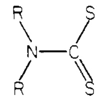
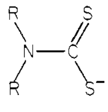
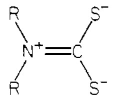
kinetics of the electrode processes. Thus, $[Cr(pdtc)_2(opdtc)]^+$, the initial product formed on oxidation of $Cr(pdtc)_2(opdtc)$, is substantially more stable in the kinetic sense than $[Cr(pdtc)_3]^+$, which is derived from $Cr(pdtc)_3$. On electrochemical reduction of $Cr(pdtc)_2(opdtc)$, $[pdtc]^-$ is preferentially released to generate the complex Cr(pdtc)(opdtc), indicating the considerable kinetic stability of $[opdtc]^-$ when coordinated to chromium. Thermodynamically, differences between the $Cr(pdtc)_2(opdtc)$ and $Cr(pdtc)_3$ complexes are not very large with respect to redox potentials. However, $Cr(pdtc)_2(opdtc)$ is easier to oxidize than $Cr(pdtc)_3$ so that thermodynamically, as well as kinetically, enhanced stability of the chromium(IV) species is obtained by the oxygen insertion. A less detailed study of analogous diethyldithiocarbamate complexes shows the same overall pattern of behavior, indicating some generality may apply to these observations. Other workers[1-4] have shown that the dithiocarbamate ion may be represented by resonance forms I–III, where resonance form III is claimed to be the most dominant the higher the oxidation state of the metal.[1-4] The increased stability with inclusion of an oxygen atom is possibly due to stabilization of the analogous resonance form IV.



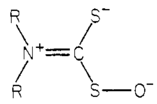
I



II



III



IV

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Registry No. $Cr(pdtc)_3$, 38532-19-3; $Cr(pdtc)_2(opdtc)$, 89437-75-2; $Hg(pdtc)_2$, 41060-60-0; $K_2Cr_2O_7$, 7778-50-9; Au, 7440-57-5; Pt, 7440-06-4; C, 7440-44-0; Hg, 7439-97-6; ammonium pyrrolidine dithiocarbamate, 5108-96-3.

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Kinetics and Mechanism of Some Fast Substitution Reactions of a Series of Methyl-Substituted dien Complexes of Palladium(II) in Aqueous Solution[1]

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The kinetics of the substitution reactions of $Pd(1,4,7\text{-}Me_3dien)Cl^+$, $Pd(1,1,7,7\text{-}Me_4dien)Cl^+$, and $Pd(1,1,4,7,7\text{-}Me_5dien)Cl^+$ by OH^- and I^- were studied as a function of [entering ligand], temperature, and pressure up to 1 kbar. The rate constants for both the solvolysis and direct substitution paths decrease significantly with increasing steric hindrance. For the Me_3dien and Me_4dien complexes, they exhibit meaningful $[OH^-]$ dependencies, and the corresponding volumes of activation ($+21 \pm 2$ and $+25 \pm 4$ $cm^3\ mol^{-1}$, respectively) provide strong evidence for a conjugate-base substitution process. The results are discussed in comparison with those previously reported for a corresponding series of ethyl-substituted dien complexes.

Introduction

Although substitution reactions of square-planar complexes in general, and of Pt(II) and Pd(II) in particular, have received much attention from various investigators over the last two decades, the interest in such reactions continues uninterruptedly as demonstrated by the significant number of contributions appearing annually. This interest mainly focuses on the effect of steric hindrance, chelation of ligands, antitumor activity, and substituents of biological importance. Our own interest originated in the remarkable effect of steric hindrance on simple substitution processes, which was originally interpreted[2-4] as evidence for a change from an associative to a dissociative reaction mode with increasing steric hindrance.

