Intramolecular Catalysis of Olefin Exchange in *trans*-Dichloro(η-olefin)-(pyridine)platinum(II) Complexes by the Hydroxy-group of a Side Chain in the 2-Position of the Pyridine Ligand †

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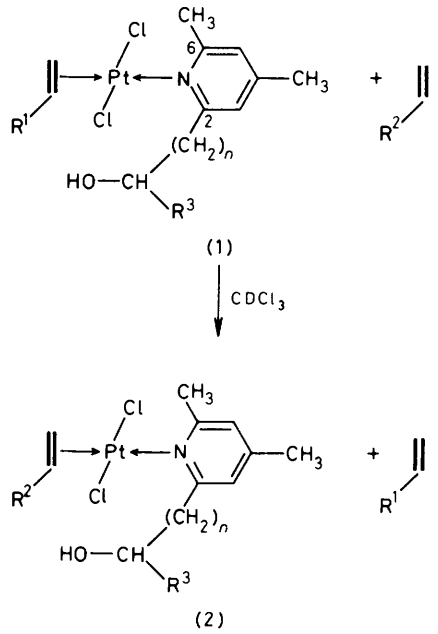
Whereas olefin exchange in *trans*-dichloro(η-olefin)(pyridine)platinum(II) complexes is hindered by the presence of 2,6-substituents on the pyridine ligand, a hydroxy-group, either primary or secondary, borne by a side chain in the 2-position of this ligand can give an intramolecular catalysis of the olefin exchange reaction. This catalysis leads to a reaction that is first order in the complex and zero order in the olefin. The catalysis is dependent on the length of the side chain bearing the hydroxy-group. Kinetic data, for the substitution of 3,3-dimethylbut-1-ene by styrene, suggest that the catalysis is due to the transient formation of a (hydroxyalkylpyridine-*O*,*N*)platinum chelate.

Kinetic studies of olefin exchange in square-planar *trans*-aminedichloro(olefin)platinum(II) complexes have established a direct second-order substitution pathway in non-co-ordinating solvents.[1,2] It has also been reported that this substitution process is very slow when the amine ligand is a 2,6-dimethylpyridine.[3,4] However, in the course of previous work,[5] we observed a fast olefin exchange when the reaction of Scheme 1 (where R^1 = H, R^2 = various aliphatic or functional chains, R^3 = H or Me, and n = 1 or 2) was used to prepare the corresponding complexes of type (2).

We found that the presence of the hydroxy-group on the side chain in the 2-position of the pyridine ligand is necessary to obtain this rate enhancement. We report herein a study of the role of the hydroxy-group in the displacement of 3,3-dimethylbut-1-ene (R^1 = Bu^t) by styrene (R^2 = Ph) [reaction (i), Scheme 1] for complexes (1a)—(1e).



(1a); n = 0, R^3 = H (2a); n = 0, R^3 = H
(1b); n = 1, R^3 = H (2b); n = 1, R^3 = H
(1c); n = 2, R^3 = H (2c); n = 2, R^3 = H
(1d); n = 2, R^3 = Me (2d); n = 2, R^3 = Me
(1e); n = 3, R^3 = H (2e); n = 3, R^3 = H

Scheme 1. For reaction (i) R^1 = Bu^t and R^2 = Ph

Experimental

Starting Materials.—Zeise's salt was prepared according to the method of Cramer *et al.*[6] from potassium tetrachloroplatinate and ethylene gas. Di-μ-chloro-bis[dichloro(η-ethene)-platinum] was prepared from Zeise's salt by the method of Chatt and Searle.[7] 3-(2′-Pyridyl)- and 3-(2′,4′-dimethyl-6′-pyridyl)-propan-1-ol, 4-(2′-pyridyl)- and 4-(2′,4′-dimethyl-6′-pyridyl)-butan-1-ol, and 4-(2′-pyridyl)- and 4-(2′,4′-dimethyl-6′-pyridyl)-butan-2-ol were prepared according to the method of Lüning and Lundin.[8] 2-(2′-Pyridyl)- and 2-(2′,4′-dimethyl-6′-pyridyl)-ethan-1-ol were prepared according to Proft.[9] (2′-Pyridyl)- and (2′,4′-dimethyl-6′-pyridyl)-methanol were prepared according to Boekelheide and Linn.[10] 18-Crown-6 ether (1,4,7,10,13,16-hexaoxacyclo-octadecane) was supplied from Aldrich (99%) and used without further purification. The 222 cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) was Merck Kryptofix 222, and was used after lyophilisation of its benzene solution.

