Photochemical Preparation and Reactivity of Platinum(II) Complexes with Oxygen-donor Ligands. Description and Synthesis of Di-μ-chloro-dichlorobis(substituted pyridine)diplatinum(II)

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The complexes $[PtCl_2YL]$ (Y = substituted pyridine, L = oxygen-donor ligand) have been obtained by irradiation of $[PtCl_2Y(CH_2{=}CH_2)]$ in the appropriate solvent. Substitutions of the oxygenated ligands by dimethyl sulphide, ethylene, and acetonitrile have been studied. At room temperature and in the absence of external ligands, loss of the oxygen-donor ligand is observed and dichloro-bridged diplatinum complexes $[(PtCl_2Y)_2]$ are formed with *cis* and *trans* configurations. The *cis–trans* proportion of the diplatinum complexes can be shifted by u.v. irradiation and compounds with *cis* configurations have been isolated for the first time by this process.

Platinum(II) (soft acid) complexes with hard bases are supposed to be unstable and only a few examples of neutral platinum(II) complexes with oxygen-donor ligands have been described in the literature.[1] Most complexes of this type which have been reported are positively charged.[1] As far as neutral compounds are concerned, in most cases they have been obtained *in situ* and studied directly at low temperature in the reaction medium, since any attempt to isolate them afforded only dimers.[2] In the complex $[PtCl_2\{CH_2{=}C(Me)CH_2COMe\}]$[3] the oxygen-donor ligand is also bonded to platinum through a double bond. Aqua complexes of platinum(II) have also been studied in solution. They generally present several water molecules as ligands and, if the solvent is not rigorously dried, such complexes can interfere with the observation of other unstable species.

We have observed[4] that the isomerization reactions of olefins photo-assisted by platinum(II) complexes were inhibited when the reactions took place in solvents such as diethyl ether or thf (tetrahydrofuran). It was concluded that this could be due to the formation of an intermediate stabilized by a solvent molecule. The present paper reports the preparation of platinum(II) complexes of general formula $[PtCl_2YL]$ [Y = pyridine (py), 2-methyl-(2Me-py), 4-methyl-(4Me-py), 2,6-dimethyl-(2,6Me_2-py), or 2,4,6-trimethyl-pyridine (2,4,6Me_3-py); L = oxygen-donor ligand]. The physical properties of these compounds and the dynamic n.m.r. behaviour of ketonic complexes is reported. The substitution of the ligand L by stronger ligands is also described, as well as the 'dimerization' reaction to form dichloro-bridged diplatinum complexes. In the last part of this paper, the *cis–trans* thermal equilibria of the dichloro-bridged species and their modifications by irradiation are reported.

Results and Discussion

The preparation of $[PtCl_2(2,4,6Me_3\text{-py})L]$ has been reported in a preliminary communication.[5] As for other platinum(II) complexes containing a crowded substituted pyridine group as a ligand, all these complexes have a *trans* configuration. We are now able to present a generalization of the synthesis of these compounds and to discuss the stereochemical characteristics of the reaction.

Compounds (**1**)—(**5**) have been obtained by irradiation of *cis*- or *trans*-$[PtCl_2Y(CH_2{=}CH_2)]$ complexes in a suitable solvent. The process shown in reaction (1) was observed, where Y =

$$\textit{cis}\text{- or }\textit{trans}\text{-}[PtCl_2Y(CH_2{=}CH_2)] \xrightarrow[L]{h\nu} [PtCl_2YL] \quad (1)$$

2,4,6Me_3-py (**1**), 2,6Me_2-py (**2**), 2Me-py (**3**), 4Me-py (**4**), or py (**5**) and L = Et_2O (**a**), Me_2CO (**b**), thf (**c**), $MeCO_2Et$ (**d**), or $MeCO_2Me$ (**e**).

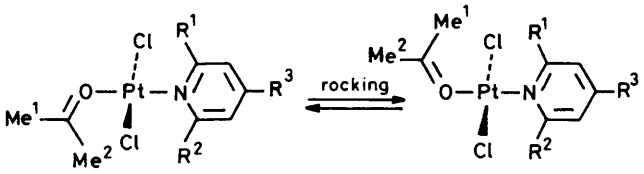
Compounds (**1**)—(**5**) have been obtained, after evaporation of the solvent at low temperature, as crystalline powders (yields 85—95%). They are stable at −20 °C for several days in the solid state, and for several hours in halogenated solvents. Their main physical properties are reported in the Experimental section.

Complexes of type (**a**) (with an Et_2O ligand) show a band near 1 040 cm^{-1} in their i.r. spectra, attributed to a ν(C–O–C) vibration (this band is 85 cm^{-1} higher in the free ligand). In the ^1H n.m.r. spectra the diethyl ether protons are deshielded by 0.5 p.p.m. for CH_2 and Me relative to the free ligand, and coupled to platinum, J(Pt–H) 20 for CH_2 and 6 Hz for Me.

The ν(C=O) vibrations of complexes of type (**b**) (with ketone ligands) are lowered from the free ligand value to 1 650 cm^{-1}. As with other metals,[6] such a lowering is characteristic of platinum–oxygen bonding. In the ^1H n.m.r. spectrum of (**1b**) deshielding of the acetone methyl protons by 0.6 p.p.m. (at 2.75 p.p.m.) and a small J(Pt–H) coupling constant of 6 Hz favour the platinum–acetone bonding being effective through one free non-bonding doublet of oxygen acting as a σ donor.

