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Formation Mechanism of Head-to-Head Amidato-Bridged Acetonylplatinum(III) Binuclear Complexes – Kinetic Evidence for π-Coordination of the Enol Form of a Ketone in a Ligand Substitution Reaction

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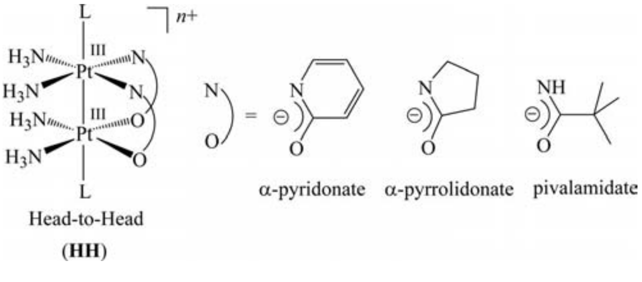
Keywords: Platinum / Reaction mechanisms / Enols

Reactions of head-to-head (HH) α-pyridonato- and pivalamidato-bridged platinum(III) binuclear complexes with acetone were investigated kinetically. The reactions with acetone proceeded slowly to form acetonyl Pt^{III} binuclear complexes in two steps. A mechanism, which involves π-coordination of the enol form of acetone in the first step, followed by the π–σ bond conversion in the second step, is proposed. π-Coordination of the enol was strongly supported by kinetic analyses of a ligand substitution reaction involving the pivalamidato-bridged Pt^{III} binuclear complex with (4-hydroxyphenyl)pyruvic acid. Only the enol form was reactive towards the Pt^{III} dimer complex.

Introduction

Head-to-head (HH) Pt^{III} binuclear complexes $[(L)Pt(NH_3)_2(\mu\text{-amidato})_2Pt(NH_3)_2(L)]^{n+}$ (amidato = α-pyridonato, α-pyrrolidonato, and pivalamidato; L = NO_3^-, NO_2^-, H_2O, Cl^-, and Br^-) have two inequivalent Pt atoms. The upper platinum atom is coordinated by two ammine and two amidate nitrogen atoms $\{Pt(N_4)\}$, and the other is coordinated by two ammine nitrogen and two amidate oxygen atoms $\{Pt(N_2O_2)\}$ with a Pt–Pt bond.[1] These complexes act as catalysts towards the oxidation of olefins to aldehydes, ketones, epoxides, and α,β-diols.[2–5] In these reactions, initial π-coordination of the olefins has been suggested.[2–5]



A four-step reaction mechanism (Scheme 1)[6,7] proposed in our previous kinetic studies involves the initial π-coordination of the double bond of the olefin to the $Pt(N_2O_2)$ moiety to produce a mono-π complex. The olefin then coordinates to the $Pt(N_4)$ moiety to form a di-π complex when $C_{HH} << C_L$, where C_{HH} and C_L denote the total concentrations of the HH Pt^{III} binuclear complex and the olefin, respectively. These steps are followed by conversion of the π bond to a σ bond on the $Pt(N_2O_2)$ atom and dissociation of the olefin on the $Pt(N_4)$ atom. If the σ complex is not stable, it is reduced to produce the corresponding Pt^{II} binuclear complex and a ketone.

It has been reported that the pivalamidato-bridged Pt^{III} binuclear complex reacts with acetone to produce an acetonyl Pt^{III} binuclear complex, for which there are three plausible reaction routes A–C, as shown in Scheme 2.[8] Route A involves electrophilic displacement of H^+ from acetone by an electrophilic Pt^{III} atom. Route B involves homolytic cleavage of the C–H bond forming an acetonylplatinum(III) complex, and route C involves coordination of the enol form of the acetone to the $Pt(N_2O_2)$ atom, followed by nucleophilic attack of a water molecule, proton release, and elimination of one molecule of H_2O.[8]

In this paper, we report detailed kinetic studies involving the formation of acetonylplatinum(III) complexes in acidic aqueous solutions and propose a plausible formation mechanism. In addition, kinetic studies of a ligand substitution reaction of the HH Pt^{III} dimer complex with (4-hydroxyphenyl)pyruvic acid were carried out in order to obtain information about the initial π-coordination of the ketone.

