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## Kinetics and Mechanism of the Formation, Aquation, and Base Hydrolysis Reactions of a Series of Monodentate Carbonato Complexes of Palladium(II)<sup>1</sup>

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The formation reactions of a series of complexes of the type Pd(R<sub>3</sub>dien)OCO<sub>2</sub>, where R<sub>3</sub>dien = dien (diethylenetriamine), 1,1,7,7-Me<sub>4</sub>dien, and 1,1,7,7-Et<sub>4</sub>dien, were studied as a function of pH, [total carbonate], and temperature. The kinetic data clearly demonstrate that these complexes are not produced via the expected CO<sub>2</sub>-uptake mechanism (as found for octahedral complexes) but rather via anation of the aquo complex by bicarbonate/carbonate ion. These complexes also undergo acid-catalyzed aquation and base hydrolysis reactions. The temperature and pressure dependencies of the last reactions were studied in detail, and the activation parameters suggest an associative solvolysis reaction path. The results are discussed in reference to the previously reported data for the formation and acidification reactions of octahedral carbonato complexes, and the substitution reactions of square-planar Pd(II) complexes.

### Introduction

The formation reactions and reactivity of transition-metal carbonato and carbon dioxide complexes have received significant attention from numerous groups in recent years.<sup>2</sup> This is partly due to the advances in the area of metal carbon dioxide complexes, i.e. organometallic chemistry, the greater interest from biologists, environmentalists, geochemists, and oceanographers in such complexes, and the generally improved understanding of the underlying reaction mechanisms. These aspects were emphasized in a recent review article,<sup>2</sup> which called our attention to a number of areas in need of detailed investigations to complete the overall picture. One of these is the topic of the present report.

Harris and co-workers<sup>3</sup> have demonstrated unequivocally that nonlabile octahedral metal aquo and hydroxo species can react rapidly with dissolved CO<sub>2</sub> in aqueous medium to produce carbonato complexes via CO<sub>2</sub> addition to coordinated hydroxide, i.e. without metal-oxygen bond cleavage. This reaction route has significant advantages over the conventional substitution route involving slow metal-oxygen bond breakage. Later work<sup>4-11</sup> showed that O-bonded nitrito and sulfito complexes are also formed via the addition of NO<sup>+</sup> and SO<sub>2</sub> to coordinated hydroxide, respectively. It is, however, unknown how labile metal aquo and hydroxo species, for instance the corresponding square-planar complexes of Pd(II) and Pt(II), would behave under such conditions. Competition between substitution reactions involving bicarbonate and carbonate ion, and addition and elimination reactions involving carbon dioxide, are expected to occur in such systems.

In contrast to the large number of octahedral carbonato complexes investigated along these lines before,<sup>3</sup> very little has been reported on analogous square-planar complexes.<sup>2,12-15</sup> More has been reported with respect to carbon dioxide complexes of Pt(II) and Pd(II),<sup>16</sup> including fixation and insertion reactions. Furthermore, our interest in the spontaneous solvolysis reactions of

square-planar complexes in general<sup>17,18</sup> and of sterically hindered Pd(II) complexes in particular<sup>19</sup> has emphasized the importance of intermediate solvento complex species and the possible role they could play in the antitumor and catalytic activity of such complexes. The behavior of such square-planar aquo/hydroxo species in the presence of the carbon dioxide/bicarbonate/carbonate system is, therefore, of fundamental importance.

In this study we have selected a series of dien (diethylenetriamine) and substituted dien complexes of Pd(II) for which the lability of the aquo ligand varies over several orders of magnitude. The kinetics and mechanism of the formation, aquation, and base hydrolysis reactions of the corresponding monodentate carbonato complexes were investigated.

### Experimental Section

**Materials.** The following complexes were prepared as described in the literature:<sup>20,21</sup> [Pd(dien)Cl]ClO<sub>4</sub>; [Pd(1,1,7,7-Me<sub>4</sub>dien)Cl]ClO<sub>4</sub>; [Pd(1,1,7,7-Et<sub>4</sub>dien)Cl]ClO<sub>4</sub>. These were subjected to chemical analyses (Hoechst Analytical Laboratory, Frankfurt, West Germany), and the results were in excellent agreement with the theoretically expected values. The chloro complexes were converted into the aquo analogues in solution by adding an equivalent amount of AgClO<sub>4</sub>, heating to 40 °C for 1 h and removing the AgCl precipitate by filtering through a 0.1 μm pore membrane filter. Great care was taken to ensure that the resulting solutions were free of Ag<sup>+</sup> ions and that the chloro complexes had been converted completely into the aquo species.

Various procedures were adopted to synthesize the corresponding monodentate carbonato complexes in solution. It has been reported<sup>22</sup> that octahedral carbonato complexes involving nonlabile metal centers can in general be synthesized by bubbling CO<sub>2</sub> gas through or adding NaHCO<sub>3</sub> to a solution of the metal hydroxo complex, prepared by the addition of base to a solution of the corresponding aquo complex. In this study it was found that addition of NaHCO<sub>3</sub> introduced small quantities of chloride impurities into the solution, which rapidly reacted with the labile metal aquo species to produce the corresponding chloro complex. We therefore adopted the CO<sub>2</sub> gas method and constantly added 1 M NaOH dropwise to control the pH of the solution between 8.5 and 9.0. Special care was taken to avoid chloride contamination during pH measurements with a glass electrode. In contrast to earlier work involving less labile metal centers,<sup>22</sup> a significant excess of bicarbonate ion in solution was required to stabilize the carbonato complex. We were unsuccessful in our attempts to isolate the carbonato complexes in their pure form due to the presence of this large excess of NaHCO<sub>3</sub>. Stock solutions of the complexes were found to be stable at pH ~8.5 over several days.