Preparation of Complexes.—*trans*-Dichloro(η-3,3-dimethylbut-1-ene)(pyridine)platinum complexes were prepared from di-μ-chloro-bis[dichloro(η-3,3-dimethylbut-1-ene)platinum] according to Brause *et al.*[11] The complexes were purified by column chromatography on Florisil (150—250 μm) with a chloroform–methanol mixture (99 : 1) as eluant. Products were obtained as yellow viscous liquids in 60—70% yield. The analytical and spectroscopic data are collected in Tables 1 and 2.

Kinetic Data.—The n.m.r. technique was used despite the fact it is less accurate than u.v. spectroscopy because the difference between the u.v. spectra of reagents and products was too small. ^{1}H N.m.r. spectra were recorded with a Varian EM 390 spectrometer using $CDCl_3$ as solvent and hexamethyldisiloxane (hmds) as internal standard. The probe temperature was adjusted with a variable-temperature probe accessory.

Complexes (1) were dissolved in $CDCl_3$ containing hmds (0.025 mol dm^{-3}). Solutions were prepared so that the final concentrations in the n.m.r. tube were 0.05 mol dm^{-3} of complex (1) and 0.25—1 mol dm^{-3} of styrene. In a typical

† Throughout this paper the word pyridine is used as a generic name for the various substituted pyridines studied.

experiment, complex (1) (0.4 cm^3 of a 0.0625 mol dm^{-3} solution) was added to $CDCl_3$ (0.05 cm^3) and the spectrum recorded. At time $t = 0$ styrene in $CDCl_3$ (0.05 cm^3 of a 5 mol dm^{-3} solution) was added. Four different styrene concentrations were used for each complex at each temperature. All the experiments were repeated at least in duplicate runs.

The chemical shift of the Bu^t group in co-ordinated 3,3-dimethylbut-1-ene was 1.33 p.p.m. while it is 1 p.p.m. for the free olefin thus enabling us to follow the appearance of the free ligand. Its concentration *versus* time was calculated by monitoring the integration area of the Bu^t group signal, using hmds as internal standard. The first-order rate constant was given by the relation $k = -\ln[(a_0 - x)/a_0]/t$ where a_0 is the initial concentration of the complex and x is the concentration of free olefin at time t. Reactions were monitored during the first half-life and correlation coefficients are better than 0.99. Ten to 20 measurements were made for each run, except with complex (1b) for which the shorter half-life allowed only five to six measurements.

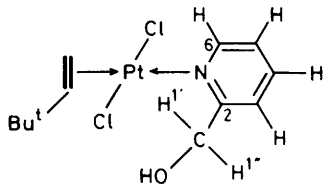
The reactions of *trans*-dichloro(η-3,3-dimethylbut-1-ene)-(2,4,6-trimethylpyridine)platinum with styrene in the presence of MeOD were followed in $CDCl_3$ solutions. Concentrations in the kinetic runs were 0.04 mol dm^{-3} of the complex and 1 mol dm^{-3} of styrene; calculated concentrations of MeOD were checked *versus* the integration area of its methyl peak. Pseudo-first-order rate constants were determined by the same method used for the olefin exchange of complexes (1): [MeOD] = 0.5 mol dm^{-3}, $k_{obs.} = (1.0 \pm 0.2) \times 10^{-5}$ s^{-1}; [MeOD] = 0.7 mol dm^{-3}, $k_{obs.} = 1.4 \pm 0.2) \times 10^{-5}$ s^{-1}; [MeOD] = 1 mol dm^{-3}, $k_{obs.} = (2.0 \pm 0.3) \times 10^{-5}$ s^{-1}.

