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Proton, Carbon-13, and Platinum-195 Nuclear Magnetic Resonance Spectroscopy of Hydroxypyridinate-Bridged Dinuclear Platinum(III) Complexes. Equilibria and Mechanism of Bridging Ligand Rearrangement

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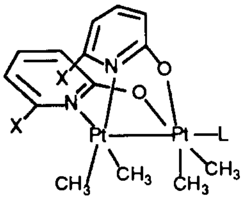
The proton, carbon-13, and platinum-195 nuclear magnetic resonance spectra of some *o*-hydroxypyridinate-bridged dinuclear platinum(III) complexes have been analyzed and used to study some of their reactions. These complexes feature two Pt(III) ions joined by a metal-metal bond. Each Pt has two methyl groups on it in a cis configuration. Two hydroxypyridinate groups bridge the dinuclear unit. Derivatives of the parent compound have fluorine, chlorine, or a methyl group at the 6-position of the hydroxypyridinate. The bridging ligands may bind in head-to-head (HH) or head-to-tail (HT) arrangements. The HH complex has either a single pyridine or a single diethyl sulfide coordinated to the platinum ion to which the hydroxypyridinate oxygen atoms are also bound. In the HH complexes this ligand is in slow exchange with free ligand and binds at the sites coaxial to the metal-metal bond. For complexes with the bridging ligands hydroxypyridinate and 6-fluorohydroxypyridinate, increased pyridine concentration results in the isomerization of the ligand bridge to form HT complexes. The HT complexes have pyridine bound to both axial sites and in fast exchange with free pyridine at room temperature. The formation constants of the HT complexes from HH and pyridine are 120 L mol^{-1} for the hydroxypyridinate complex and 25 L mol^{-1} for the 6-fluorohydroxypyridinate complex at 25 °C. The mechanism of the HH to HT rearrangement may involve a preequilibrium of the HH complex with pyridine. Rearrangement of the bridge is dissociative but does not involve complete dissociation from the complex. The $\Delta H^{\ddagger}$ is 84 kJ mol^{-1} and $\Delta S^{\ddagger}$ is -29 J mol^{-1} K^{-1} for this rearrangement. For the conversion of HT to HH, $\Delta H^{\ddagger}$ = 105 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 16 J mol^{-1} K^{-1}.

Introduction

During the past two decades it has become clear that there is an extensive chemistry of Pt(III).[1,2] Most of the complexes that have been reported are dinuclear with a Pt-Pt bond and are quite stable. Recently, dinuclear Pt(III) complexes have been prepared with 6-substituted 2-hydroxypyridinate ligands bridging the metal ions. X-ray crystallography reveals that their structures are as represented in I.[3-5] Platinum-195 is a spin $^1/_2$ nucleus and is 34% abundant. This plus the presence of protons and carbon-13 nuclei makes multinuclear NMR studies attractive as a means of probing structure, solution reactions, and other important properties in these metal cluster compounds.



I (X = H, F, Cl, Br, CH_3; L = py, Et_2S)

The structure shown in formula I has a head-to-head (HH) arrangement of bridging ligands. For two derivatives, addition of pyridine converts the complex to a head-to-tail (HT) type structure, as indicated in eq 1.[5] In a previous paper several of us suggested that both the steric bulk of the 6-substituent as well as the trans-donating ability of the axial ligand were important factors determining the coordination geometry of these complexes.[5] The present paper utilizes multinuclear NMR techniques to investigate the properties of these complexes in greater detail.

$$\underset{\substack{\text{red-orange HH}\\ \text{(head-to-head)}}}{[Pt_2(CH_3)_4(xhp)_2py]} \underset{-py}{\overset{+py}{\rightleftharpoons}} \underset{\substack{\text{yellow HT}\\ \text{(head-to-tail)}}}{[Pt_2(CH_3)_4(xhp)_2(py)_2]} \quad (1)$$

Experimental Section

NMR Measurements. The complexes were prepared by the previously published methods.[3-5] The following abbreviations are used: Hhp = 2-hydroxypyridine; Hfhp = 2-hydroxy-6-fluoropyridine; Hchp = 2-hydroxy-6-chloropyridine; Hbhp = 2-hydroxy-6-bromopyridine; Hmhp = 2-hydroxy-6-methylpyridine; HH = head-to-head; HT ; head-to-tail.