We recently reported[5] kinetic data and temperature and pressure parameters for some substitution reactions of dien (diethylenetriamine) and a series of ethyl-substituted dien complexes of palladium(II) in aqueous solution. A significant $[OH^-]$ dependence of the observed rate constant was found for one of the complexes, viz. $Pd(1,1,7,7\text{-}Et_4dien)Cl^+$, in agreement with earlier observations.[2,3] The accompanying activation parameters differed markedly from those reported for other substitution reactions of this complex[6-8] and required the suggestion of a conjugate-base mechanism[3,5] to account for the extraordinary kinetic behavior. The present investigation was undertaken to extend the previously studied[5] series of palladium(II) complexes, viz. dien, Et_3dien (1,1,4 and 1,4,7 isomers), $1,1,7,7\text{-}Et_4dien$, $4\text{-}Me\text{-}1,1,7,7\text{-}Et_4dien$, and $1,1,4,7,7\text{-}Et_5dien$, to include some methyl-substituted complexes, viz. $1,4,7\text{-}Me_3dien$, $1,1,7,7\text{-}Me_4dien$, and $1,1,4,7,7\text{-}Me_5dien$, in order to establish whether a similar $[OH^-]$ dependence exists for one of these species. Additionally, the data enable an overall comparison of the substitution behavior of a wide range of palladium(II)-substituted dien complexes, emphasizing the role played by steric hindrance during such processes.

Experimental Section

The complexes $[Pd(1,4,7\text{-}Me_3dien)Cl_2]HCl$, $[Pd(1,1,7,7\text{-}Me_4dien)Cl]ClO_4$, and $[Pd(1,1,4,7,7\text{-}Me_5dien)Cl]ClO_4$ were prepared as described before.[3,9,10] Analytical data for these complexes and

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Table I. k_{obsd} as a Function of $[Y^-]$ and Temperature for the Reaction $Pd(L)Cl^+ + Y^- \rightarrow Pd(L)Y^+ + Cl^-$ ($[Pd] = 1 \times 10^{-3}$ mol dm^{-3}; Ionic Strength 0.1 mol dm^{-3}; Wavelength 320 nm (Y = OH), 400 nm (Y = I))