Chemicals of analytical reagent grade and doubly distilled water were used to prepare all stock solutions. Sodium perchlorate was used to adjust the ionic strength of the test solutions.

**Measurements.** UV-visible absorption spectra were recorded on a Perkin-Elmer 555 spectrophotometer. Acid dissociation constants of the various aquo complexes were determined spectrophotometrically according to the method described before.<sup>21</sup> A Radiometer PHM 64 in-

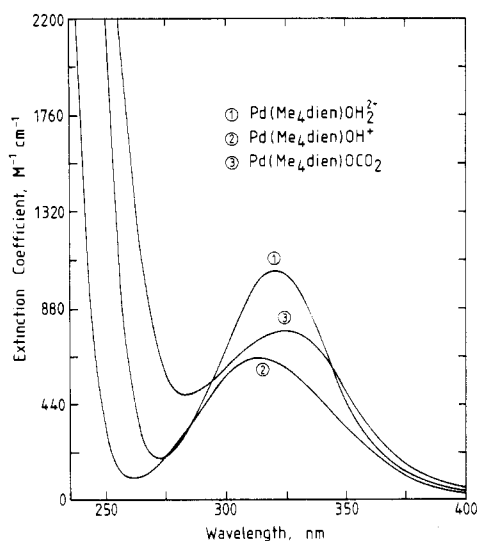
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**Table I.** Spectral Data for a Series of dien Complexes of Pd(II)

complex species	$\lambda_{\max}^a$ , nm	$\epsilon^a$ , $M^{-1} cm^{-1}$	$\lambda_{\max}^b$ , nm	$\epsilon^b$ , $M^{-1} cm^{-1}$	$\epsilon$ at 260 nm, <sup>a</sup> $M^{-1} cm^{-1}$
Pd(dien)Cl <sup>+</sup>	330	460	330–332	460–480 <sup>c</sup>	
Pd(dien)OH <sub>2</sub> <sup>2+</sup>	313	480	313	511 ± 2	60
Pd(dien)OH <sup>+</sup>	309	380	309	410 ± 4	50
Pd(dien)OCO <sub>2</sub>	316	470			800
Pd(Me <sub>4</sub> dien)Cl <sup>+</sup>	332	805	332–340	810–800 <sup>c</sup>	
Pd(Me <sub>4</sub> dien)OH <sub>2</sub> <sup>2+</sup>	320	1052	320	1088 ± 16	657
Pd(Me <sub>4</sub> dien)OH <sup>+</sup>	313	635	313	644 ± 9	110
Pd(Me <sub>4</sub> dien)OCO <sub>2</sub>	325	800			1500
Pd(Et <sub>4</sub> dien)Cl <sup>+</sup>	346	890	348	860	
Pd(Et <sub>4</sub> dien)OH <sub>2</sub> <sup>2+</sup>	327	1120	329	1140	2000
Pd(Et <sub>4</sub> dien)OH <sup>+</sup>	322	696	322	728	180
Pd(Et <sub>4</sub> dien)OCO <sub>2</sub>	338	810			1720

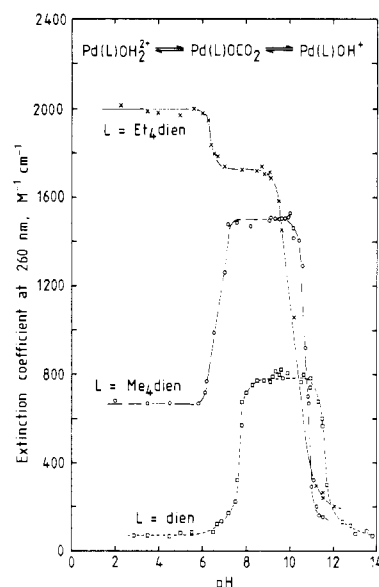
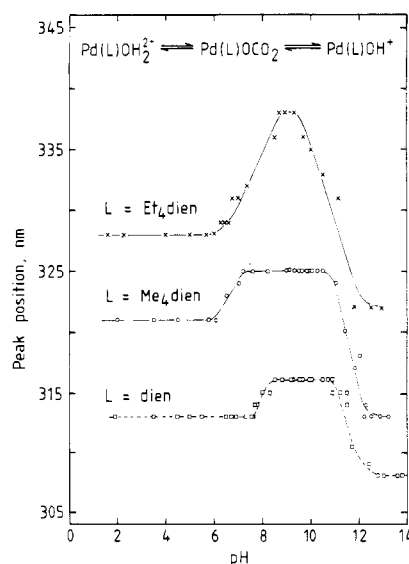
<sup>a</sup>This work. <sup>b</sup>Data reported in ref 20, 21, and 35. <sup>c</sup>Spectral differences due to spontaneous solvolysis.<sup>19,21</sup>

**Figure 1.** UV-visible absorption spectra of a series of 1,1,7,7-Me<sub>4</sub>dien complexes of Pd(II).

strument whose reference electrode was filled with a 3 M NaCl solution was used for all pH measurements. Kinetic measurements at ambient pressure were performed in the thermostated cell compartment of the mentioned spectrophotometer and on an Aminco stopped-flow instrument. At elevated pressures up to 150 MPa a Zeiss PMQ II spectrophotometer equipped with a high-pressure cell<sup>23</sup> and a specially designed high-pressure stopped-flow unit<sup>24</sup> was used. First-order rate constants were calculated in the usual way, and the corresponding first-order plots proved to be linear for at least 3 half-lives of the reaction.