Most measurements were made with a Bruker WM-250 spectrometer operating at 250.132 MHz for proton, 62.80 MHz for carbon-13, and 53.518 MHz for platinum-195 spectroscopy. Chemical shifts are referred to internal TMS for proton and carbon-13 spectra. For platinum-195, the standard is 1 M hexachloroplatinate(IV) in 1 M HCl. Proton-carbon-correlated spectra were obtained on a Varian VXR-500 spectrometer. Nuclear Overhauser enhancements were measured by the difference method.

Equilibrium and Rate Constant Measurements. Equilibrium constants for the interconversion of HH and HT complexes were determined from the proton spectrum in deuteriochloroform solution. The HT complex is in fast exchange with free pyridine, while the HH complex is in slow exchange. Integration of the pyridine α-proton resonances gives a measure of the ratio of HH complex to the total HT complex plus free pyridine. The 5-H resonances of xhp ligands in the HH and HT are well separated. Integration of this region gives the ratio of HH to HT complex. Knowledge of the total complex concentration makes possible the calculation of all relevant concentrations from these ratios.

Equilibrium is achieved slowly in these cases, and so samples were kept at 25 °C and studied occasionally. Equilibrium constants were measured four times. In these measurements pyridine concentration was varied by a factor of 5. Kinetic analyses were carried out at complex concentrations from 0 to 10 mM and pyridine concentrations from 0 to 0.5 M.

Most of the kinetic analyses for these reactions were executed on systems approaching equilibrium under pseudo-first-order conditions.[6] After demonstrating that the HH + py → HT reaction was first order in pyridine by varying the pyridine concentration over a factor of 5, we calculated second-order rate constants by dividing the pseudo-first-order rate constants by the pyridine concentration.

Results and Discussion

Chemical Shift Assignments. Tables I-V contain the chemical shift and coupling constant data for this series of complexes. Protons on the hydroxypyridine ligands were readily assigned by comparison of the unsubstituted complex with the 6-substituted complexes. The 5-H resonance is a multiplet in the former case but is a doublet in the latter cases. The 3- and 4-H's are the remaining doublet and multiplet, respectively. Single-frequency

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Table I. ^{1}H Chemical Shifts (ppm) of Pyridine Adducts of Selected Pt(III) Dimeric Complexes[a]

	3-H	4-H	5-H	6-H	CH_3	CH_3'	α-H	β-H	γ-H
$[Pt_2(hp)_2(CH_3)_4(py)_2]$	6.55 (d)	7.22 (m)	6.07 (m)	7.16 (d)			8.70	7.40	7.84
$[Pt_2(fhp)_2(CH_3)_4(py)_2]$	6.38 (d)	7.30 (m)	5.74 (d)		1.33	0.83	8.68	7.32	7.75
$[Pt_2(hp)_2(CH_3)_4py]$	6.55 (d)	7.46 (m)	6.34 (m)	7.41 (d)					
$[Pt_2(fhp)_2(CH_3)_4py]$	6.45 (d)	7.26 (m)	6.07 (d)		1.61	1.12	8.46	7.40	7.92
$[Pt_2(mhp)_2(CH_3)_4py]$[a]	6.48 (d)	7.14 (m)	6.22 (d)		1.50	1.02	8.46	7.41	7.9
$[Pt_2(chp)_2(CH_3)_4py]$	6.51 (d)	7.18 (m)	6.42 (d)		1.51	1.12	8.48	7.36	7.82

[a] 6-CH_3 resonance at 2.34 ppm.

Table II. ^{1}H Chemical Shifts (ppm) of Diethyl Sulfide Adducts of Selected Pt(III) Dimeric Complexes[a]

							Et_2S	
	3-H	4-H	5-H	6-H	CH_3	CH_3'	CH_2	CH_3
$[Pt_2(hp)_2(CH_3)_4Et_2S]$	6.51	7.29	6.32	7.74	1.27	1.09	2.8	1.37
$[Pt_2(mhp)_2(CH_3)_4Et_2S]$[a]	6.42 (d)	7.14 (m)	6.23 (d)		1.15	1.04	2.8	1.38
$[Pt_2(fhp)_2(CH_3)_4Et_2S]$	6.33	7.27	5.99		1.25	1.10	2.76	1.36

[a] 6-CH_3 resonance at 232 ppm.

