

concentrations higher than 2.5 M, where the metathetic reaction is probably better described by eq 6, solvation effects should be minimized and the enthalpy change of  $-8 \text{ kcal mol}^{-1}$  should result from the balance of the exothermic ligand field contribution and the endothermic contribution due to the disappearance of 1 mol of aqueous  $\text{Na}^+$  and  $\text{Cl}^-$  ions.

### Conclusions

The general suggestion to the synthetic chemist wishing a design ligands that stabilize high oxidation states of transition-metal ions is to look at strongly coordinating systems. This tip arises from the consideration that a  $\text{M}^{(n+1)+}$  metal center will profit from ligand field stabilization energy effects to a greater extent than the corresponding  $\text{M}^{n+}$  cation. Considering things from a thermodynamic standpoint, this should be defined as a pure *enthalpy* effect. Another reasonable tip could be to put several negative charges on the coordinating system: intuitively, the energy to be

spent to increase the positive charge of the metal center should be lower in a negatively charged coordinative environment. The present investigation has demonstrated that this latter effect is not a ligand field enthalpy effect but is essentially an *entropy* effect and, in particular, it arises from the gain in translational entropy that occurs when the overall negative charge of the metal complex decreases in absolute value and water molecules are released from the hydration sphere. It is reasonable to predict that the ligand's negative charge effect on the stabilization of metal centers in unusually high oxidation states, being strictly related to solute-solvent interactions, should vary significantly with the nature of the solvent employed.

**Acknowledgment.** We are indebted to the Ministry of Public Education of Italy for financial support (MPI 40%).

**Registry No.**  $[\text{Ni}^{\text{III}}\text{Y}]$ , 87306-48-7;  $[\text{Ni}^{\text{II}}\text{Y}]^-$ , 82980-33-4;  $[\text{Ni}^{\text{III}}\text{L}_2]^{3+}$ , 86709-81-1;  $[\text{Ni}^{\text{III}}\text{L}_2]^{2+}$ , 59034-11-6;  $\text{NaCl}$ , 7647-14-5;  $\text{Ni}$ , 7440-02-0.

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## Water Exchange of *trans*-Dichlorodiaquaplatinum(II) and Tetraaquaplatinum(II) Studied by an Oxidative-Addition Quenching Technique. Isotopic Shifts and Platinum-195 NMR Chemical Shifts for Mixed Chloro-Aqua Complexes of Platinum(II) and Platinum(IV)

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Water exchange on  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  and *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  has been studied by means of a new  $^{18}\text{O}$ -tracing technique. The exchange between a platinum(II) complex and  $^{18}\text{O}$ -enriched water has been rapidly quenched by addition of excess chlorine, which gives a substitution-inert platinum(IV) complex. The time-dependent  $^{16}\text{O}/^{18}\text{O}$  distributions of the platinum(II) complexes are obtained from the  $^{195}\text{Pt}$  NMR spectra of the corresponding oxidized complexes, which display well-resolved oxygen isotopic shifts in the 78-MHz signal. Product identification based on the isotopic splitting of the NMR signal due to both  $^{16}\text{O}/^{18}\text{O}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  shows that the oxidation takes place without scrambling and involves the formation of a  $\text{Cl-Pt-OH}_2$  axis perpendicular to the original coordination plane of platinum(II). The oxidation products of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ , *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ , and  $\text{PtCl}_4^{2-}$  are thus found to be  $\text{PtCl}(\text{H}_2\text{O})_5^{3+}$ , *mer*- $\text{PtCl}_3(\text{H}_2\text{O})_3^+$ , and  $\text{PtCl}_5\text{H}_2\text{O}^-$ , respectively. There is no observable exchange of *trans*- and *cis*-aqua ligands in those platinum(IV) complexes during the time required to accumulate the spectra. Water exchange of *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  is slower than that of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  by a factor of 30. The statistically corrected rate constants are  $k_{\text{ex}}^{298} = (1.58 \pm 0.03) \times 10^{-5} \text{ s}^{-1}$  and  $k_{\text{ex}}^{298} = (4.8 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ , respectively. Variable-temperature measurements (278–303 K) gave  $\Delta H^\ddagger = (92 \pm 2) \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = (0 \pm 5) \text{ J K}^{-1} \text{ mol}^{-1}$  for exchange on  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ . The effect of the nonreacting ligands is basically the same as that previously reported for the chloride anation reactions of these two substrates. The chemical shifts of the complexes  $\text{PtCl}_{4-n}(\text{H}_2\text{O})_n^{2-n}$ ,  $n = 0-4$ , have been measured in a 1.00 M  $\text{HClO}_4$  medium. The increment in the chemical shift for substitution of water by chloride is smaller *trans* to water than *trans* to chloride but increases with the number of chloride ligands in a *cis* position to the replaced water molecule. This might be consistent with a large ground-state *trans* influence of chloride compared to water and a negligible relative *cis* influence.

### Introduction

Rate data for exchange of water on square-planar metal complexes were hitherto only available for the tetraqua ions of platinum(II)<sup>1,2</sup> and palladium(II).<sup>3</sup> Volumes of activation have been determined to be  $-4.6 \text{ cm}^3 \text{ mol}^{-1}$  and  $-2.2 \text{ cm}^3 \text{ mol}^{-1}$ , respectively.<sup>2,3</sup> The mechanistic interpretation of these volume changes is still an open question.<sup>2,3</sup>

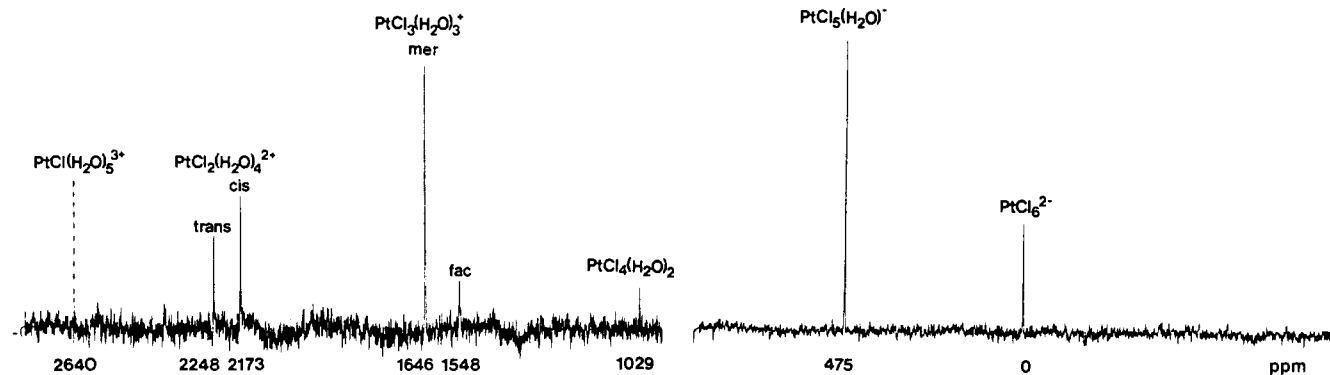
Halide anation of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  is more than 2 orders of magnitude faster than that of *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ .<sup>4</sup> The former reaction is favored thermodynamically and by the 2+ ionic charge of the complex. Neutral as well as anionic ligands react rather rapidly with the *trans* complex, replacing one of the chloride ligands,<sup>5</sup> but there are no data for the replacement of the aqua

ligands, except for the chloride anation. It was therefore of interest to study the water exchange on *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  in order to evaluate the effect of the two *cis* chlorides. The exchange reaction occurs with  $\Delta G^\circ = 0$  and with conservation of ionic charge, and the data are therefore of particular interest in relation to previous data for halide anation.<sup>4,6,7</sup>

The small chemical shift range in oxygen-17 NMR makes the conventional isotopic dilution technique unsuitable for study of water exchange in mixtures of aqua complexes. Evaluation of rate constants from the absolute oxygen-17 signal intensity is difficult when the complexes are not stable with time due to side reactions or when the accumulation of spectra is time consuming compared to the half-life of exchange.

