ring in the BCEN or BCMEN complex.[27,28] The very large dissociative rate constant in $[Cu(BCHTN)]^{2+}$ is attributed to both the large steric strains among the three linked chelate rings and the low basicity of the ligand.

It is interesting to note that the rate constants for the dissociation reactions of these copper(II)–diamino diamides are smaller than those for the analogous reactions of the nickel(II) diamino diamides.[1] Of the transition-metal ions copper(II) is one of the most kinetically labile.[29,30] The small values of k^{CuL} and $k_H{}^{CuL}$ relative to k^{NiL} and $k_H{}^{NiL}$ reside in low $(k_1k_2/k_{-1}k_{-2})$ values for the reactions of these copper(II) complexes.

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Registry No. BCEN, 3216-87-3; BCTN, 34740-97-1; BCMEN, 89709-74-0; BCHTN, 89709-75-1; Cu, 7440-50-8.

Supplementary Material Available: Figures showing the results of Job's method of isomolar solutions of copper(II)–BCEN, copper(II)–BCTN, copper(II)–BCMEN, and copper(II)–BCHTN at 25.0 ± 0.1 °C (4 pages). Ordering information is given on any current masthead page.

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Leaving-Group Effects on Kinetic Parameters for Solvolysis Reactions of Sterically Hindered Palladium(II) Complexes in Aqueous Solution

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The solvolysis kinetics of a series of sterically hindered square-planar complexes of the type $Pd(R_5dien)X^{n+}$, where dien = diethylenetriamine, was studied as a function of temperature and pressure for differently charged leaving groups X, viz. Cl^-, Br^-, I^-, py, NH_3, and $C_2O_4{}^{2-}$. The results underline earlier observations that the leaving group has a marked influence on the volume of activation for the process, which varies between −3 and −12 cm³ mol⁻¹. This trend is discussed in terms of an earlier suggested gradual changeover in substitution mechanism from an associative to an associative interchange mechanism. It is, however, concluded that various factors can account for the observed trend such that solvolysis may proceed according to an associative mechanism in all cases.

Introduction

Our longstanding interest in the intimate nature of substitution reactions of sterically hindered Pd(II) complexes has resulted in a rather complete series of accurately measured activation parameters (ΔH^*, ΔS^*, and ΔV^*) for various degrees of steric hindrance.[1-3] These data clearly demonstrate that ΔS^* and ΔV^* for the solvolysis reactions of a series of $Pd(R_5dien)Cl^+$ complexes (R_5dien = substituted diethylenetriamine) are independent of the degree of steric hindrance.[2,3] The 6 orders of magnitude variation in the solvolysis rate constants can all be accounted for in terms of an increase in ΔH^* with increasing steric hindrance.[3] In addition, the activation parameters clearly demonstrated that an increase in steric hindrance in this system does not lead to a changeover in substitution mechanism from associative to dissociative.[4-6] ΔV^* has an average value of -12 ± 2 cm^3 mol^{-1} for solvolysis of the mentioned chloro comlexes, where R was varied from H to CH_3 and C_2H_5 in all five positions. However, in a few cases, for other leaving groups, significantly less negative ΔV^* values were found, viz. -7.8 ± 0.2 $(Pd(MeEt_4dien)I^+)^2$, -8.2 ± 0.3 $(Pd(Et_5dien)I^+)^2$, and -3 ± 1 cm^3 mol^{-1} $(Pd(Et_4dien)NH_3{}^{2+})$.[1] It is also rather surprising that similar ΔV^* values were reported[7] for water exchange of $Pd(H_2O)_4{}^{2+}$ and $Pt(H_2O)_4{}^{2+}$, viz. -2.2 ± 0.2 and -4.6 ± 0.2 cm^3 mol^{-1}, respectively. The possible changeover from an associative to an associative interchange mechanism was suggested, or at least could not be ruled out completely.