L	Y	temp/ °C	$[Y^-]$/ mol dm^{-3}	$k_{obsd}{}^a$/s^{-1}	k_1/s^{-1}	$\Delta H_1^{\ddagger\,b}$/ kcal mol^{-1}	$\Delta S_1^{\ddagger\,b}$/ cal K^{-1} mol^{-1}	k_2/ dm^3 mol^{-1} s^{-1}	$\Delta H_2^{\ddagger\,b}$/ kcal mol^{-1}	$\Delta S_2^{\ddagger\,b}$/ cal K^{-1} mol^{-1}
1,4,7-Me$_3$dien	OH	11.5	0.01	11.4 ± 0.1	11.1 ± 0.0	8.7 ± 0.8	−22.8 ± 2.8	28.0 ± 0.3	17.3 ± 1.0	+9.2 ± 3.4
			0.03	11.9 ± 0.2						
			0.05	12.5 ± 0.1						
		18.2	0.01	18.6 ± 0.3	17.9 ± 0.2			67.3 ± 5.1		
			0.03	19.8 ± 0.3						
			0.05	21.3 ± 0.6						
		25.0	0.01	26.9 ± 0.5	25.7 ± 0.3			130 ± 8		
			0.03	29.7 ± 1.0						
			0.05	32.1 ± 0.8						
		31.4	0.01	34.6 ± 0.7	32.4 ± 0.2			225 ± 6		
			0.03	39.3 ± 1.0						
			0.05	43.6 ± 0.5						
	I	11.5	0.005	24.2 ± 0.5	11.3 ± 1.7	9.2 ± 1.0	−20.9 ± 3.6	2486 ± 91	5.1 ± 0.9	−25.1 ± 3.0
			0.01	36.5 ± 0.4						
			0.02	58.9 ± 0.5						
			0.03	87.0 ± 0.6						
		18.2	0.005	33.9 ± 0.4	19.8 ± 4.1			3183 ± 308		
			0.01	54.2 ± 1.0						
			0.02	82.5 ± 0.6						
		25.0	0.005	40.9 ± 1.0	25.0 ± 4.2			3542 ± 319		
			0.01	63.2 ± 0.8						
			0.02	94.9 ± 3.4						
		31.4	0.005	61.8 ± 0.2	36.9 ± 0.3			4980 ± 34		
			0.01	86.7 ± 0.9						
1,1,7,7-Me$_4$dien	OH	11.5	0.01	0.34 ± 0.01	0.32 ± 0.00	11.9 ± 0.4	−18.5 ± 1.3	2.13 ± 0.07	11.5 ± 1.6	−16.6 ± 5.5
			0.03	0.39 ± 0.01						
			0.05	0.43 ± 0.01						
		18.2	0.01	0.61 ± 0.01	0.57 ± 0.00			3.25 ± 0.03		
			0.03	0.67 ± 0.01						
			0.05	0.74 ± 0.01						
		25.0	0.01	0.94 ± 0.01	0.90 ± 0.01			4.53 ± 0.19		
			0.03	1.04 ± 0.02						
			0.05	1.12 ± 0.01						
		31.4	0.01	1.49 ± 0.01	1.40 ± 0.01			9.08 ± 0.07		
			0.03	1.67 ± 0.04						
			0.05	1.85 ± 0.02						
	I	11.5	0.01	0.37 ± 0.00		11.8 ± 0.2	−18.9 ± 0.6			
		18.2	0.01	0.61 ± 0.01						
		25.0	0.01	0.98 ± 0.01	0.99 ± 0.02			0.28 ± 0.53		
			0.03	1.01 ± 0.02						
			0.05	0.99 ± 0.01						
		31.4	0.01	1.57 ± 0.01						
1,1,4,7,7-Me$_5$dien	OH	11.5	0.01	(0.89 ± 0.02) × 10^{-1}		12.1 ± 0.5	−20.5 ± 1.8			
		18.2	0.01	(1.61 ± 0.02) × 10^{-1}						
		25.0	0.01	(2.41 ± 0.03) × 10^{-1}	(2.44 ± 0.04) × 10^{-1}					
			0.05	(2.47 ± 0.03) × 10^{-1}						
		31.4	0.01	(3.98 ± 0.02) × 10^{-1}						
	I	11.5	0.01	(1.04 ± 0.02) × 10^{-1}		11.9 ± 0.2	−21.1 ± 0.7			
		18.2	0.01	(1.69 ± 0.01) × 10^{-1}						
		25.0	0.01	(2.78 ± 0.04) × 10^{-1}	(2.76 ± 0.04) × 10^{-1}					
			0.05	(2.73 ± 0.05) × 10^{-1}						
		31.4	0.01	(4.41 ± 0.04) × 10^{-1}						

[a] Mean value of at least six kinetic runs. [b] Presented in non-SI units for direct comparison with available literature data.

Table II. k_{obsd} as a Function of [Y^-] and Pressure for the Reaction $Pd(L)Cl^+ + Y^- \rightarrow Pd(L)Y^+ + Cl^-$ ([Pd] = 1×10^{-3} mol dm^{-3}; Ionic Strength 0.1 mol dm^{-3}; Temperature 25 °C; Wavelength 320 nm (Y = OH), 400 nm (Y = I))