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**Figure 1.** Platinum-195 NMR spectra showing signals for the complexes  $\text{PtCl}_{6-n}(\text{H}_2\text{O})_n^{4-n}$  ( $n = 0-5$ ). The left part of the spectrum was recorded by using a solution of  $0.15 \text{ M PtCl}(\text{H}_2\text{O})_5^{3+}$  (dotted line). The right part of the spectrum was recorded by using  $\text{PtCl}_6^{2-}$  ( $0.1 \text{ M}$ ) and  $\text{PtCl}_5(\text{H}_2\text{O})^-$  prepared by oxidation of  $\text{PtCl}_4^{2-}$  ( $0.1 \text{ M}$ ) with excess chlorine.

In the present work, we have used platinum-195 NMR and a new convenient oxygen-18 isotopic dilution technique. It involves instantaneous quenching of the water exchange on the platinum(II) complexes by rapid oxidation with chlorine. The oxidation results in formation of much more substitution-inert platinum(IV) complexes and also effectively removes the chemical shift anisotropy.<sup>1</sup> The signals from the oxygen isotopomers can therefore be well resolved at high magnetic fields and their relative intensities can be evaluated at ambient conditions, independent of the exchange kinetics. The method can therefore be used for studies of relatively fast water-exchange reactions. It does not require high metal concentrations.

We also report chemical and isotopic shifts for platinum(IV)- and platinum(II)-chloro-aqua complexes. Some isotopic shifts in the 195-platinum NMR signal due to oxygen-18 substitution in platinum(II) complexes have been published previously.<sup>1</sup>

### Experimental Section

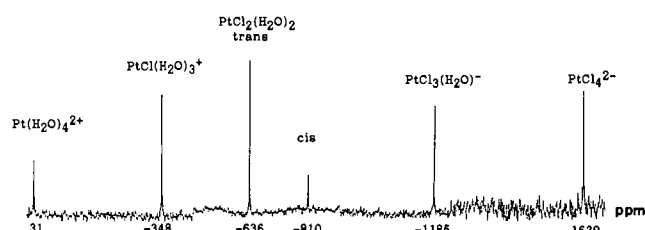
**Chemicals and Solutions.** Stock solutions of  $10 \text{ mM Pt}(\text{H}_2\text{O})_4^{2+}$  in  $1.0 \text{ M}$  perchloric acid (Baker, p.a.) were prepared from  $\text{K}_2\text{PtCl}_4$  (Johnson and Matthey) and  $\text{AgClO}_4$  (G. F. Smith) as described previously.<sup>8</sup> They were concentrated by freeze-drying and addition of water suspensions of  $\text{KHCO}_3$  (Merck, p.a.) to give a final concentration of  $0.15 \text{ M Pt}(\text{H}_2\text{O})_4^{2+}$  and  $2.0 \text{ M}$  perchloric acid. During this procedure, the perchloric acid concentration of the solution was always  $0.5 \text{ M}$  or larger, in order to prevent polynuclear hydrolysis.<sup>8</sup>

The final solutions were characterized by their absorption spectra in the region  $225-450 \text{ nm}$  and by their platinum-195 NMR spectra, which both had characteristics similar to those of the solutions used previously.<sup>1,8</sup> Solutions of *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  with  $0.50 \text{ M}$  free chloride were prepared from the  $0.15 \text{ M Pt}(\text{H}_2\text{O})_4^{2+}$  stock solutions by dissolving calculated quantities of solid  $\text{NaCl}$  (Merck p.a.). After the solution was aged at  $25^\circ\text{C}$  for  $20 \text{ min}$ , the conversion to *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  was complete,<sup>6,7</sup> and the isotopic exchange experiment was started. Water was doubly distilled from quartz, and  $99.8 \text{ mol } \%$  enriched  $\text{H}_2^{18}\text{O}$  from Ventron was used for isotopic dilution.

**Procedure.** Weighed samples of the platinum(II) solutions and ordinary water or oxygen-18 enriched water were mixed under well-motated conditions (water thermostats between  $30.0$  and  $5.0 \pm 0.1^\circ\text{C}$ ) to give  $0.075 \text{ M}$  platinum and  $1.00 \text{ M}$  perchloric acid and a total volume of ca.  $3 \text{ mL}$ . In the case of *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  this dilution decreased the concentration of free chloride to  $250 \text{ mM}$ , which was sufficient to suppress hydrolysis and contributions to the exchange by  $\text{PtCl}(\text{H}_2\text{O})_3^{3+}$ .<sup>6,7</sup>

After an appropriate interval of time, the water exchange was rapidly quenched by flushing dry chlorine through the solutions. The color changed instantaneously from light to darker yellow, indicating oxidation. The gas flow was continued for  $30 \text{ s}$  to ensure complete oxidation. Excess chlorine was then removed by flushing with nitrogen, and  $0.4 \text{ mL}$  of  $\text{D}_2\text{O}$  was added to the solution for shimming of the NMR magnet.

Rapid oxidation was checked by mixing a  $1 \text{ mM}$  solution of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  with a  $5 \text{ mM}$  solution of chlorine in a  $1.00 \text{ M HClO}_4$  medium by use of a Durrum-Gibson stopped-flow instrument. Reaction was complete within the dead time of the instrument (a few milliseconds). In order to test the effect of chloride on the redox step and on the water-exchange rate, several qualitative experiments were carried out. For the experiments with  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ , a solution of  $1 \text{ M NaCl}$  in  $\text{H}_2^{18}\text{O}$  water



**Figure 2.** Platinum-195 NMR spectra with chemical shifts relative to  $\text{PtCl}_6^{2-}$  for the complexes  $\text{PtCl}(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0-4$ ).  $C_{\text{Pt}} \approx 40 \text{ mM}$ . Medium:  $1.0 \text{ M HClO}_4$ .

was mixed with an equal volume of the  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  stock solution. In one experiment, the temperature was held at  $-2^\circ\text{C}$  and oxidation was carried out immediately (ca.  $2 \text{ s}$ ) after mixing. In another at  $25^\circ\text{C}$ , the anation was allowed to go to completion (ca.  $12 \text{ min}$ ) before oxidation. Only one oxidation product could be detected in both these experiments and the  $^{18}\text{O}$  content of the respective oxidation products showed very clearly that the chloride media had no effect on the redox step or the water-exchange rate.

**NMR Measurements.** The instrumentation was the same as that used previously.<sup>1</sup> Most of the platinum-195 NMR spectra were recorded by using a Nicolet 360 Fourier transform spectrometer with an Oxford Instrument  $8.5\text{-T}$   $12\text{-mm}$ -bore superconducting magnet. Measurements of the spin-lattice relaxation time for  $\text{PtCl}(\text{H}_2\text{O})_3^{3+}$  at  $8.5 \text{ T}$  gave  $T_1 = 0.28 \text{ s}$ . The line width for  $\text{Pt}^{35}\text{Cl}(\text{H}_2^{16}\text{O})_3^{3+}$  was never better than about  $10 \text{ Hz}$  probably due to temperature gradients in the sample. About  $1000$  scans with a repetition time of  $0.5 \text{ s}$  were needed to achieve an acceptable signal to noise ratio, and about  $9000$  scans were accumulated for quantitative treatment of a spectrum. Shimming was done on internal  $\text{D}_2\text{O}$  for each sample. All spectra were recorded at ambient temperature ( $23^\circ\text{C}$ ), and temperature equilibration was achieved about  $20 \text{ min}$  after the sample was placed in the probe. Spectra accumulated  $1/2 \text{ h}$  after sample preparation could be reproduced the following day. During longer periods of time, gradual changes of the initial spectra were observed.