### Results and Discussion

UV-visible absorption spectral data for the chloro, aquo, hydroxo, and carbonato complexes are summarized along with the available literature data in Table I. The present results are in good agreement with the earlier reported data. A typical example of the spectra for one of the series of complexes is given in Figure 1. Carbonate complex formation is accompanied by significant spectral changes in the UV region. This is in agreement with the general tendency observed for octahedral monodentate carbonato complexes.<sup>2</sup> The absorbance around 260 nm is significantly higher for the carbonato than for the corresponding hydroxo complexes (see Figure 2). These charge-transfer bands can be ascribed<sup>25,26</sup> to intramolecular hydrogen bonding between the monodentate carbonate and the dien ligands. In the case of the unsubstituted ligand this interaction most probably involves the N-H protons, whereas for the substituted ligands hydrogen bonding with the

**Figure 2.** pH dependence of the extinction coefficient at 260 nm for a series of dien and substituted dien complexes of Pd(II).**Figure 3.** pH dependence of the peak position for a series of dien and substituted dien complexes of Pd(II).

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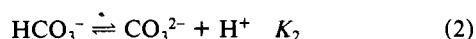
methyl or ethyl protons is bound to occur. Since these are removed further away from the coordinating atom, smaller spectral changes are expected to accompany them.

The stability of the carbonato complexes can be well characterized by studying their UV-visible spectra as a function of pH,

for which the results are summarized in Figures 2 and 3. The molar extinction coefficient at 260 nm and the position of the peak maximum exhibit distinct pH dependencies. These data were obtained by adding acid or base to solutions of the carbonato complexes and demonstrate that these complexes are usually stable over a pH range between 8 and 10. The trend in the shift in the absorbance maximum is the same for all the studied complexes, viz. a shift to longer wavelength in going from the hydroxo to the aquo to the carbonato complexes. Despite our inability to isolate the carbonato complexes in their pure form, we are confident that our earlier experience with such systems<sup>2,19,21,27,28</sup> and our understanding of the chemistry involved enable us to interpret the very characteristic spectral properties outlined above. The large spectral changes around 260 nm were employed in the kinetic analysis of the formation, aquation, and hydrolysis reactions of the carbonato complexes.

The acid dissociation constants of the aquo complexes were found to be 7.5, 8.1, and 8.2 at 25 °C and 1 M ionic strength for the dien, Me<sub>4</sub>dien, and Et<sub>4</sub>dien complexes, respectively. These values are in close agreement with those reported elsewhere,<sup>21</sup> especially when the difference in ionic strength is taken into account.

**Carbonato Complex Formation.** The nature of the complex formation process is of fundamental importance in the understanding of the chemistry involved. As pointed out above, two possible reaction routes exist, viz. CO<sub>2</sub> uptake by the metal hydroxo species or substitution of the aquo/hydroxo ligand by bicarbonate/carbonate ion. CO<sub>2</sub>-uptake reactions can be studied according to two different kinetic procedures,<sup>29</sup> viz. (i) the acidification method and (ii) the equilibration method. In method i a sodium bicarbonate solution (usually 0.02 M) is carefully acidified to pH ~3 and then mixed with a buffered solution of the metal hydroxo species (usually at pH ~8–9). The uncatalyzed rate of CO<sub>2</sub> hydrolysis is considerably slower than the CO<sub>2</sub>-uptake reaction.<sup>2</sup> This method could not be used in the present study since most of the employed buffers tended to react with the labile metal aquo/hydroxo species and complicated the kinetic interpretation. Buffers of low coordination ability<sup>30</sup> unfortunately completely overruled the spectral properties of the studied complexes in the UV region. In method ii the metal aquo complex is mixed with a bicarbonate/carbonate buffer solution for which the equilibrium concentration of CO<sub>2</sub>(aq) is determined by equilibria 1 and 2. [CO<sub>2</sub>(aq)] can be calculated from eq 3. At



$$[\text{CO}_2(\text{aq})] = \frac{[\text{H}^+]^2[\text{total carbonate}]}{([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2)} \quad (3)$$

low [total carbonate] or at high pH, [CO<sub>2</sub>(aq)] is such that it is not in excess over the complex ion, and micromolar quantities of carbonic anhydrase were introduced to ensure rapid maintenance of equilibria 1 and 2. In this way pseudo-first-order conditions could be secured in case the process does follow the suggested CO<sub>2</sub>-uptake reaction path. In this case the carbonate system is self-buffering and the introduction of foreign buffers could be avoided.