Although the nature of the leaving group is not expected to influence the intimate nature of the substitution process in case of a limiting associative mechanism, these data do indicate significant differences that may be related to other contributions toward ΔV^*. In this respect it is important to realize that leaving-group effects in substitution reactions of square-planar complexes, in general, have received significant attention from kineticists.[1,8,9] Different factors such as steric hindrance, trans effects, nucleophilicity, charge, etc. have been used to account for the observed trends. For systems in which marked leaving-group effects occur, it was suggested[8] that bond breakage of the five-coordinate intermediate produced during an associative substitution process may contribute significantly toward the observed kinetic parameters and may even be the rate-determining step under extreme conditions, for instance for strongly bonded leaving groups. It is, however, difficult to detect the presence of such a second transition state kinetically, especially for solvolysis reactions where it is difficult to measure the concentration dependence of the rate constant (see Results and Discussion). We have, therefore, extended the series of leaving groups studied before to include neutral and doubly charged species such as NH_3, pyridine, and $C_2O_4{}^{2-}$ and have concentrated on the 4-Me-1,1,7,7-Et_4dien and 1,1,4,7,7-Et_5dien complexes, in an effort to obtain more information on the effect of the leaving group.

Experimental Section

The complexes $[Pd(MeEt_4dien)Cl]ClO_4$, $[Pd(MeEt_4dien)Br]PF_6$, $[Pd(MeEt_4dien)I]ClO_4$, $Pd(MeEt_4dien)py^{2+}$, and $[Pd(Et_5dien)Cl]ClO_4$, where $MeEt_4$dien = 4-Me-1,1,7,7-Et_4diethylenetriamine and Et_5dien = 1,1,4,7,7-Et_5dien, were prepared as described before.[10,11] The [Pd-

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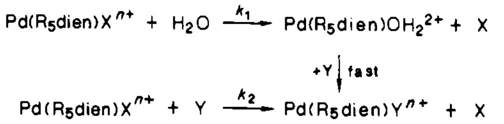
$(MeEt_4dien)NH_3](ClO_4)_2$ complex was synthesized according to the following method: Concentrated ammonia was added to a solution of the corresponding aquo complex[12] in the ratio 10:1, and the resulting mixture was slowly evaporated to dryness on a water bath. Light yellow crystals formed, which were recrystallized from a concentrated ammonia solution in the same way as above. The $Pd(MeEt_4dien)C_2O_4$ complex was prepared in solution by treating the corresponding aquo complex[12] with an equimolar $Na_2C_2O_4$ solution. Chemical analyses (Hoechst Analytical Laboratory, Frankfurt) for all the isolated complexes were in good agreement with the theoretically expected values. UV–vis spectral data were similar to those reported elsewhere for some of the complexes characterized before[11,13] and are as follows for the newly synthesized species: ammonia complex $\lambda_{max} = 311$ nm, $\epsilon = 910 \pm 10$ M^{-1} cm^{-1}; oxalato complex $\lambda_{max} = 328$ nm, $\epsilon = 1020 \pm 20$ M^{-1} cm^{-1}. Chemicals of analytical reagent grade and doubly distilled water were used throughout this study.

Kinetic measurements at ambient pressure were performed in the thermostated (±0.1 °C) cell compartment of a Zeiss DMR 10 or a Shimadzu UV 250 spectrophotometer. Similar measurements at elevated pressures were performed with the aid of a thermostated (±0.1 °C) high-pressure cell[14] built into the Zeiss spectrophotometer. All reactions were followed under pseudo-first-order conditions, and a linearity standard of 2–3 half-lives of the reaction was set for the corresponding plots.

Results and Discussion

Substitution reactions of the type $Pd(R_5dien)X^{n+} + Y \rightarrow Pd(R_5dien)Y^{n+} + X$ generally proceed according to the mechanism



$$\begin{array}{l} Pd(R_5dien)X^{n+} + H_2O \xrightarrow{k_1} Pd(R_5dien)OH_2{}^{2+} + X \\ \qquad\qquad\qquad\qquad\qquad\qquad\downarrow {+Y}\ \text{fast} \\ Pd(R_5dien)X^{n+} + Y \xrightarrow{k_2} Pd(R_5dien)Y^{n+} + X \end{array} \qquad (1)$$

