me$_2$-py derivatives respectively to ν[Pt(C$_2$H$_4$)]. These bands are absent from the spectrum of complexes (1) and (2) indicating, once more, that they have no π-bonded ethylene.

N.M.R. Data.—The n.m.r. spectra of solutions of complexes (1) and (2) in CDCl$_3$ at 0 °C showed a single resonance for the ethylene protons having the same chemical shift and ^{195}Pt coupling constant as that observed for the *trans*-[Pt(C$_2$H$_4$)Cl$_2$L] starting complexes. Moreover, a single resonance was observed for each type of equivalent proton of the pyridines, and the chemical shift was intermediate between that of the free amine and that of the co-ordinated amine in *trans*-[Pt(C$_2$H$_4$)Cl$_2$L]. Therefore it is clear that under these conditions complexes (1) and (2) are completely dissociated into the starting materials, and a fast exchange process takes place between free and co-ordinated pyridine [equation (1)]. On decreasing the temperature below -40 °C, other proton resonances assignable to a

$$\text{*trans*-[Pt(C}_2\text{H}_4\text{)Cl}_2\text{L]} + \text{L}' \longrightarrow$$
$$\text{*trans*-[Pt(C}_2\text{H}_4\text{)Cl}_2\text{L}'] + \text{L} \quad (1)$$
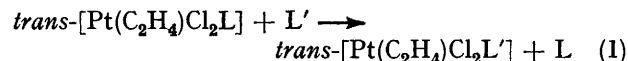
zwitterion of the type (B) began to appear and at -65 °C the amount of zwitterion was *ca.* 50% of the total platinum species [Figures 1 and 2; the n.m.r. resonances are at δ 2.43, 2.77, 4.52, 7.13, 7.77, 8.79, and 8.88 for (1) and at 2.32, 2.62, 4.62, 7.40, 8.06, 8.52, and 8.60 p.p.m. for (2)].

These results allow the following conclusions. (*i*) Reaction (1) is fast, in the n.m.r. time scale, even at -65 °C
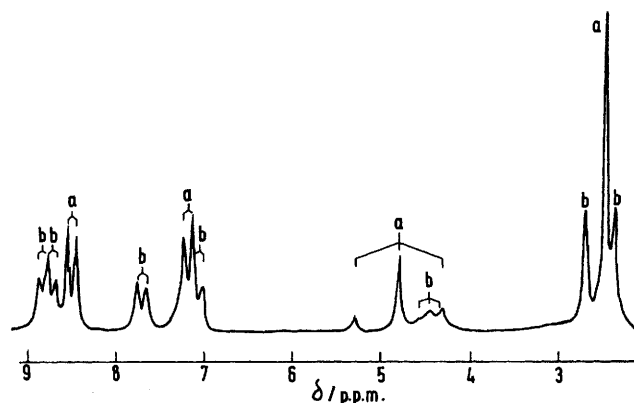

FIGURE 1 Low-temperature n.m.r. spectrum (-65 °C) of *trans*-[Pt(CH$_2$CH$_2$NC$_5$H$_4$Me-4)Cl$_2$(4Me-py)] dissolved in CDCl$_3$. Peaks referring to the fast reaction *trans*-[Pt(C$_2$H$_4$)Cl$_2$(4Me-py)] + (4Me-py)' ⇌ *trans*-[Pt(C$_2$H$_4$)Cl$_2$(4Me-py)'] + 4Me-py are indicated by a, the proton resonances of *trans*-[Pt(CH$_2$CH$_2$NC$_5$H$_4$Me-4)Cl$_2$(4Me-py)] by b

and it does not occur through an intermediate species such as a zwitterion as suggested by other workers (in this case the resonance of the zwitterion could not be

observed distinctly), but probably through a five-co-ordinate intermediate of the type (A) as will be discussed later. (*ii*) In the zwitterion there is no fast exchange between free and co-ordinated pyridine.