A series of preliminary experiments was performed to elucidate the nature of the carbonato complex formation process. The kinetics of the reaction was studied in the pH range 8–9 as a function of [total carbonate], pH, and [carbonic anhydrase]. The first-order rate constant,  $k_{\text{obsd}}$ , increases with increasing [total carbonate], decreases with increasing pH, and exhibits no meaningful dependence on [carbonic anhydrase] (see Table II for

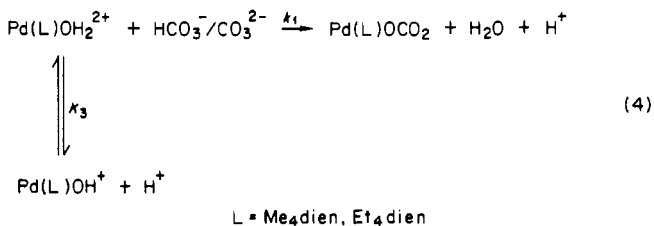
**Table II.** Preliminary Rate Data for the Formation of Pd(II) Carbonato Complexes<sup>a</sup>

complex species	[total carbonate], M	[CA], <sup>b</sup> μM	pH	10 <sup>3</sup> × [CO <sub>2</sub> ], <sup>c</sup> M	$k_{\text{obsd}}$ , <sup>d</sup> s <sup>-1</sup>	
Pd(Me <sub>4</sub> dien)OH <sub>2</sub> <sup>2+</sup>	0.33	...	8.3	1.7	13.2	
			8.4	1.0	9.7	
			8.6	0.83	7.6	
			8.7	0.65	6.5	
			8.9	0.40	5.3	
			3	8.3	1.7	11.4
				8.4	1.0	9.2
				8.6	0.83	6.8
				8.7	0.65	6.4
				8.9	0.40	5.3
Pd(Et <sub>4</sub> dien)OH <sub>2</sub> <sup>2+</sup>	0.33	...	8.4	...	0.15	
			0.25	0.12		
			0.21	0.092		
			0.16	0.074		
			0.11	0.062		
Pd(Me <sub>4</sub> dien)OH <sub>2</sub> <sup>2+</sup>	0.33	...	8.4	...	10.3	
				0.25	6.2	
				0.21	5.3	
				0.16	3.2	
				0.11	1.8	
				0.02	0.41	

<sup>a</sup> Conditions: temperature 25 °C, ionic strength 1 M, [Pd(II)] = 0.5 × 10<sup>-3</sup> M. <sup>b</sup> CA = carbonic anhydrase (see Results and Discussion). <sup>c</sup> Calculated by using eq 3 with pK<sub>1</sub> = 6.03 and pK<sub>2</sub> = 9.80. <sup>d</sup> Mean value of at least four kinetic runs.

some typical results). Furthermore, excellent first-order plots were observed in the absence of carbonic anhydrase under conditions where [CO<sub>2</sub>(aq)] is less than [Pd(II)], i.e. under non-pseudo-first-order conditions since the spontaneous formation of CO<sub>2</sub>(aq) from H<sub>2</sub>CO<sub>3</sub> and HCO<sub>3</sub><sup>-</sup> occurs at a rate of (2–6) × 10<sup>-4</sup> s<sup>-1</sup> under these conditions.<sup>2,31,32</sup> In addition, the formation reaction goes to completion under all conditions. These observations clearly indicate that the formation of the carbonato complexes does not proceed via the CO<sub>2</sub>-uptake route but rather via substitution by HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup> in this pH range. The decrease in  $k_{\text{obsd}}$  with increasing pH must be due to the formation of hydroxo complexes which are known to be substitutionally inert and therefore reduce  $k_{\text{obsd}}$ .<sup>33</sup>

A complete set of rate data for the formation of the carbonato complexes as a function of pH and temperature is given in Table III. The kinetic data can be fitted to the suggested mechanism outlined in (4), where  $K_3$  is the acid dissociation constant of the



aquo complex species determined before. On the assumption that the hydroxo complexes do not participate in the substitution process,<sup>33</sup>  $k_{\text{obsd}}$  can be expressed as in (5). Under the present

$$k_{\text{obsd}} = k_1[\text{H}^+][\text{total carbonate}]/(K_3 + [\text{H}^+]) \quad (5)$$

experimental conditions, HCO<sub>3</sub><sup>-</sup> is the main carbonate species in solution (pK<sub>1</sub> = 6.03; pK<sub>2</sub> = 9.80 at 25 °C<sup>2</sup>), and we suggest that  $k_1$  mainly represents the rate constant for anation by HCO<sub>3</sub><sup>-</sup>. The base hydrolysis of the carbonato complexes at higher pH (see Figures 2 and 3), the drastic decrease in the fraction of complex present in the aquo form, and the possible participation of con-

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**Table III.** Rate Data for the Formation of Pd(II) Carbonato Complexes as a Function of pH and Temperature<sup>a</sup>