This scheme is in agreement with the generally observed two-term rate law $k_{obsd} = k_1 + k_2[Y]$, where k_1 is the first-order rate constant for the solvolysis path and k_2 the second-order rate constant for the direct substitution path. For sterically hindered complexes and especially for weak nucleophiles Y, the direct substitution is usually very slow and almost no [Y] dependence of k_{obsd} is observed.[2,3] This is also the case in the present investigation as illustrated by the [Y] independence of k_{obsd} in Table A (supplementary material). It follows that the rate expression can be simplified to $k_{obsd} = k_1$; i.e., the solvolysis reaction path presents the main substitution route. Earlier studies[2,3] have clearly demonstrated that this k_1 is independent of the nature of the entering group Y and cannot be associated with a reverse anation reaction, which would have resulted in a similar rate expression.[11,15]

For NH_3 and py as leaving groups the pH of the solution increases significantly during the substitution reaction due to the protonation of the released ligand. This increase in pH may complicate the measurement of the solvolysis kinetics since the usually rapid subsequent anation step may become rate-determining at higher pH.[17,18] To rule out this possibility, the solvolysis reaction of $Pd(MeEt_4dien)NH_3{}^{2+}$ was measured in a different way, viz. via acidification. In the presence of acid the NH_3 released during solvolysis (k_1 in (1)) is protonated to $NH_4{}^+$, which cannot anate the produced aquo complex. In this way the solvolysis reaction can be followed directly, and the corresponding spectral changes exhibit clean isosbestic points at 286 and 319 nm. The observed rate contstants (i.e. k_1) in 0.1 M $HClO_4$ and at 39.5, 50.0, and 60.0 °C are $(0.42 \pm 0.02) \times 10^{-4}$, $(1.3 \pm 0.1) \times 10^{-4}$, and $(4.6 \pm 0.02) \times 10^{-4}$ s^{-1}, respectively, and are in close agreement with those measured for the substitution reaction with I^- (see Table A). It follows that solvolysis is the rate-determining step in the latter and similar reactions and that its measurement is not complicated by the increase in pH during the release of NH_3 or py.

The temperature and pressure dependencies of k_{obsd} $(=k_1)$ in Table A were used to calculate ΔH^*, ΔS^*, and ΔV^* in the usual way. Plots of ln k_{obsd} vs. pressure are linear in all cases, indicating that ΔV^* exhibits no meaningful pressure dependence over the investigated pressure range. The activation parameters for solvolysis are summarized along with the available literature data in Table I. From the overall 35 sets of rate parameters, 9 originate from this study. Furthermore, the data sets cover a significant range of complex species, leaving groups, ionic strengths, and temperatures, from which a number of interesting conclusions can be drawn.

In our earlier paper[2] we reported significantly more positive ΔV^* values for the solvolysis of $Pd(MeEt_4dien)I^+$ and $Pd(Et_5dien)I^+$ than for the corresponding chloro complexes (see Table I). In addition, Palmer and Kelm[1] reported an exceptionally slight negative ΔV^* value for the solvolysis of $Pd(Et_4dien)NH_3{}^{2+}$. It is, therefore, encouraging to note that we could reproduce our earlier data under closely related conditions and that we found a similar trend for other complexes with X = NH_3 and py. From this we can only conclude that there is a definite leaving-group effect, which requires a more detailed discussion. The data in Table I also demonstrate that small changes in ionic strength have no significant effect on ΔV^*. In one case, viz. the solvolysis of $Pd(MeEt_4dien)Cl^+$, an increase in the ionic strength to 1.0 M had no effect on the value of ΔV^*. Furthermore, temperatures of between 15 and 50 °C do not have a marked influence on ΔV^*. It follows that the observed deviations cannot be accounted for in terms of ionic strength and/or temperature effects. For a particular leaving group like Cl^-, Br^-, $CO_3{}^{2-}$, or NH_3, the decrease in k_1 with increasing steric hindrance on the dien ligand is accompanied by a significant increase in ΔH^* and approximately constant values for ΔS^* and ΔV^*. This trend has been discussed for the chloro and carbonato complexes elsewhere,[12,16] and similar arguments can be adopted for the other leaving groups.

The most complete sets of data, demonstrating the leaving-group dependence of ΔV^*, are available for the Et_4dien[1] and $MeEt_4dien$ complex series. In the case of the Et_4dien species the lowest absolute values of ΔV^* were observed for the NH_3 and $CO_3{}^{2-}$ complexes, whereas those for the $MeEt_4dien$ species are the lowest for the I^-, py, and NH_3 complexes. There are two obvious ways to interpret these trends in the ΔV^* values, viz. (i) due to a gradual changeover in substitution mechanism from an associative to an associative interchange mechanism or (ii) due to differences in the partial molar volumes of the reactant and transition-state species during the solvolysis process. In both cases intrinsic volume contributions due to changes in bond lengths and bond angles, as well as solvational volume contributions due to changes in electrostriction during the solvolysis reaction, may contribute to the observed effects.