In complexes of types (**d**) and (**e**) the acetate ligand can be bonded to platinum either through the carbonyl or the alkoxy oxygen. In the ^1H n.m.r. spectra the complexed acetates show a deshielding of the MeCO signal (by *ca.* 0.8 p.p.m.) as well as a coupling with platinum [J(Pt–H) 6 Hz], analogous to those observed with acetone in complexes (**1b**)—(**5b**). Unlike the diethyl ether signals in complexes (**1a**)—(**5a**) the complexed acetates exhibit a small deshielding of the MeO– or CH_2–O protons (by *ca.* 0.2 p.p.m.) and no coupling with platinum. These data are in good agreement with bonding of the carbonyl oxygen of the acetate ligands to platinum(II).

Proton and ^{13}C n.m.r. spectra of complexes (**1**)—(**5**) show only one isomer, whatever the initial *cis* or *trans* configuration of the olefinic complex may be, independently of the nature of the ligand, L, and of the pyridine substitution. In the i.r. spectra compounds (**1**)—(**5**) show only one ν(Pt–Cl) vibration near 360 cm^{-1} and only one ν(Pt–N) vibration near 327 cm^{-1}, indicative of a *trans* configuration for the complex as reported in the literature.[7] The occurrence of a unique *trans* configuration is easily understood when a crowded substituted pyridine ligand (2,6Me_2-py or 2,4,6Me_3-py) with a strong steric effect is present. However, with a less crowded pyridine (py, 2Me-py, or 4Me-py),



Scheme 1. R^1, R^2, R^3 = H or Me

such a situation is not obvious. Considering the anti-symbiotic behaviour of platinum(II), a soft base with a strong *trans* influence is supposed to stabilize, in a *trans* configuration, the complexation of a hard base (oxygen-donor ligand). However pyridines are not very soft bases and they do not exert a strong influence. So, neither the unique *trans* configuration nor the stability of our complexes compared to *trans*-$[PtCl_2(PR_3)L]$ (R = alkyl) complexes (as reported by Shaw and co-workers[2] in solution at low temperature) can be explained by anti-symbiotic[1] behaviour of platinum(II). Even at low temperature, no *cis* configuration of complexes (**1**)—(**5**) can be detected. We have obtained and isolated, for the first time, oxygen-donor ligand complexes of platinum(II), and we now describe their physical and chemical properties.

N.M.R. Study of trans-$[PtCl_2Y(Me_2CO)]$, *Complexes* (**1b**)—(**5b**).—Co-ordinated acetone in complexes (**1b**)—(**5b**) is characterized in the ^1H n.m.r. spectra by a singlet with two satellites near 2.75 p.p.m., J(Pt–H) 6 Hz. The signal broadens at −50 °C and splits near −72 °C to give, at −95 °C, two broad singlets near 2.95 and 2.45 p.p.m. The coalescence temperature is not solvent dependent and shows very small variation with pyridine substitution (a few degrees). No shift in resonance is observed for the methyl protons of substituted pyridines. Splitting of acetone methyl carbons is also observed in the ^{13}C n.m.r. spectra for compounds (**3b**), (**4b**), and (**5b**). The singlet peak with satellites at 33.5 p.p.m. [J(Pt–C) 32 Hz] broadens at −50 °C and yields, at −95 °C, two broad singlets at 33.2 and 34 p.p.m. The coalescence temperature has not been determined exactly by ^{13}C n.m.r. No shift in the signals of methyl groups, at −92 °C, of substituted pyridines and of acetone carbonyl at 228 p.p.m. is observed. Such a situation may be explained by bonding of acetone to platinum through one *n* doublet of oxygen, with a Pt–O–C angle smaller than 180°. We assume a 'rocking' movement of acetone (Scheme 1), analogous to the inversion around sulphur atoms co-ordinated to platinum(II).[8,9]

At temperatures higher than coalescence this movement is fast and the acetone methyl groups are magnetically equivalent. Compared to the n.m.r. time-scale, there is, at low temperature, a slowing down of this rocking movement. The acetone methyl groups then become different (^{13}C and ^1H n.m.r.). The results do not depend on the pyridine substitution and the n.m.r. signals of the pyridine methyl groups always remain unchanged. Such a situation might be due either to the absence of mutual interaction between pyridine and acetone or to a fast rotation of acetone (or pyridine) around the Pt–O (or Pt–N) bond.

In order to confirm these results we decided to replace acetone with a non-symmetrical ketone (2-butanone), and with another symmetrical ketone (3-pentanone). These new compounds are obtained in the same way as the acetone analogue (95% yield). In the ^1H n.m.r. spectra, even at −90 °C, complex $[PtCl_2(2,4,6Me_3\text{-py})(EtCOMe)]$ shows no shift in the butanone signals, whereas signals for 3-pentanone in complexes with py and $2,4,6Me_3$-py do split at −80 °C. These data would suggest that only complexes with a symmetrically substituted ketone present splitting of the ligand signal. The absence of such a splitting in complexed butanone (unsymmetrical ketone) may be explained by the presence of a preferential conformation.

Table 1. Activation parameters for complexes (**1a**)—(**1d**)

Compound	(**1a**)	(**1b**)	(**1d**)	(**1c**)
Ligand	Et_2O	Me_2CO	$MeCO_2Et$	thf
$\tau_{\frac{1}{2}}$ at 20 °C/min	118	126	21	49
$\Delta H^{\ddagger}$/kJ mol^{-1}	95.8 ± 2.0	83.3 ± 2.0	93.3 ± 2.0	95.0 ± 2.5
$\Delta S^{\ddagger}$/kJ K^{-1} mol^{-1}	4.2 ± 2.5	39.3 ± 7.5	10.5 ± 5.9	13.4 ± 7.5

The smallest group of this ketone probably adopts an 'internal' position in the complex. At low temperature in the ^1H n.m.r. spectrum, the chemical shift of the methyl group of complexed butanone is in good agreement with this hypothesis. The signal of this group at 2.88 p.p.m. is only slightly different from the signal of one methyl group of acetone at 2.95 p.p.m. (second methyl group, δ 2.45 p.p.m.).