L	Y	pressure/ bar	[Y^-]/ mol dm^{-3}	$k_{\mathrm{obsd}}{}^a$/s^{-1}	k_1/s^{-1}	$\Delta V_1^\ddagger$/ cm^3 mol^{-1}	k_2/ dm^3 mol^{-1} s^{-1}	$\Delta V_2^\ddagger$/ cm^3 mol^{-1}
1,4,7-Me_3dien	OH	50	0.01	27.2 ± 0.7	24.9 ± 0.2	−12.2 ± 0.6	223 ± 6	+21.2 ± 1.6
			0.03	31.4 ± 0.3				
			0.05	36.1 ± 0.7				
		250	0.01	30.8 ± 0.2	28.7 ± 1.3		175 ± 37	
			0.03	33.1 ± 0.4				
			0.05	37.9 ± 0.9				
		500	0.01	34.0 ± 0.7	31.8 ± 1.8		153 ± 53	
			0.03	35.2 ± 0.2				
			0.05	40.1 ± 0.4				
		750	0.01	37.3 ± 0.2	35.8 ± 0.6		126 ± 16	
			0.03	39.2 ± 0.9				
			0.05	42.3 ± 0.5				
		1000	0.01	41.5 ± 0.7	40.6 ± 0.2		93.0 ± 5.5	
			0.03	43.5 ± 0.3				
			0.05	45.2 ± 0.7				
	I	50	0.005	43.4 ± 1.0	21.9 ± 0.4	−9.2 ± 0.6	4318 ± 73	−18.9 ± 0.3
			0.01	65.0 ± 0.7				
		250	0.005	49.1 ± 0.6	24.0 ± 0.3		5036 ± 63	
			0.01	74.3 ± 1.0				
		500	0.005	57.0 ± 0.1	26.5 ± 0.1		6100 ± 19	
			0.01	87.5 ± 0.4				
		750	0.005	65.8 ± 0.9	28.1 ± 0.3		7542 ± 72	
			0.01	103 ± 1				
		1000	0.005	76.4 ± 0.8	31.7 ± 0.3		8934 ± 92	
			0.01	121 ± 1				
1,1,7,7-Me_4dien	OH	50	0.01	0.97 ± 0.01	0.90 ± 0.02	−15.5 ± 0.6	6.85 ± 0.52	+25.2 ± 3.6
			0.03	1.09 ± 0.01				
			0.05	1.25 ± 0.02				
		250	0.01	1.10 ± 0.01	1.04 ± 0.02		6.63 ± 0.48	
			0.03	1.25 ± 0.02				
			0.05	1.36 ± 0.02				
		500	0.01	1.26 ± 0.06	1.21 ± 0.02		5.43 ± 0.48	
			0.03	1.39 ± 0.00				
			0.05	1.48 ± 0.01				
		750	0.01	1.48 ± 0.04	1.45 ± 0.01		3.43 ± 0.33	
			0.03	1.56 ± 0.01				
			0.05	1.61 ± 0.02				
		1000	0.01	1.65 ± 0.02	1.63 ± 0.00		2.80 ± 0.06	
			0.03	1.71 ± 0.01				
			0.05	1.77 ± 0.02				
	I	50	0.01	1.00 ± 0.01				
		250	0.01	1.17 ± 0.02		−13.4 ± 1.9		
		500	0.01	1.44 ± 0.01				
		750	0.01	1.57 ± 0.03				
		1000	0.01	1.67 ± 0.02				
1,1,4,7,7-Me_5dien	OH	50	0.01	0.27 ± 0.01		−11.6 ± 0.5		
		250	0.01	0.29 ± 0.01				
		500	0.01	0.32 ± 0.01				
		750	0.01	0.37 ± 0.02				
		1000	0.01	0.42 ± 0.00				
	I	50	0.01	0.31 ± 0.01		−10.9 ± 0.3		
		250	0.01	0.34 ± 0.01				
		500	0.01	0.37 ± 0.02				
		750	0.01	0.42 ± 0.01				
		1000	0.01	0.47 ± 0.01				

[a] Mean value of at least six kinetic runs.

UV–visible spectra data for the dissolved species and the corresponding substitution products were reported elsewhere.[10] The investigated reactions are all of stopped-flow rate necessitating special instrumentation.[10,11] The pseudo-first-order rate constants k_{obsd} were determined in the usual way from the slopes of plots of ln ($A_\infty - A_t$) vs. *t*, each value being the mean for six successive kinetic runs and each plot being subjected to a linearity standard of at least 3 half-lives.