In terms of the Langford and Gray classification of substitution reactions,[9] it is helpful to distinguish between limiting A, A, and I_a mechanisms to account for leaving-group effects. The first two mechanisms are characterized by the formation of an intermediate of higher coordination number, i.e. two transition states separated by a minimum in the energy profile, whereas the I_a mechanism is a synchronous, single-transition-state process.[8,9] Systems in which the formation of the five-coordinate intermediate is rate-determining are referred to as limiting A, whereas those in which the subsequent bond breakage step (i.e. the second transition state) significantly affects the observed kinetics are referred to as A. It follows that bond formation as well as bond breakage will contribute to the observed activation parameters for both A and I_a mechanisms, such that these could account for leaving-group effects. However, to distinguish kinetically between an A and I_a process is difficult since this is directly related to the problem of synchronous (I_a) vs. stepwise (A) processes.

If some of the sterically hindered complexes aquate according to an A or I_a mechanism, the Pd–X bond must lengthen during the formation of the transition state. This would lead to a positive intrinsic contribution toward ΔV^*, which would at least partially

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Table I. Summary of Rate and Activation Parameters for the Solvolysis of $Pd(R_5dien)X^{n+}$ Complexes in Aqueous Solution during the Overall Reaction $Pd(R_5dien)X^{n+} + Y \rightarrow Pd(R_5dien)Y^{n+} + X$