### Results

**Chemical Shifts.** Addition of excess chlorine to an acidic solution of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  results in rapid formation of  $\text{PtCl}(\text{H}_2\text{O})_3^{3+}$ , which displays a signal at  $+2640 \text{ ppm}$  relative to  $\text{PtCl}_6^{2-}$ . Over a period of several months, this line at  $2640 \text{ ppm}$  slowly decreases and new resonances appear at lower frequencies, due to formation of higher chloro-aqua complexes of platinum(IV). This is shown in Figure 1, which also includes resonances for the  $\text{PtCl}_6^{2-}$  reference and for  $\text{PtCl}_5(\text{H}_2\text{O})^-$  obtained independently by oxidation of  $\text{PtCl}_4^{2-}$  with chlorine. Assignment of the resonances from  $\text{PtCl}(\text{H}_2\text{O})_3^{3+}$ , *mer*- $\text{PtCl}_3(\text{H}_2\text{O})_3^+$  and  $\text{PtCl}_5(\text{H}_2\text{O})^-$  in Figure 1 have been based on observed  $^{16}\text{O}/^{18}\text{O}$  isotopic shifts of the platinum-195 signal. In the case of  $\text{PtCl}(\text{H}_2\text{O})_3^{3+}$ ,  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopic shifts were also resolved. The other resonances have been assigned by interpolation and assuming that signals from isomeric forms are closely spaced.

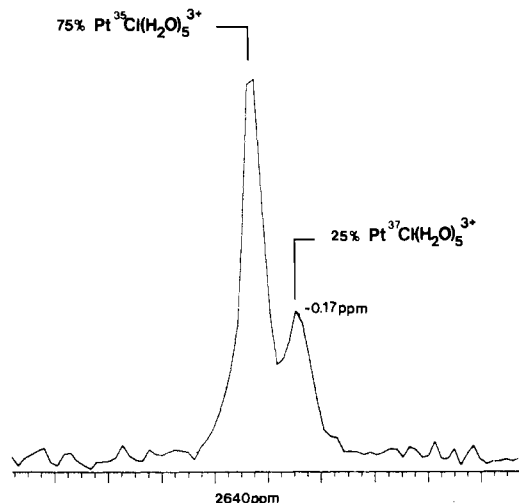
In Figure 2, 195-Pt NMR chemical shifts for the chloro-aquaplatinum(II) complexes  $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  are shown. The spectra for  $\text{PtCl}_4^{2-}$ ,  $\text{PtCl}_3(\text{H}_2\text{O})^-$ , and *cis*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  were obtained by use of a ca.  $40 \text{ mM}$  solution of  $\text{K}_2\text{PtCl}_4$  aged for ca.  $24 \text{ h}$  at  $25^\circ\text{C}$  in  $1.00 \text{ M HClO}_4$ .<sup>4,6,7</sup> Similarly, those of Pt-

(8) Elding, L. I. *Inorg. Chim. Acta* 1976, 20, 65.

**Table I.** Internuclear Oxygen-18 and Chlorine-37 Isotopic Shifts in  $\sigma_{\text{Pt}}$  in ppm<sup>a</sup>

complex	<sup>16</sup> O/ <sup>18</sup> O	<sup>35</sup> Cl/ <sup>37</sup> Cl	ref
Pt(H <sub>2</sub> O) <sub>4</sub> <sup>2+</sup>	-1.00		1
<i>trans</i> -PtCl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	-0.83	<i>b</i>	1
<i>trans</i> -PtCl <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup>	-0.63	<i>b</i>	1
PtCl(H <sub>2</sub> O) <sub>5</sub> <sup>3+</sup>	-0.72 (-0.71 <i>trans</i> )	-0.17	<i>c</i>
<i>mer</i> -PtCl <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> <sup>+</sup>	-0.82 (-0.82 <i>trans</i> )	≈0.2	<i>c</i>
PtCl <sub>5</sub> (H <sub>2</sub> O) <sup>-</sup>	-0.65	-0.17	<i>c</i>
PtCl <sub>6</sub> <sup>2-</sup>		-0.167	9

<sup>a</sup>Uncertainty ca. 0.01 ppm. <sup>b</sup>Not observed. <sup>c</sup>This work.



**Figure 3.** High-resolution spectrum of PtCl(H<sub>2</sub>O)<sub>5</sub><sup>3+</sup> showing a 0.17 ppm low-field isotopic shift of <sup>37</sup>Cl compared to <sup>35</sup>Cl. The relative intensities are determined by the natural occurrence (3:1) of the two isotopes. A negative (-10 Hz) exponential weight function for resolution enhancement has been applied.

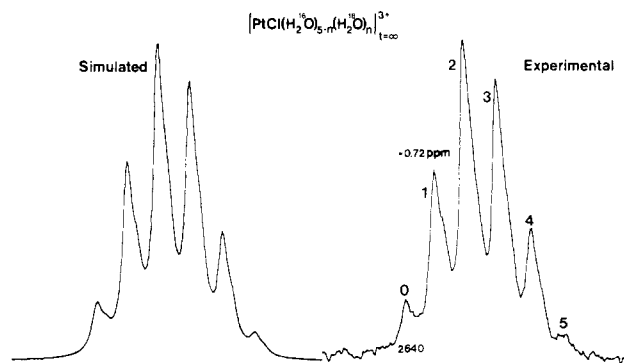
(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, PtCl(H<sub>2</sub>O)<sub>3</sub><sup>+</sup>, *trans*-PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, and *cis*-PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> were recorded by use of an equilibrated 0.10 M solution of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> in 1.00 M HClO<sub>4</sub> with 0.15 M chloride added.<sup>6,7</sup> All isotopic shifts have been summarized in Table I.

**Oxidation of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> with Chlorine.** The high-resolution spectrum in Figure 3 of the 2640 ppm resonance obtained by oxidation of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> in ordinary water shows the splitting due to the two <sup>35</sup>Cl/<sup>37</sup>Cl isotopomers of PtCl(H<sub>2</sub>O)<sub>5</sub><sup>3+</sup>. The relative intensity of the lines is approximately 3:1 in agreement with the natural abundance of the chlorine isotopes. The isotopic shift for <sup>37</sup>Cl relative to <sup>35</sup>Cl was measured to be -0.17 ppm, which is close to the value of -0.167 ppm reported for PtCl<sub>6</sub><sup>2-</sup>.<sup>9</sup>

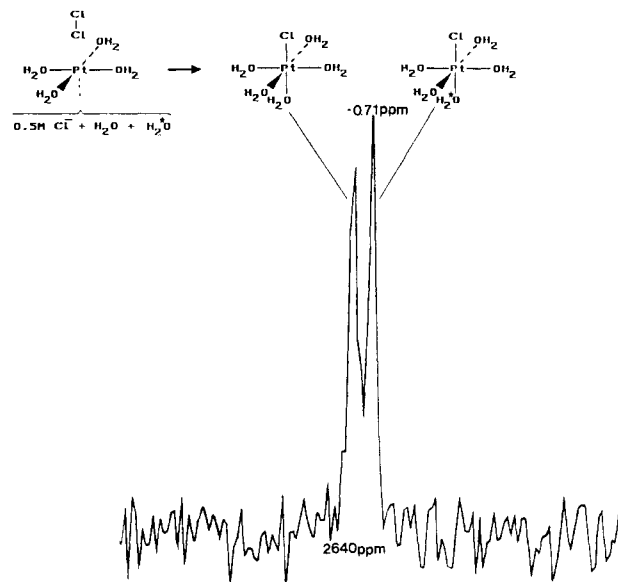
Figure 4 shows high-resolution spectra of the 2640 ppm signal for a solution obtained by oxidation of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, which had first been preequilibrated in oxygen-18 water. In this case, signals from all the six isotopomers (PtCl(H<sub>2</sub><sup>16</sup>O)<sub>5-n</sub>(H<sub>2</sub><sup>18</sup>O)<sub>n</sub><sup>3+</sup>, *n* = 0-5) are observed. The signals are equidistant within the experimental uncertainty, and the isotopic shift for H<sub>2</sub><sup>18</sup>O relative to H<sub>2</sub><sup>16</sup>O is 0.71 ppm.