complex	temp, °C	pH	$k_{\text{obsd}},^b \text{ s}^{-1}$	$k_1,^c \text{ M}^{-1} \text{ s}^{-1}$	$\bar{k}_1, \text{ M}^{-1} \text{ s}^{-1}$	$\Delta H^\ddagger, \text{ kJ mol}^{-1}$	$\Delta S^\ddagger, \text{ J K}^{-1} \text{ mol}^{-1}$
Pd(Me <sub>4</sub> dien)OCO <sub>2</sub>	15.1	8.15	11.5	7.18	6.8 ± 1.1	33 ± 5	-115 ± 17
		8.25	8.45	5.92			
		8.50	5.86	5.79			
		8.67	4.97	6.48			
		8.90	4.43	8.79			
	25.0	8.05	16.0	10.6	9.9 ± 1.1		
		8.15	12.7	9.47			
		8.40	9.2	9.83			
		8.57	5.8	8.25			
		8.80	5.3	11.6			
	34.1	7.95	27.8	17.4	17.0 ± 0.4		
		8.05	24.5	17.2			
		8.30	16.6	16.4			
		8.47	13.0	16.9			
Pd(Et <sub>4</sub> dien)OCO <sub>2</sub>	15.1	8.15	0.112	6.3 × 10 <sup>-2</sup>	(5.5 ± 0.5) × 10 <sup>-2</sup>	68 ± 6	-32 ± 22
		8.25	0.093	5.8 × 10 <sup>-2</sup>			
		8.50	0.060	5.1 × 10 <sup>-2</sup>			
		8.67	0.046	5.1 × 10 <sup>-2</sup>			
		8.90	0.033	5.4 × 10 <sup>-2</sup>			
	25.0	8.05	0.285	0.16	0.13 ± 0.02		
		8.15	0.215	0.13			
		8.40	0.150	0.13			
		8.57	0.086	0.095			
		8.80	0.075	0.12			
	34.1	7.95	0.750	0.42	0.35 ± 0.05		
		8.05	0.637	0.40			
		8.30	0.376	0.32			
		8.47	0.282	0.31			
		8.70	0.171	0.28			

<sup>a</sup> Conditions: [Pd(II)] = 0.5 × 10<sup>-3</sup> M; [total carbonate] = 0.33 M; ionic strength 1 M; wavelength 260 nm. <sup>b</sup> Mean value of at least three kinetic runs with an average error limit of less than 3%. <sup>c</sup>  $k_1 = k_{\text{obsd}}(K_3 + [\text{H}^+])/[\text{H}^+][\text{total carbonate}]$ ; see eq 5.

**Table IV.** Rate Data for Anation Reactions of a Series of Pd(II) dien Complexes

complex ion	entering ligand	ionic strength, M	$k$ at 25 °C, M <sup>-1</sup> s <sup>-1</sup>	$\Delta H^\ddagger, \text{ kJ mol}^{-1}$	$\Delta S^\ddagger, \text{ J K}^{-1} \text{ mol}^{-1}$	$\Delta V^\ddagger, \text{ cm}^3 \text{ mol}^{-1}$	ref
Pd(Me <sub>4</sub> dien)OH <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	0.1	1908 ± 50	40 ± 2	-49 ± 6	-7.2 ± 0.2	21
	Br <sup>-</sup>	0.1	3130 ± 120	39 ± 1	-47 ± 5	-7.6 ± 0.3	21
	I <sup>-</sup>	0.1	8080 ± 890	34 ± 2	-55 ± 6	-9.3 ± 0.8	21
	N <sub>3</sub> <sup>-</sup>	0.1	2.2 × 10 <sup>4b</sup>	32 ± 2	-53 ± 5	...	21
	HCO <sub>3</sub> <sup>-</sup>	1.0	9.9 ± 1.1	33 ± 5	-115 ± 17	...	a
Pd(Et <sub>4</sub> dien)OH <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	0.1	4.2 ± 0.1	56 ± 2	-45 ± 5	-3.0 ± 0.2	24
	HCO <sub>3</sub> <sup>-</sup>	1.0	0.13 ± 0.02	68 ± 6	-32 ± 22	...	a

<sup>a</sup> This work. <sup>b</sup> Extrapolated from quoted activation parameters.

jugate base species<sup>33</sup> (deprotonation of the central coordinated N atom on the dien ligand) complicate a study of the anation by CO<sub>3</sub><sup>2-</sup> at higher pH. Values for  $k_1$  were calculated from the  $k_{\text{obsd}}$  data by using eq 5 and the quoted values for  $K_3$ . These are included in Table III, from which it follows that they exhibit no meaningful pH dependence, underlining the validity of the suggested substitution mechanism. A comparison with earlier reported anation data for related species is given in Table IV.

It is important to note that the formation of the Pd(dien)OCO<sub>2</sub> species was too fast to be followed by stopped-flow methods. This is in agreement with earlier findings on the general substitution behavior of the very labile Pd(dien)OH<sub>2</sub><sup>2+</sup> species;<sup>21</sup> even at high pH where only a small fraction of the complex is in the aquo form, no substitution data could be measured.<sup>33</sup> The volumes of activation for the substitution by HCO<sub>3</sub><sup>-</sup> could not be measured due to the extreme pH sensitivity of the reaction. It follows from the data in Table IV that bicarbonate is a weak nucleophile. The value of the anation rate constant is accounted for by a more negative  $\Delta S^\ddagger$  value in the case of the Me<sub>4</sub>dien complex and a more positive  $\Delta H^\ddagger$  value for the Et<sub>4</sub>dien species. The latter could partially be due to the effect of steric hindrance on the dien ligand. These complex formation rate data cannot be compared with those for octahedral systems, since the latter all proceed via the CO<sub>2</sub>-uptake route.<sup>2</sup>

**Acid-Catalyzed Aquation.** Figures 2 and 3 clearly show that the carbonato complexes decompose to the aquo and hydroxo complexes at lower and higher pH, respectively. Acidification