Although fairly stable in the solid state, complexes (**1**)—(**5**) loose their oxygen ligand in solution at room temperature, to give new reactions in the presence or absence of other ligands.

Thermal Reactivity of trans-$[PtCl_2YL]$ *Complexes.—Formation of dichloro-bridged diplatinum complexes.* Complexes (**1**)—(**5**) show good stability in solution in the corresponding solvent. However, when these complexes are dissolved in solvents such as $CDCl_3$, CD_2Cl_2, or C_6D_6 they loose their oxygen-donor ligand at room temperature, to yield dichloro-bridged diplatinum compounds according to reaction (2).

$$2[PtCl_2YL] \longrightarrow [Pt_2(\mu\text{-}Cl)_2Cl_2Y_2] + 2L \quad (2)$$

Kinetic studies of these dimerization reactions by ^1H n.m.r. spectroscopy allow us better to understand the mechanism. They follow first-order kinetics, in agreement with two possible reaction schemes. In the first step, the three-co-ordinate, unstable intermediate $[PtCl_2Y]$ would be formed, and in the second step the reaction could follow two different paths; either a fast reaction with one molecule of the initial complex or a co-condensation with another unstable intermediate [see reactions (3)—(5)].

$$[PtCl_2YL] \xrightarrow{k^1} [PtCl_2Y] + L \quad (3)$$

$$[PtCl_2YL] + [PtCl_2Y] \xrightarrow{k^2} [(PtCl_2Y)_2] + L \quad (4)$$

$$2[PtCl_2Y] \xrightarrow{k_2'} [(PtCl_2Y)_2] \quad (5)$$

In both mechanisms, the first step would be the slower one, corresponding to dissociation of the complex, and would govern the rate of the 'dimerization reaction.' Determination of kinetic constants at different temperatures allowed us to calculate the activation parameters of the reaction for several complexes [(**1a**), (**1b**), (**1c**), and (**1d**)] (Table 1) and this, to our knowledge, is the first time that such quantitative data have been obtained for these types of reactions. The different values of kinetic constants at 20 °C show the importance of the nature of the oxygen-donor ligand in the 'dimerization' kinetics.

The complexes can be graded in order of decreasing reactivity as follows: $[PtCl_2Y(MeCO_2Et)] > [PtCl_2Y(thf)] > [PtCl_2Y(Et_2O)] > [PtCl_2Y(Me_2CO)]$. Substitution of the pyridine ligand gives little change in kinetic constants, which show the following values at 20 °C in $CDCl_3$: 55×10^{-5} for $[PtCl_2(2,4,6Me_3\text{-py})(MeCO_2Et)]$, 60.8×10^{-5} for $[PtCl_2(2,6Me_2\text{-py})(MeCO_2Et)]$, and 52.5×10^{-5} s^{-1} for $[PtCl_2(2Me\text{-py})(MeCO_2Et)]$.

Thermal Exchange of Oxygen-donor Ligands.—Although our complexes are stable when dissolved in the oxygen-donor

Table 2. Yields for thermal substitution reactions of (**3b**)

Ligand, L	[$PtCl_2$(2Me-py)L] *cis*/%	*trans*/%
SMe_2	0	100
$CH_2{=}CH_2$	25	75
MeCN (1 equivalent)	75	25
(10 equivalents)	25	75

ligand, as solvent, an n.m.r. study shows an interesting exchange reaction of the oxygen-donor ligand. The complex [$PtCl_2$-(2,4,6Me_3-py)(Me_2CO)]), (**1b**), has been studied in more detail. When dissolved in $(CD_3)_2CO$ complex (**1b**) exchanges its ketonic ligand with deuteriated acetone as in reaction (6). This

$$[PtCl_2(2,4,6Me_3\text{-py})(Me_2CO)] + (CD_3)_2CO \rightleftharpoons [PtCl_2(2,4,6Me_3\text{-py})\{(CD_3)_2CO\}] + Me_2CO \quad (6)$$

reaction is slow, its rate constant at 20 °C (10^{-4} s^{-1}) being similar to that obtained for the dimerization reaction (9.1×10^{-5} s^{-1}). This process probably takes place through a dissociative mechanism which involves the formation of a 'T'-shaped intermediate followed by addition of $(CD_3)_2CO$ to this species.

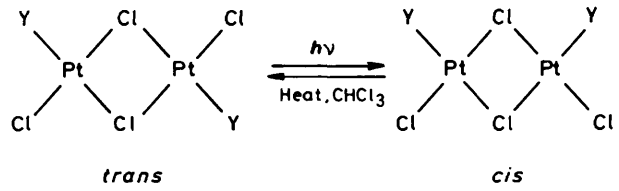
In dilute solutions, the dimer [{$PtCl_2$(2,4,6Me_3-py)}$_2$] which may be formed by condensation of two 'T'-shaped intermediates is not identified and, as the cleavage of the chloro-bridges by acetone is very slow, we can conclude that the acetone-exchange reaction does not take place through a process involving the formation of a dichloro-bridged dimer followed by bridge splitting of this latter compound.

Thermal Substitution of Oxygen-donor Ligands by Softer Bases.—Substitution reactions of ligands on platinum(II) square-planar complexes are known to occur with retention of configuration, probably through a mechanism involving a trigonal-bipyramidal intermediate. Only substitution of acetone in complex (**3b**), [$PtCl_2$(2Me-py)(Me_2CO)], will be reported here, the weakly crowded pyridine allowing the formation of the final product with *cis* and *trans* configurations.[10] The substitutions were carried out with dimethyl sulphide (dms), ethylene, and acetonitrile. The softest base (dms) should yield the most stable complexes, whereas acetonitrile (the hardest base) should give less stable complexes with platinum(II).