It is apparent from the isotopic labeling experiments that the stereochemistry of the redox step involves a simple addition of one water molecule and one chloride trans to each other and perpendicular to the original coordination plane of platinum(II). No scrambling or water exchange of the four aqua ligands in the original platinum(II) coordination plane takes place.

Thus, when the spectrum of PtCl(H<sub>2</sub>O)<sub>5</sub><sup>3+</sup> was recorded by use of a solution of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> that had been oxidized immediately after addition of oxygen-18-enriched water, i.e. before any water exchange had occurred, only two oxygen isotopomers were observed as shown by Figure 5. The signal splitting is 0.71 ppm, and the intensity ratio is equal to the <sup>16</sup>O/<sup>18</sup>O mole ratio in the bulk. The two lines are assigned to *trans*-PtCl(H<sub>2</sub><sup>16</sup>O)<sub>4</sub>(H<sub>2</sub><sup>18</sup>O)<sup>3+</sup>



**Figure 4.** Spectra for oxygen isotopomers of PtCl(H<sub>2</sub>O)<sub>5</sub><sup>3+</sup>. The spectrum for the equilibrium distribution of PtCl(H<sub>2</sub><sup>18</sup>O)<sub>5-n</sub>(H<sub>2</sub><sup>16</sup>O)<sub>n</sub><sup>3+</sup> is shown on the right. The statistical distribution <sup>16</sup>O:<sup>18</sup>O = 0.536:0.464 is shown by the simulated spectra to the left. The spectrum was recorded by using a solution of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> (ca. 75 mM) that had been preequilibrated in oxygen-18-enriched water for 24 h before oxidation with chlorine. 10-Hz noise filtering removed most of the additional splitting due to the chlorine isotopic shift.



**Figure 5.** Spectrum of PtCl(H<sub>2</sub>O)<sub>5</sub><sup>3+</sup> recorded by use of a solution of Pt(H<sub>2</sub><sup>16</sup>O)<sub>4</sub><sup>2+</sup> in oxygen-18-enriched water immediately before oxidation with chlorine. The two signals originate from PtCl(H<sub>2</sub><sup>16</sup>O)<sub>5</sub><sup>3+</sup> and *trans*-PtCl(H<sub>2</sub><sup>16</sup>O)<sub>4</sub>(H<sub>2</sub><sup>18</sup>O), which are formed during the oxidation. The relative intensities are, within experimental error, H<sub>2</sub><sup>16</sup>O:H<sub>2</sub>O<sup>18</sup> = 0.47:0.53.

and *trans*-PtCl(H<sub>2</sub><sup>16</sup>O)<sub>4</sub>(H<sub>2</sub><sup>18</sup>O)<sup>3+</sup> formed in the redox step as one water molecule from the bulk adds. The same product is also obtained in 0.5 M chloride medium.

When H<sub>2</sub><sup>18</sup>O was added to PtCl(H<sub>2</sub><sup>16</sup>O)<sub>5</sub><sup>3+</sup>, no new lines appeared in the NMR spectrum over 12 h. Thus, the water exchange of both the *trans*- and the *cis*-aqua ligands in PtCl(H<sub>2</sub>O)<sub>5</sub><sup>3+</sup> is very slow. For the present purpose, only exchange of the *cis*-aqua ligands is critical, since the *trans* axis equilibrates during oxidation. However, the slow exchange in the *trans* position shows that it will be possible to study substrates like PtCl<sub>3</sub>(H<sub>2</sub>O)<sup>-</sup> where a nonequilibrated Cl-Pt-OH<sub>2</sub> axis will be inert after oxidation by use of the present technique.

**Oxidation of *trans*-PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> with Chlorine.** Oxidation of the *trans* isomer takes place in a manner similar to that of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>. In the exchange experiments with long aging times in oxygen-18 water and with excess chloride added, a substantial amount of the *trans* complex is converted to PtCl<sub>4</sub><sup>2-</sup>.<sup>6,7</sup> After oxidation, these two complexes are recovered as *mer*-PtCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub><sup>+</sup> and PtCl<sub>5</sub>(H<sub>2</sub>O)<sup>-</sup>, respectively.

**Kinetic Analysis.** The nonequilibrium distribution of oxygen isotopomers of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> and *trans*-PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> are recovered as frozen distributions in the corresponding platinum(IV) com-

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**Table II.** Rate Constants and Activation Parameters for Chloride Anation and Water Exchange of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  and *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ 

reaction	$k^{298}/\text{s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	ref
$\text{Pt}(\text{H}_2\text{O})_4^{2+} + {}^{18}\text{OH}_2$	$(4.8 \pm 0.1) \times 10^{-4a}$	$92.2 \pm 2$	$0 \pm 5$	e
$\text{Pt}(\text{H}_2\text{O})_4^{2+} + {}^{17}\text{OH}_2$	$(3.9 \pm 0.3) \times 10^{-4b}$	$89.7 \pm 2.4$	$-9 \pm 8$	3
$\text{Pt}(\text{H}_2\text{O})_4^{2+} + \text{Cl}^-$	$(6.65 \pm 0.04) \times 10^{-3c}$	$81.5 \pm 1$	$-13 \pm 2$	28, 7
<i>trans</i> - $\text{PtCl}_2(\text{H}_2\text{O})_2 + {}^{18}\text{O}_2$	$(1.6 \pm 0.2) \times 10^{-5}$	$100 \pm 3^d$	$-5 \pm 11^d$	e
<i>trans</i> - $\text{PtCl}_2(\text{H}_2\text{O})_2 + \text{Cl}^-$	$(2.92 \pm 0.04) \times 10^{-5c}$	$96 \pm 4$	$-13 \pm 13$	4, 6

<sup>a</sup>0.075 M  $\text{Pt}(\text{H}_2\text{O})_4(\text{ClO}_4)_2$  in 1.0 M  $\text{HClO}_4$ . <sup>b</sup>0.25 M  $\text{Pt}(\text{H}_2\text{O})_4(\text{ClO}_4)_2$  in 1.5 M  $\text{HClO}_4$ . <sup>c</sup>Unit:  $\text{s}^{-1} \text{M}^{-1}$ . <sup>d</sup>Estimated from  $\Delta G^\ddagger = 101.3 \text{ kJ mol}^{-1}$ , assuming that  $\Delta S^\ddagger$  is approximately the same as for the reaction with  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ . <sup>e</sup>This work.

plexes  $\text{PtCl}(\text{H}_2\text{O})_5^{3+}$  and *mer*- $\text{PtCl}_3(\text{H}_2\text{O})_3^+$ , respectively. Since the oxidation step only involves a simple addition of a  $\text{Cl}-\text{Pt}-\text{OH}_2$  axis perpendicular to the original coordination plane, the frozen distribution in the platinum(IV) complex is simply related to the original time-dependent distribution in the platinum(II) complex. The explicit expression giving the relative amounts of the six oxygen isotopomers of  $\text{PtCl}(\text{H}_2\text{O})_5^{3+}$  and the four oxygen isotopomers of *mer*- $\text{PtCl}_3(\text{H}_2\text{O})_3^+$  are given in eq 1 and 2, respectively.

