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Substitution Kinetics of Diethylenetriamine Complexes of Palladium(II) with Tris(hydroxymethyl)aminomethane in Aqueous Solution

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The reaction of aqueous Pd(1,4,7-Me_3dien)Cl^+ and Pd(1,1,7,7-Me_4dien)Cl^+ with Tris (tris(hydroxymethyl)aminomethane) buffer solutions covering $7 < pH < 9$ comprises two consecutive steps, which both depend on added [Cl^-], for which the pseudo-first-order rate constants were measured by stopped-flow spectrophotometry. Neither of the rate laws correspond with the simple two-term expression for square-planar substitution, the observations being consistent with a rapid equilibration resulting from an added contribution to the forward aquation of the complex by reverse chloride anation for the first step and the formation of a Tris complex via slow anation of the aqua intermediate for the second step. The rate constants for both steps are discussed in reference to available kinetic data in the literature.

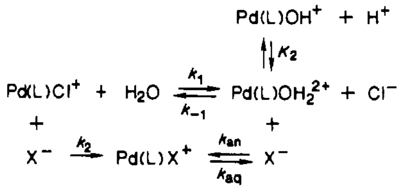
Introduction

In a pH-dependence study[1] of the fast anation reaction (k_{an}) following the rate-determining aquation reaction (k_1) in Scheme I, with L = various methyl/ethyl-substituted diethylenetriamines and X = I, the Tris (tris(hydroxymethyl)aminomethane) buffer species, which was used to effectively stabilize the pH over the range $6 < pH < 10$, caused a slow substitution reaction that interfered with the substitution process under study and led to erroneous kinetic results. The complication was overcome by adding the buffer to the ligand solution instead of to the complex solution prior to mixing. The observation, however, stimulated interest to study the substitution reaction with X = Tris as part of extending the investigation of square-planar substitution by this laboratory to more uncommon ligands. Among these are ligands having no net charge,[2] ligands of biological nature whose interactions with palladium(II) complexes serve as models for analogous reactions involving antitumor complexes[3] and ligands, like Tris and HCO_3^-,[4] which may exhibit unfamiliar square-planar substitution kinetics due to their pH-changing capability. The earlier work[1] demonstrated that only the aqua and not the hydroxo complex undergoes substitution and that the anation of the first-mentioned complex strongly depends on pH, emphasizing the importance of studying substitution with ligands causing a pH change.

Experimental Section

The complexes Pd(1,4,7-Me_3dien)Cl^+ and Pd(1,1,7,7-Me_4dien)Cl^+ and their corresponding aqua analogues were chosen on account of their relative lability to study the slow substitution reaction with the Tris species. The first-mentioned complex was isolated as [Pd(1,4,7-Me_3dien)Cl_2]HCl,[5] the free hydrogen ion in solution per complex molecule being left unneutralized since the reaction with Tris turned out to be kinetically unaffected by the lower than neutral pH at the selected buffer concentration. The synthesis of the other complex, as well as the conversion of both chloro complexes into the aqua form by precipitating chloride with $AgClO_4$, is described elsewhere.[6] The concentrations of the complex and of the Tris solutions were 1×10^{-3} and 5×10^{-2} mol dm^{-3}, respectively, on mixing equal volumes, in fulfilment of pseudo-first-order requirements. The various Tris solutions covering the range $7 < pH < 9$ were prepared by blending a constant concentration Tris base with precalculated amounts of a standard $HClO_4$ solution and adding the necessary amounts of a standard $NaClO_4$ solution to fix the total ionic strength of the final reaction mixture at 0.1 mol dm^{-3}. The initial acidities of the ligand solutions were checked, and the changes in acidity on mixing with the complex solutions were monitored by pH measurements with a Metrohm E520 pH meter. The chloride ion dependence of the title reactions has been studied by varying the amount of NaCl added or, in the case of [Pd(1,4,7-Me_3dien)Cl_2]HCl, which has two chloride ions per complex molecule free in solution, also by varying the number of equivalents of chloride precipitated from the complex solution. The spectral changes that occur on mixing equal volumes of complex and ligand solutions were recorded over the range $250 < \lambda < 400$ nm by using a Perkin-Elmer Lambda 5 spectrophotometer and cuvettes of 1-cm path length. The kinetic measurements were performed with a Durrum D110 stopped-flow spectrophotometer connected to a Tektronix 5111A oscilloscope and an Apple II microcomputer loaded with a locally updated version of the Hi-Tech[7] data aquisition and analysis program. The solutions were carefully thermostated at 25 °C by linking the closed-circuit temperature bath of the stopped-flow apparatus to a Haake NK22 cryostat.