Table 1. Analytical data for the complexes (1)

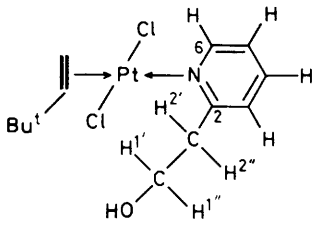
Complex	Molecular formula	Analysis * (%) C	H	N
(1a)	$C_{14}H_{23}Cl_2NOPt$	34.25 (34.50)	4.55 (4.70)	2.80 (2.85)
(1b)	$C_{15}H_{25}Cl_2NOPt$	35.15 (35.95)	5.10 (5.00)	2.85 (2.80)
(1c)	$C_{16}H_{27}Cl_2NOPt$	37.20 (37.30)	5.20 (5.25)	2.45 (2.70)
(1d)	$C_{17}H_{29}Cl_2NOPt$	38.55 (38.55)	5.30 (5.50)	2.90 (2.65)
(1e)	$C_{17}H_{29}Cl_2NOPt$	38.35 (38.55)	5.60 (5.50)	2.45 (2.65)

* Calculated values are given in parentheses.

(Hydroxyalkylpyridine-O,N)platinum Chelates of Complexes (3a) *and* (3b).—Complexes (3a) and (3b) (0.125 mol dm^{-3} in $CDCl_3$) were treated with Na_2CO_3 (100 mg) in an n.m.r. tube.



(3a)



(3b)

The following ^1H n.m.r. and i.r. data support the formation of the (hydroxyalkylpyridine-*O*,*N*)platinum chelates. (*a*) The most important ^1H n.m.r. modifications are a large downfield shift of H^6 of pyridine (that still presents a ^{195}Pt–^1H coupling), a strong upfield shift of the protons of the hydroxyalkyl chain, together with the appearance of a non-equivalence of the $H^{1'}$ and $H^{1''}$ protons [$J_{gem} \approx 18$ Hz observed in the case of (3a)] [12] (Table 3). (*b*) In the i.r. spectra ($CDCl_3$ solution in CsI cells), the disappearance of the ν(OH) bands at 3 600 and 3 440 cm^{-1} is observed together with decreased intensity of the ν(Pt–Cl) band at 340 cm^{-1}.

Results and Discussion

In all the cases studied, reaction (i) (Scheme 1) was run with complex (1) (0.05 mol dm^{-3} in $CDCl_3$) with a five- to twenty-fold excess of styrene. At equilibrium, at 22 °C, the proportion of complex (2) was larger than 90%. The olefin exchange reaction was monitored by ^1H n.m.r. up to 50—60% completion. For all the complexes studied, with $n = 0$—3, reaction (i)

Table 2. ^1H N.m.r. data for the complexes (1) [a]

Complex	Olefin Bu^t	−CH=	=CH_2	Pyridine ring 6-Me	4-Me	$H^{3,5}$	Hydroxyalkyl side chain [b]
(1a)	1.33	5.9—6.15 (m)	4.7—4.9 (m)	3.2 (12.5)	2.4	7.15 (10) 7.6 (10)	5.5 (12)
(1b)	1.33	5.8—6.05 (m)	4.65—4.8 (m)	3.2 (12.5)	2.37	7.03 (10) 7.15	3.9—4.3 (m, α-CH_2 + β-CH_2)
(1c)	1.33	5.8—6.05 (m)	4.65—4.8 (m)	3.2 (12.5)	2.35	7.03 7.08	3.92 (t, α-CH_2) 3.72 (t, γ-CH_2) 2.15 (m, β-CH_2)
(1d)	1.33	5.8—6.05 (m)	4.65—4.8 (m)	3.2 (12.5)	2.37	7.00 7.05	3.8—4.1 (m, γ-CH_2 + α-CH) 1.9—2.2 (m, β-CH_2) 1.27 (d, β-CH_3)
(1e)	1.33	5.8—6.05 (m)	4.65—4.8 (m)	3.2 (12.5)	2.37	7.03 (2 H)	3.7—3.9 (m, α-CH_2 + δ-CH_2) 1.7—2.15 (m, β-CH_2 + γ-CH_2)

[a] All spectra were recorded in $CDCl_3$ solution, δ in p.p.m. relative to $SiMe_4$; d = doublet, t = triplet, m = multiplet. $J(^{195}Pt$–$^1H)$ coupling constants in Hz are given in parentheses. [b] α-CH and α-CH_2 refer to the carbon bearing the OH group.