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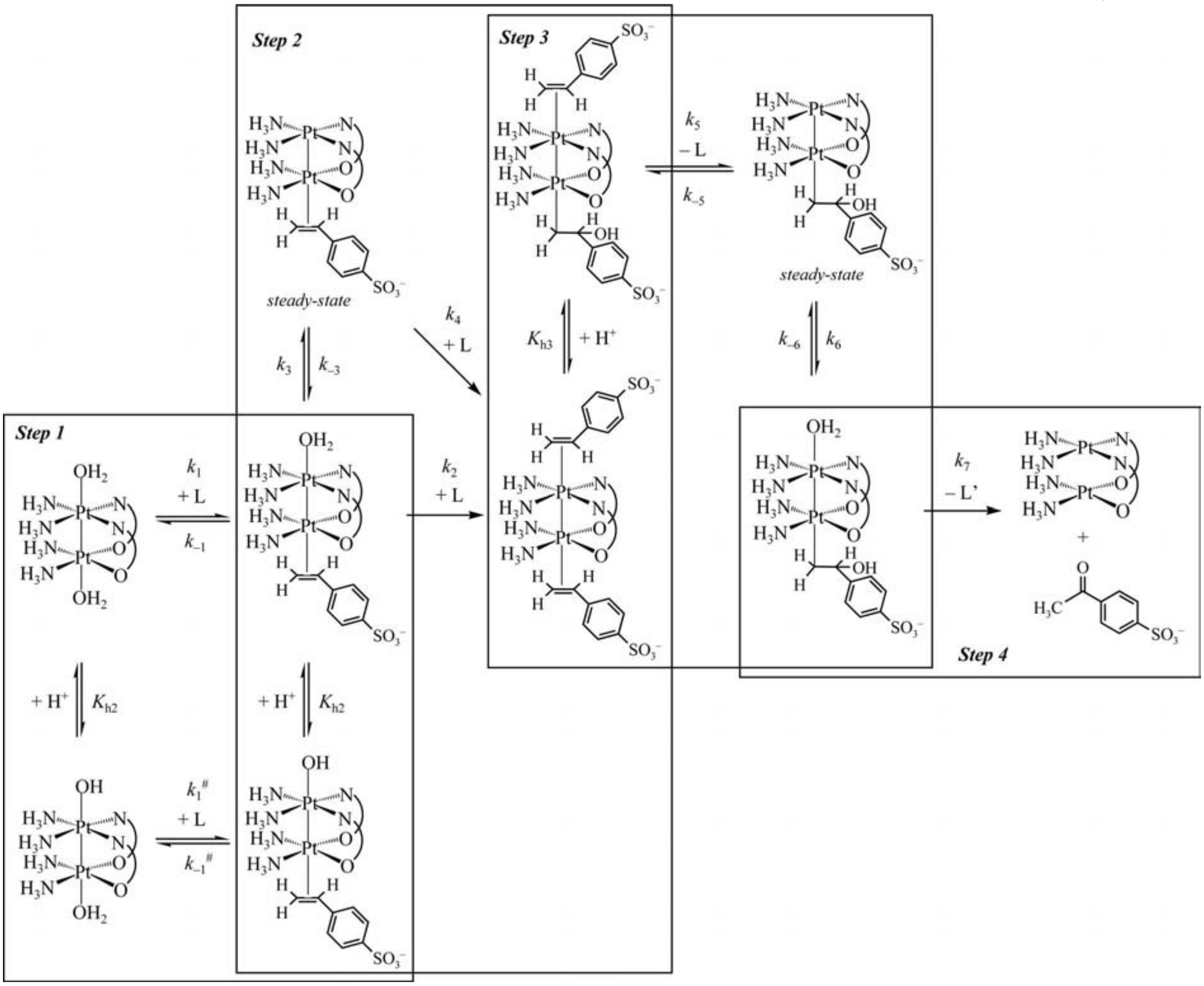
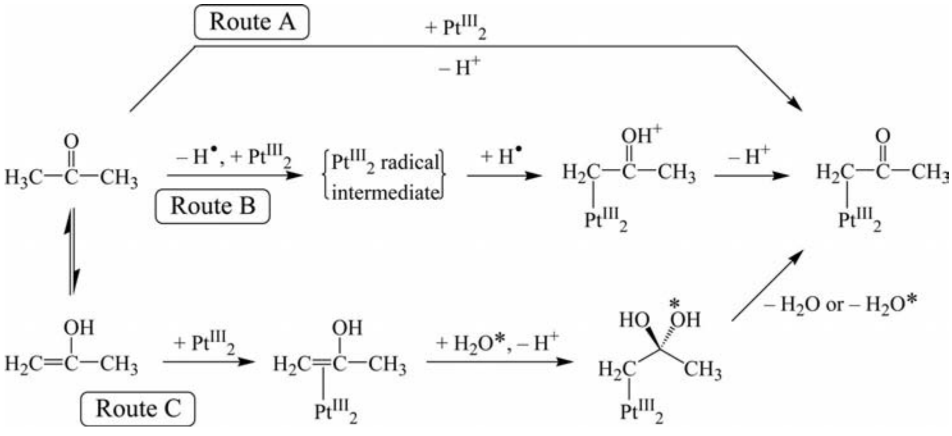


Scheme 1. Mechanism for the reaction of the HH α-pyridonato-bridged Pt^{III} binuclear complex with *p*-styrenesulfonate in a strongly acidic aqueous solution.