Scheme I



Results and Discussion

Figure 1 shows the UV/visible spectra of the chloro, aqua, and hydroxo forms of the unreacted Pd(Me_3dien) complex and of the product obtained by reacting the chloro form of this complex with Tris solutions of equal concentration but different pH. The product formation is clearly pH dependent. The distinct isosbestic point (λ = 324 nm) indicates that the product is formed by an equilibrium. The latter proceeds via the aqua species, since no isosbestic point is observed for the UV/visible spectra for various Tris solutions reacting directly with the aqua complex. The failure of the product spectrum involving the Tris solution of the highest pH to pass through the isosbestic point in Figure 1 is ascribed to partial formation of the hydroxo species at this pH value. The OH^- and Tris entities namely compete mutually for the aqua intermediate. A reaction with OH^- deprotonates the aqua and produces the hydroxo species, the latter being substitutionally inert even at a large excess of Tris.

The spectral changes in Figure 1 result from two consecutive reaction steps that, by the use of the oscilloscope, could be readily separated in time to facilitate the measurement of the kinetics of each step. The pseudo-first-order rate constants k_{obsd} for both steps and the contribution of each step to the overall change in absorbance ΔA are summarized in Table I for the Pd(Me_3dien)Cl^+ and in Table II for the Pd(Me_4dien)Cl^+ complex. The faster reaction step is not observed when, instead of the chloro species, the aqua species is reacted with Tris. The kinetic data for only the slower reaction step observable under such conditions are

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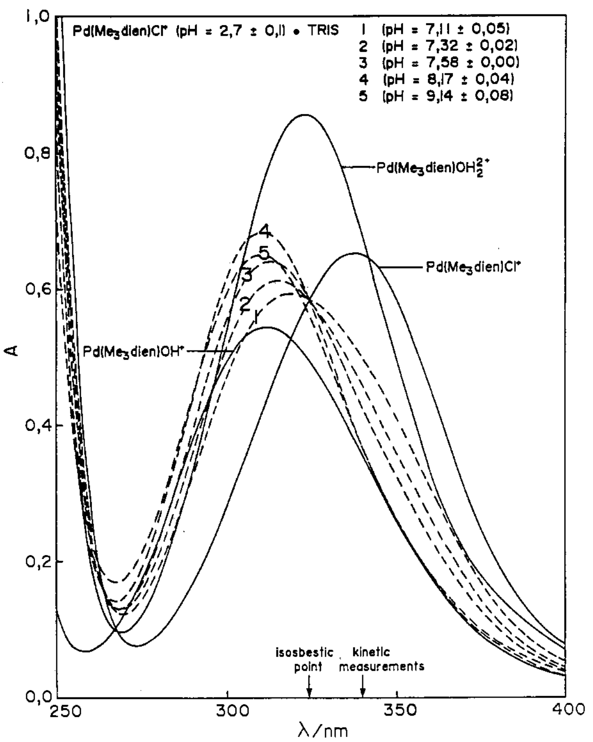

Figure 1. Spectral change during reaction of Pd(Me$_3$dien)Cl$^+$ with Tris: [complex] = 1 × 10^{-3} mol dm^{-3}; [Tris] = 5 × 10^{-2} mol dm^{-3}; ionic strength = 0.1 mol dm^{-3}; added [Cl$^-$] = 2 × 10^{-3} mol dm^{-3}.