$$\begin{aligned} \alpha_0(t) &= 1 \\ \alpha_1(t) &= Q_\infty + 4Q_t \\ \alpha_2(t) &= 4Q_\infty Q_t^2 + 6Q_t^2 \\ \alpha_3(t) &= 6Q_\infty Q_t^2 + 4Q_t^3 \\ \alpha_4(t) &= 4Q_\infty Q_t^3 + Q_t^4 \\ \alpha_5(t) &= Q_\infty Q_t^4 \end{aligned} \quad (1)$$

$$\begin{aligned} \alpha_0(t) &= 1 \\ \alpha_1(t) &= Q_\infty + 2Q_t \\ \alpha_2(t) &= 2Q_\infty Q_t + Q_t^2 \\ \alpha_3(t) &= Q_\infty Q_t^2 \end{aligned} \quad (2)$$

The equations are valid for a simple exchange process that occurs stepwise. Derivation of these expressions and the mechanistic information contained in the nonequilibrium isotopomer distribution are discussed further in the Appendix. The symbols in eq 1 and 2 are defined by eq 3, where  $X_{\text{O}^*}$  and  $X_{\text{O}}$  denote the bulk mole fraction of oxygen-18 and oxygen-16 water, respectively, and

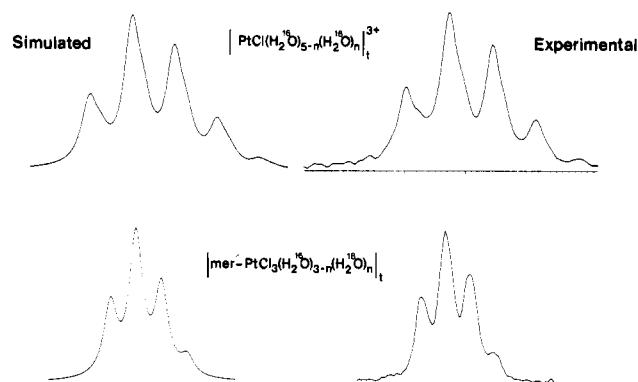
$$Q_t = \frac{X_{\text{O}^*} - X_{\text{O}^*} e^{-k_{\text{ex}} t}}{X_{\text{O}} + X_{\text{O}^*} e^{-k_{\text{ex}} t}} \quad (3)$$

$k_{\text{ex}}$  is the exchange frequency of a particular aqua ligand. In eq 1 and 2,  $Q_t$  is the only unknown parameter in each run that is needed to describe the relative intensities of the NMR signals.

Examples of experimental and calculated spectra for  $\text{PtCl}(\text{H}_2^{16}\text{O})_{5-n}(\text{H}_2^{18}\text{O})_n^{3+}$  ( $n = 0-5$ ) and *mer*- $\text{PtCl}_3(\text{H}_2^{16}\text{O})_{3-n}(\text{H}_2^{18}\text{O})_n^+$  ( $n = 0-3$ ) are shown in Figure 6. A line-shape function that fits the pure oxygen-16 complex was used in the fittings. The calculated spectra are within small random errors mirror images of the experimental ones, which gives a strong support for eq 1 to 3 and allows an accurate calculation of  $k_{\text{ex}}$ .

Water exchange on  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  was studied at 5.2, 15.2, 25.2 and 28.4 °C, giving the exchange rate constants  $3.03 \times 10^{-5}$ ,  $1.205 \times 10^{-4}$ ,  $4.78 \times 10^{-4}$  and  $7.00 \times 10^{-4} \text{ s}^{-1}$ , respectively. All simulated spectra using eq 1 gave excellent fits to the experimental spectra, which were recorded in the time interval  $(0.34-1.2)t_{1/2}$ .

Rate constants and activation parameters for the water exchanges and related chloride anations have been collected in Table II. An Arrhenius plot of  $\ln k_{\text{ex}}$  vs  $1/T$  for water exchange on  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  was strictly linear (5–30 °C). The trans complex was only studied at 25 °C, but the enthalpy change observed for the two chloride anation reactions in Table II and the parallel kinetic behavior for the water-exchange reaction suggest that the decrease in rate due to the change of cis ligand is mainly due to a change in activation enthalpy. Data for water exchange of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  has previously been obtained with two other methods.<sup>1,3</sup> The most accurate data obtained from a recent study<sup>3</sup> using oxygen-17 NMR are included in Table II for comparison with the present



**Figure 6.** Water exchange of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  and *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  visualized from nonequilibrium distributions of oxygen isotopomers in  $\text{PtCl}(\text{H}_2\text{O})_5^{3+}$  (top) and *mer*- $\text{PtCl}_3(\text{H}_2\text{O})_3^+$  (bottom). The relative intensities of the simulated spectra were obtained from eq 1 and 2, respectively, and  $k_{\text{ex}}$  was obtained from the parameter  $Q_t$  of eq 3.

results. All data for  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  agree within experimental errors.

## Discussion

The rate constants for halide anation and acid hydrolysis reactions of square-planar complexes of the type  $\text{MCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0-4$ ;  $\text{M} = \text{Pt}, \text{Pd}$ ) have been described previously by use of simple empirical relationships containing parameters for entering and leaving ligands and relative cis and trans effects.<sup>4,10</sup> The relative cis effect for a pair of ligands is smaller and of opposite sign compared to their relative trans effect. Attempts have been made to rationalize this behavior in terms of ligand field theory.<sup>11-13</sup> The 30-fold decrease of the water-exchange rate of *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  compared to  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  due to the presence of the two cis chlorides show that the cis effect operates for those simple water-exchange reactions, too.

If we apply a free energy relationship of the type shown in eq 4 to water exchange and chloride anation reactions of the series

$$\log(k_{\text{an}}/k_{\text{ex}}) = \alpha \log K_f + \beta \quad (4)$$

of complexes  $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0-4$ ), it is possible to use the two present exchange rate constants for  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  and *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  together with previous kinetic and thermodynamic data<sup>4,6-7</sup> to calculate  $\alpha = 0.62$  and  $\beta = -1.57$ .

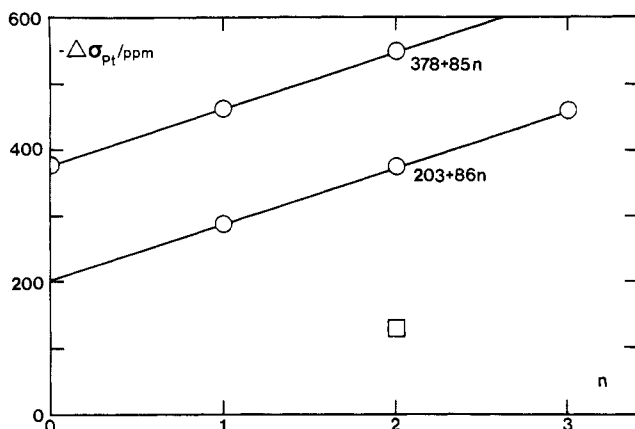
Equation 4 can then be used to estimate the rate constants for water exchange trans to chloride in the complexes  $\text{PtCl}(\text{H}_2\text{O})_3^+$ , *cis*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  and  $\text{PtCl}_3(\text{H}_2\text{O})^-$ . The calculated values are given in Table III. Although the calculation may be somewhat uncertain, it is probably quite safe to predict that the water exchange on all those three complexes is considerably faster than water exchange on  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ . In particular, the calculated water-exchange rate constant trans to chloride in  $\text{PtCl}(\text{H}_2\text{O})_3^+$  can be described by a relative trans effect  $\text{Cl}/\text{H}_2\text{O}$  of 140, in good agreement with previous estimations based on rate constants for