The yields from the substitution reactions are given in Table 2. The reactions were followed in deuteriated chloroform by ^1H n.m.r. spectroscopy at −10 °C or at room temperature. We have checked that there was no rapid *cis–trans* isomerization of terminal products under our reaction conditions. Substitution by ethylene was carried out at room temperature in a sealed tube with an excess of ethylene. Reactions with acetonitrile were also carried out at room temperature in $CDCl_3$ in the presence of 1 or 10 equivalents of acetonitrile.

The reactions with ethylene and acetonitrile are slow (3—4 h at room temperature) and do not yield the only expected *trans* isomer. In the course of the reaction we have shown, by ^1H n.m.r., the transient formation of the dichloro-bridged [{$PtCl_2$-(2Me-py)}$_2$] compound (10%). This diplatinum complex slowly disappears from the solution by reacting with ethylene or acetonitrile to give, *via* splitting of the halide bridges, either an equimolar mixture of *cis*- and *trans*-[$PtCl_2$(2Me-py)($CH_2{=}CH_2$)] or *cis*-[$PtCl_2$(2Me-py)(MeCN)], as shown by Courtot *et al.*[10]

The formation of the mixture of *cis* and *trans* isomers is probably due to a dissociative process forming the 'T'-shaped intermediate [$PtCl_2$(2Me-py)] which either dimerizes to give the dichloro-bridged diplatinum complex or is attacked, before



Scheme 2. Y = Substituted pyridine

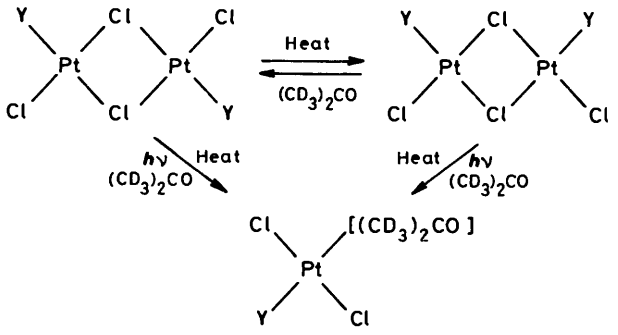
or after isomerization, by ethylene or acetonitrile. In order to demonstrate this hypothesis, an excess of acetonitrile was added to (**3b**). These new reaction conditions favour the second pathway but also, if there is competition between addition and isomerization in the 'T'-shaped intermediate, they should increase the proportion of the *trans* isomer in the first process. Our results are in good agreement with this theory, though high concentrations of complex do not increase notably the proportion of *cis* isomer.

Substitution by dms is very fast at −10 °C (10—15 min) and it is not possible to detect by ^1H n.m.r. the formation of the dichloro-bridged diplatinum complex. The reaction yields only the *trans*-[$PtCl_2$(2Me-py)(dms)] complex and this is probably indicative of a direct substitution of acetone in (**3b**) *via* an associative process. This absence of the formation of the diplatinum complex during the process is confirmed through the reaction of *trans*-[$PtCl_2$(2,4,6Me_3-py)(Me_2CO)] (**1b**) with dms which yields *trans*-[$PtCl_2$(2,4,6Me_3-py)(dms)], whereas reaction of [{$PtCl_2$(2,4,6Me_3-py)}$_2$] with dms yields another diplatinum mono dimethyl sulphide-bridged complex [{$PtCl_2$-(2,4,6Me_3-py)}$_2$(dms)].[11]

We now report the interesting structure of the dichloro-bridged diplatinum complexes formed at room temperature in halogenated solvents by the loss of the oxygen-donor ligand from [$PtCl_2YL$].

cis–trans *Equilibrium of Dichloro-bridged Diplatinum Complexes* [$Pt_2(\mu\text{-}Cl)_2Cl_2Y_2$].—Several dichloro-bridged diplatinum complexes, of general formula [$Pt_2(\mu\text{-}Cl)_2X_2L^1{}_2$], have been reported in the literature.[12–15] When X = Cl and L^1 = PMe_2Ph, these compounds are present in solution with *cis* and *trans* configurations which interconvert very quickly.[12] These dichloro-bridged complexes are usually *trans* when X = halide[13] and *cis* when X = alkyl or aryl.[14] Compounds with X = Cl and L^1 = pyridine or, more generally, amine have been reported only with the *trans* configuration.[15] We have shown by ^1H n.m.r. in a preliminary communication[5] that the complex [{$PtCl_2$(2,4,6Me_3-py)}$_2$] shows both *cis* and *trans* configurations in a solvent such as $CDCl_3$, which is not a potential ligand. Although a precise determination of the *cis* to *trans* ratio is difficult, due to the proximity of their respective signals (*o*-methyl of pyridine at 3.49 p.p.m. for *trans* and 3.47 p.p.m. for *cis* isomers), an estimation of 90% for the *trans* isomer and 10% for the *cis* can be deduced from the n.m.r. study. Results concerning [{$PtCl_2$(2,6Me_2-py)}$_2$] (a complex with another crowded pyridine) are of the same order. Temperature has no influence on the equilibrium ratios in the range explored (−50 to +50 °C). This equilibrium can be shifted by irradiating [{$PtCl_2$(2,4,6Me_3-py)}$_2$] or [{$PtCl_2$(2,6Me_2-py)}$_2$] in chloroform or dichloromethane with a medium-pressure mercury lamp. After the irradiation the proportion of *cis* isomer reaches 70% and thermal reversion to the initial equilibrium can be followed by ^1H n.m.r. spectroscopy ($\tau_{\frac{1}{2}}$ = 1 h at 25 °C) (Scheme 2).