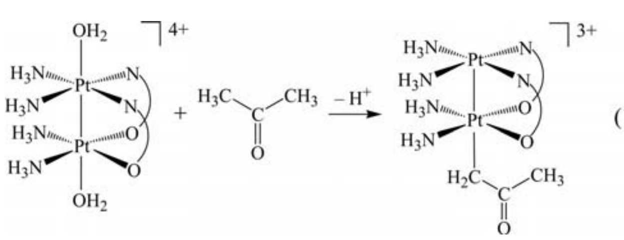


Scheme 2. Three possible routes (A–C) for the formation of the acetonyl Pt^{III} binuclear complex.

Results and Discussion

Kinetic Studies of Reactions of HH α-Pyridonato-Bridged and Pivalamidato-Bridged Pt^{III} Dimer Complexes with Acetone

Amidato-bridged Pt^{III} dimers react with acetone to give acetonyl complexes, as shown in Equation (1).[8]



(1)

Changes in UV/Vis absorption spectra with time under pseudo first-order conditions $C_{HH} << C_L$ are shown in parts a and b of Figure 1 for the reactions of α-pyridonato-bridged and pivalamidato-bridged dimers, respectively. Figure 2 (a, b) show the changes in the absorbances in Figure 1 (a, b) with time, respectively. Both traces in Figure 2 indicate that the reaction consists of two steps. In other words, no further reaction was observed. In contrast, the reactions of these complexes with olefins consist of four steps (Scheme 1). In addition, the dimers react much slower with acetone than they do with olefins. Inset in Figure 2 is shown that the reaction consists of two consecutive first-order reactions. The pseudo first-order rate constants k_{obs1} and k_{obs2} for steps 1 and 2, respectively, were calculated by nonlinear least-squares fitting of the data in Figure 2. k_{obs1} is linearly dependent on C_L at a given [H$^+$], as shown in Figure 3, and thus is expressed as Equation (2). The slopes (k_f) of the straight lines with zero intercept decrease with an increase in [H$^+$], which is consistent with the trend observed in the first steps [the substitution on the Pt(N_2O_2) atom] of the reactions of amidato-bridged Pt^{III} dimers with halide ions and some olefins. On the other hand, k_{obs2} is independent of both C_L and [H$^+$] (Figure 4). Therefore, k_{obs2} is expressed as Equation (3), which suggests that step 2 is an intramolecular process. The k_2 values were calculated from the data in Figure 4 (a, b) to be 6.3×10^{-5} and $6.9\times10^{-5}\,s^{-1}$, respectively.

$$k_{obs1} = k_f\, C_L \qquad (2)$$

$$k_{obs2} = k_2 \qquad (3)$$

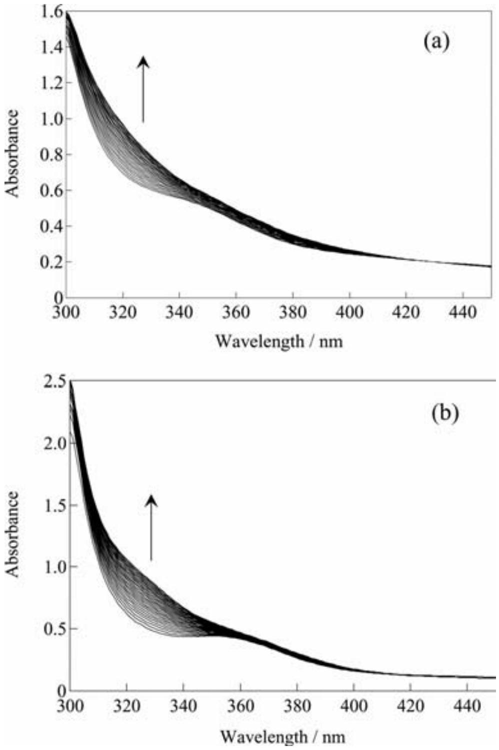


Figure 1. Time-resolved UV/Vis spectra for the reactions of (a) the α-pyridonato-bridged Pt^{III} binuclear complex and (b) the pivalamidato-bridged Pt^{III} binuclear complex with acetone in an acidic aqueous solution at I = 0.40 м and 38.5 °C. C_{HH} = 1.0×10^{-4} м, C_L = 0.500 м (a), 1.00 м (b), [H$^+$] = 0.100 м.