We recorded the variable-temperature n.m.r. spectra of an equimolar mixture of trans-[Pt(C$_2$H$_4$)Cl$_2$L] and free base for a series of different pyridines in order to see whether other pyridines can give the zwitterion at low temperature and to determine the effect of basicity and steric hindrance of the amine on the rate of reaction (1). In addition to 4Me-py and 3,5Me$_2$-py,·py itself also gave
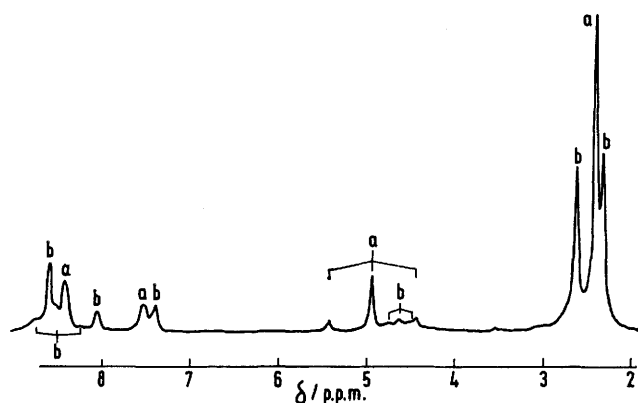
Figure 2 Low-temperature n.m.r. spectrum (−60 °C) of trans-[Pt(CH$_2$CH$_2$NC$_5$H$_3$Me$_2$-3,5)Cl$_2$(3,5Me$_2$-py)] dissolved in CDCl$_3$. Peaks referring to the fast reaction trans-[Pt(C$_2$H$_4$)Cl$_2$(3,5Me$_2$-py)] + (3,5Me$_2$-py)′ ⇌ trans-[Pt(C$_2$H$_4$)Cl$_2$(3,5-Me$_2$py)′] + 3,5Me$_2$-py are indicated by a, those of trans-[Pt(CH$_2$CH$_2$NC$_5$H$_3$Me$_2$-3,5)Cl$_2$(3,5Me$_2$-py)] by b

spectroscopic evidence for the formation at low temperature of the zwitterion, starting from an equimolar mixture of trans-[Pt(C$_2$H$_4$)Cl$_2$(py)] and free pyridine; however, in this case the amount of zwitterion at −65 °C was less than 20% of the total complexed species. These results are in line with the conclusions of Hollings et al.[2] for aliphatic amines in that only bases of high basicity and relative freedom from steric hindrance are able to form σ-bonded compounds.

Pyridine Exchange.—The rate of exchange between free and complexed amine was fast on the n.m.r. time scale even at −65 °C for all the complexes with the exception of the 2,4,6Me$_3$-py derivative in which the rate of exchange was slow even at 90 °C. The effect of the basicity of pyridines on the ligand lability in some trans-[Pt(C$_2$H$_4$)Cl$_2$(4Z-py)] complexes was considered by Kaplan et al.[7] who found an inverse relation between the ligand lability and basicity of the amine. The effect of the steric hindrance of the amine on the ligand exchange was studied by Chottard et al.[8] who found that by using two amines of equal basicity but different steric hindrance such as 2,4Me$_2$-py and 2,6Me$_2$-py the rate of exchange at room temperature was fast (on the n.m.r. time scale) in the former case and slow in the latter.

The exchange processes we have so far examined were

[7] P. D. Kaplan, P. Schmidt, A. Brause, and M. Orchin, *J. Amer. Chem. Soc.*, 1969, **91**, 85.

either fast even at −65 °C or slow even at 90 °C. More specific information could be obtained by studying exchange processes in which the coalescence temperature
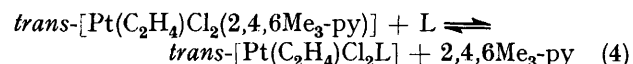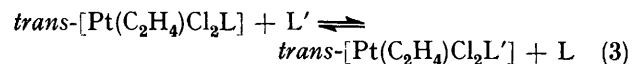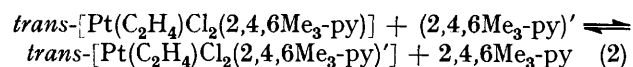
TABLE 1

Proton chemical shifts * (δ/p.p.m., downfield from SiMe$_4$) of complexed and free pyridines, L (upper and lower lines respectively), and estimated free energies of activation for ligand exchange in the reaction: trans-[Pt(C$_2$H$_4$)Cl$_2$L] + L′ ⇌ trans-[Pt(C$_2$H$_4$)Cl$_2$L′] + L

L	ΔG‡ kJ mol⁻¹	H²	H³	H⁴	2-Me	3-Me	4-Me
2,4,6Me$_3$-py	>80		7.04		3.17		2.37
			6.80		2.51		2.28
2,5Me$_2$-py	<42	8.52	7.29	7.56	3.13	2.41	
		8.31	7.02	7.34	2.52	2.28	
2Me-py	<42	8.66	7.39, 7.33	7.74			3.15
		8.46	7.10, 7.04	7.54			2.56
2Cl-py	<42	8.66	7.59, 7.51	7.87			
		8.38	7.32, 7.23	7.65			
3,5Me$_2$-py	<42	8.53		7.53		2.39	
		8.22		7.26		2.29	
4Me-py	<42	8.70	7.35			2.51	
		8.46	7.08			2.35	
4Cl-py	<42	8.90	7.52				
		8.50	7.28				
py	<42	8.93	7.51	7.95			
		8.61	7.26	7.66			