Table 3. ^{1}H N.m.r. data for complexes (3a) and (3b) and for their platinum chelates [a]

Complex	H^6	H^{3-5}	$H^{1'}$, $H^{1''}$	$H^{2'}$, $H^{2''}$
(3a)	8.73 (d) (33)	7.87—7.94 (m), 7.76 (d) 7.42—7.48 (m)	5.4 (8)	
Chelate of (3a)	9.25 (d) (33)	7.86—7.92 (m) 7.36—7.50 (m)	5.08, 4.80 ($J_{gem} \approx 18$) [b]	
(3b)	8.74 (d) (35)	7.77—7.83 (m), 7.55 (d) 7.35—7.41 (m)	4.28 (m)	3.88 (m)
Chelate of (3b)	9.07 (d) (40)	7.87—7.93 (m) 7.35—7.41 (m)	3.1—3.5 (m, 4 H)	

[a] Spectra were recorded in $CDCl_3$ on a 250-MHz Cameca TSN 250 spectrometer; chemical shifts δ in p.p.m. relative to $SiMe_4$; $J(^{195}Pt-^1H)$ coupling constants in Hz are given in parentheses. [b] The $J(^{195}Pt-^1H)$ could not be determined accurately.

Table 4. Kinetic data, activation parameters, and effective molarity (e.m.) for the reaction of complexes (1) with styrene

Complex	n	R^3	T/°C	10^3k/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	e.m./ mol dm^{-3}
(1a)	0	H	22	1.0 ± 0.1			50
(1b)	1	H	22	10 ± 2 *			500
(1c)	2	H	22	1.7 ± 0.2			85
			32	4.3 ± 0.4	45 ± 8	−(140 ± 20)	
			43	6.5 ± 0.3			
(1d)	2	Me	22	0.6 ± 0.1			
			32	1.5 ± 0.1	49 ± 6	−(140 ± 20)	
			40	2 ± 0.15			
(1e)	3	H	22	0.02 ± 0.002			1
			32	0.11 ± 0.02	88 ± 8	−(34 ± 10)	
			43	0.25 ± 0.03			

[a] The half-life for this reaction is 70 s which explains the smaller precision on the rate constant value determined by ^{1}H n.m.r. (see Experimental section).

is first order in complex (1) and zero order in styrene. The same rate constants are obtained when non-1-ene is used instead of styrene. The first-order rate constants for 3,3-dimethylbut-1-ene substitution depend on the value of n (Table 4) with a maximum for $n = 1$. This suggests an intramolecular participation of the hydroxy-group of the pyridine side chain to the olefin exchange process.

Under similar conditions, when the amine ligand is 2,4,6-trimethylpyridine (0.04 mol dm^{-3} complex, 1 mol dm^{-3} styrene) displacement of 3,3-dimethylbut-1-ene is too slow to give a measurable rate. However, this reaction is catalysed by addition of methanol. The slow rates observed are proportional to the methanol concentration in the range 0.5—1 mol dm^{-3} and independent of styrene concentration. For these methanol concentrations no decomposition of the complex is detectable during the reaction and the same rate constant is obtained when non-1-ene is used instead of styrene. The rate constant at 22 °C for this intermolecularly catalysed reaction is 2×10^{-5} dm^3 mol^{-1} s^{-1}. This allows the determination of the effective molarity (e.m.) of the side chain primary hydroxy-group, as a function of n, for the olefin exchange reaction (i) [13] (Table 4). The largest value of 500 mol dm^{-3} corresponds to $n = 1$.

In three cases, the activation parameters of reaction (i) have been determined (Table 4). It is noteworthy that the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are very similar for complexes (1c) and (1d), with a primary and a secondary hydroxy-group respectively, showing that the length of the side chain is the determining factor for the hydroxy-group assistance to the olefin substitution.