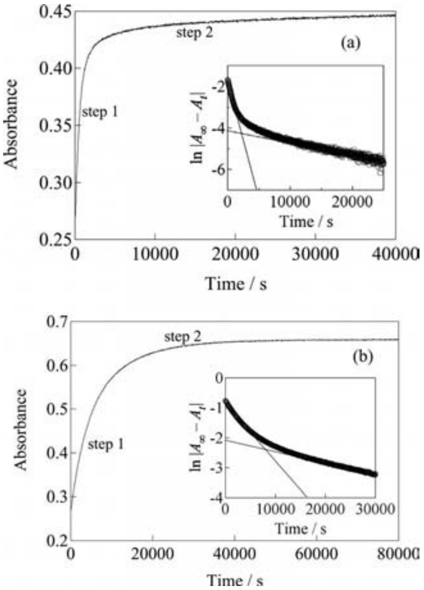


Figure 2. Change in absorbance with time for the reactions of (a) the α-pyridonato-bridged Pt^{III} binuclear complex at 336 nm and (b) the pivalamidato-bridged Pt^{III} binuclear complex with acetone at 325 nm in an acidic aqueous solution at I = 0.40 м and 38.5 °C. C_{HH} = 1.0×10^{-4} м, C_L = 4.00 м (a), 3.00 м (b), [H$^+$] = 0.100 м. The inset in each Figure shows the semi-log plot of the data.

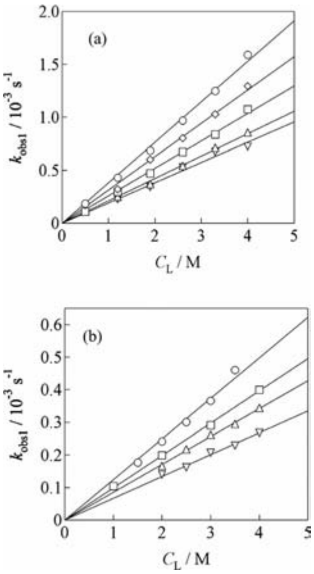


Figure 3. Dependence of k_{obs1} on C_L at various [H$^+$] for the reactions of (a) the α-pyridonato-bridged Pt^{III} binuclear complex and (b) the pivalamidato-bridged Pt^{III} binuclear complex with acetone in an acidic aqueous solution at I = 0.40 м and 38.5 °C. C_{HH} = 1.0×10^{-4} м, [H$^+$]/M = 0.100 (○), 0.150 (◇), 0.200 (□), 0.300 (△), 0.400 (▽) in (a); 0.0500 (○), 0.0750 (□), 0.100 (△), 0.150 (▽) in (b).

When simple nucleophilic attack of the carbonyl oxygen in acetone occurs, as in the case of the initial substitution reactions with halides shown in Scheme 3, Equation (4) is

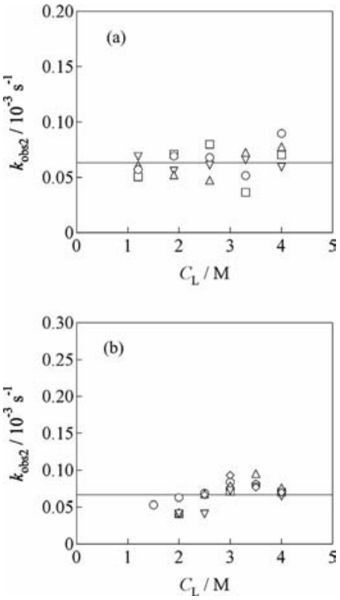
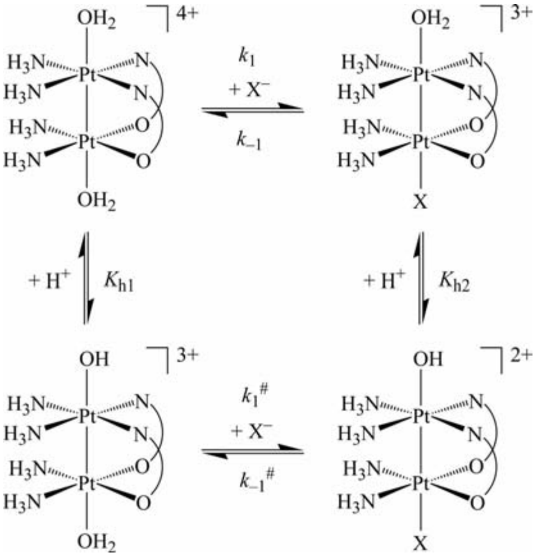


Figure 4. Dependence of k_{obs2} on C_L at various [H$^+$] for the reactions of (a) the α-pyridonato-bridged Pt^{III} binuclear complex and (b) the pivalamidato-bridged Pt^{III} binuclear complex with acetone in an acidic aqueous solution at I = 0.40 M and 38.5 °C. C_{HH} = 1.0×10^{-4} M, [H$^+$]/M = 0.100 (○), 0.200 (□), 0.300 (△), 0.400 (▽) in (a); 0.0500 (○), 0.0750 (□), 0.100 (△), 0.150 (▽), 0.200 (◇) in (b).