presented in the $[\mathrm{Cl}]_\mathrm{T} = 0$ columns of Tables I and II. The reaction pH values in these tables are being arrived at in different ways for the two reaction steps. They are *calculated* for the faster reaction step from

$$\mathrm{pH} = \mathrm{p}K + \log \{([\mathrm{base}] - [\mathrm{H}^+]_{\mathrm{complex}})/([\mathrm{acid}] + [\mathrm{H}^+]_{\mathrm{complex}})\} \quad (1)$$

where pK = 8.08,[8] [acid] and [base] are obtained from the measured pH values of the various Tris solutions (cf. Figure 1 and Tables I and II) and $[\mathrm{H}^+]_{\mathrm{complex}}$ is the fixed contribution of the complex solutions (pH 2.7 ± 0.1 for Pd(Me$_3$dien), pH 4.5 ± 0.1 for Pd(Me$_4$dien)) to the reaction pH on mixing with the Tris solutions. For the slower reaction step the reaction pH is taken to be equal to the pH *measured* after mixing, since the major change in pH is expected to occur during the mixing stage and the faster reaction step.

The absence of the faster reaction step when the substitution with Tris is performed with the aqua complex suggests that this reacton step corresponds with the conversion of the chloro into the aqua species, i.e. with aquation according to the k_1 path in Scheme I. The aquation rate constants k_1 for the Pd(Me$_3$dien)Cl$^+$ and Pd(Me$_4$dien)Cl$^+$ complexes were determined by reacting these complexes with iodide ion over an extended range of concentrations, the respective values k_1 = 30.8 ± 0.8 s^{-1} and k_1 = 1.01 ± 0.01 s^{-1} obtained from the corresponding intercepts of k_{obsd} versus [I$^-$] being in good agreement with previously[9] estimated values. The rate constants k_{obsd} for the faster reaction step in Tables I and II are such that $k_{\mathrm{obsd}} \gg k_1$ at low pH and $k_{\mathrm{obsd}} \rightarrow k_1$ at high pH. This implies that a parallel, pH-dependent forward or reverse reaction is also contributing to these k_{obsd} values. The significant [Cl$^-$] dependence of the k_{obsd} values strongly suggests that the additional contribution stems from the k_{-1} path in the scheme above, according to which an increase in [Cl$^-$] would lead to an increase in the contribution of k_{-1} to result in increasing values of k_{obsd} and decreasing changes in absorbance ΔA as are indeed observed. The faster reaction step can thus be regarded as a solvolysis process proceeding according to an equilibration com-

Table I. Rate Data for the Reaction of Pd(Me$_3$dien)OH$_2$$^{2+}$ ($[\mathrm{Cl}]_\mathrm{T} = 0$) and Pd(Me$_3$dien)Cl$^+$ ($1 \times 10^{-3} < [\mathrm{Cl}]_\mathrm{T} < 11 \times 10^{-3}$ mol dm^{-3}) with Tris[a]

pH of Tris[b]	reacn pH[c]	reacn step	$[\mathrm{Cl}]_\mathrm{T} = 0$		$[\mathrm{Cl}]_\mathrm{T} = 1 \times 10^{-3}$		$[\mathrm{Cl}]_\mathrm{T} = 2 \times 10^{-3}$		$[\mathrm{Cl}]_\mathrm{T} = 3 \times 10^{-3}$		$[\mathrm{Cl}]_\mathrm{T} = 6 \times 10^{-3}$		$[\mathrm{Cl}]_\mathrm{T} = 11 \times 10^{-3}$	
			k_{obsd}	ΔA	k_{obsd}	ΔA	k_{obsd}	ΔA	k_{obsd}	ΔA	k_{obsd}	ΔA	k_{obsd}	ΔA
6.90 ± 0.00	6.72	fast							111 ± 8	0.04				
	6.62	slow							0.96 ± 0.01	0.13				
7.11 ± 0.05	7.00	fast			56.1 ± 0.7	0.08	72.3 ± 1.7	0.07	83.2 ± 3.6	0.06	169 ± 10	0.02		
	6.88	slow	1.90 ± 0.07	0.20	1.34 ± 0.03	0.18	1.15 ± 0.01	0.18	1.08 ± 0.01	0.20	0.85 ± 0.00	0.12		
7.32 ± 0.02	7.25	fast			56.7 ± 0.3		71.4 ± 0.5	0.10	82.0 ± 1.6	0.08	161 ± 10	0.04		
	7.12	slow	2.22 ± 0.09	0.20	1.55 ± 0.01	0.23	1.30 ± 0.01		1.22 ± 0.01	0.20	0.91 ± 0.03	0.12		
7.58 ± 0.00	7.53	fast			52.3 ± 0.3	0.15	62.9 ± 0.2		71.0 ± 2.7	0.12	125 ± 8	0.07	209 ± 4	0.03
	7.41	slow	2.60 ± 0.03	0.15	1.86 ± 0.06		1.57 ± 0.01	0.23	1.41 ± 0.01	0.23	1.06 ± 0.05	0.20	0.97 ± 0.01	
8.17 ± 0.04	8.14	fast			38.4 ± 1.0	0.25	44.2 ± 3.3	0.30	52.0 ± 0.9	0.25	68.7 ± 0.7	0.15	101 ± 6	0.10
	8.00	slow	2.39 ± 0.07	0.10	2.11 ± 0.09	0.20	1.93 ± 0.16		1.83 ± 0.04	0.23	1.53 ± 0.00	0.20	1.34 ± 0.01	0.20
9.14 ± 0.08	9.03	fast			36.1 ± 0.0	0.35	36.6 ± 0.1	0.38	37.1 ± 1.2	0.40	39.4 ± 2.1	0.40	43.4 ± 1.7	0.35
	8.97	slow	0.99 ± 0.01	0.04	1.06 ± 0.03	0.05		0.08	1.09 ± 0.01	0.10	1.06 ± 0.01	0.10	1.04 ± 0.02	0.10