Table III. Carbon-13 Chemical Shifts (ppm) of Diethyl Sulfide Adducts of Pt(III) Dimers

								Et_2S	
	C_2	C_3	C_4	C_5	C_6	CH_3	CH_3'	CH_2	CH_3
$[Pt_2(hp)_2(CH_3)_4Et_2S]$	168.0	116.56	138.06	110.74	144.18	−12.74	−2.48	28.55	11.40
$[Pt_2(mhp)_2(CH_3)_4Et_2S]$[a]	168.24	113.34	137.26	111.09	153.69	−12.33	−2.33	28.29	11.38
$[Pt_2(fhp)_2(CH_3)_4Et_2S]$	167.13[b]	111.23	140.30[c]	92.61[d]	161.10[e]	−12.02	−1.83	28.45	11.37

[a] 6-CH_3 resonance at 2.40 ppm. [b] Doublet J_{CF} = 6.1 Hz. [c] Doublet J_{CF} = 10.2 Hz. [d] Doublet J_{CF} = 30.5 Hz. [e] Doublet J_{CF} = 246 Hz.

Table IV. Carbon-13 Chemical Shifts (ppm) of Pyridine Adducts of Selected Pt(III) dimers

	C_2	C_3	C_4	C_5	C_6	α-C	β-C	γ-C	CH_3	CH_3'
$[Pt_2(fhp)_2(CH_3)_4py]$	167.15	111.3	140.4[a]	92.81[b]	161.20[c]	149.9	125.4	138.8	−8.89	−0.77
$[Pt_2(fhp)_2(CH_3)_4(py)_2]$	170.12	112.6	139.8[d]	91.51[e]	160.68[f]	148.47	124.2	136.9	−11.15	−7.84
$[Pt_2(chp)_2(CH_3)_4py]$	168.9	114.05	138.65	110.62	150.0	149.7	125.3	137.6	−8.77	−2.05
$[Pt_2(mhp)_2(CH_3)_4py]$	168.35	113.45	137.46	111.27	153.45	150.02	125.17	138.58	−9.02	−1.43
$[Pt_2(hp)_2(CH_3)_4py]$	169.16	116.57	137.83	110.27	144.3	149.7	125.08	138.1	−9.90	−4.17

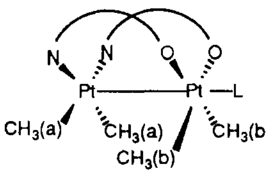
[a] Doublet J_{CF} = 10.2 Hz. [b] Doublet J_{CF} = 30.5 Hz. [c] Doublet J_{CF} = 246 Hz. [d] Doublet J_{CF} = 12.2 Hz. [e] Doublet J_{CF} = 31.7 Hz. [f] Doublet J_{CF} = 251 Hz.

Table V. Platinum-195 Chemical Shifts (ppm) and Coupling Constants (Hz) for Selected Pt(III) Dimeric Complexes

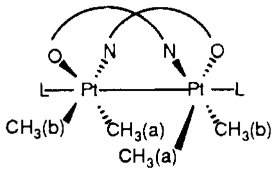
	δ(Pt)	$^1J_{Pt-Pt}$	$^1J_{Pt-C}{}^{CH_3}$	$^1J_{Pt-C}{}^{CH_3'}$	$^2J_{Pt-C}{}^{CH_3}$	$^2J_{PT-C}{}^{CH_3'}$	$^2J_{Pt-H}{}^{CH_3}$	$^2J_{Pt-H}{}^{CH_3'}$	$^3J_{Pt-H}{}^{CH_3'}$
$[Pt_2(hp)_2(CH_3)_4Et_2S]$	−2607, −2436	10599	610.3	740.0	29.6	24.0	79.7	70.9	10.7
$[Pt(mhp)_2(CH_3)_4Et_2S]$	−2672, −2367	11311	618.2	730.4	25.6	23.6			14.8
$[Pt_2(fhp)_2(CH_3)_4Et_2S]$	−2058, −1867	11250	618.5	750.7	28.4	24.4	79.1	72	11.0
$[Pt_2(fhp)_2(CH_3)_4py]$	−3123, −1740	11680	661.2	740.5	34.6	24.9	80.4	71.6	7.3
$[Pt_2(fhp)_2(CH_3)_4(py)_2]$	−2323		781.2	725.1		27.5	77.5	74.5	
$[Pt_2(chp)_2(CH_3)_4py]$	−3016, −1785	12353	667.0	736.8	34.9	28.3	79.6	70.2	5.5
$[Pt_2(mhp)_2(CH_3)_4py]$	−2922, −1635	12060	662.6	719	32.7	26.1	78.3	70.8	
$[Pt_2(hp)_2(CH_3)_4py]$	−1894, −1793	10823	724.6	796.9	31.5	23.6	78.7	69.9	4.88

decoupling confirmed these assignments.