Scheme 3. The initial ligand substitution step for the reaction of the HH amidato-bridged Pt^{III} binuclear complex with halide ions.

obtained. Comparison of Equation (4) with (2) gives Equation (5), since $C_L \approx [L]$ when $C_{HH} << C_L$. Analysis based on Equation (5) gives straight lines, as shown in Figure 5, from which the values of k_1 and $k_1^\#$ were obtained (Table 1).

$$k_{obs1} = \frac{k_1 + \frac{k_1^\# K_{h1}}{[H^+]}}{1 + \frac{K_{h1}}{[H^+]}}[L] \tag{4}$$

$$\left(1 + \frac{K_{h1}}{[H^+]}\right)k_f = k_1 + \frac{k_1^\# K_{h1}}{[H^+]} \tag{5}$$

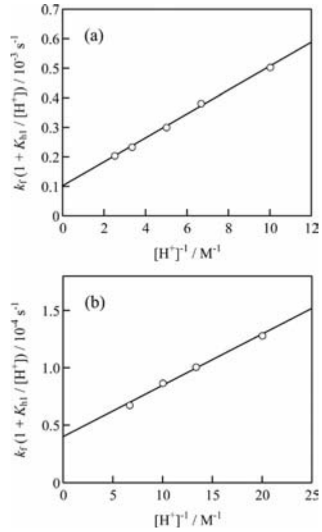


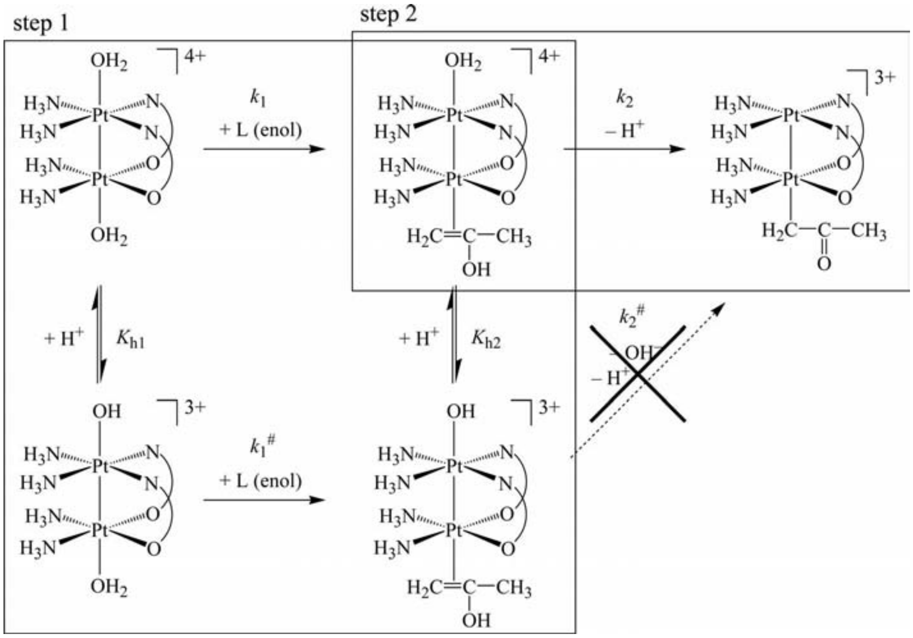
Figure 5. Dependence of k_f on [H$^+$] for the reactions of (a) the α-pyridonato-bridged Pt^{III} binuclear complex and (b) the pivalamidato-bridged Pt^{III} binuclear complex with acetone in an acidic aqueous solution at I = 0.40 M and 38.5 °C.

The k_1 and $k_1^\#$ values for the reaction with acetone, summarized in Table 1 under the heading "acetone", are unusually low compared with those for the reactions with halides and olefin. The slowness of the reactions with acetone suggests that the first step is not initiated by the simple attack of acetone. It should be noted that, in the first step of the reactions with olefins, olefins π-coordinate to the Pt(N$_2$O$_2$) center (Scheme 1).[6,7] It has been reported that acetone exists in equilibrium with its enol tautomer (keto ⇌ enol, the equilibrium constant, K_{ke} = [enol]/[keto] = $10^{-8.46}$).[9] These observations suggest that the enol form of acetone π-coordinates to the Pt(N$_2$O$_2$) atom in the first step. In ^{1}H NMR spectra for the present reaction over time

Table 1. Rate constants for the reactions of the HH amidato-bridged Pt^{III} binuclear complexes with various ligands.