[a] [Complex] = 1 × 10^{-3} mol dm^{-3}; pH of complex = 2.7 ± 0.1 (mean of *measured* pH for complex solutions prior to mixing with Tris solutions); [Tris] = 5 × 10^{-2} mol dm^{-3}; ionic strength = 0.1 mol dm^{-3}; temperature = 25 °C; wavelength = 340 nm. [b] Mean of *measured* pH for Tris solutions prior to mixing with complex solution. [c] Taken as *calculated* pH according to (1) for faster reaction step and as *measured* pH after mixing for slower reaction step.

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Table II. Rate Data for the Reaction of $Pd(Me_4dien)OH_2^{2+}$ ($[Cl]_T = 0$) and $Pd(Me_4dien)Cl^+$ ($1 \times 10^{-3} < [Cl]_T < 11 \times 10^{-3}$ mol dm^{-3}) with Tris[a]

pH of Tris[b]	reacn pH[c]	reacn step	$[Cl]_T = 0$		$[Cl]_T = 1 \times 10^{-3}$		$[Cl]_T = 6 \times 10^{-3}$		$[Cl]_T = 11 \times 10^{-3}$	
			k_{obsd}	ΔA	k_{obsd}	ΔA	k_{obsd}	ΔA	k_{obsd}	ΔA
7.11 ± 0.01	7.11	fast			1.93 ± 0.02	0.07	8.88 ± 0.90	0.02	16.2 ± 0.2	0.01
	7.04	slow	0.375 ± 0.002	0.02	0.240 ± 0.008		0.126 ± 0.003		0.143 ± 0.003	
7.31 ± 0.01	7.31	fast			1.87 ± 0.02	0.09	8.35 ± 1.81	0.03	15.4 ± 1.1	0.02
	7.24	slow	0.407 ± 0.001	0.02	0.247 ± 0.004	0.01	0.159 ± 0.002			
7.57 ± 0.02	7.57	fast			1.73 ± 0.09	0.13	6.58 ± 1.16	0.05	11.8 ± 0.09	0.03
	7.50	slow			0.255 ± 0.003		0.163 ± 0.001	0.01	0.182 ± 0.002	
8.17 ± 0.02	8.17	fast			1.26 ± 0.08	0.20	2.74 ± 0.10	0.12	4.36 ± 0.12	0.08
	8.09	slow					0.185 ± 0.001	0.02	0.160 ± 0.001	
9.18 ± 0.04	9.18	fast			1.03 ± 0.00	0.35	1.23 ± 0.04	0.30	1.44 ± 0.02	0.27
	9.05	slow								

[a] [Complex] = 1×10^{-3} mol dm^{-3}; pH of complex = 4.5 ± 0.1 (mean of *measured* pH for complex solutions prior to mixing with Tris solutions); [Tris] = 5×10^{-2} mol dm^{-3}; ionic strength = 0.1 mol dm^{-3}; temperature = 25 °C; wavelength = 340 nm. [b] Mean of *measured* pH for Tris solutions prior to mixing with complex solution. [c] Taken as *calculated* pH according to (1) for faster reaction step and as *measured* pH after mixing for slower reaction step.