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**Table III.** Experimental and Calculated Values for Water-Exchange Rate Constants and Activation Parameters

complex	$\Delta V^\ddagger/\text{cm}^3 \text{ mol}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\text{mol}^{-1} k_{\text{ex}}/\text{s}^{-1}$	$(k_{\text{an}}/k_{\text{ex}})/M^{-1}$	$K_f/M^{-1}{}^c$	ref
$d^6\text{-Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	+1.2	111.3	$0.57 \times 10^{-5}$	0.5	1.6	14 <sup>d</sup>
$d^5\text{-Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	-3.2	91.5	$2.3 \times 10^{-4}$	2	$1.4 \times 10^2$	14
$d^6\text{-Rh}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	-4.1	102.9	$0.87 \times 10^{-5}$	2	$1.6 \times 10^2$	14 <sup>d</sup>
$d^6\text{-Ir}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	-4.0	117.6	$6.1 \times 10^{-8}$	4 <sup>a</sup>	$3.6 \times 10^3$ <sup>a</sup>	14 <sup>d</sup>
$d^8\text{-Pt}(\text{H}_2\text{O})_4^{2+}$	-4.6	92	$4.75 \times 10^{-4}$	14	$2.4 \times 10^4$	2, 4-7
$d^8\text{-PtCl}(\text{H}_2\text{O})_3^{2+}$			$6.5 \times 10^{-2b}$	7 <sup>b</sup>	$5.0 \times 10^3$	4-7; eq 4
$d^8\text{-trans-PtCl}_2(\text{H}_2\text{O})_2$		100	$1.58 \times 10^{-5}$	2	$9.0 \times 10^2$	4-7
$d^8\text{-cis-PtCl}_2(\text{H}_2\text{O})_2$			$1.8 \times 10^{-2b}$	2 <sup>b</sup>	$1.5 \times 10^3$	4-7; eq 4
$d^8\text{-PtCl}_3(\text{H}_2\text{O})^-$			$4.3 \times 10^{-3b}$	1 <sup>b</sup>	$5.0 \times 10^2$	4-7; eq 4

<sup>a</sup>  $(k_{\text{an}}/k_{\text{ex}})$  and  $K_f$  at 95 °C;  $k_{\text{ex}}$  at 25 °C. <sup>b</sup> Calculated from eq 4 with  $\alpha = 0.62$  and  $\beta = -1.57$ . <sup>c</sup>  $K_f$  denotes the formation constant for the higher chloro complex. The value has been corrected for the statistical factor. <sup>d</sup> From references quoted in ref 14.



**Figure 7.** Increments in  $\Delta\sigma_{\text{Pt}}$  for substitution of water by chloride as a function of cis and trans ligands in the  $\text{PtCl}_{4-n}(\text{OH}_2)_{2-n}$  system.  $n$  denotes the number of cis-chloride ligands in the complex.  $n = 0, 1, 2$ . A  $\square$  denotes  $\Delta\sigma_{\text{Pt}}$  for a complex in which the trans ligand is S-bonded  $\text{Me}_2\text{SO}$ .<sup>17</sup>

halide anation and acid hydrolysis reactions.<sup>4,6</sup>

The values given in Table III show that the experimental and calculated exchange rate constants parallel the previously determined chloride anation rate constants for those complexes. Such parallel behavior can also be observed for octahedral complexes, which is shown by the  $k_{\text{an}}/k_{\text{ex}}$  ratios for such complexes also given in Table III.

We have tried to use the NMR chemical shifts for an evaluation of the ground-state effects in the  $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}$  complexes. The increments in  $\sigma_{\text{Pt}}$  for the simple complexes considered here can be interpreted according to eq 5, which expresses the predominant

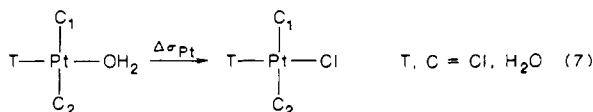
$$\Delta\sigma_{\text{Pt}} = -16\beta^2(r^{-3})_{\text{5d}}\Delta(C_{a_{1g}}^2 C_{\pi}^2 (\Delta E)^{-1}) \quad (5)$$

contributions to the paramagnetic term. The  $C$ 's denote the coefficients for the metal d orbitals in the LCAO expressions of  $D_{4h}$  symmetry with  $C_{a_{2g}} \approx C_{e_g} = C_{\pi}$ .  $\Delta E$  is the weighted average of the related spectroscopic energy differences.<sup>15,16</sup>

Since  $\pi$ -bonding should be unimportant in the chloro aqua complexes of platinum(II), eq 5 can be further simplified to eq 6 where  $C_{a_{1g}}^2$  is the coefficient for the metal  $d_{x^2-y^2}$  orbital.

$$\Delta\sigma_{\text{Pt}} \propto \Delta(C_{a_{1g}}^2/\Delta E) \quad (6)$$

In Figure 7, the six possible increments in  $\Delta\sigma_{\text{Pt}}$  for a substitution of the type shown in eq 7 have been plotted vs the number of cis-chloride ligands in the complex.



For a given trans ligand ( $\text{Cl}^-$  or  $\text{H}_2\text{O}$ ), the magnitude of  $\Delta\sigma_{\text{Pt}}$  increases with the number of chloride ligands in the cis position ( $n = 0, 1, 2$ ). On the other hand, when the trans ligand is changed from water to chloride, the increment is reduced significantly. The increase of  $\Delta\sigma_{\text{Pt}}$  when the cis chlorides are changed from water to chloride is independent of the nature of the trans ligand and all observed increments can therefore be described by additive contributions of opposite sign for trans- and cis-chloride ligands in the complex.

Both ligand field effects and covalency must be of importance for the bond strength. In the absence of any reliable theory, empirical correlations of the increments against known parameters such as bond distances are preferable. In Figure 7, a point for *trans*- $\text{PtCl}_2(\text{Me}_2\text{SO})(\text{H}_2\text{O})$  has also been included.<sup>17</sup> In this case, the decrease in the increment for trans-S-bonded  $\text{Me}_2\text{SO}$  compared to trans water parallels the increase in Pt-O bond length from 2.00 Å trans to oxygen to 2.05 Å trans to S-bonded  $\text{Me}_2\text{SO}$ .<sup>18,19</sup> The effect on  $\Delta\sigma_{\text{Pt}}$  for substitution of chloride by bromide has been extensively investigated.<sup>16,20</sup>

If it is assumed that a reduced interaction with the metal d orbital for the substituted water ligand is reflected in the increments, we arrive at the conclusion that the ground-state effect of halide on coordinated water is significant but mainly trans directional in these chloro aqua complexes of platinum(II). The trans influence is probably important for the large difference in water exchange rate between *cis*- and *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ .

A perturbation calculation<sup>21</sup> has shown, that the introduction of a better  $\sigma$ -donor ligand  $L'$  into square-planar  $d^8\text{-ML}_4$  or octahedral  $d^6\text{-ML}_6$  complexes always weakens the bond to the ligand  $L$  in the trans position by a reduction of the s- and d-orbital contributions to the bond. For the cis ligands, these two contributions must change in opposite directions, and the net effect on total bond strength may be of any sign. As a rule the d component should decrease, but the opposite trend cannot be excluded.<sup>21</sup>

It is clear that the rate of water exchange is not only a function of the metal-water bond properties in the ground state. However, irrespective of mechanism, it seems reasonable to assume that a significant ground-state bond weakening should increase rather than decrease the water-exchange rate. We therefore found the relations between the empirical and theoretical ground-state effects described above worth noting.