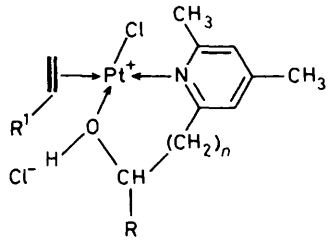
These data suggest that the formation of an intermediate complex, with chelation of the metal by the pyridine nitrogen and the hydroxy-group, occurs in the rate-determining step. The fastest reaction with complex (1b) would correspond to the involvement of a six-membered platinum chelate. Such a chelation process would be in agreement with the larger enthalpy of activation determined for the olefin exchange reaction with complex (1c) than with complexes (1c) and (1d), because the largest enthalpies of activation for cyclisation reactions are usually encountered for making eight-membered rings.[14] A more complete set of data is needed to discuss the rather large entropies of activation found for complexes (1c) and (1d). The preceding results are in favour of the transient binding of the hydroxy-group to the metal, in the rate-determining step of the olefin exchange.

Several (hydroxyalkylpyridine-*O*,*N*)platinum chelates can be postulated. We could not detect the formation of a five-co-ordinate complex at low temperature (down to −60 °C) for (1b) (R^1 = H) (0.2 mol dm^{-3} in $CDCl_3$) by looking for the ^{1}H n.m.r. upfield shift of the ethene signal, known to be characteristic of five-co-ordination.[15-17] Olefin exchange has been established and studied for five-co-ordinate complexes dichloro(diamine)(η-olefin)platinum(II) [18] and dichloro(α-di-imine)(η-olefin)platinum; [19] however a trigonal-bi-pyramidal structure is not expected to favour the olefin displacement *via* an associative process. The mechanism proposed in the case of the α-di-imine complexes involves a platinum–nitrogen bond dissociation as the initial step.[19]

The formation of a cationic (hydroxyalkylpyridine-*O*,*N*)-platinum chelate (4), by displacement of a chloride ligand by the hydroxy-group, could be the rate-determining step.

We did not detect the neutral (hydroxyalkylpyridine-*O*,*N*)-platinum chelates, that could have derived from complexes (4) (n = 0 or 1, R = H), upon treatment of chloroform solutions of (1a) and (1b) with sodium carbonate for 4 d [20] or with 0.2 mol dm^{-3} aqueous sodium hydroxide for 3 h.* It is

* A longer time leads to decomposition of the complexes (1).



(4)

noteworthy that in the former conditions the neutral derived chelates are slowly formed (75% after 20 h) from the complexes (3a) and (3b) which are identical to the corresponding complexes (1) without the 4- and 6-methyl groups on the pyridine ligand (see Experimental section). A comparable chloro(η-ethene)(8-quinolinato-*O*,*N*)platinum(II) complex has already been described.[21]

Complex (1e) (0.06 mol dm^{-3} in $CDCl_3$) was treated with one equivalent of silver tetrafluoroborate in acetone, in the presence of two equivalents of styrene, in order to generate the corresponding cationic complex (4) ($n = 3$, R = H) [20] and to detect an eventual acceleration of the olefin exchange process. This reaction led to the decomposition of the complex to a black precipitate with release of the olefin and pyridine ligands * (40% after 30 min). The proportions of the released ligands rule out an olefin exchange that would occur on complex (4) faster than the observed decomposition.

Reaction (i) in $CDCl_3$ between complex (1d) (0.05 mol dm^{-3}) and styrene (1 mol dm^{-3}) at 32 °C in the presence of MeOD was studied. Methanol, at a concentration of 0.4 mol dm^{-3}, increases the rate constant from 1.5×10^{-3} s^{-1} to 6.2×10^{-3} s^{-1}, and for a concentration of 0.8 mol dm^{-3} the constant is larger than 10^{-2} s^{-1}. At these concentrations, methanol cannot compete with the intramolecular catalysis and the acceleration of the catalytic process can result from an increase of the polarity of the medium. This would support the involvement of an ionic intermediate of type (4). It has been shown that cationic complexes of the type $[PtCl(C_2H_4)(N{-}N)]^+$ (where N–N is a chelating diamine ligand) occur as intermediates during the decomposition in methanol of the corresponding five-co-ordinate $[PtCl_2(C_2H_4)(N{-}N)]$ complexes to ethene and $[PtCl_2(N{-}N)]$, whereas in dichloromethane (at 20 °C) the loss of ethene occurs in a single step.[22] No such decomposition occurs with the complexes (1) under our conditions. As the hydroxy-group is a rather weak ligand,[23a] the loss of olefin to give the dichloro(hydroxyalkylpyridine-*O*,*N*)platinum complex does not appear to be a favourable route of evolution for an intermediate complex of type (4).