prising the k_1 and k_{-1} paths. The pH-dependence of the solvolysis process is governed by the aqua/hydroxo equilibrium in Scheme I through controlling the contribution of the k_{-1} path only, since the k_1 path is pH independent. An increase in pH favors the formation of the hydroxo species, whereby the contribution of the k_{-1} path is reduced such that $k_{obsd} \rightarrow k_1$ and ΔA increases. Similarly a decrease in pH favors the formation of the aqua species, whereby the contribution of the k_{-1} path is enhanced such that $k_{obsd} \gg k_1$ and ΔA decreases.

The rate constant for the faster reaction step is mathematically given by

$$k_{obsd} = k_1 + k_{-1}f_{Pd(L)OH_2^{2+}}[Cl^-] = k_1 + k_{-1}\{[H^+]/(K_2 + [H^+])\}[Cl^-] \quad (2)$$

which permits the calculation of k_1 and k_{-1} for each complex from the intercept and slope of plots of k_{obsd} versus $\{[H^+]/(K_2 + [H^+])\}[Cl^-]$ as illustrated in Figure 2. The values of K_2 required for these plots were obtained from the previously[6] measured pK_2 values 7.05 ± 0.01 and 7.54 ± 0.01 for $Pd(Me_3dien)OH_2^{2+}$ and $Pd(Me_4dien)OH_2^{2+}$ respectively, whereas the values of $[Cl^-]$ were calculated from

$$[Pd(L)OH_2^{2+}] = \{K_1/(K_1 + [Cl^-])\}[Pd]_T \quad (3)$$

through inserting the added chloride ion concentration in this expression and correcting it for the chloride ion released by the chloro complex by repeating the calculation in such a way that each newly calculated value of $[Cl^-]$ was introduced for the next calculation until constant values were obtained. The K_1 values $(4.5 \pm 0.5) \times 10^{-4}$ and $(4.3 \pm 0.6) \times 10^{-4}$ mol dm^{-3} used in this calculation for $Pd(Me_3dien)Cl^+$ and $Pd(Me_4dien)Cl^+$, respectively, were taken from literature,[6,10] the first-mentioned value being an estimation based on the K_1 values obtained for a series of palladium(II) dien complexes for which $K_1 = k_1/k_{-1}$ (cf. Scheme I) remains fairly constant despite a variation of k_1 and k_{-1} by at least 6 orders of magnitude. The values $k_1 = 40.1 \pm 0.3$ s^{-1} and $k_1 = 1.02 \pm 0.14$ s^{-1} obtained for $Pd(Me_3dien)Cl^+$ and $Pd(Me_4dien)Cl^+$, respectively, are in satisfactory agreement with the known values mentioned above, especially when the indirect way of determination is taken into consideration and allowance is made for slight deviations at low $[Cl^-]$ when the reverse chloride anation reaction, which contributes minimally under such conditions, is not strictly first order. There is no literature value available with which $k_{-1} = (5.7 \pm 0.3) \times 10^4$ dm^3 mol^{-1} s^{-1} obtained for $Pd(Me_3dien)Cl^+$ can be compared, but it neatly fits into a sequence of decreasing k_{-1} values with increasing steric hindrance for a series of substituted dien complexes of palladium(II).[10] The value $k_{-1} = (2.17 \pm 0.04) \times 10^3$ dm^3 mol^{-1} s^{-1} for $Pd(Me_4dien)Cl^+$ neatly agrees with the literature value $k_{-1} = (1.91 \pm 0.05) \times 10^3$ dm^3 mol^{-1} s^{-1}.