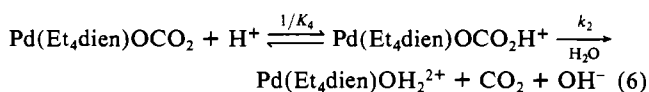
results in the protonation of the carbonate ligand to produce a bicarbonate species that can either decarboxylate (loss of CO<sub>2</sub> without metal-oxygen bond cleavage), as in the case of octahedral carbonato complexes, or spontaneously aquate (via metal-oxygen bond cleavage) in agreement with the general behavior of square-planar complexes.<sup>19</sup> Acidification of the released HCO<sub>3</sub><sup>-</sup> in the latter case results in the formation of CO<sub>2</sub>(aq), which cannot participate in the reverse anation process. Of the three carbonato complexes investigated, the Pd(Et<sub>4</sub>dien)OCO<sub>2</sub> complex is the only one for which acid-catalyzed aquation rate data could be measured. The less sterically hindered complexes aquate too fast in acidic medium to be followed by stopped-flow methods. The pH dependence of the aquation of Pd(Et<sub>4</sub>dien)OCO<sub>2</sub> could only be studied over a limited pH range since secondary reactions with the buffer medium occurred at lower pH. The observed rate constants are subjected to large errors due to the formation of CO<sub>2</sub> bubbles in the observation cell of the stopped-flow instrument during the acidification of the carbonato complex solution. An excess of NaHCO<sub>3</sub> is present in the latter, in order to have a maximum concentration of the complex present in solution (see previous section), causing this problem. Furthermore, the absorbance increase at 260 nm during the acidification of Pd(Et<sub>4</sub>dien)OCO<sub>2</sub> is rather small and makes it almost impossible to follow this reaction in the high-pressure stopped-flow instrument, where the higher pressure would have eliminated the CO<sub>2</sub>-bubble problem. An average decarboxylation rate constant of 2.4 ± 0.2 s<sup>-1</sup> at 25 °C and ionic strength 1 M was found over the range 1

Table V. Rate Data for the Base Hydrolysis of Pd(II) Carbonato Complexes as a Function of [OH<sup>-</sup>], Temperature, and Pressure<sup>a</sup>

complex	temp, °C	pressure, MPa	[OH <sup>-</sup> ], M	$k_{\text{obsd}}^b$ , s <sup>-1</sup>	rate parameter
Pd(dien)OCO <sub>2</sub>	25.0	0.1	0.2	1.72	$k_3 = 1.74 \pm 0.08 \text{ s}^{-1}$
			0.25	1.76	
			0.3	1.78	
			0.35	1.77	
			0.4	1.74	
			0.45	1.69	
			0.5	1.72	
	10.1	0.1	0.5	0.607	$\Delta H^\ddagger = 41 \pm 5 \text{ kJ mol}^{-1}$
	14.6		0.970	$\Delta S^\ddagger = -101 \pm 15 \text{ J K}^{-1} \text{ mol}^{-1}$	
	19.4		1.30		
	24.2		1.70		
	29.3		2.03		
	25.0	4.0	0.5	1.82	$\Delta V^\ddagger = -9.7 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$
			26.1	2.01	
			51.7	2.23	
	76.9		2.43		
	99.5		2.67		
Pd(Me <sub>4</sub> dien)OCO <sub>2</sub>	25.0	0.1	0.2	$5.46 \times 10^{-2}$	$k_3 = (5.49 \pm 0.05) \times 10^{-2} \text{ s}^{-1}$
			0.25	$5.50 \times 10^{-2}$	
			0.3	$5.50 \times 10^{-2}$	
			0.35	$5.50 \times 10^{-2}$	
			0.4	$5.45 \times 10^{-2}$	
			0.45	$5.50 \times 10^{-2}$	
			0.5	$5.50 \times 10^{-2}$	
	10.9	0.1	0.5	$2.35 \times 10^{-2}$	$\Delta H^\ddagger = 52 \pm 4 \text{ kJ mol}^{-1}$
	16.0		$3.36 \times 10^{-2}$	$\Delta S^\ddagger = -95 \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$	
	19.2		$3.54 \times 10^{-2}$		
	25.1		$5.50 \times 10^{-2}$		
	29.4		$7.15 \times 10^{-2}$		
	36.4	$10.6 \times 10^{-2}$			
	25.0	3.4	0.5	$5.0 \times 10^{-2}$	$\Delta V^\ddagger = -8.6 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$
			25.8	$5.5 \times 10^{-2}$	
	50.8		$6.0 \times 10^{-2}$		
	75.5		$6.4 \times 10^{-2}$		
	95.0		$7.0 \times 10^{-2}$		
Pd(Et <sub>4</sub> dien)OCO <sub>2</sub>	25.0	0.1	0.2	$3.36 \times 10^{-3}$	$k_3 = (3.5 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$
			0.25	$3.42 \times 10^{-3}$	
			0.3	$3.46 \times 10^{-3}$	
			0.35	$3.58 \times 10^{-3}$	
			0.4	$3.28 \times 10^{-3}$	
			0.45	$3.57 \times 10^{-3}$	
			0.5	$3.58 \times 10^{-3}$	
	11.0	0.1	0.5	$8.67 \times 10^{-4}$	$\Delta H^\ddagger = 62 \pm 2 \text{ kJ mol}^{-1}$
	16.1		$1.53 \times 10^{-3}$	$\Delta S^\ddagger = -82 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$	
	19.3		$1.93 \times 10^{-3}$		
	25.0		$3.44 \times 10^{-3}$		
	29.5		$5.16 \times 10^{-3}$		
	34.1	$7.97 \times 10^{-3}$			
	25.0	5	0.5	$1.47 \times 10^{-3}$	$\Delta V^\ddagger = -6.7 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$
			25	$1.50 \times 10^{-3}$	
	50		$1.75 \times 10^{-3}$		
	75		$1.77 \times 10^{-3}$		
	100		$1.91 \times 10^{-3}$		
	125		$2.07 \times 10^{-3}$		
	150		$2.15 \times 10^{-3}$		