Due to the slow rate of equilibration between the *cis* and *trans* isomers of [{$PtCl_2$(2,4,6Me_3-py)}$_2$] and [{$PtCl_2$(2,6Me_2-py)}$_2$] we have been able to isolate the *cis* compounds. These *cis* dichloro-bridged diplatinum complexes are the first of this type to be reported.



Scheme 3.

More problems have been encountered in the determination of the $[\{PtCl_2(2Me\text{-}py)\}_2]$ equilibrium. The *cis* and *trans* isomers cannot be discriminated by ^1H n.m.r. spectroscopy at room temperature: the 2-methyl hydrogens on pyridine only show one broad signal at 3.36 p.p.m. Co-existence of both *cis* and *trans* isomers could however be demonstrated through variable-temperature n.m.r. experiments in $CDCl_3$. A progressive separation of methyl signals is observed when the temperature is decreased below −10 °C and a Δν separation of 3.6 Hz can be measured between the two signals at −50 °C (3.33 and 3.29 p.p.m.). After checking that this separation is not due to a coalescence phenomenon (at 50 °C the signal shows a shoulder at high field), it can be concluded that an equilibrium takes place between *cis* and *trans* isomers of $[\{PtCl_2(2Me\text{-}py)\}_2]$ in a ratio of 50:50. U.v. irradiation does not shift this equilibrium, even at low temperature. This lack of reaction does not exclude the possibility of a photochemical transformation if the thermal equilibration is much more rapid than in the preceding case (Y = $2,6Me_2$-py and $2,4,6Me_3$-py).

The influence of the solvent on the equilibrium has been studied for complexes $[\{PtCl_2(2,6Me_2\text{-}py)\}_2]$ and $[\{PtCl_2(2,4,6Me_3\text{-}py)\}_2]$. These compounds were dissolved in $(CD_3)_2CO$ and the reactions monitored by ^1H n.m.r. spectroscopy. A rapid equilibration takes place (15 min at 20 °C) between *cis* and *trans* isomers in a ratio 60:40. The acetone complexes (**1b**) or (**2b**) are formed slowly when the solution is left in the dark at 25 °C (40% of the mixture after 5 d) (Scheme 3).

U.v. irradiation of $[\{PtCl_2(2,4,6Me_3\text{-}py)\}_2]$ in acetone gives a quantitative yield of the *trans* complex (**1b**) (Scheme 3).

Information about the mechanism of *cis–trans* isomerization of diplatinum complexes can be deduced from the preceding results. The observation of a fast thermal *cis–trans* isomerization of the diplatinum complexes in a solution of a potential ligand, without noticeable formation of the monomeric complex $[PtCl_2Y(Me_2CO)]$, allows us to suggest an associative mechanism for this thermal isomerization, since a dissociative process or even a semi-open intermediate would lead to the formation of a consistent proportion (at least 50%) of monomer (**1b**). On the other hand, the photochemical *cis–trans* isomerization observed in solvents which are not potential ligands ($CHCl_3$ or CH_2Cl_2) probably follows a dissociative process or takes place *via* a semi-open monochloro-bridged intermediate, as we observe the rapid formation of a ketonic complex when irradiation is performed in acetone.

Experimental

Proton and ^{13}C n.m.r. spectra were obtained using a JEOL FX 100 spectrometer. Chemical shifts are given in δ(p.p.m.) relative to $SiMe_4$. I.r. spectra were recorded as CsBr pellets on a SP 2000 Pye-Unicam instrument. The complexes $[PtCl_2Y(CH_2{=}CH_2)]$ or $[(PtCl_2Y)_2]$ were prepared according to procedures reported by our laboratory.[15] Only physical constants of the most characteristic compounds are reported.

Synthesis of trans-$[PtCl_2YL]$.—*General procedure.* The complex $[PtCl_2Y(CH_2{=}CH_2)]$ (100 mg) dissolved in previously deoxygenated solvent (40 cm^3) was introduced into a muff-shaped (5-cm diameter) Schlenk tube surrounding a 125-W medium-pressure mercury lamp, Philips HPK 125. Quantitative yields were obtained after irradiation for 15 min at room temperature. Wavelengths lower than 310 nm were eliminated by a Pyrex filter. The solvent was removed under reduced pressure at −30 °C. The yellow residual solid was recrystallized at −30 °C in pentane–dichloromethane (10:90). Yields: 85—95%. The complexes were kept at −20 °C and n.m.r. spectra were recorded at −10 °C.

trans-*Acetonedichloro*(2,4,6-*trimethylpyridine*)*platinum*(II) (**1b**). Yield 95%; m.p. 140 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 2.36 (3 H, s, *para* Me), 2.75 [6 H, s + d, *J*(Pt–H) 6, MeCO], 3.45 [6 H, s + d, *J*(Pt–H) 16, 2 *ortho* Me], and 6.9 (2 H, m, aromatic H); ^{13}C, δ 228.4 (1 C, s, CO), 167.54 (2 C, s, *ortho* C), 157.67 (1 C, s, *para* C), 124.44 (2 C, s, *meta* C), 33.56 [2 C, s + d, *J*(Pt–C) 35 Hz, *Me*CO], 28.02 (2 C, s, *ortho* Me), and 20.7 p.p.m. (1 C, s, *para* Me). I.r.: ν(CO) 1 650, ν(Pt–Cl) 360 cm^{-1}.