R_5dien	X	Y	k_1(25 °C), s^{-1}	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	$\Delta V^\ddagger$, cm^3 mol^{-1}	ionic strength, M	ref
dien	Cl^-	OH^-	37.8 ± 0.4	40 ± 5	−82 ± 18	−12.2 ± 0.8 (25)	0.1	2
		I^-	43.8 ± 0.5	43 ± 3	−69 ± 12	−10.0 ± 0.6 (25)		
	CO_3^{2-}	OH^-	1.74 ± 0.08	41 ± 5	−101 ± 15	−9.7 ± 0.4 (25)	1.0	16
1,4,7-Me_3dien	Cl^-	OH^-	25.7 ± 0.3	36 ± 3	−95 ± 12	−12.2 ± 0.6 (25)	0.1	3
		I^-	25.0 ± 4.2	38 ± 4	−87 ± 15	−9.2 ± 0.6 (25)		
1,4,7-Et_3dien	Cl^-	OH^-	10.8 ± 0.0	43 ± 1	−79 ± 3	−10.8 ± 0.7 (25)	0.1	2
		I^-	10.0 ± 0.1	41 ± 5	−86 ± 18	−10.8 ± 1.0 (25)		
1,1,7,7-Me_4dien	Cl^-	OH^-	0.90 ± 0.01	50 ± 2	−77 ± 5	−15.5 ± 0.6 (25)	0.1	3
		I^-	0.99 ± 0.02	49 ± 1	−79 ± 2	−13.4 ± 1.9 (25)		
	CO_3^{2-}	OH^-	(5.49 ± 0.05) × 10^{-2}	52 ± 4	−95 ± 12	−8.6 ± 0.4 (25)	1.0	16
1,1,4-Et_3dien	Cl^-	OH^-	0.74 ± 0.02	52 ± 2	−71 ± 9	−14.2 ± 0.6 (25)	0.1	2
		I^-	0.77 ± 0.01	51 ± 1	−76 ± 3	−14.5 ± 1.2 (25)		
1,1,4,7,7-Me_5dien	Cl^-	OH^-	(2.44 ± 0.04) × 10^{-1}	51 ± 2	−86 ± 7	−11.6 ± 0.5 (25)	0.1	3
		I^-	(2.76 ± 0.04) × 10^{-1}	50 ± 1	−88 ± 3	−10.9 ± 0.3 (25)		
1,1,7,7-Et_4dien	Cl^-	OH^-	(2.08 ± 0.11) × 10^{-3}	71 ± 2	−57 ± 6	−13.0 ± 0.6 (25)	0.1	2
		I^-	(2.16 ± 0.40) × 10^{-3}	66 ± 1	−74 ± 3	−14.9 ± 0.2 (25)	0.05	1
	Br^-	N_3^-	(1.74 ± 0.07) × 10^{-3}	66 ± 3	−75 ± 10	−13.3 ± 0.2 (25)	0.05	1
	N_3^-	I^-	(4.59 ± 0.05) × 10^{-4}	72 ± 1	−71 ± 2	−13.9 ± 0.5 (25)	0.05	1
	I^-	Br^-	(2.65 ± 0.05) × 10^{-4}	71 ± 1	−69 ± 3	−11.5 ± 0.2 (25 + 40)	0.05	1
	NCS^-	I^-	(1.52 ± 0.03) × 10^{-4}	75 ± 2	−67 ± 6	−10.3 ± 0.2 (40)	0.05	1
	NH_3	I^-	(0.13 ± 0.01) × 10^{-4}	93 ± 2	−28 ± 7	−3.0 ± 0.9 (40)	0.05	1
	CO_3^{2-}	OH^-	(3.5 ± 0.1) × 10^{-3}	62 ± 2	−82 ± 8	−6.7 ± 0.5 (25)	1.0	16
4-Me-1,1,7,7-Et_4dien	Cl^-	OH^-	(6.0 ± 0.2) × 10^{-4}				0.05	2
			(6.5 ± 0.4) × 10^{-4}	69 ± 1	−74 ± 4	−12.2 ± 0.6 (25)	0.1	*a*
						−13.2 ± 1.0 (40)	0.1	*a*
			(6.2 ± 0.6) × 10^{-4} [b]			−13.5 ± 1.8 (30)	1.0	*a*
		I^-	(6.7 ± 0.1) × 10^{-4}	66 ± 7	−84 ± 25	−14.3 ± 0.6 (30)	0.05	2
	I^-	OH^-	(1.8 ± 0.1) × 10^{-4}	72 ± 2	−75 ± 5	−7.8 ± 0.2 (30)	0.05	2
			(1.82 ± 0.03) × 10^{-4}	72 ± 2	−74 ± 5	−8.4 ± 0.6 (30)	0.1	*a*
	Br^-	OH^-	(4.5 ± 0.1) × 10^{-4}	73 ± 3	−63 ± 11	−11.9 ± 0.5 (25)	0.1	*a*
	py	OH^-	(8.6 ± 0.5) × 10^{-6}	78 ± 2	−80 ± 6	−3.7 ± 0.4 (50)	0.1	*a*
	NH_3	I^-	(1.24 ± 0.06) × 10^{-5}	83 ± 8	−59 ± 25	−3.0 ± 0.4 (50)	0.1	*a*
	$C_2O_4^{2-}$	OH^-	(4.0 ± 0.3) × 10^{-3}	48 ± 4	−128 ± 13	−10.6 ± 0.2 (14)	0.1	*a*
1,1,4,7,7-Et_5dien	Cl^-	OH^-	(7.0 ± 0.2) × 10^{-4}	74 ± 1	−56 ± 3	−11.6 ± 0.2 (25)	0.1	*a*
		I^-	(7.2 ± 0.1) × 10^{-4}	59 ± 3	−106 ± 9	−12.8 ± 0.8 (25)	0.05	2
	I^-	OH^-	(2.2 ± 0.3) × 10^{-4}	76 ± 3	−60 ± 11	−8.2 ± 0.3 (30)	0.05	2

[a] This work—calculated from the rate data in Table A. [b] Value at 30 °C.

be compensated for by electrostriction resulting from charge separation in the case of X being an ionic ligand. The major contribution to $\Delta V^\ddagger$ will result from the associative entrance of the solvent molecule, such that an overall negative $\Delta V^\ddagger$ is observed in all cases. In general, the gradual changeover from limiting A to A or I_a is expected to depend on the degree of steric hindrance and the nature of the leaving group. However, for the series of chloro complexes included in Table I the activation parameters do not reveal any significant trend in $\Delta S^\ddagger$ and $\Delta V^\ddagger$ with increasing steric hindrance.[2,3] Only $\Delta H^\ddagger$ increases significantly with increasing steric hindrance and accounts for the significant decrease in solvolysis rate constant. It follows that steric hindrance alone cannot initiate such a changeover and that the nature of the leaving group must play a dominant role.