* All the spectra were recorded in CDCl$_3$ solution at room temperature.

occurs between −65 and 90 °C. Therefore we studied the exchange of the amine ligands in an equimolar mixture of trans-[Pt(C$_2$H$_4$)Cl$_2$(2,4,6Me$_3$-py)] and L = (*i*) 2Me-py, (*ii*) 4Me-py, and (*iii*) py. In all three cases, soon after the mixing of the reagents amine exchange occurred and the two possible complexes containing different pyridines and the two free pyridines were formed in comparable yields. Three different exchange processes, (2)—(4), can therefore take place.

trans-[Pt(C$_2$H$_4$)Cl$_2$(2,4,6Me$_3$-py)] + (2,4,6Me$_3$-py)′ ⇌ trans-[Pt(C$_2$H$_4$)Cl$_2$(2,4,6Me$_3$-py)′] + 2,4,6Me$_3$-py (2)

trans-[Pt(C$_2$H$_4$)Cl$_2$L] + L′ ⇌ trans-[Pt(C$_2$H$_4$)Cl$_2$L′] + L (3)

trans-[Pt(C$_2$H$_4$)Cl$_2$(2,4,6Me$_3$-py)] + L ⇌ trans-[Pt(C$_2$H$_4$)Cl$_2$L] + 2,4,6Me$_3$-py (4)

Reaction (2) is slow on the n.m.r. time scale even at 90 °C and therefore it cannot lead to equivalence of the proton resonances of free and complexed 2,4,6Me$_3$-py. Reaction (3) is fast on the n.m.r. time scale even at −65 °C and led to equivalence of the proton resonances of free and complexed L. Depending on the rate of reaction (4) (whether fast or slow with respect to the n.m.r. time scale), one or two distinct resonances will be observed for the ethylene protons of the two complexes and for equivalent protons of free and complexed 2,4,6Me$_3$-py. In all three cases examined, on varying the temperature we could attain a slow or fast rate for reaction (4) and the calculated free energies of activation are summarized

[8] J. C. Chottard, D. Mansuy, and J. F. Bartoli, *J. Organometallic Chem.*, 1974, **65**, C19.

in Table 2. The results indicate that the steric effect is the most important factor in determining the rate of
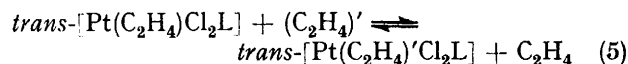
TABLE 2

Estimated free energies of activation * for ligand exchange in the reaction: $trans$-[Pt(C$_2$H$_4$)Cl$_2$(2,4,6Me$_3$-py)] + L $\rightleftharpoons$ $trans$-[Pt(C$_2$H$_4$)Cl$_2$L] + 2,4,6Me$_3$-py

L	$\Delta G^{\ddagger}$/kJ mol^{-1}
2Me-py	77
4Me-py	65
py	60

* Errors are estimated to be ca. ±2 kJ mol^{-1}.

pyridine exchange in this type of complex, and this is compelling experimental evidence that the exchange process occurs through a five-co-ordinate transition state (A) whose energy depends mainly on the steric interaction between the *ortho* substituents of the equatorial pyridine ligands.

Ethylene Exchange.—The large effect of the *ortho* substituents of the pyridine on the free energy of activation of the pyridine-exchange reaction is probably determined also by the presence, in the trigonal plane of the five-co-ordinate transition state, of an ethylene molecule. The steric hindrance of the olefin cannot be compared with that of a normal unidentate ligand for two reasons: first because two atoms are simultaneously at a bond distance from the central metal; secondly because in the five-co-ordinate species the ethylene molecule virtually lies in the trigonal plane. Therefore the olefin molecule has to be considered as a bulky ligand. If this view is correct the steric hindrance of the pyridine ligand should have a large effect on the rate of exchange of free and complexed ethylene [reaction (5)]. The n.m.r. spectrum of the complexes *trans*-

$$trans\text{-}[Pt(C_2H_4)Cl_2L] + (C_2H_4)' \rightleftharpoons$$
$$trans\text{-}[Pt(C_2H_4)'Cl_2L] + C_2H_4 \quad (5)$$