Results and Discussion

The values of k_{obsd} measured for the substitution reactions $Pd(L)Cl^+ + Y^- \rightarrow Pd(L)Y^+ + Cl^-$ for various L and Y as a function of [Y^-], temperature, and pressure are presented in Tables I and II. Such reactions generally follow the well-known two-term rate law for square-planar substitution according to which $k_{\mathrm{obsd}} = k_1 + k_2[Y^-]$. The values of k_1 (solvolysis path) and k_2 (direct substitution path) were estimated by using a least-squares analysis of the k_{obsd} vs. [Y^-] data. These are included in Tables I and II along with the corresponding activation parameters. $\Delta V_1^\ddagger$ and $\Delta V_2^\ddagger$ were determined from the slopes of linear plots of ln k_1 and ln k_2 vs. pressure.

The values of k_{obsd} at ambient pressure for the substitution of the Me_5dien complex by OH^- and I^- are in good agreement with some preliminary data reported elsewhere.[3,12] They exhibit no meaningful [OH^-] dependence, in contrast with

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Table III. Kinetic Parameters for the k_1 Path of the Substitution Reaction[a] $Pd(L)Cl^+ + Y^- \rightarrow Pd(L)Y^+ + Cl^-$

L	Y	k_1[c]/s^{-1}	$\Delta H_1^{\ddagger}$[d]/ kcal mol^{-1}	$\Delta S_1^{\ddagger}$[d]/ cal K^{-1} mol^{-1}	$\Delta V_1^{\ddagger}$[c]/ cm^3 mol^{-1}	ref
dien	OH	37.8 ± 0.4	9.5 ± 1.3	−19.6 ± 4.4	−12.2 ± 0.8	5
	I	43.8 ± 0.5	10.3 ± 0.8	−16.5 ± 2.8	−10.0 ± 0.6	
1,4,7-Me$_3$dien	OH	25.7 ± 0.3	8.7 ± 0.8	−22.8 ± 2.8	−12.2 ± 0.6	this work
	I	25.0 ± 4.2	9.2 ± 1.0	−20.9 ± 3.6	−9.2 ± 0.6	
1,4,7-Et$_3$dien	OH	10.8 ± 0.0	10.4 ± 0.2	−18.8 ± 0.8	−10.8 ± 0.7	5
	I	10.0 ± 0.1	9.9 ± 1.3	−20.6 ± 4.3	−10.8 ± 1.0	
1,1,7,7-Me$_4$dien	OH	0.90 ± 0.01	11.9 ± 0.4	−18.5 ± 1.3	−15.5 ± 0.6	this work
	I	0.99 ± 0.02	11.8 ± 0.2	−18.9 ± 0.6	−13.4 ± 1.9	
1,1,4-Et$_3$dien	OH	0.74 ± 0.02	12.5 ± 0.6	−17.1 ± 2.1	−14.2 ± 0.6	5
	I	0.77 ± 0.01	12.1 ± 0.2	−18.1 ± 0.8	−14.5 ± 1.2	
1,1,4,7,7-Me$_5$dien	OH	(2.44 ± 0.04) × 10^{-1}	12.1 ± 0.5	−20.5 ± 1.8	−11.6 ± 0.5	this work
	I	(2.76 ± 0.04) × 10^{-1}	11.9 ± 0.2	−21.1 ± 0.7	−10.9 ± 0.3	
1,1,7,7-Et$_4$dien	OH	(2.08 ± 0.11) × 10^{-3}	17.0 ± 0.4	−13.6 ± 1.4	−13.0 ± 0.6	5
	I	(2.16 ± 0.40) × 10^{-3}	16.5 ± 0.5	−16 ± 2	−14.9 ± 0.2	6, 8[b]
4-Me-1,1,7,7-Et$_4$dien	OH	(6.0 ± 0.2) × 10^{-4}				5[b]
	I	(6.8 ± 0.1) × 10^{-4}	15.8 ± 1.7	−20 ± 6	−14.3 ± 0.6	
1,1,4,7,7-Et$_5$dien	I	(6.7 ± 0.1) × 10^{-4}	14.2 ± 0.7	−25.4 ± 2.2	−12.8 ± 0.8	5[b]

[a] Ionic strength 0.1 mol dm^{-3} unless otherwise indicated. [b] Ionic strength 0.05 mol dm^{-3}. [c] Temperature 25 °C. [d] Presented in non-SI units for direct comparison with available literature data.