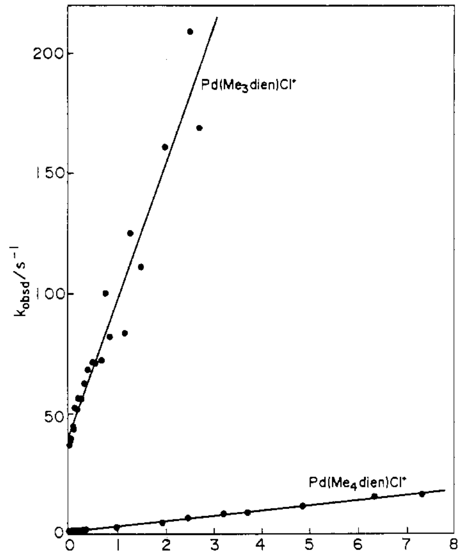

Figure 2. Mathematical treatment (eq 2) of kinetic data for faster reaction of $Pd(Me_3dien)$ and $Pd(Me_4dien)$ complexes with Tris. Data were taken from Tables I and II.

The corresponding solvolysis equilibrium constant $K_1 = k_1/k_{-1}$ turns out to be $(7.0 \pm 0.4) \times 10^{-4}$ and $(4.7 \pm 0.7) \times 10^{-4}$ mol dm^{-3} for the two complexes, respectively, whereby the values of K_1 chosen from the literature to facilitate the calculation of $[Cl^-]$ for the presentation of the kinetic data in Figure 2 are justified. The validity of the mathematical description of the faster reaction step is finally confirmed by satisfactory mutual agreement between any value of k_{obsd} in Tables I and II and a corresponding value of k_{theor} calculated from (2).

The rate constants k_{obsd} in Tables I and II for the slower reaction step are best accounted for by the anation of the aqua complex by the Tris species according to the k_{an} path in Scheme I. Since the Tris species is a significantly weaker nucleophile than chloride ion, the aqua complex is not rapidly taken up by the Tris species, allowing the reverse anation reaction with chloride ion according to the k_{-1} path in Scheme I, to be kinetically observed during the faster reaction step. The slowness of the anation reaction with Tris is further attributed to the fact that, in the pH range concerned (cf. measured pH for the slower reaction step in Tables I and II), only a fraction of the solvolysis product is present as the aqua species and that, in terms of the equilibrium

$$H^+{\cdot}Tris \overset{K}{\rightleftharpoons} Tris + H^+ \quad (4)$$

(pK = 8.08 as stated before), only free Tris can react with the aqua species. These pH-related limitations and the low nucleophilicity require provision to be made in reaction Scheme I for reverse aquation according to the k_{aq} path when X = Tris. The

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(10) Kotowski, M.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 3310.
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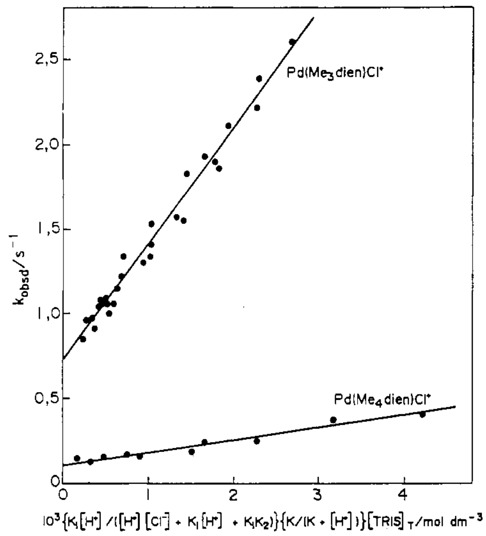

Figure 3. Mathematical treatment (eq 5) of kinetic data for slower reaction of Pd(Me$_3$dien) and Pd(Me$_4$dien) complexes with Tris. Data were taken from Tables I and II.

values of ΔA for the slower reaction in Tables I and II indeed support the idea that this reaction step is an equilibration, since these values initially increase with increasing pH due to increased availability of free Tris (cf. equilibrium 4) but finally decrease towards higher pH due to partial formation of hydroxo complex (cf. Scheme I) to represent the net contribution from two opposing reactions.