[Pt(C$_2$H$_4$)Cl$_2$L] at temperatures up to 90 °C did not show significant line broadening or loss of coupling of the

TABLE 3

Proton chemical shifts ^{a} (δ/p.p.m., downfield from SiMe$_4$) of complexed ethylene and estimated free energies of activation for olefin exchange in the reaction: $trans$-[Pt(C$_2$H$_4$)Cl$_2$L] + (C$_2$H$_4$)' $\rightleftharpoons$ $trans$-[Pt(C$_2$H$_4$)'Cl$_2$L] + C$_2$H$_4$

L	$\Delta G^{\ddagger}$ ^{b}/kJ mol^{-1}	δ (C$_2$H$_4$) ^{c}
2,4,6Me$_3$-py	$\geqslant$76	4.82(61)
2,5Me$_2$-py	>76	4.91(61)
2Me-py	>76	4.90(61)
2Cl-py	55	4.93(65)
3,5Me$_2$-py	44	4.89(60)
4Me-py	<43	4.90(60)
4Cl-py	<43	4.92(62)
py	<43	4.92(61)

^{a} All the spectra were recorded in CDCl$_3$ solution. ^{b} Errors are estimated to be ca. ±2 kJ mol^{-1}. ^{c} Coupling constants (in Hz) with ^{195}Pt are given in parentheses.

ethylene resonance with platinum; when, however, free ethylene was added to the solution an exchange process,

the rate of which depended on the nature of the pyridine, was generally observed. We recorded the variable-temperature n.m.r. spectra of an approximately equi-molar mixture of $trans$-[Pt(C$_2$H$_4$)Cl$_2$L] and free ethylene, and the measured free energy of activation for the exchange process is reported in Table 3. Assuming that unco-ordinated ethylene protons absorb at δ 5.42 p.p.m. while the signal of co-ordinated ethylene in these complexes occurs in a narrow range at δ ca. 4.85 p.p.m., it follows that for each complex the coalescence of the signals of free and co-ordinated ethylene will be reached when the rate constant for the exchange process is $\frac{1}{2}\tau = \Delta v \pi/2^{\frac{1}{2}} = 76$ s^{-1}. The range of temperature which could be explored was −65 to 90 °C corresponding to a range of $\Delta G^{\ddagger}$ values of 43—76 kJ mol^{-1}. The complex
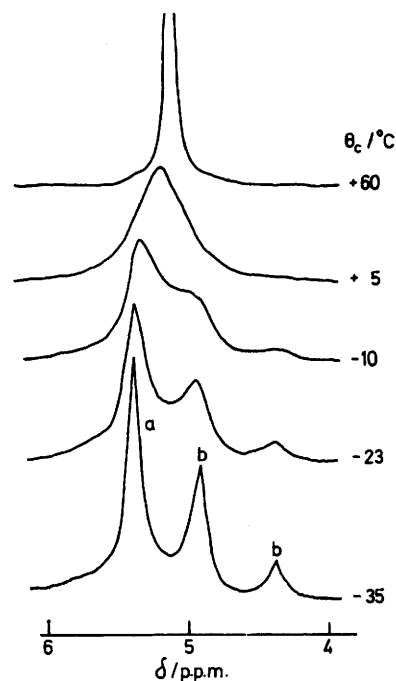

FIGURE 3   Variable-temperature n.m.r. spectrum in the region of ethylene resonances relative to the reaction: $trans$-[Pt(C$_2$H$_4$)Cl$_2$(2Cl-py)] + (C$_2$H$_4$)' $\rightleftharpoons$ $trans$-[Pt(C$_2$H$_4$)'Cl$_2$(2Cl-py)] + C$_2$H$_4$. Peaks a and b refer to free and complexed ethylene respectively

of 2,4,6Me$_3$-py did not show any broadening of the ethylene signal even at 90 °C, indicating that the free energy of activation for ethylene exchange in this complex is $\geqslant$76 kJ mol^{-1}. The complexes of 2,5Me$_2$-py and 2Me-py showed line broadening at high temperature, but coalescence did not occur at 90 °C and therefore the $\Delta G^{\ddagger}$ for these two complexes is >76 kJ mol^{-1}. In the case of the complex of 2Cl-py, on varying the temperature we could attain the conditions of slow exchange (two sharp resonances for free and co-ordinated ethylene) and fast exchange (one sharp signal) (Figure 3), and from the coalescence temperature we calculated an activation energy of 55 kJ mol^{-1}. The complex of 3,5Me$_2$-py underwent fast exchange of ethylene at room temperature, but at −65 °C two distinct signals for free and

complexed olefin began to appear; the calculated $\Delta G^{\ddagger}$ value is 44 kJ mol⁻¹. The complexes of 4Me-py, 4Cl-py, and py underwent fast exchange of ethylene even at −65 °C where only a broadening of the proton resonance was apparent; the $\Delta G^{\ddagger}_{\ddagger}$ values for these three complexes are therefore <43 kJ mol⁻¹.