We have tried to study the influence of a sufficient chloride-ion concentration, in the chloroform solution, on reaction (i) between complex (1d) (0.05 mol dm^{-3}) and styrene (1 mol dm^{-3}). However, the addition of $[NMe_2(CH_2C_6H_5)_2]Cl$ (0.1 mol dm^{-3}) to complex (1d) leads to the formation of a new complex resulting from the substitution of the pyridine ligand by a chloride ion. This is shown by the appearance of the characteristic ^1H n.m.r. signals of the free ligand (pyridine 6-Me and 4-Me at 2.5 and 2.3 p.p.m.) and of a new Bu^t signal (1.25 p.p.m.) for the co-ordinated 3,3-dimethylbut-1-ene. The use of 18-crown-6 ether did not allow us to dissolve enough potassium chloride in the chloroform solution to run a kinetic experiment. Finally a (cryptand 222)potassium chloride solution in chloroform (>0.1 mol dm^{-3}), obtained from extraction of an aqueous cryptate solution, also led to a partial substitution of the pyridine ligand of complex (1d), probably by one nitrogen atom of free cryptand 222 that we could not eliminate.

The displacement of the pyridine nitrogen by the side chain hydroxy-group in the rate-determining step is another hypothesis to take into account. A comparable ethanol-assisted pathway has been proposed as one possibility in the substitution of styrene by pent-1-ene in *trans*-(aniline)dichloro(olefin)-platinum complexes in reagent chloroform, where the presence of the alcohol was shown to decrease the rate of the second-order substitution pathway.[1] We have seen that methanol catalyses the olefin exchange for the type (1) complex having 2,4,6-trimethylpyridine as the amine ligand. Displacement of the pyridine ligand by methanol is an unfavourable process [23b] and the catalysis would imply a very large reactivity of the resulting *trans*-(alcohol)(olefin) complex *versus* olefin exchange.

For the complex $[PtCl_2(C_2H_4)(N{-}N)]$ (where N–N = *NNN'N'*-tetramethylbutane-1,4-diamine) which gives no five-co-ordinate structure and which does not decompose with ethylene release, there is a fast exchange on the n.m.r. time-scale at room temperature, of the two equivalent diamine groups.[17] For complex (1b), $^{195}Pt{-}^1H$ coupling ($J = 12.5$ Hz) of the 6-methyl group of the pyridine ligand at 22 °C is observed. The coalescence of this coupling would correspond to a rate constant of 56 s^{-1} for the exchange between the pyridine nitrogen and the hydroxy-group.[24] From the rate constant of the olefin exchange ($k = 10^{-2}$ s^{-1} at 22 °C) this could be very roughly expected to occur at about 140 °C. However upon heating complex (1b) up to 115 °C in pentachloroethane † no beginning of coalescence could be seen.

In conclusion, a hydroxy-group (either primary or secondary) of a side chain in the 2-position of the pyridine ligand in *trans*-dichloro(η-olefin)(pyridine)platinum(II) complexes (1) can give a significant intramolecular catalysis of the olefin exchange. This catalysis depends on the length of the side chain and occurs *via* a pathway that is first order in complex and zero order in olefin. The results of our investigations do not allow the assignment of a structure to the intermediate complex actually involved in the catalysis. However the kinetic data suggest the formation of a (hydroxyalkylpyridine-*O*,*N*)platinum chelate in the rate-determining step. The fastest reaction, observed with complex (1b), would involve a six-membered chelate corresponding to a 500 mol dm^{-3} effective molarity of the primary hydroxy-group.

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* This decomposition also occurs in the absence of styrene.
† Decomposition of (1b) occurred at higher temperature.

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