All complexes give two methyl resonances, each of which is split by two- and three-bond coupling to each platinum-195. Formulas II and III depict the platinum–methyl skeleton in the HH and HT cases discussed herein. In the HH case, there are two magnetically equivalent methyl groups on each platinum atom. In the HT case, each platinum atom has two different methyl groups on it but each of the two methyl resonances of one platinum ion is identified with one of the two platinum methyl groups of the other platinum ion. This is because in the HT case, each platinum will have one methyl group trans to a nitrogen and one methyl group trans to an oxygen. The letters "a" and "b" each identify identical methyl groups in II and III. If a HT complex had a single axial substituent, four different methyl resonances would be anticipated. Such a situation was not encountered in this study.



II



III

Nuclear Overhauser enhancements served to identify the methyl groups in the HH complex in the case where the axial ligand is pyridine. Irradiation of the downfield methyl resonance resulted in enhancement of the pyridine α-proton resonances. In the fhp case, the upfield methyl resonance shows a small coupling to 6-F consistent with the downfield resonance being closest to the coordinated pyridine. For the HT complexes irradiation of each methyl resonance resulted in equal enhancement of the pyridine α protons, as expected. In the fhp HT complex, the lowest field methyl resonance in the proton spectrum shows a small coupling to 6-F. This may mean that for the HT cases the lowest field methyl resonance is cis to the coordinated nitrogen of the hydroxypyridinate bridge.

In the carbon-13 spectra, the 3-, 4-, and 5-carbon resonances of the coordinated hydroxypyridinate were assigned by proton–carbon-correlated spectra. Confirmation comes from observations on the fhp complex where fluorine–carbon coupling constants and fluorine perturbations of pyridine ring chemical shifts agree closely with literature values.[7] Proton–carbon correlations show that

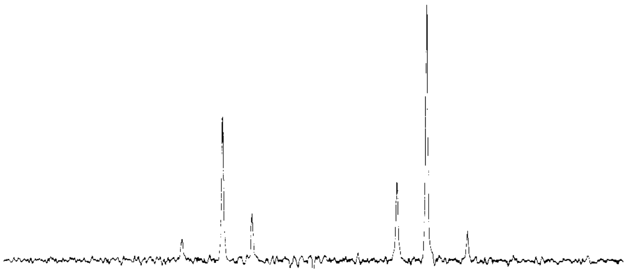


Figure 1. Platinum-195 spectrum of the head-to-head complex $[Pt_2(mhp)_2(CH_3)_4Et_2S]$ recorded at 107.04 MHz. The two largest peaks are at the centers of gravity of the A and B parts of an AB pattern and correspond to the case where only one platinum-195 nucleus is in the complex. The different intensities of the two halves of the spectrum are a consequence of sharper resonances in the upfield part.

for the mhp case the highest field methyl carbon resonance arises from the lowest field methyl carbon resonance in the proton spectrum. Since the chemical shifts are fairly constant throughout the series, this crossing over was assumed to be the case for all of the HH complexes.

Figure 1 shows a typical platinum-195 spectrum for a HH complex. The very large $^1J_{Pt-Pt}$ coupling constants result in AB type spectra even though the two platinum resonances are separated by more than 100 ppm. Each half of the AB pattern consists of two resonances comprising about 30% of the intensity corresponding to the case where the platinum-195 observed is split by a second platinum-195. The single peak at the center of gravity of these two peaks corresponds to about 70% of the intensity and arises from the case where the platinum-195 observed is next to a platinum isotope with no spin. The $^1J_{Pt-Pt}$ constants are the largest of any dimeric platinum compounds yet reported. This is probably the consequence of a large amount of s character in the metal–metal bond. The ^{195}Pt chemical shifts can be assigned on the basis of known chemical shift trends from other platinum complexes. With pyridine in the axial site, analysis of the spectra shows that in each case the downfield resonances correspond to the more highly substituted platinum atom, with the upfield resonances corresponding to the platinum nucleus with two carbon and two nitrogen atoms (C_2N_2) in the equatorial coordination sphere.