Bridging ligand	Reaction path	Acetone 38.5 °C	Enol acetone[a] 38.5 °C	Enol pHPP[b] 25.0 °C	p-Styrenesulfonate[c] 25.0 °C	Cl$^-$[d] 25.0 °C	Br$^-$[d] 25.0 °C
α-Pyridonate	k_1 /M^{-1} s^{-1}	1.02×10^{-4}	2.94×10^4	–	1.3×10^3	3.1×10^3	7.2×10^3
	$k_1^\#$ /M^{-1} s^{-1}	1.28×10^{-3}	3.69×10^5	–	4.4×10^3	4.6×10^5	2.4×105
Pivalamidate	k$_1$ /M^{-1} s^{-1}	3.99×10^{-5}	1.15×10^4	6.34×10^2	1.09×10^2[e]	1.12×10^3	1.12×10^3
	$k_1^\#$ /M^{-1} s^{-1}	3.39×10^{-3}	9.77×10^5	7.57×10^4	6.76×10^4[e]	1.76×10^6	1.13×10^6

[a] The enol form of acetone. [b] The enol form of (4-hydroxyphenyl)pyruvic acid. [c] Ref.[6] [d] Ref.[12,13] [e] Unpublished results.



Scheme 4. Proposed formation mechanism for the acetonyl Pt^{III} binuclear complex.

(see Figure S1 in the Supporting Information), the intensity of the peaks for the acetonyl complex increased as that for the diaqua Pt^{III} dimer decreased, and the dimer was completely converted into the acetonyl complex, i.e. no reverse reaction was observed. It was shown by X-ray crystallography that the acetonyl group is bound to the $Pt(N_2O_2)$ atom.[10] A two-step reaction was observed by UV/Vis spectrophotometry, as mentioned above. The dependence of the observed rate constants on both C_L and $[H^+]$ in the first step is similar to those for the olefin and halide systems, and an intramolecular process was suggested in the second step. These observations suggest that only one acetone molecule coordinates to the dimer, which is followed by an acid-independent intramolecular irreversible process. From these results, we propose the formation mechanism of the acetonyl complex shown in Scheme 4. In Scheme 4, the enol form of acetone π-coordinates to the $Pt(N_2O_2)$ moiety in step 1, and the π complex formed undergoes intramolecular conversion to the σ complex in step 2. Step 2 does not involve an acid-dependent path ($k_2^{\#}$) because k_{obs2} is independent of $[H^+]$. Thus, Equations (2) and (4) can be rewritten as Equations (6) and (7), respectively, since $C_L = (1 + 1/K_{ke})[\text{enol}] \approx [\text{enol}]/K_{ke}$.

$$k_{obs1} = k_f C_L = \frac{k_f}{K_{ke}}[\text{enol}] \tag{6}$$

$$k_{obs1} = \frac{k_1 + \frac{k_1^{\#} K_{h1}}{[H^+]}}{1 + \frac{K_{h1}}{[H^+]}}[\text{enol}] \tag{7}$$

Therefore,

$$\frac{k_f}{K_{ke}} = \frac{k_1 + \frac{k_1^{\#} K_{h1}}{[H^+]}}{1 + \frac{K_{h1}}{[H^+]}} \tag{8}$$

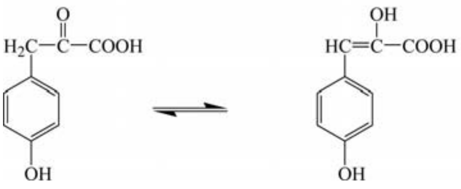
The values of the rate constants obtained using Equation (8) are listed under the heading "enol acetone" in Table 1 and are comparable to those for the other systems.

Thus, we think that only the enol form of acetone, which is in fast equilibrium with the keto form, coordinates to the $Pt(N_2O_2)$ moiety to form the π complex in step 1 and then the π complex irreversibly changes to the acetonyl complex in step 2. As mentioned above, the mechanism for the reactions of the HH amidato-bridged Pt^{III} binuclear complex with acetone under the conditions of $C_{HH} << C_L$ is given in Scheme 4, and the reaction is first order with respect to the concentration of the HH dimer [HH]. This is because, in these reactions, the concentration of the reactive enol acetone, [enol], is kept virtually constant during the reaction, though [enol] is much smaller than C_{HH}, because $K_{ke} = [\text{enol}]/[\text{keto}] = 10^{-8.46}$. In addition, because of $C_{HH} >> [\text{enol}]$, the intermediate having two axial π-bonds as shown in Scheme 1 is not included in Scheme 4. In order to obtain the further kinetic evidence for the initial π-coordination of enol tautomer proposed in Scheme 4, additional experiments were carried out.

Kinetics for the Reaction of the HH Pivalamidato-Bridged Pt^{III} Dimer with (4-Hydroxyphenyl)pyruvic Acid (pHPP)

It is known that pHPP adopts an enol form in the solid state and that it isomerizes very slowly to the keto form in solution as observed by UV/Vis spectrophotometry (Figure S2) [Equation (9)].[11]

Changes in UV spectra for the isomerization reaction with time were first order (Figure S2 and S3), and the first-order rate constant was independent of $[H^+]$ in the range of 0.1–0.4 м. If only the enol form of pHPP reacts with the HH Pt^{III} dimer, the rate constant in step 1 for the reaction should decrease with time. Thus, the reaction of the HH



(9)

pivalamidato-bridged dimer complex with pHPP was followed spectrophotometrically under pseudo first-order conditions ($C_{Pt} << C_L$). The reaction was fast enough (Figure S3) compared with the isomerization reaction (Figure S2) such that the concentration of the enol form of pHPP could be regarded as being constant during the fast reaction.