trans-*Acetonedichloro*(2,6-*dimethylpyridine*)*platinum*(II) (**2b**). Yield, 95%; m.p. 135 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 2.77 [6 H, s + d, *J*(Pt–H) 6, MeCO], 3.51 [6 H, s + d, *J*(Pt–H) 16, 2 *ortho* Me], and 7.25 (3 H, m, aromatic H); ^{13}C, δ, 228.6 (1 C, s, CO), 162.63 (2 C, s, *ortho* C), 139.37 (1 C, s, *para* C), 123.4 [2 C, s + d, *J*(Pt–C) 36, *meta* C], 33.56 [2 C, s + d, *J*(Pt–C) 32 Hz, *Me*CO], and 28.38 p.p.m. (1 C, s, *ortho* Me). I.r.: ν(CO) 1 650, ν(Pt–Cl) 355 cm^{-1}.

trans-*Acetonedichloro*(2-*methylpyridine*)*platinum*(II) (**3b**). Yield, 90%; m.p. 130 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 2.75 [6 H, s + d, *J*(Pt–H) 6, MeCO], 3.3 [3 H, s + d, *J*(Pt–H) 16, *ortho* Me], and 7.0 (4 H, m, aromatic H); ^{13}C, δ 228 (1 C, s, CO), 162.5 (1 C, s, *ortho* C), 155.1 (1 C, s, *ortho* C), 138.0 (1 C, s, *para* C), 126.5 and 122.8 (2 C, 2 s, *meta* C), 33.8 [2 C, s + d, *J*(Pt–C) 31 Hz, *Me*CO], and 27.41 p.p.m. (1 C, s, *ortho* Me). I.r.: ν(CO) 1 655, ν(Pt–Cl) 355 cm^{-1}.

trans-*Dichloro*(*diethyl ether*)(2,4,6-*trimethylpyridine*)*platinum*(II) (**1a**). Yield, 95%; m.p. 125 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 1.73 [6 H, m, *J*(H–H) 7, *J*(Pt–H) 6, ether Me], 2.36 (3 H, s, *para* Me), 3.41 [6 H, s + d, *J*(Pt–H) 20, 2 *ortho* Me], 3.96 [4 H, m, *J*(H–H) 7, *J*(Pt–H) 20, CH_2–O], and 6.85 (2 H, m, aromatic H); ^{13}C, δ 161.3 (2 C, s, *ortho* C), 150.7 (1 C, s, *para* C), 124.2 [2 C, s + d, *J*(Pt–C) 40, *meta* C], 75.0 (2 C, CH_2O), 27.8 [2 C, s + d, *J*(Pt–C) = 38 Hz, *ortho* Me], 20.47 (1 C, s, *para* Me), and 15.40 p.p.m. (2 C, CH_2–*Me*). I.r.: ν(C–O–C) 1 040, ν(Pt–Cl) 363 cm^{-1}.

trans-*Dichloro*(*tetrahydrofuran*)(2,4,6-*trimethylpyridine*)-*platinum*(II) (**1c**). Yield 85%, oil difficult to crystallize; m.p. 115 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 1.95 (4 H, m, CH_2–CH_2), 2.33 (3 H, s, *para* Me), 3.37 [6 H, s + d, *J*(Pt–H) 18 Hz, 2 *ortho* Me], 4.2 (4 H, m, CH_2–O), and 7.15 p.p.m. (2 H, m, aromatic H). I.r.: ν(C–O–C) 1 035, ν(Pt–Cl) 358 cm^{-1}.

trans-*Dichloro*(*ethyl acetate*)(2,4,6-*trimethylpyridine*)*platinum*(II) (**1d**). Yield, 85%, oily compound difficult to crystallize, m.p. 120 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 1.26 [3 H, t, *J*(H–H) 7, *Me*–CH_2], 2.3 (3 H, s, *para* Me), 2.8 [3 H, s + d, *J*(Pt–H) 6, MeCO], 3.37 [6 H, s + d, *J*(Pt–H) 20, 2 *ortho* Me], 4.19 [2 H, q, *J*(H–H) 7, CH_2–O], and 7.15 (2 H, m, aromatic H); ^{13}C, δ 171.6 (1 C, CO), 160.8 (2 C, *ortho* C), 151.6 (1 C, *para* C), 124.25 [2 C, s + d, *J*(Pt–C) 35 Hz, *meta* C], 60.6 (1 C, CH_2O), 27.95 (2 C, *ortho* Me), 21.32 (1 C, *Me*CO), 20.7 (1 C, *para* Me), and 14.2 p.p.m. (1 C, Me–CH_2). I.r.: ν(CO) 1 700, ν(C–O–C) 1 235, ν(Pt–Cl) 360 cm^{-1}.

trans-*Dichloro*(*methyl acetate*)(2,4,6-*trimethylpyridine*)*platinum*(II) (**1e**). Yield, 85%; oily compound difficult to crystallize,

m.p. 110 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 2.36 (3 H, s, *para* Me), 2.86 [3 H, s + d, *J*(Pt–H) 6, MeCO], 3.42 [6 H, s + d, *J*(Pt–H) 21 Hz, 2 *ortho* Me], 3.91 (3 H, s, MeO), and 7.2 (2 H, m, aromatic H); ^{13}C, δ 172 (1 C, CO), 160.8 (2 C, *ortho* C), 151.6 (1 C, *para* C), 124.5 (2 C, *meta* C), 52.0 (1 C, MeO), 27.96 (2 C, *ortho* Me), 21.01 (1 C, *Me*CO), and 20.65 p.p.m. (1 C, *para* Me). I.r.: ν(C=O) 1 710, ν(C–O–C) 1 250, ν(Pt–Cl) 358 cm^{-1}.