In two previous ^{195}Pt NMR studies of Pt(III) complexes by Hall et al., asymmetry was introduced into the systems by exchanging one of the axial ligands of symmetric sulfate- and phosphate-bridged complexes, thus making the Pt atoms magnetically nonequivalent.[8,9] None of the asymmetric complexes prepared in those stuides were isolated. One important result from these studies, however, was the observation that the Pt–Pt coupling constants did not correlate well with the metal–metal bond distances as determined by X-ray crystallography. The authors concluded that the Pt–Pt coupling must be extremely sensitive to minor differences in the electronic structures of the complexes.[8,9] Our results are consistent with and support the conclusions drawn from Hall et al.'s studies in that we also do not see any correlation between Pt–Pt coupling and metal–metal bond distances. In fact, the coupling constants determined for the asymmetric hydroxypyridinate-bridged complexes are nearly twice as large in magnitude as the coupling constants determined for the sulfate- and phosphate-bridged complexes, which have significantly shorter metal–metal bonds.[10,11] Furthermore, the coupling constant for a structurally analogous complex, $[Pt_2(en)_2(hp)_2(NO_3)(NO_2)](NO_3)_2\cdot 0.5H_2O$, is nearly half the magnitude of the coupling constants reported herein for these hydroxypyridinate-bridged complexes.[12,13]

HH and HT Equilibria. Addition of pyridine to the HH fhp and hp complexes results in the progressive conversion to the HT isomer. Dissolution of pure HT isomers of these complexes results in dissociation into equilibrium mixtures of HH complex and free pyridine. Equilibrium is achieved in about 1 day for the fhp case and about 10 days in the hp cases at 25 °C. Addition of pyridine to HH complexes of mhp and of chp resulted in no detectable HT complex even after several months.

For the equilibrium given in eq 2, equilibrium constants were measured over a 5-fold variation of pyridine concentration by the method described in the Experimental Section. For the hp case

$$\text{pyridine} + \text{HH} \rightleftharpoons \text{HT} \qquad (2)$$

K is 120 L mol^{-1} and for the fhp case it is 25 L mol^{-1} at 25 °C in chloroform. The failure of mhp and chp to form **HT** complexes is attributed to the steric bulk of the 6-X substituent in each case.

If diethyl sulfide is substituted for pyridine as the axial ligand, the type of equilibrium described in eq 2 for the pyridine-substituted complexes is shifted so far to the left that the equilibrium constants are too small to measure by magnetic resonance methods for any of the complexes. Since the hp- and fhp-bridged complexes do not have sterically large substituents inhibiting coordination of a second diethyl sulfide molecule, it can be concluded that the ability of the axial ligand to exert a trans influence on the axial ligand across the metal–metal bond is important. These results are consistent with those of Vrieze,[13] where asymmetric carboxylate bridged complexes, which were resistant to further axial substitution, were formed when strong trans-donating axial ligands were used. Vrieze's results indicate that axial ligands such as diethyl sulfide and phosphines exert such strong trans influences across the metal–metal bond that the axial ligands opposite to them are no longer coordinated. This is also consistent with the crystallographic results for the hp- and fhp-bridged complexes, where a significant lengthening (0.16 Å) of the axial bond distances is observed upon coordination of a second pyridine molecule.

Low-Temperature Studies. At room temperature, separate resonances are observed for the proton resonances of free and coordinated pyridine in the HH complexes. The two α protons of the pyridine are equivalent, and spin coupling to platinum-195 is observed. This indicates that pyridine exchange is slow but rotation may be rapid around the metal–nitrogen bond. In the HT case, separate resonances were not observed for free and coordinated pyridine. Pyridine α-proton resonances show no spin coupling to platinum-195. Progressive reduction of temperature in both the hp and fhp HT complexes results in similar changes in the spectra. Free-pyridine resonances begin to broaden at 0 °C and reach maximum breadth at −20 °C. At −40 °C separate, well-resolved resonances are observed for free and for coordinated pyridine in the **HT** case. Integration shows two coordinated pyridine molecules per HT complex, and the methyl resonances remain as two peaks—further supporting a symmetrical complex with two axial ligands in the HT case. In both the hp and fhp cases the chemical shift of the HH methyl resonances are strongly temperature dependent. In the fhp case, the methyl resonance next to coordinated pyridine shifts about 0.1 ppm between −20 and −50 °C while the other methyl resonance does not shift. In the hp case both methyl resonances shift progressively and equally to higher field over the temperature range of ±25 to −50 °C. The HT resonances do not shift significantly in either case.