Table IV. Kinetic Parameters for the k_2 Path of the Substitution Reaction[a] $Pd(L)Cl^+ + I^- \rightarrow Pd(L)I^+ + Cl^-$

L	k_2[c]/ dm^3 mol^{-1} s^{-1}	$\Delta H_2^{\ddagger}$[d]/ kcal mol^{-1}	$\Delta S_2^{\ddagger}$[d]/ cal K^{-1} mol^{-1}	$\Delta V_2^{\ddagger}$[c]/ cm^3 mol^{-1}	ref
dien	4446 ± 41	4.0 ± 1.8	−28 ± 6	−10.3 ± 1.0	5
1,4,7-Me$_3$dien	3542 ± 319	5.1 ± 0.9	−25.1 ± 3.0	−18.9 ± 0.3	this work
1,4,7-Et$_3$dien	932 ± 4	7.9 ± 0.8	−18.3 ± 2.7	−11.1 ± 0.8	5
1,1,4-Et$_3$dien	21.2 ± 0.3	8.7 ± 0.03	−23.2 ± 0.1	−11.3 ± 1.3	5
1,1,7,7-Me$_4$dien	0.28 ± 0.53				this work
1,1,7,7-Et$_4$dien	8.0 × 10^{-4}				7[b]

[a] Ionic strength 0.1 mol dm^{-3} unless otherwise indicated. [b] Ionic strength 0.5 mol dm^{-3}. [c] Temperature 25 °C. [d] Presented in non-SI units for direct comparison with available literature data.

Table V. Kinetic Parameters for the k_2 Path of the Substitution Reaction[a] $Pd(L)Cl^+ + OH^- \rightarrow Pd(L)OH^+ + Cl^-$

L	k_2[b]/dm^3 mol^{-1} s^{-1}	$\Delta H_2^{\ddagger}$[c]/ kcal mol^{-1}	$\Delta S_2^{\ddagger}$[c]/ cal K^{-1} mol^{-1}	$\Delta V_2^{\ddagger}$[b]/ cm^3 mol^{-1}	ref
1,4,7-Me$_3$dien	130 ± 8	17.3 ± 1.0	+9.2 ± 3.4	+21.2 ± 1.6	this work
1,1,7,7-Me$_4$dien	4.53 ± 0.19	11.5 ± 1.6	−16.6 ± 5.5	+25.2 ± 3.6	this work
1,1,7,7-Et$_4$dien	(3.76 ± 0.49) × 10^{-2}	15.3 ± 0.4	−13.6 ± 1.2	+6.4 ± 0.9	5

[a] Ionic strength 0.1 mol dm^{-3}. [b] Temperature 25 °C. [c] Presented in non-SI units for direct comparison with available literature data.

those for the Me$_3$dien and Me$_4$dien complexes for which a significant [OH$^-$] dependence is observed. Moreover, for the Me$_3$dien species a k_2 path is observed for substitution by either OH$^-$ or I$^-$, whereas for the Me$_4$dien species a k_2 path is observed only for substitution by OH$^-$ and for the Me$_5$dien species no k_2 path could be detected. This illustrates the significant influence the methyl substituents have on the substitution processes. The reversal in the case of the Me$_4$dien species of the nucleophilicity order I$^-$ > OH$^-$ that applies for substitution of the Me$_3$dien complex was also reported for the ethyl-substituted dien complexes[5,7] and emphasizes the unique behavior of the Me$_4$dien and Et$_4$dien species (cf. further discussion).