trans-(2-*Butanone*)*dichloro*(2,4,6-*trimethylpyridine*)*platinum*(II). Yield, 85%; m.p. 140 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 1.09 [3 H, t, *J*(H–H) 7 *Me*–CH_2], 2.34 (3 H, s, *para* Me), 2.86 [3 H, s + d, *J*(Pt–H) 7, MeCO], 3.37 (8 H, m, CH_2CO and *ortho* Me), and 6.98 (2 H, m, aromatic H); ^{13}C, δ 230.9 (1 C, CO), 161.8 (2 C, *ortho* C), 151.7 (1 C, *para* C), 124.52 [2 C, s + d, *J*(Pt–C) 36, *meta* C], 39.93 [1 C, s + d, *J*(Pt–C) 29, *C*H_2CO], 32.24 [1 C, s + d, *J*(Pt–C) 30, *Me*CO], 28.13 [2 C, s + d, *J*(Pt–C) 18 Hz, *ortho* Me], 20.84 (1 C, *para* Me), and 8.57 p.p.m. (1 C, *Me*CH_2). I.r.: ν(CO) 1 650, ν(Pt–Cl) 355 cm^{-1}.

trans-*Dichloro*(3-*pentanone*)(2,4,6-*trimethylpyridine*)*platinum*(II). Yield, 85%; m.p. 130 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 1.26 [6 H, t, *J*(H–H) 7, 2 *Me*CH_2], 2.33 (3 H, s, *para* Me), 3.08 [4 H, q + satellites, *J*(H–H) 7, *J*(Pt–H) 7, 2 CH_2CO], 3.34 [6 H, s + d, *J*(Pt–H) 16.5, 2 *ortho* Me], and 7.15 (2 H, m, 2 aromatic H); ^{13}C, δ 233.9 (1 C, CO), 161.82 (2 C, *ortho* C), 151.67 (1 C, *para* C), 124.52 [2 C, s + d, *J*(Pt–C) 37.5, *meta* C], 38.1 [2 C, s + d, *J*(Pt–C) 30, CH_2CO], 28.14 [2 C, s + d, *J*(Pt–C) 37.5 Hz, 2 *ortho* Me], 20.8 (1 C, *para* Me), and 9.1 p.p.m. (2 C, *Me*CH_2). I.r.: ν(CO) 1 650, ν(Pt–Cl) 352 cm^{-1}.

Low-temperature ^1H *N.M.R. of trans*-[$PtCl_2YL$] *Complexes* (L = *Ketone*).—Complexes (**1b**)—(**5b**), obtained as crystalline powders, were dissolved in cold CD_2Cl_2 or $(CD_3)_2CO$ (0.6 cm^3). Spectra were recorded with 9×10^{-2} mol dm^{-3} solutions and at temperatures from −10 to −90 °C. Only a few examples of our results are reported here.

Complexes with acetone as the oxygen-donor ligand. Only the acetone signals are temperature dependent.

For [$PtCl_2$(2,4,6Me_3-py)(Me_2CO)] (**1b**). Acetone resonances: at −30 °C, singlet + satellites at 2.73 p.p.m. [*J*(Pt–H) 6 Hz]; at −70 °C, splitting; at −90 °C, two broad singlets at 2.98 and 2.47 p.p.m.

For [$PtCl_2$(2Me-py)(Me_2CO)], (**3b**). Acetone resonances: at −20 °C, singlet + satellites at 2.75 p.p.m. [*J*(Pt–H) 6 Hz]; at −70 °C, splitting; at −90 °C, two broad singlets at 2.96 and 2.44 p.p.m.

Complexes with 2-butanone or 3-pentanone. For [$PtCl_2$(2,4,6-Me_3-py)(EtCOMe)]. There is no noticeable change in ^1H n.m.r. signals with temperature variation.

For [$PtCl_2$(2,4,6Me_3-py)(Et_2CO)]. Only the signals of 3-pentanone show a temperature dependence, as follows: at −20 °C, triplet at 1.26 [*J*(H–H) 7], quadruplet + satellites at 3.08 p.p.m. [*J*(H–H) 7 and *J*(Pt–H) 7 Hz]; at −80 °C, splitting.

Low-temperature ^{13}C *N.M.R. of* [$PtCl_2YL$] *where* L = *Ketone*.—The relevant complex (100 mg) was dissolved in CD_2Cl_2 (1.5 cm^3).

For [$PtCl_2$(2Me-py)(Me_2CO)]. Only acetone methyls show a temperature dependence, as follows: at −30 °C, singlet + satellites at 33.8 p.p.m. [*J*(Pt–C) 31 Hz]; at −90 °C, two singlets at 33.99 and 33.26 p.p.m. The coalescence temperature has not been determined.

For [$PtCl_2$(2,4,6Me_3-py)(EtCOMe)]. Only signals for 3-pentanone, excluding the carbonyl, show a temperature dependence, as follows: at −30 °C, singlet + satellites at 38.10 p.p.m. [*J*(Pt–C) 30 Hz], singlet at 9.09 p.p.m.; at −90 °C, four broad singlets at 38.46, 36.96, 9.52, and 8.20 p.p.m.

Thermal Reactivity of [$PtCl_2YL$] *Complexes*.—Solutions of the complexes (18×10^{-2} mol dm^{-3}) in CD_2Cl_2 were used at low temperature. The kinetics was studied in the probe of the n.m.r. spectrometer at various temperatures. Dichloro-bridged diplatinum complexes were identified by comparison with the n.m.r. characteristics of compounds reported in the literature[15] or with samples which will be described later.