Mechanism of HH to HT Rearrangement. The fhp complex affords a convenient opportunity to study the mechanism of the rearrangement from HH to HT. Reactions at varying pyridine concentration established that the reaction is first order in pyridine and first order in HH complex. Addition of free Hmhp to the reaction mixture showed no formation of a mixed mhp, fhp

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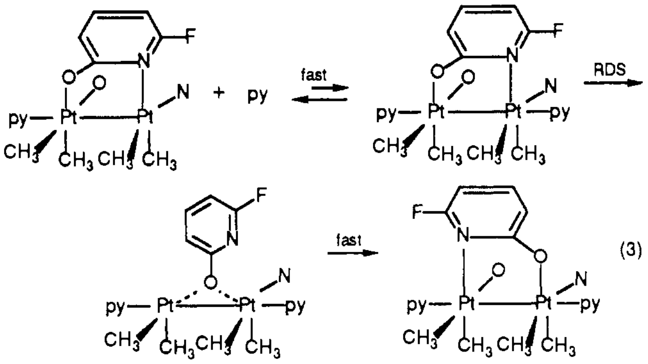
Table VI. Rate Constants and Equilibrium Constants Measured for the Reaction

$$[Pt_2(fhp)_2(CH_3)_4py] + py \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Pt_2(fhp)_2(CH_3)_4(py)_2]$$

temp, K	k_f, L mol^{-1} K^{-1}	k_r, s^{-1}	K, mol^{-1} [a]	K, mol^{-1} [b]
296	5.43×10^{-4}	2.05×10^{-5}	26.4	22.6
307	1.81×10^{-3}	2.05×10^{-5}	18.6	20.9
318	5.20×10^{-3}	3.46×210^{-4}	15.01	18.5

[a] Calculated from k_f/k_r. [b] Measured at equilibrium.

complex even after 20 half-lives for the HH to HT rearrangement. These facts taken together suggest one of two mechanisms. In reaction 3 a preequilibrium in which pyridine binds the HH complex is followed by a rate-determining, somewhat dissociative but concerted rearrangement of an fhp bridge perhaps involving bridging of the dinuclear unit by the hydroxypyridinate oxygen. In reaction 4, pyridine attacks in a rate-determining associative step displacing one bond to the fhp. The fhp subsequently rearranges to form an HT complex. The possibility of a mechanism involving rupture of the metal-metal bond was also considered. In principle, addition of pyridine to HH could not occur on the same Pt to which the first pyridine is coordinated. If this were followed by disproportionation, it would result in a mononuclear four-coordinate Pt(II) complex and a mononuclear six-coordinate Pt(IV) complex. Each complex would contain one bidentate xhp. Recombination of these two complexes could result in HT formation. This mechanism was rejected on the basis of experiments in which the hp complex and fhp complex were present in the same solution. After 10 half-lives for the HH to HT conversion, no mixed complex containing both fhp and hp could be detected. This observation does not, of course, preclude mechanisms in which the metal-metal bond is broken but one xhp continues to bridge the metal ions.



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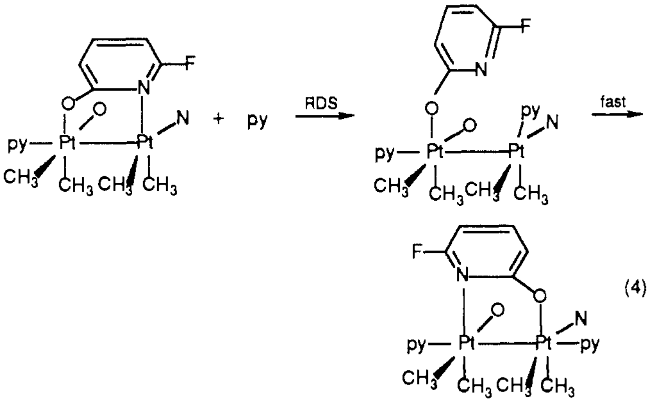