Only k_{obs1} for step 1 (corresponding to the fast step in Figure S4) was calculated and plotted against the concentration of the enol form of pHPP (C_{enol}), which was calculated from the rate constant ($k_{iso} = 2.10 \times 10^{-4}$ s^{-1} at 25 °C and I = 0.40 M) for the isomerization reaction in Figure S2. In Figure 6, k_{obs1} decreased linearly to zero with a decrease in C_{enol} and an increase in the acidity of the solution. This result indicates that only the enol form of pHPP is reactive towards the Pt^{III} dimer because k_{obs1} in Figure 6 would deviate from the straight line at low C_{enol}, i.e. at high concentration of the keto form, if the keto form is reactive towards the Pt^{III} dimer. The values of k_1 and $k_1{}^{\#}$ for this system were obtained using a similar procedure to that employed for the other ligand substitution systems mentioned previously and are summarized in Table 1. These values are also comparable to those for the other systems in Table 1.

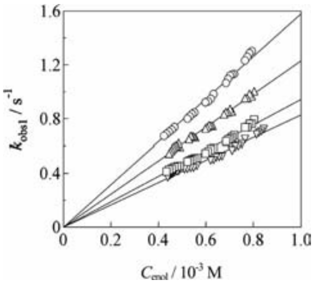


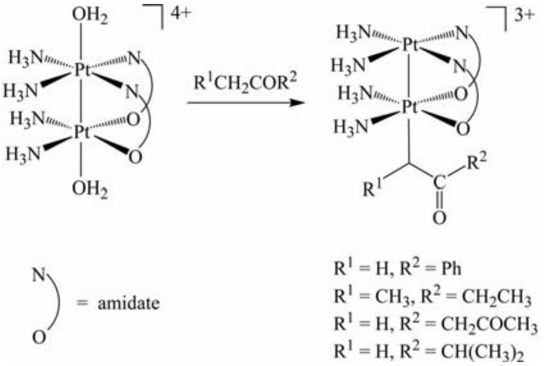
Figure 6. Dependence of k_{obs1} on C$_{enol}$ (the concentration of the enol form of pHPP) at various [H$^+$] for the reaction of the pivalamidato-bridged Pt^{III} binuclear complex with pHPP at I = 0.40 M and 25.0 °C. $C_{HH} = 5.0 \times 10^{-5}$ M, [H$^+$]/M = 0.100 (○), 0.200 (△), 0.300 (□), 0.400 (▽).

In Table 1, the k_1 values for the reactions of the α-pyridonato-bridged Pt^{III} binuclear complex with halide ions are somewhat larger than those for the reactions of the pivalamidato-bridged complex with corresponding halide ions, however this relation is reversed for the $k_1{}^{\#}$ values. These were explained as follows; the k_1 and $k_1{}^{\#}$ values may reflect that the H_2O–Pt(N_2O_2) bond in the α-pyridonato-bridged diaqua complex [H_2O–Pt(N_4)–Pt(N_2O_2)–OH_2]$^{4+}$ is weaker than that in the pivalamidato-bridged complex, since the H_2O–Pt(N_4) bond in the former complex which has a smaller pK_{h1} (1.71), is stronger than that in the latter complex, which has a larger pK_{h1} (2.88), and once the diaqua complexes are deprotonated, the H_2O–Pt(N_2O_2) bond in the aquahydroxo complex [HO–Pt(N_4)–Pt(N_2O_2)–OH_2]$^{3+}$ becomes weaker for the latter complex, as the opposite HO–Pt(N_4) bond becomes stronger in the deprotonated complex.[12] In view of Table 1, the k_1 and $k_1{}^{\#}$ values for the reactions of the α-pyridonato-bridged and pivalamidato-bridged complexes with enol acetone and *p*-styrenesulfonate are in line with the explanation just mentioned.