Water exchange data showing the effect of cis and trans halide for the inert octahedral  $d^6$  systems are still lacking. However, cis and trans effects for halide anation in the dissociatively activated rhodium(III) chloro-aqua system are very similar to those found in the present platinum(II) system.<sup>22</sup>

**Isotopic Shifts.** The magnitudes of the oxygen isotopic shifts at different sites on the same complex are virtually the same trans to chloride and trans to water; cf. Table I. In *mer*- $\text{PtCl}_3(\text{H}_2\text{O})_3^+$ , no difference could be observed, and for  $\text{PtCl}(\text{H}_2\text{O})_5^{3+}$ , the dif-

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ference is ca. 10 times smaller than the total range observed. It does not seem very likely that the two sites are equivalent. A substantial trans influence much larger than the cis influence has been observed in the analogous  $\text{PtCl}_{5-n}\text{F}_n^{2-}$  system.<sup>23</sup> In  $\text{PtClF}_5^{2-}$  the force constant for the Pt-F stretching trans to Cl is 2.87 N/cm while it is 3.35 N/cm cis to Cl.<sup>23</sup> The Pt-F spin coupling data give a similar trend with values of 1000 Hz trans to Cl and 2000 Hz trans to F.<sup>24</sup> A similar ratio of the trans/cis influence is expected for the chloro-aqua system.

It might also be of interest to compare the magnitudes of the chloride and the oxygen isotopic shifts in  $\text{PtCl}(\text{H}_2\text{O})_3^+$  by taking the differences in relative masses of the isotopes into account. As a first approximation, the mass dependence is given by eq 8 where

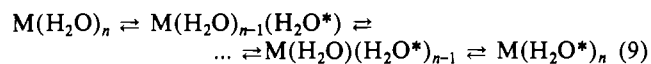
$$\sigma_{m_1} - \sigma_{m_2} \propto [1 - (m_1/m_2)^{1/2}] \quad (8)$$

$m_1$  and  $m_2$  are the masses of the lighter and heavier isotopes, respectively.<sup>25</sup> A correction for this factor will increase the  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopic shift relative to that of  $^{16}\text{O}/^{18}\text{O}$  by a factor of 2, which is too small to reverse the observed magnitudes with ratios around 1:4. A comparable change in relative mass will then produce a larger isotopic shift for coordinated water than for coordinated chloride in these platinum(IV)-chloro-aqua complexes. It should also be noted that the smaller isotopic shift for *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  compared to  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  is not accompanied by a similar trend in the cooperative chemical shift due to Cl/ $\text{H}_2\text{O}$  substitution: the value for  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  of -379 ppm is considerably smaller than that observed for *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ , which is -549 ppm, cf. Figure 2.

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#### Appendix

Consider a water-exchange reaction initiated by isotopic dilution of a complex  $\text{M}(\text{OH}_2)_n$  where all the ligands to be exchanged are at equivalent positions. It is assumed for simplicity that the metal concentration is much smaller than the molarity of water so that the isotopic composition in the bulk will not change significantly during a run. The equilibrium system is indicated by eq 9. In



order to simplify the treatment we introduce the fraction  $f_k(t)$  defined as the subgroup of all metal ions where precisely  $n - k$  of the aqua ligands present at zero time remain unexchanged at time  $t$ .

The fraction of a particular species of composition  $\text{M}(\text{H}_2\text{O})_{n-k}(\text{H}_2\text{O}^*)_k$  denoted  $\alpha_i(t)$  will be equal to  $f_k(t)$  if the mole fraction of labeled ligand in the bulk is equal to unity. In a more general case, we obtain  $\alpha_i(t)$  as a sum over all  $f_k(t)$  with  $k \geq i$  according to eq 10. The distribution within each such group is

$$\alpha_i(t) = \sum_{k=i}^n \binom{n}{k} X_{\text{O}^*}^{k-i} X_{\text{O}}^{i-k} f_k(t) \quad (10)$$

constant with time since consecutive exchanges only cause statistical fluctuations. The probability  $P_i$  for no exchange at one particular site during the time interval is related to the water exchange frequency  $k_{\text{ex}}$  at that site by the general expression  $P_i = e^{-k_{\text{ex}}t}$ . In addition, the relation between population mean values and probabilities assures that the numerical value of  $f_k(t)$  can be expressed as the probability for no exchange at  $n - k$  sites and

at least one exchange at the remaining  $k$  sites.

An expression for  $f_k(t)$  in terms of  $P_i$  would then easily be obtained if it could be assumed that the exchange at different sites in the same molecule are independent events.

However, this is not a general condition for isotopic exchange of equivalent ligands in a  $\text{ML}_n$  complex, and accurate nonequilibrium distributions of isotopomers may therefore give a unique insight into a complex mechanism.<sup>26,27</sup> However, from a practical point of view, it seems most expedient first to compare the experimental values of  $\alpha_i(t)$  with a theoretical expression that is valid for independent exchange. Other alternatives can be examined if significant deviations between experimental and theoretical distributions are observed. Thus, in the case of independent exchange at the different sites in the  $\text{M}(\text{H}_2\text{O})_n$  complex,  $f_k(t)$  is given by eq 11. After rearrangement, eq 10 and 11 give eq 12,

$$f_k(t) = \binom{n}{k} P_i^{n-k} (1 - P_i)^k \quad (11)$$

which is transformed to eq 13. Expressing these values relative

$$\alpha_i(t) = \binom{n}{i} [X_{\text{O}^*} - X_{\text{O}^*} P_i]^i \sum_{k=i}^n \binom{n-i}{n-k} [X_{\text{O}} + X_{\text{O}^*} P_i^{k-i}] P_i^{n-k} \quad (12)$$

$$\alpha_i(t) = \binom{n}{i} [X_{\text{O}^*} - X_{\text{O}^*} e^{-k_{\text{ex}}t}]^i [X_{\text{O}} + X_{\text{O}^*} e^{-k_{\text{ex}}t}]^{n-i} \quad (13)$$

to  $\alpha_0(t)$  gives eq 14, where  $Q_i$  is defined by eq 15. The char-

$$\alpha_i(t) = \frac{\alpha_i(t)}{\alpha_0(t)} = \binom{n}{i} Q_i^i \quad (14)$$

$$Q_i = \frac{X_{\text{O}^*} - X_{\text{O}^*} e^{-k_{\text{ex}}t}}{X_{\text{O}} + X_{\text{O}^*} e^{-k_{\text{ex}}t}} \quad (15)$$

acteristic feature of eq 14 is that the distribution of the different species  $\text{M}(\text{H}_2\text{O})_{n-i}(\text{H}_2\text{O}^*)_i$  looks like an equilibrium distribution at all times except that the molar ratios of the isotopes are replaced by the single parameter  $Q_i$ . Equation 3, which was used in the fitting procedure, is obtained from eq 13 by considering the effect of oxidation;  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  gives statistical amounts of  $\text{PtCl}(\text{H}_2\text{O})_3^{3+}$  and  $\text{PtCl}(\text{H}_2\text{O})_4(\text{H}_2^{18}\text{O})^{3+}$ , etc. Equation 3 contains information on both  $Q_i$  and  $Q_{\infty}$ , and the spectrum is therefore self-consistent with  $k_{\text{ex}}$  as the only unknown parameter.

**Side Reactions.** In the experiments with *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  the total concentration of the complex decreased irreversibly due to a second-order chloride anation. The time dependence of this drift is denoted  $dC_i/dt$  and the absolute concentration of a par-

(26) Intermediates of exceedingly low concentrations in equilibrium with the substrate may cause deviations from independent exchange, if the intermediate contributes to the exchange of the substrate studied. For example, consider the effect of a symmetric *tbp* intermediate in true equilibrium with the  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  substrate (A mechanism). Exchange of equatorial water ligands in the *tbp* by a mechanism that opens the trigonal plane and passes via a six-coordinated transition state is then possible. Equation 13 will then be modified to eq 19 where the pa-

$$\alpha_i(t) = \sum_{i=j+j'} f_j f_{j'} \quad i \in \{0, 1, 2, 3, 4\} \quad j, j' \in \{0, 1, 2\} \quad (19)$$

$f_j =$

$$\binom{?}{j} [(X_{\text{O}^*} - X_{\text{O}^*} e^{-k_{\text{ex}}t})^j (X_{\text{O}} + X_{\text{O}^*} e^{-k_{\text{ex}}t})^{2-j} + (-1)^j X_{\text{O}^*}^2 (e^{-2k_{\text{ex}}t/(1+\lambda)} - e^{-2k_{\text{ex}}t})]$$

rameter  $\lambda$  ranges from unity when the exchange is fast compared to the average lifetime of the *tbp* to zero when exchange is slow on this time scale. A similar expression is also valid for an second-order axial equatorial inversion process. Deviation from eq 14 will be large if inversion is slow compared to axial exchange.