The values of k_1 (k_{obsd} in case no [Y$^-$] dependence was observed) are independent of the nature of the entering ligand for the various complexes as illustrated by the data in Tables I and II. This is in agreement with a rate-determining solvolysis step prior to the fast anation step[10] that completes the substitution process. The significant decrease in the values of k_1 with increasing substitution by methyl groups on the dien ligand is accompanied by an increase in $\Delta H_1^{\ddagger}$ and almost constant values of $\Delta S_1^{\ddagger}$ and $\Delta V_1^{\ddagger}$. A summary of the present values of k_1 at 25 °C and their activation parameters along with those obtained for previously investigated complexes[5] (Table III) illustrates a reactivity order dien > Me$_3$dien > 1,4,7-Et$_3$dien > Me$_4$dien ~ 1,1,4-Et$_3$dien > Me$_5$dien > Et$_4$dien > MeEt$_4$dien ~ Et$_5$dien. This is expected to be in accordance with the degree of steric hindrance, which accounts for the decrease in k_1 and increase in $\Delta H_1^{\ddagger}$.

The distinctly negative values of $\Delta V_1^{\ddagger}$ underline the associative nature of the solvolysis process. The average value $\Delta V_1^{\ddagger} = -13 \pm 2$ cm^3 mol^{-1} is close to the maximum value expected[13,14] for the associative entrance of a water molecule into the coordination sphere of an octahedral complex ion. Moreover, $\Delta V_1^{\ddagger}$ is expected to mainly represent volume changes due to intrinsic changes in bond lengths and angles since major changes in electrostriction are not expected to occur during an associative solvolysis process. Apparently steric hindrance has no significant effect on the magnitude of $\Delta V_1^{\ddagger}$ (and $\Delta S_1^{\ddagger}$) and, therefore, on the nature of the substitution process.

The values of k_2 summarized in Table IV for substitution by I$^-$ decrease along the series dien > Me$_3$dien > 1,4,7-Et$_3$dien > 1,1,4-Et$_3$dien > Me$_4$dien > Et$_4$dien in close agreement with the sequence for the k_1 path mentioned above and for the anation reactions of the corresponding aquo complexes previously[10] observed. The decrease in k_2 is accompanied by an increase in $\Delta H_2^{\ddagger}$ and near constancy in $\Delta S_2^{\ddagger}$. The value of $\Delta V_2^{\ddagger}$ for the Me$_3$dien complex notably differs from the remaining almost constant $\Delta V_2^{\ddagger}$ values. They are all negative, in line with an associative reaction mode for which the intrinsic

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volume decrease is partially cancelled by the volume increase resulting from changes in solvation due to charge neutralization. It is the latter component that may be less significant in the case of the Me$_3$dien species to account for its deviating value of $\Delta V_2^{\ddagger}$. The difference in behavior between this and the others species is further exemplified by the values of k_2 and the activation parameters for substitution by OH$^-$ (cf. further discussion).

It follows from Table V, in which data for complexes exhibiting a meaningful [OH$^-$] dependence are summarized, that k_2 decreases significantly with increasing steric hindrance and that no apparent trend exists for any of the activation parameters. The fact that k_2 for substitution by I$^-$ greatly exceeds k_2 for substitution by OH$^-$ in the case of the Me$_3$dien species (cf. Tables IV and V) confirms the weak nucleophilicity normally observed for OH$^-$. The order is reversed in the case of the Me$_4$dien and Et$_4$dien complexes, indicating a common mechanistic feature of these species. This may probably be related to the unsubstituted fourth position of the dien ligand that can deprotonate under typical experimental conditions to result in a reactive conjugate-base species.[3,5] However, despite the parallelism between the values of $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ for these two complex species, a significant difference in the values of $\Delta V_2^{\ddagger}$ exists and calls for further discussion.