The rate of the substitution process representing the slower reaction step is given by

$$k_{obsd} = k_{an}f_{Pd(L)OH_2^{2+}}f_{Tris}[Tris]_T + k_{aq} = k_{an}\{K_1[H^+]/([H^+] \times [Cl^-] + K_1[H^+] + K_1K_2)\}\{K/(K + [H^+])\}[Tris]_T + k_{aq} \quad (5)$$

with K_1, K_2, and K having the values cited earlier in the text, $[H^+]$ being taken as the measured pH after the complex and ligand solutions are mixed (cf. Tables I and II) and $[Cl^-]$ being calculated from the sum of the equations

$$[Pd(dien)OH_2^{2+}] = \{K_1[H^+]/([H^+][Cl^-] + K_1[H^+] + K_1K_2)\}[Pd]_T \quad (6a)$$

$$[Pd(dien)OH^+] = \{K_1K_2/([H^+][Cl^-] + K_1[H^+] + K_1K_2)\}[Pd]_T \quad (6b)$$

in a similar way as for (3). Equation 5 implies that k_{obsd} for the slower reaction of both complexes with Tris, when plotted as a function of $f_{Pd(L)OH_2^{2+}}f_{Tris}[Tris]_T$, should yield straight lines with slope k_{an} and intercept k_{aq}. This is indeed the case, as Figure 3 illustrates. The validity of the mathematical description is also supported by the mutual agreement between the values of k_{obsd} for the slower reaction step in Tables I and II and the corresponding values of k_{theor} calculated from (5). The anation rate constant turns out to be k_{an} = (689 ± 20) dm^3 mol^{-1} s^{-1} for Pd(Me$_3$dien)OH$_2^{2+}$ and k_{an} = (72.0 ± 5.8) dm^3 mol^{-1} s^{-1} for Pd(Me$_4$dien)OH$_2^{2+}$, the ratio 10:1 between these two values being in fair accordance with the ratios roughly ranging from 5:1 to 25:1 between the anation rate constants of the two complexes for a few other anating reagents listed in Table III. It follows from the tabulated data that Tris and HCO$_3^-$ are indeed very weak nucleophiles, explaining why the slower reaction step also involves a reverse aquation reaction. The rate constant for the latter reaction turns out to be k_{aq} = 0.72 ± 0.03 s^{-1} for Pd(Me$_3$dien)-Tris^{2+} and k_{aq} = 0.11 ± 0.01 s^{-1} for Pd(Me$_4$dien)Tris^{2+}, and very similar values are obtained for the analogous complexes with HCO$_3^-$.[4]

Table III. Anation Rate Constant for the Reaction Pd(L)OH$_2^{2+}$ + X^{n-} → Pd(L)X$^{(2-n)+}$ + H$_2$O[a]

L	X^{n-}	k_{an}/dm^3 mol^{-1} s^{-1}	ref
1,4,7-Me$_3$dien	Cl$^-$	57055 ± 3009	*e*
	Tris	689 ± 20	*e*
	HCO$_3^-$	116 ± 6[b]	4
1,1,7,7-Me$_4$dien	Cl$^-$	2169 ± 44	*e*
		1908 ± 50	6
	Br$^-$	3126 ± 119	6
	I$^-$	8081 ± 287	5, 6
	N$_3^-$	22009 ± 1873[c]	6
	Tris	72 ± 6	*e*
	HCO$_3^-$	29 ± 2	4
		10 ± 1[d]	11

[a] Temperature = 25 °C; ionic strength = 0.1 mol dm^{-3} unless otherwise specified. [b] Mean of values determined at two different complex solution pH (2.7 and 6.5). [c] Extrapolated value using reported activation parameters. [d] Ionic strength = 1.0 mol dm^{-3}. [e] This work.

In summary, this study not only confirms previous[12] findings that systems involving square-planar substitution can under certain circumstances come to equilibrium but also shows that in the particular situation of having an incoming ligand with strong pH-changing capability and weak nucleophilicity two successive equilibrations are observed. This represents uncommon kinetic behavior that might be expected to occur whenever ligands of high basicity and low nucleophilicity are involved in such square-planar substitution reactions.

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Registry No. Pd(1,4,7-Me$_3$dien)Cl$^+$, 89397-60-4; Pd(1,1,7,7-Me$_4$dien)Cl$^+$, 89397-61-5; Pd(1,4,7-Me$_3$dien)OH$_2^{2+}$, 88717-42-4; Pd-(1,1,7,7-Me$_4$dien)OH$_2^{2+}$, 88717-44-6; Tris, 77-86-1; Cl$^-$, 16887-00-6.

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