A mechanistic changeover from limiting A to A is likely in cases where the leaving group is strongly bonded to the metal center, since in such cases the second transition state (bond breakage process) could lie significantly higher than for a limiting A mechanism and so affect the substitution process. In some cases bond strength correlates with the nucleophilicity of the ligand, and accordingly the less negative $\Delta V^\ddagger$ values found for the solvolysis of $Pd(MeEt_4dien)I^+$ and $Pd(Et_5dien)I^+$ could indicate a positive contribution arising from Pd–I bond breakage due to the relative high nucleophilicity of iodide. However, in many cases this correlation does not hold, and complexes with weak nucleophilic ligands such as OH^-, NH_3, and py are extremely stable and exhibit strong metal–ligand bonds. The slightly negative $\Delta V^\ddagger$ values for the solvolysis of the NH_3 and py complexes in Table I indicate that bond breakage could play a significant role. Alternatively, these effects can be ascribed to a changeover from a limiting A to an I_a mechanism, as suggested before.[1] However, the vacant p_z orbital in square-planar d^8 complexes should favor an associative reaction mode in which a five-coordinate intermediate is formed. This is further demonstrated by the isolation of numerous five-coordinate complexes of such d^8-metal centers. It is understandable that a synchronous interchange type of mechanism will operate in the case of a coordinatively saturated species as found for octahedral d^6 complexes but not for square-planar d^8 species.

It is also possible to interpret all the observed $\Delta V^\ddagger$ data in terms of a limiting A mechanism. Partial molar volume data for some of the complexes referred to in Table I demonstrate[1] the expected tendency that such values depend on the size of X and the overall charge on the complex, which is determined by the charge on X. Since $\Delta V^\ddagger$ for solvolysis presents the difference in volume between the five-coordinate transition state and the reactant species (according to a limiting A mechanism), its magnitude is determined by the ability of the complex to accommodate the additional ligand on a volume basis. Larger complex species may be able to accommodate the additional solvent molecule more effectively, which will result in a more negative $\Delta V^\ddagger$ value, and vice versa for smaller complexes. However, once again the results for the series of chloro complexes in Table I do not show any specific trend, indicating that the absolute size of the reactant complex plays a minor role in determining the value of $\Delta V^\ddagger$. Such effects can probably account for small diffferences in $\Delta V^\ddagger$, viz. −8 compared to −11 cm^3 mol^{-1}, but surely not for large differences, viz. −3 compared to −11 cm^3 mol^{-1}.

The most positive $\Delta V^\ddagger$ values in Table I are for the NH_3 and py complexes, i.e. species with a neutral leaving group and an overall charge of 2+. Furthermore, these values are in excellent agreement with those reported for solvolysis (solvent exchange) of $Pd(H_2O)_4^{2+}$ and $Pt(H_2O)_4^{2+}$, in which case we are also dealing with a neutral leaving group and an overall charge of 2+. These values suggest that there must be an additional negative contribution toward $\Delta V^{\ddagger}$ when the leaving group is a 1– or a 2– species. This negative component most probably originates from changes in dipole interaction when the square-bipyramidal transition state, in which the dien ligand most probably occupies the trigonal plane. This component will depend on the size and nature (especially charge) of the leaving group X. In addition, such volume differences may be more significant in the trigonal-bipyramidal transition state than in the square-planar ground state. It then follows that a $\Delta V^{\ddagger}$ of -3 cm^3 mol^{-1} could present the intrinsic component for the limiting associative attack of a water molecule on a 2+-charged square-planar complex with neutral ligands. The additional -9 cm^3 mol^{-1} usually observed for solvolysis reactions of 1+ and neutral Pd(II) complexes must then be due to solvational effects resulting from the described dipole interactions. The intrinsic component of -3 cm^3 mol^{-1} is significantly smaller than that observed and expected for associative solvolysis of octahedral complexes.[19,20] This is quite understandable since the geometry of the square-planar complex is such that the entering solvent molecule may be close to the vacant coordination site (i.e. above or below the plane in the second coordination sphere), such that relatively small volume changes are observed. Futhermore, structural changes from tetragonal pyramidal to trigonal bipyramidal are expected to cause an increase in volume that will counterbalance the intrinsic volume decrease due to bond formation.