It is clear that the complexes in which the pyridine ligand has two substituents in the *ortho* positions have an exceptionally high free energy of activation for ethylene exchange; on the other hand, complexes in which the pyridine ligand has no *ortho* substituents have a very low $\Delta G^{\ddagger}$ value for olefin exchange, and intermediate behaviour is shown by complexes in which the pyridine ligand has only one substituent in the *ortho* position. The influence of the steric hindrance of the pyridine on the rate of ethylene exchange and the fact that fast exchange is observed only in the presence of free olefin indicate that the reaction is bimolecular and therefore analogous to that observed for bis(ethylene)-(pentane-2,4-dionato)rhodium(I) [9] and ethylenebis-(triphenylphosphine)platinum(0).[10]

The study of ethylene exchange allows a direct measure of the steric retardation exerted by the *trans* ligand alone (the pyridine) on the reaction rate. It has been suggested that in a five-co-ordinate transition state of trigonal-bipyramidal structure the destabilization due to an *ortho*-substituted aromatic group is much less if the aromatic ligand is in the equatorial plane than if it occupies an apical position; in fact, in the second case, the *ortho* substituents would extend just into the trigonal plane.[11] In our case the aromatic amine is in the equatorial plane and, nevertheless, the effect of the *ortho* substituents on the reaction rate is very high. A possible explanation is that the two equatorial ethylene molecules, since they tend to be coplanar in the trigonal plane, are in direct steric competition with the third ligand lying in the equatorial plane. That the steric retardation caused by the *trans* ligand also depends on the steric requirements of the entering and leaving groups both lying in the equatorial plane of the trigonal

transition state is evident by comparing our data with those for reaction (6) (R = phenyl, *o*-tolyl, or mesityl).[12]

$$trans\text{-}[PtRCl(PEt_3)_2] + CN^- \rightleftharpoons$$
$$trans\text{-}[PtR(CN)(PEt_3)_2] + Cl^- \quad (6)$$
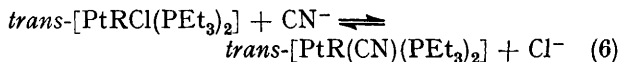
An increase in activation energy of 17 kJ mol⁻¹ was found on going from phenyl to mesityl; in our case [reaction (5), Table 3] the increase in $\Delta G^{\ddagger}$ on going from py to 2,4,6Me₃-py is ≫33 kJ mol⁻¹, although the steric hindrance of py, 2Me-py, and 2,4,6Me₃-py is very similar to that of phenyl, *o*-tolyl, and mesityl respectively.

In conclusion our experiments indicate that pyridines can exhibit nucleophilic attack either on platinum or on co-ordinated ethylene. In the first case the reaction leads to pyridine exchange and the steric factors provide the major contribution to the $\Delta G^{\ddagger}$ value; in the second case the reaction leads to formation of a zwitterion and is influenced by the steric and electronic properties of the attacking pyridine. The hypothesis of pyridine exchange occurring through a preliminary attack on the ethylene [1] is ruled out since at low temperature fast exchange between free and complexed pyridine of *trans*-[Pt(C₂H₄)Cl₂L] occurs but not between free and complexed pyridine of the zwitterion. We have also shown that the broadening of the ethylene resonance and loss of coupling with platinum observed for *trans*-[Pt(C₂H₄)-Cl₂L] at >30 °C is not caused, as suggested, by a fast exchange between ethylene and free base but eventually by a fast exchange between the co-ordinated ethylene and the small amount of free olefin displaced from the substrate. It has been demonstrated that the steric retardation caused by the *trans* ligand depends also on the steric requirements of the entering and leaving groups; the exceptionally large effect of the pyridine substituent on the rate of ethylene exchange indicates that the olefin ligands, for their peculiar manner of co-ordination, behave as very bulky groups.

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