Table 3. N.m.r. data for [$Pt_2(\mu\text{-}Cl)_2Cl_2$(2Me-py)$_2$]

Temperature/°C	δ/p.p.m. (2-Me)
20	3.36
−10	3,36, 3.33
−18	3.35, 3.32
−30	3.33, 3.30
−50	3.33, 3.29
+60	3.36, 3.35(sh)

Thermal Exchange of Acetone with $(CD_3)_2CO$.—The complex [$PtCl_2Y(Me_2CO)$] (50 mg) was dissolved in $(CD_3)_2CO$ (0.6 cm^3). The exchange reaction was followed by ^1H n.m.r. spectroscopy by integrating the signals of co-ordinated acetone at 2.75 and of free acetone at 2.05 p.p.m.

Thermal Substitution of Oxygen-donor Ligands by Softer Bases.—The relevant [$PtCl_2YL$] complex (50 mg) was dissolved in CD_2Cl_2 (0.6 cm^3) at room temperature. To the solution, in an n.m.r. tube, was added either 1 equivalent of dimethyl sulphide, 1 or 10 equivalents of acetonitrile, or an excess of ethylene (ethylene was trapped at low temperature in the n.m.r. tube which was then sealed). Reactions were followed by n.m.r. spectroscopy at room temperature by comparison with the n.m.r. characteristics of products reported in the literature.[10]

Equilibria of Dichloro-bridged Diplatinum Compounds, [$Pt_2(\mu\text{-}Cl)_2Cl_2Y_2$].—The thermal equilibria were studied by ^1H n.m.r. spectroscopy in non-ligand solvents ($CDCl_3$, CD_2Cl_2) on 5.5×10^{-2} mol dm^{-3} solutions of the diplatinum compounds. The ratio of each isomer was evaluated by integrating the *o*-methyl signals of the pyridine. The temperature range used was −50 to +60 °C. The methyls of pyridine show, at −20 °C, the following signals: for [{$PtCl_2$(2,4,6Me_3-py)}$_2$], *cis* isomer, 3.47 and 2.35, *trans* isomer, 3.49 and 2.35 p.p.m.; for [{$PtCl_2$(2,6Me_2-py)}$_2$], *cis* isomer, 3.55, *trans* isomer, 3.58 p.p.m. In both cases 90% *trans* and 10% *cis* was found. Temperature has a very small influence on these equilibria. The evolution of the 2-Me signal of [$Pt_2(\mu\text{-}Cl)_2Cl_2$(2Me-py)$_2$] is shown in Table 3. The integration of these signals shows that an equimolar mixture of *cis* and *trans* isomers is present.

In $(CD_3)_2CO$. Identification of compounds was performed through the n.m.r. signals of pyridine or ketone methyl signals in $(CD_3)_2CO$, as follows: for [{$PtCl_2$(2,4,6Me_3-py)}$_2$], *trans* isomer, 3.49 and 2.43; *cis* isomer, 3.47 and 2.39; compound (**1b**), 3.40 and 2.39 p.p.m.; for [{$PtCl_2$(2,6Me_2-py)}$_2$], *trans* isomer, 3.51; *cis* isomer, 3.48; compound (**2b**), 3.44 p.p.m. In both cases a rapid equilibration takes place between the *cis* and *trans* isomers (*ca.* 20 min), followed by slow formation of the monomers (**1b**) or (**2b**) (15 d).

Photostationary Equilibria.—Non-ligand solvents. Irradiations were performed on solutions of the diplatinum complexes (80 mg) in CH_2Cl_2 or $CHCl_3$ (20 cm^3), followed by evaporation of the solvent at low temperature. Proton n.m.r. spectroscopy at −10 °C allows identification of the compounds (*cf.* thermal equilibria). For [{$PtCl_2$(2Me-py)}$_2$] no variation of the equilibrium was observed after irradiation.

Synthesis of dichloro-bridged diplatinum cis *complexes*. The

complexes $[\{PtCl_2(2,4,6Me_3\text{-py})\}_2]$ or $[\{PtCl_2(2,6Me_2\text{-py})\}_2]$ were irradiated at −20 °C for 10 min. The solvent was removed at low temperature and the residue crystallized from cold CH_2Cl_2–pentane (10:90).

Di-μ-chloro-dichlorobis(2,4,6-trimethylpyridine)diplatinum-(II). Yield 35%, m.p. 250 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 2.35 (6 H, br s, *para* Me), 3.47 [12 H, br s + d, *J*(Pt–H) 12, *ortho* Me], and 6.94 (4 H, m, aromatic H); ^{13}C, 160.64 (4 C, *ortho* C), 151.52 (2 C, *para* C), 122.44 [4 C, s + d, *J*(Pt–C) 37, *meta* C], 27.85 [4 C, s + d, *J*(Pt–C) 28 Hz, *ortho* Me], and 20.56 p.p.m. (2 C, *para* Me). I.r.: ν(Pt–Cl) 358, 333, 317, and 295 cm^{-1}.

Di-μ-chloro-dichlorobis(2,6-dimethylpyridine)diplatinum(II). Yield 20%, crystalline powder, m.p. 245 °C (decomp.). N.m.r. ($CDCl_3$): ^1H, δ 3.55 [12 H, s + d, *J*(Pt–H) 12 Hz, *ortho* Me] and 7.3 p.p.m. (6 H, m, aromatic H). I.r.: ν(Pt–Cl) 340, 330 (sh), 323, and 300 cm^{-1}.

Ligand solvent. The complexes $[(PtCl_2Y)_2]$ (80 mg) were irradiated in acetone (20 cm^3) for 10 min. Reduced-pressure evaporation at −30 °C yielded a residual oil, analyzed by ^1H n.m.r. spectroscopy at −10 °C. The *trans*-$[PtCl_2Y(Me_2CO)]$ complexes were obtained in all cases.

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