(27) The time-dependent fraction of label in the whole metal system, which usually is measured in isotopic dilution kinetics, is  $F = n^{-1} \sum \alpha_i(t)$ . It should be noted that  $F$  approaches its equilibrium value as a first-order process. This relation is invariant for all possible mechanisms and therefore gives no further mechanistic information.

(28) All values in Table III have been corrected for the statistical factor. The reaction  $\text{Pt}(\text{H}_2\text{O})_4^{2+} + \text{Cl}^- \rightarrow \text{PtCl}(\text{H}_2\text{O})_3^+ + \text{H}_2\text{O}$  has been studied in the temperature range -2 to +60 °C, giving  $\Delta S^\ddagger = -1.6 \pm 1.6 \text{ J K}^{-1} \text{ mol}^{-1}$  or, corrected for statistics,  $-13.1 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$ .

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ticular isotopomer is denoted  $y_i$ . The fraction  $\alpha_i(t)$  is defined as  $\alpha_i(t) = y_i/C_i$ . If the water exchange is first-order in complex, we get eq 16, where  $c_j$  in the sum accounts for mole fractions,

$$dy_i/dt = \sum c_j y_j + \alpha_i(t) dC_i/dt \quad \alpha_i(0) = 1 \quad (16)$$

$$j = 0, 1, 2$$

statistical factors, and exchange constants for the isotopic equilibration process. The last term originates from the fact that isotopic effects on the irreversible side reaction are negligible. The time derivative of  $\alpha_i(t)$  is given by eq 17, where the expression for  $dy_i/dt$  can be substituted into eq 16 to give eq 18. An identical

$$d\alpha_i(t)/dt = C_i^{-1} dy_i/dt - y_i C_i^{-2} dC_i/dt \quad (17)$$

$$d\alpha_i(t)/dt = C_i^{-1} \sum c_j y_j = \sum c_j \alpha_j(t) \quad (18)$$

equation can be derived when the substrate concentration is constant with time (divide eq 16 with  $C_0$  and let  $dC_i/dt = 0$ ). Thus, a complex undergoing side reactions can be treated as any stable  $MS_n$  complex as long as (i) water exchange is first-order with respect to complex and (ii) the relative concentrations  $\alpha_i(t)$  of isotopomers can be measured.

Registry No.  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ , 60911-98-0; *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ , 13876-96-5; Pt, 7440-06-4.

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## Di(phosphine)-Bridged Complexes of Palladium. Parahydrogen-Induced Polarization in Hydrogenation Reactions and Structure Determination of Tris( $\mu$ -bis(diphenylphosphino)methane)dipalladium, $\text{Pd}_2(\text{dppm})_3$

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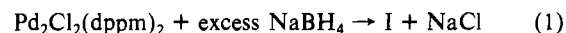
Reduction of  $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$  ( $\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$ ) with excess  $\text{NaBH}_4$  produces a dark purple solid, I, which shows a reaction chemistry consistent with the stoichiometry  $\text{Pd}_2\text{H}_x(\text{dppm})_2$ . Reaction of I with excess  $\text{dppm}$  produces the known compound  $\text{Pd}_2(\text{dppm})_3$ . Crystals of  $\text{Pd}_2(\text{dppm})_3$  are monoclinic in space group  $P2_1/c$  with cell dimensions  $a = 14.733$  (5) Å,  $b = 14.760$  (5) Å,  $c = 29.720$  (6) Å, and  $\beta = 97.44$  (1)°. The structure of  $\text{Pd}_2(\text{dppm})_3$  is similar to that of the structurally characterized  $\text{Pt}_2(\text{dppm})_3$  analogue with approximate  $C_{3h}$  symmetry. A total of 1 equiv of  $\text{H}_2$  and 1 equiv of methane is evolved per 3  $\text{Pd}(\text{dppm})$  units when I is treated with aqueous HCl and methyl iodide, respectively. The corresponding metal-containing products are  $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$  and a mixture of  $[\text{Pd}_2\text{I}(\text{CH}_3)(\text{dppm})_2]\text{I}$  and  $\text{PdI}_2(\text{dppm})$ . The latter compound is also obtained upon oxidation of I with  $\text{I}_2$ . Reaction of I with  $\text{CH}_2\text{I}_2$  in dichloromethane yields a mixture of  $\text{Pd}_2\text{I}_2(\mu\text{-CH}_2)(\text{dppm})_2$  and  $\text{Pd}_2\text{Cl}_2(\mu\text{-CH}_2)(\text{dppm})_2$ , while reaction with either  $\text{Me}_3\text{SiCl}$  or  $\text{Me}_2\text{SiCl}_2$  produces  $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$ . Complex I is active in the catalytic hydrogenation of alkenes and alkynes. Parahydrogen-induced polarization (PHIP) is observed in the styrene product when solutions of I and phenylacetylene in  $\text{CDCl}_3$  are stored at  $-196$  °C under 3–4 atm of  $\text{H}_2$  for >8 h prior to reaction at 60–70 °C. Similar results are obtained when para-enriched  $\text{H}_2$  is used without the storage time. Complex I decomposes upon heating in  $\text{CDCl}_3$  to mixtures of  $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$ ,  $\text{PdCl}_2(\text{dppm})$ , and an unidentified red palladium compound. While this mixture is also active in hydrogenation and gives rise to PHIP,  $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$  by itself gives weak polarization under hydrogenation conditions and  $\text{PdCl}_2(\text{dppm})$  gives no polarization.

### Introduction

Binuclear di(phosphine)-bridged hydride complexes incorporate two key features for the study of metal-catalyzed reactions. First, metal hydrides play an important role in hydrogenation, hydroformylation, and CO reduction chemistry,<sup>1,2</sup> and second, the proximity of two metal centers in binuclear systems can lead to unusual reactivity.<sup>3–5</sup> For these reasons, the preparation and reaction chemistry of binuclear  $\text{dppm}$ -bridged ( $\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$ ) hydride complexes have been a focus of our research. Recently, our interest in this class of compounds was stimulated by an unusual series of observations in the reaction chemistry of  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$  with unsaturated organic substrates.<sup>6–9</sup> Specifically, when hydrogenation reactions of

alkynes by  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$  were monitored by  $^1\text{H}$  NMR spectroscopy at early reaction times, extraordinary NMR absorptions and emissions were observed in the product resonances.<sup>7</sup> This series of observations, which has now been shown to be due to parahydrogen-induced polarization,<sup>8</sup> prompted efforts to prepare  $\text{dppm}$ -bridged complexes containing other platinum group elements that would show similar properties in hydrogenation catalysis.

In this paper, we report one such system that forms in the reaction of  $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$  with excess  $\text{NaBH}_4$ , eq 1. This system,



which we refer to as I, has not been characterized definitively, although it is an effective hydrogenation catalyst and its reaction chemistry shows it to be consistent with  $\text{Pd}_2\text{H}_x(\text{dppm})_2$ . In the course of characterizing I, we found that its reaction with excess  $\text{dppm}$  led to the formation of  $\text{Pd}_2(\text{dppm})_3$ , which we have examined by X-ray diffraction. This structure determination is fully described in this paper.

The complex  $\text{Pd}_2(\text{dppm})_3$  was reported in 1972 by Stern and Maples,<sup>10</sup> who examined its catalytic activity with regard to ho-

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