As mentioned in our previous paper,[13] the rate constants for the substitution reactions on the hexaaqua metal ions [$M(H_2O)_6$]$^{n+}$ are smaller by 2–3 orders of magnitude than the corresponding pentaaquahydroxo metal ions [$M(H_2O)_5(OH)$]$^{(n-1)+}$.[14] The reactions of [$M(H_2O)_6$]$^{n+}$ ions proceed with an associative interchange (I$_a$) mechanism or a dissociative interchange (I$_d$) mechanism depending on the central metal ion, whereas the reactions of [$M(H_2O)_5$-(OH)]$^{(n-1)+}$ occur always with I$_d$ mechanism.[15] Table 1 shows that the same tendency holds for the k_1 for the diaqua complex and $k_1{}^{\#}$ for the aquahydroxo complex for all the reaction systems of α-pyridonato-bridged and pivalamidato-bridged Pt^{III} binuclear complexes with halide ions, which means that the *trans* effect of OH$^-$ also operates in the substitution of the water molecule on the Pt(N_2O_2) with the halide ion in the Pt^{III} binuclear complexes through the Pt–Pt bond. On the other hand, for the reactions of α-pyridonato-bridged Pt^{III} binuclear complex with enol acetone and *p*-styrenesulfonate the $k_1{}^{\#}$ is only one order of magnitude greater than the k_1 for the former reaction ($k_1{}^{\#}/k_1$ = 13), and the $k_1{}^{\#}$ for the latter reaction is comparable to k_1 ($k_1{}^{\#}/k_1$ = 3.4) but significantly greater than the k_1 as is obvious from the original data (Figure 3(a) in ref.[6]). The $k_1{}^{\#}$ value for the latter reaction would be too low, since the $k_1{}^{\#}$ value for the reaction of α-pyridonato-bridged Pt^{III} binuclear complex is expected to be in the order of 10^5, if the $k_1{}^{\#}$ path is dissociatively activated like pentaaquahydroxo metal ions. This low value may come from sterically hindered approach of *p*-styrenesulfonate involving a bulky substituted-phenyl group to the Pt(N_2O_2) in the transition state, in other words the mechanism may be close to D but not D because there is no intermediate. Similar lowering of $k_1{}^{\#}$ due to steric hindrance is also observed to a lesser extent for the systems of the pivalamidato-bridged Pt^{III} binuclear complex with enol pHPP and *p*-styrenesulfonate, both of which have a bulky susbstituted-phenyl group.

Conclusions

HH α-pyridonato-bridged and pivalamidato-bridged Pt^{III} binuclear complexes react with only the enol tautomer of acetone to form acetonyl Pt^{III} dimer complexes in two steps. In the first step, the substitution of the water molecule ligated to the Pt(N_2O_2) atom with the enol acetone occurs to form a π complex, and then a σ (acetonyl) complex is irreversibly formed with the release of H$^+$ from the π complex in step 2. This proposed mechanism was strongly supported by the rate constants calculated using the equation derived from the mechanism. Furthermore, the fact that the enol form of (4-hydroxyphenyl)pyruvic acid reacts with HH pivalamidato-bridged Pt^{III} dimer supports the proposal that acetone π-coordinates to the Pt^{III} complex in the initial step to afford an acetonyl Pt^{III} binuclear complex. These conclusions are generalized as: all the reactions of the amidato-bridged Pt^{III} binuclear complexes with ketones as shown in Equation (10)[8] proceed with the initial π-coordination of their enol-forms to the $Pt(N_2O_2)$ atom.



(10)

Experimental Section

Reagents: Head-to-head $[(H_2O)Pt(NH_3)_2(\mu\text{-}\alpha\text{-pyridonato})_2Pt(NH_3)_2(NO_3)](NO_3)_3\cdot 2H_2O$ and head-to-head $[(H_2O)Pt(NH_3)_2(\mu\text{-pivalamidato})_2Pt(NH_3)_2(H_2O)](NO_3)_4\cdot 2H_2O$ were prepared according to literature procedures.[1,3] Perchloric acid (60 % UGR for trace analysis, Kanto), acetone (UGR, Kanto), and (4-hydroxyphenyl)pyruvic acid (ACROS) were used as received. Sodium perchlorate was prepared and purified by using a previously reported procedure.[16]

Measurements: Ionic strength was maintained at 0.40 M with perchloric acid and sodium perchlorate. All the sample solutions were prepared by using doubly distilled water just before measurement. Spectrophotometric measurements were performed using a rapid-scan/stopped-flow spectrophotometer USP-600 (Unisoku Scientific Instruments, Osaka) and a UV-2400 spectrophotometer (Shimadzu, Kyoto). Rate constants were measured by monitoring the absorbance change at 336 nm for the reaction of the HH α-pyridonato-bridged Pt^{III} complex with acetone, at 325 nm for the reaction of the HH pivalamidato-bridged complex with acetone, and at 340 nm for the reaction of the HH pivalamidato-bridged complex with (4-hydroxyphenyl)pyruvic acid. The rate constants for the consecutive reactions (k_{obs1} and k_{obs2}) were determined using the SPECFIT program[17] in relation to the following equation: $A_t = A_{eq} + \alpha\exp(-k_{obs1}t) + \beta\exp(-k_{obs2}t)$, in which A_t and A_{eq} are the absorbances at time t and infinity, respectively, and α and β are composite parameters.[18]

Acknowledgments

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