We conclude that a limiting associative mechanism can accommodate all the data in Table I, and a $\Delta V^{\ddagger}$ value of -3 cm^3 mol^{-1} could represent the intrinsic component for the associative attack of a water molecule on a square-planar complex with neutral ligands. If deviations do occur, we expect these to result from a changeover from limiting A to A, rather than from limiting A to I_a as suggested before.[1] Further investigations to clarify this point are presently under way in our laboratories.

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Registry No. $Pd(MeEt_4dien)NH_3^{2+}$, 103904-37-6; $Pd(MeEt_4dien)C_2O_4$, 103932-99-6; $Pd(MeEt_4dien)Cl^+$, 46848-25-3; $Pd(MeEt_4dien)I^+$, 58619-25-3; $Pd(MeEt_4dien)Br^+$, 58619-24-2; $Pd(MeEt_4dien)py^{2+}$, 91606-31-4; $Pd(Et_5dien)Cl^+$, 70472-44-5.

Supplementary Material Available: Table A, k_{obsd} as a function of X, Y, ionic strength, temperature, and pressure for the reaction $Pd(R_5dien)X^{n+} + Y \rightarrow Pd(R_5dien)Y^{n+} + X$ (4 pages). Ordering information is given on any current masthead page.

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Transmetalation of Tetranuclear Copper Complexes. 9. Stoichiometry and Kinetics of Transmetalation of $(\mu_4\text{-O})[NCu]_4X_6$ Complexes by $M(NS)_2$ Reagents in Aprotic Solvents

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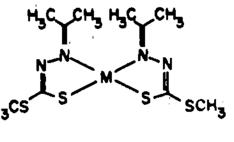
Tetranuclear copper(II) complexes $(\mu_4\text{-O})[(DENC)Cu]_4X_6$ (A; DENC = *N,N*-diethylnicotinamide; X = Cl, Br) are stoichiometrically transmetalated by 1 mol of structurally characterized $M(NS)_2$ reagents (NS is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base; M = Co, Ni, Zn) in aprotic solvents. The chromatographically isolated products are equimolar tetranuclear $(\mu_4\text{-O})[(DENC)_4Cu_3M(H_2O)]X_6$ and $Cu(NS)_2$. Reactants A and products $(\mu_4\text{-O})[(DENC)_4Cu_3M(H_2O)]X_6$ have electronic spectral features at 775 and 850 nm. The rate laws for reactions of excess A with $M(NS)_2$ in methylene chloride and nitrobenzene depend on X, M, and the structure of the NS ligand. The proposed mechanisms contain common $\overline{\text{Cu–X–M–S}}$ rings that facilitate metal replacement in A; however, metal replacement apparently is not rate-determining in the majority of the 18 systems investigated.

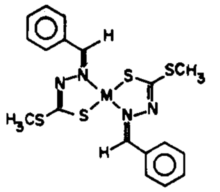
Introduction

Our previous work demonstrates that one can make polynuclear copper complexes from commonly available materials and then replace their copper centers with different metals derived from (hydrazinecarbodithioato)metal reagents $M(NS)_n$.[2-9] Attractive features of these transmetalation reactions are that they proceed under mild conditions in aprotic solvents and that they are stoichiometric, stepwise processes because of the high thermodynamic stability of easily separated Cu(NS) and $Cu(NS)_2$ coproducts.

Among the wide variety of new, polynuclear products is the series $(\mu_4\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xX_6$, obtained as discrete tetranuclear products by stoichiometric transmetalation of $(\mu_4\text{-O})[NCu]_4X_6$ complexes A with *x* mol of reagents B and C (M = Ni), eq 1. Here, N is monodentate pyridine (py), *N,N*-diethylnicotinamide (DENC), or ethyl nicotinate (ENCA), *x* is 1–4, and X is Cl or Br. One water molecule is incorporated with each new nickel center during product isolation.[3-5,8]



B



C

$$(\mu_4\text{-O})[NCu]X_6 + x(\text{B or C, M = Ni}) \rightarrow (\mu_4\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xX_6 + x(\text{B or C, M = Cu}) \quad (1)$$

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