(4)

In order to investigate the mechanism further, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were determined from the data in Table VI. The value of $\Delta H^\ddagger$ for the reaction of HH with pyridine to form HT is 84 kJ mol^{-1}, and $\Delta S^\ddagger$ is -29 J mol^{-1} K^{-1}. These values are consistent with the reaction of HH with pyridine prior to the rate-determining step, through $\Delta S^\ddagger$ is not as negative as normally encountered in an associative reaction. The reverse reaction in which HT reacts to form HH proceeds by a simple first-order process. The value of $\Delta S^\ddagger$ is 16 J mol^{-1} K^{-1}, and $\Delta H^\ddagger$ = 105 kJ mol^{-1}.

The same reactions of the hp complex were studied in less detail. For the forward reaction, the rate constant at 25 °C is 2.33×10^{-5} s mol^{-1} L^{-1}. From the equilibrium constant, the reverse rate constant is 2.1×10^{-7} s^{-1}. Both rate constants are more than 1 order of magnitude lower than for the corresponding fhp complex. The structure of the hp complex reveals a significantly shorter bond between Pt and N of hp, 2.122 (8) Å, than in the fhp case, 2.155 (10) Å, for the HH complex. The same is also true in the HT complexes, where for hp the average distance is 2.143 (13) Å, while for the fhp complex the average distance is 2.23 (3) Å. Presumably, this is a consequence of a weaker bond between platinum and the hydroxypyridinate nitrogen in the fhp complex, as might be expected on inductive grounds. The more rapid reactions of the fhp complex could then be seen as reflecting important dissociative processes of this bond in both the forward and backward reactions. These data also may provide support for mechanism 3. For both fhp and HP, the bond from platinum to the hydroxypyridinate nitrogen is longer in HT than in HH. Assuming that this lengthening is due to the presence of a second axial pyridine, then a preequilibrium such as in eq 3 should also weaken the platinum-hydroxypyridinate bond and thus accelerate a dissociative rate-determining step, as indicated.

Additional evidence for a preequilibrium of HH with pyridine was sought by studying the dependence of the chemical shift of the proton resonances of HH and HT on added pyridine. All the resonances of the HT complex shift uniformly to lower field as pyridine is added. However, in the HH complex different resonances shift by different amounts and in different directions. While this observation might be consistent with a rapid equilibrium between free pyridine and the HH complex as in 3, it could not be interpreted further in terms of a detailed mechanism.

Recently a HH to HT rearrangement has been studied in a very different system.[14] The complexes involve hydroxypyridinate-bridged Pt(II). Unlike the system we have studied, there is no Pt-Pt bond nor are axial ligands present in product or reactant. In this case $\Delta H^\ddagger$ is 114 kJ mol^{-1} and $\Delta S^\ddagger$ is 40 J mol^{-1} K^{-1}, indicating a mechanism that is clearly dissociative. These data should be compared to our data for the HT to HH reaction because in that case there is no loss of axially coordinated pyridine until after the rate-determining step. The system is sufficiently different from ours that detailed comparisons are unwise. This is compounded by the fact that the reaction was studied in water, while our work was carried out in chloroform. Nevertheless, comparison of their results to our results for the HT to HH reaction is interesting. The value of $\Delta S^\ddagger$ we observe is somewhat less positive, but given the differences in the solvents, this is hard to interpret. Both values are consistent with a dissociative concerted mechanism for bridge isomerization.

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Registry No. $[Pt_2(hp)_2(CH_3)_4(py)_2]$, 100351-35-7; $[Pt_2(fhp)_2(CH_3)_4(py)_2]$, 100351-36-8; $[Pt_2(hp)_2(CH_3)_4py]$, 124021-45-0; $[Pt_2(fhp)_2(CH_3)_4py]$, 124021-46-1; $[Pt_2(mhp)_2(CH_3)_4py]$, 124021-47-2; $[Pt_2(chp)_2(CH_3)_4py]$, 124021-48-3; $[Pt_2(hp)_2(CH_3)_4Et_2S]$, 124042-10-0; $[Pt_2(mhp)_2(CH_3)_4Et_2S]$, 124021-49-4; $[Pt_2(fhp)_2(CH_3)_4Et_2S]$, 124042-11-1; ^{195}Pt, 14191-88-9.

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