<sup>a</sup> Conditions: [Pd(II)] =  $0.5 \times 10^{-3}$  M; ionic strength 1.0 M. <sup>b</sup> Mean value of at least three kinetic runs.

$\leq \text{pH} < 3$ , with  $\Delta H^\ddagger = 35 \pm 2 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -118 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$ .<sup>34</sup> These data suggest that the acid-catalyzed aquation process can be described by the mechanism outlined in (6), where



$$k_{\text{obsd}} = k_2[\text{H}^+]/(K_4 + [\text{H}^+]) \quad (7)$$

$K_4$  is the acid dissociation constant for the protonated carbonato complex. Under the experimental conditions employed  $[\text{H}^+] \gg$

$K_4$  and  $k_{\text{obsd}} = k_2$ .<sup>35</sup> Although the value of  $k_2$  and its activation parameters are in good agreement with those reported for the decarboxylation of octahedral carbonato complexes<sup>2</sup> and the corresponding isokinetic plot,<sup>2</sup> respectively, the microscopic reversibility of the formation reaction requires that  $k_2$  must be the rate constant for the solvolysis reaction, i.e. substitution by H<sub>2</sub>O and not loss of CO<sub>2</sub>. This is also in line with the negative value for  $\Delta S^\ddagger$  (i.e. associative solvolysis) and the fact that this reaction is too fast to be measured for the less sterically hindered complexes.

(34) At pH 0.3  $k_{\text{obsd}}$  values of 1.09, 1.34, 1.95, 2.27, and  $3.00 \text{ s}^{-1}$  were measured at 10.1, 14.6, 19.4, 24.3, and 29.3 °C, respectively.

(35) The following rate constants were measured at 25 °C with use of a McIlvaine buffer (pH quoted in brackets): 2.38 (5.7), 1.75 (6.1), 1.92 (6.6), 1.33 (7.0), and  $0.99 \text{ s}^{-1}$  (7.4). From these data it follows that  $\text{p}K_4 \approx 7$ , which is in good agreement with that observed in Figures 2 and 3 and similar values reported for octahedral complexes.<sup>2</sup>

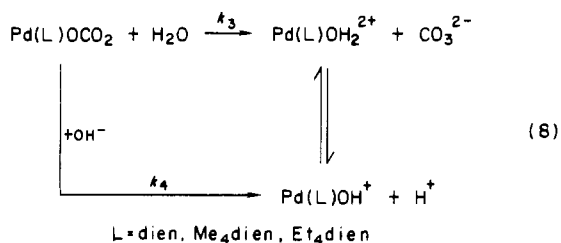
**Table VI.** Solvolysis Rate Data for a Series of Pd(II) dien Complexes

complex	ionic strength, M	$k$ at 25 °C, s <sup>-1</sup>	$\Delta H^\ddagger$ , kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ , J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta V^\ddagger$ , cm <sup>3</sup> mol <sup>-1</sup>	ref
Pd(dien)Cl <sup>+</sup>	0.1	37.8	40 ± 5	-82 ± 18	-12.2 ± 0.8	27
	0.1	43.8	43 ± 3	-69 ± 12	-10.0 ± 0.6	27
Pd(dien)OCO <sub>2</sub>	1.0	1.74	41 ± 5	-101 ± 15	-9.7 ± 0.4	<i>a</i>
Pd(Me <sub>4</sub> dien)Cl <sup>+</sup>	0.1	0.90	50 ± 2	-77 ± 5	-15.5 ± 0.6	28
	0.1	0.99	49 ± 1	-79 ± 2	-13.4 ± 1.9	28
Pd(Me <sub>4</sub> dien)OCO <sub>2</sub>	1.0	5.5 × 10 <sup>-2</sup>	52 ± 4	-95 ± 12	-8.6 ± 0.4	<i>a</i>
Pd(Et <sub>4</sub> dien)Cl <sup>+</sup>	0.1	2.1 × 10 <sup>-3</sup>	71 ± 2	-57 ± 6	-13.0 ± 0.6	27
	0.05	2.2 × 10 <sup>-3</sup>	69 ± 2	-67 ± 8	-14.9 ± 0.2	34
Pd(Et <sub>4</sub> dien)OCO <sub>2</sub>	1.0	3.5 × 10 <sup>-3</sup>	62 ± 2	-82 ± 8	-6.7 ± 0.5	<i>a</i>

<sup>a</sup> This work.