The conjugate-base mechanism (where L-H represents deprotonated L)

$$\mathrm{Pd(L)Cl^+ + OH^- \overset{K}{\rightleftharpoons} Pd(L\text{-}H)Cl + H_2O}$$

$$\mathrm{Pd(L\text{-}H)Cl \xrightarrow[H_2O]{k} Pd(L)OH^+ + Cl^-}$$

requires that $k_{\text{obsd}} = kK[\text{OH}^-]$ (cf. ref 5) and $\Delta V_2^{\ddagger} = \Delta \bar{V}(K) + \Delta V^{\ddagger}(k)$. If we assume $\Delta \bar{V}(K) \approx +22$ cm^3 mol^{-1},[15] $\Delta V^{\ddagger}(k)$ turns out to be approximately +3 and −16 cm^3 mol^{-1} for the Me$_4$dien and Et$_4$dien species, respectively. These values point toward an interchange and an associative reaction mode for the rate-determining step respectively[16,17] and, hence, indicate meaningful mechanistic differences between the substitution of the species by OH$^-$. Alternatively, the pK_a value of the remaining proton on the dien ligand is expected to be markedly higher for the Et$_4$dien than for the Me$_4$dien species due to inductive effects from the substituents, so that a conjugate-base mechanism may only be favored in the latter case. A normal associative mechanism could satisfactorily account for the substitution behavior of the Et$_4$dien complex as discussed previously.[5]

The values of $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ for the substitution of the Me$_3$dien complex by OH$^-$ differ considerably from those for the other complexes. The 1,4,7-Me$_3$dien ligand has protons available in positions 1 and 7, so that deprotonation to produce a conjugate-base species will be in a cis position with respect to the leaving group instead of the trans position as for the 1,1,7,7-Me$_4$dien and 1,1,7,7-Et$_4$dien ligands. This may partly account for the diverging trend in k_2 and the magnitudes of $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$. The positive value of $\Delta V_2^{\ddagger}$ is in close agreement with that for the Me$_4$dien species and suggests the operation of a conjugate-base mechanism in which the substitution process has an interchange character.

The results of this investigation stress the importance of the nature of the dien ligand for substitution reactions that involve bimolecular interaction with the hydroxide ion. These reactions seem to be extremely sensitive to the position and nature of the substituents on the dien ligand and thus proceed according to different mechanisms. The pK_a values of the protons in the 1 and 7 positions of the 1,4,7-Me$_3$dien ligand, for instance, are expected to be quite sensitive to the nature of the substituents in these positions, since the pK_a values of the protons in the fourth position of the 1,1,7,7-Me$_4$dien and 1,1,7,7-Et$_4$dien ligands, which are much further removed from the substituents than in the case of the 1,4,7-Me$_3$dien ligand, are influenced to such an extent that the volumes of activation suggest quite different mechanisms for these two tetrasubstituted systems. The significant role played by the 4-N hydrogen atom during hydroxide ion substitution is nicely demonstrated by the absence of such a k_2 path in the case of the Me$_5$dien complex.

Notwithstanding the outlined difficulties with the interpretation of the activation parameters for the direct substitution by OH$^-$, the very complete set of activation parameters for the solvolysis reactions of the series of dien complexes, as summarized in Table III, merits a final comment. The gradual increase in steric hindrance down the series from the dien to the Et$_5$dien complex, i.e. from a simple square-planar to a "pseudooctahedral"[2,3] geometry, causes the solvolysis rate constant (k_1) to decrease by 5 orders of magnitude. Furthermore, the activation parameters, especially $\Delta S_1^{\ddagger}$ and $\Delta V_1^{\ddagger}$, are strongly negative, suggesting that solvolysis proceeds via an associative reaction mode throughout the series. These facts have been stressed for some of the complexes in Table III[6,8,18] and related systems[19–21] before, leading to the general conclusion that it seems to be impossible to force a square-planar complex into a dissociatively activated substitution mode by increasing the steric hindrance. Some investigators, however, continue to report arguments in favor of dissociative reaction modes[22,23] for closely related, sterically hindered square-planar complexes.

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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(1,1,4,7,7-Me$_5$dien)Cl$^+$, 21007-58-9; OH$^-$, 14280-30-9; I$^-$, 20461-54-5.

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