In the case of a decarboxylation process (via O–C bond breakage), steric hindrance is not expected to have such a marked effect since it involves the breakage of a secondary ligand bond.<sup>2</sup>

**Base Hydrolysis.** Base hydrolysis to the corresponding hydroxo species could be followed for all the investigated carbonate complexes. A large excess of base was employed in these measurements to neutralize the excess of HCO<sub>3</sub><sup>-</sup> present in the complex solution, which is required to stabilize the complex (see Figures 2 and 3). The observed rate constant exhibited no meaningful [OH<sup>-</sup>] dependence (see Table V), which is in good agreement with similar observations for other dien complexes of Pd(II).<sup>27,28</sup> This indicates that OH<sup>-</sup> is a very weak nucleophile and can only substitute the carbonate ligand via the spontaneous solvolysis reaction path, as shown in (8):



The contribution of the direct substitution by OH<sup>-</sup> is negligible, and the two-term rate law can be simplified as

$$k_{\text{obsd}} = k_3 + k_4[\text{OH}^-] \approx k_3 \quad (9)$$

The values of  $k_3$  along with the corresponding activation parameters ( $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $\Delta V^\ddagger$ ) are summarized in Table V. It is clearly seen that  $k_3$  decreases significantly with increasing steric hindrance on the dien ligand, which is accompanied by a significant increase in  $\Delta H^\ddagger$ . The rate parameters, especially  $\Delta S^\ddagger$  and  $\Delta V^\ddagger$ , strongly support the associative nature of the solvolysis process. The magnitude of  $k_3$  is such that it will not contribute to  $k_{\text{obsd}}$  during the reverse formation reactions of the carbonate complexes. However, an excess of bicarbonate was always required to stabilize the carbonate complexes in the latter case. This is quite understandable in light of the spontaneous solvolysis reaction described above.

At this point we would like to comment on the large difference in the values and activation parameters of  $k_2$  and  $k_3$ , which present the solvolysis rate constants for the Pd–OCO<sub>2</sub>H and Pd–OCO<sub>2</sub> species, respectively.  $k_2$  is in all cases significantly larger than  $k_3$  and could only be measured for the most sterically hindered complex. This trend is accompanied by a significantly lower enthalpy of activation for  $k_2$ , which must point at the catalytic role of the H<sup>+</sup> ions. Protonation of the carbonate ligand pre-

sumably weakens the Pd–O bond to such an extent that the solvolysis reaction is significantly faster.

A comparison with other solvolysis rate data is given in Table VI, from which it follows that  $\Delta V^\ddagger$  for the solvolysis of the carbonate complexes is less negative than for the other complexes quoted and those reported elsewhere.<sup>27,28</sup> This difference can probably be ascribed to solvational effects resulting from changes in dipole interactions during the associative attack of a solvent molecule. To our knowledge these are the first  $\Delta V^\ddagger$  data for the solvolysis of complexes with double negatively charged leaving groups, in other words neutral complexes. In the case of single negatively charged leaving groups, i.e. complexes with an overall charge of +1,  $\Delta V^\ddagger$  usually has values between -10 and -14 cm<sup>3</sup> mol<sup>-1</sup>.<sup>27,28,36</sup> Only one example of a complex with a neutral leaving group, viz. the solvolysis of Pd(Et<sub>4</sub>dien)NH<sub>3</sub><sup>2+</sup>, has been reported,<sup>36</sup> and the corresponding value of  $\Delta V^\ddagger$  is -3.0 ± 0.9 cm<sup>3</sup> mol<sup>-1</sup>. This value was interpreted as evidence for an associative-interchange mechanism. Partial charge creation or dipole interactions are not expected to contribute to  $\Delta V^\ddagger$  in this case, and the reported value is probably the pure intrinsic component for the associative entrance of a solvent molecule. Similar  $\Delta V^\ddagger$  values were recently reported for solvent exchange on Pd(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> and Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, viz. -2.2 ± 0.2 and -4.6 ± 0.2 cm<sup>3</sup> mol<sup>-1</sup> at 51 and 24 °C, respectively.<sup>37</sup>

Finally, we wish to comment on our interesting finding that the investigated Pd(II) hydroxo complexes are not able to react with CO<sub>2</sub>(aq) to produce carbonate species according to the CO<sub>2</sub>-uptake mechanism. This inability cannot be due to steric hindrance and can possibly be analyzed in terms of the nature of the hydroxo ligand on such complexes, which is presumably completely different than for the octahedral complexes. It is well-known that these hydroxo complexes are substitutionally inert,<sup>33</sup> although hydroxide is an extremely weak nucleophile. From these observations we tend to question the coordination geometry of the hydroxy ligand in such complexes.<sup>1</sup> Various investigations are at present under way to study this peculiarity in detail.

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**Registry No.** Pd(dien)OCO<sub>2</sub>, 98777-12-9; Pd(1,1,7,7-Me<sub>4</sub>dien)OCO<sub>2</sub>, 98777-13-0; Pd(1,1,7,7-Et<sub>4</sub>dien)OCO<sub>2</sub>, 98777-14-1; Pd(dien)H<sub>2</sub>O<sub>2</sub><sup>2+</sup>, 53773-87-8; Pd(1,1,7,7-Me<sub>4</sub>dien)H<sub>2</sub>O<sub>2</sub><sup>2+</sup>, 88717-44-6; Pd(1,1,7,7-Et<sub>4</sub>dien)H<sub>2</sub>O<sub>2</sub><sup>2+</sup>, 20130-53-4; HCO<sub>3</sub><sup>-</sup>, 71-52-3.

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