Inorg. Chem. 1989, 28, 373–375

The cyclic voltammograms of the $(NH_3)_3Ru(tppz)^{2+}$ and $(NH_3)_3Ru(tppz)Ru(NH_3)_3^{4+}$ complexes are shown in Figure 3, and the results are summarized in Table II. $E_{1/2}$ for the oxidation/reduction couple of $(NH_3)_3Ru(tppz)^{2+}$ is +0.97 V (vs SCE, DMF/0.10 M TBAP, 100 mV/s; $E_{1/2}$ is the average of the anodic and cathodic waves). Although the anodic/cathodic wave separation of 75 mV is larger than the theoretical value of 59 mV, on the basis of the reproducibility of several scans and the equivalence of wave height, the electrochemical couple is judged to be reversible. The $(NH_3)_3Ru(tppz)Ru(NH_3)_3^{4+}$ complex shows two waves at $E_{1/2}(1) = +0.81$ V and $E_{1/2}(2) = +1.31$ V. The difference in $E_{1/2}(1)$ and $E_{1/2}(2)$ couples for bimetallic complexes has previously been interpreted as a measure of metal–metal communication through a bridging ligand.[2,3,8,12,23,24] The unusually large $\Delta E_{1/2}(2-1)$ value of 0.50 V for $(NH_3)_3Ru(tppz)Ru(NH_3)_3^{4+}$ indicates that substantially greater metal–metal interaction occurs through tppz as compared with similar ruthenium amine-bridged complexes ($\Delta E_{1/2}(2-1) = 390$ mV – 50 mV).[2,3,8,10,17] The $E_{1/2}(1)$ value for $(NH_3)_3Ru(tppz)Ru(NH_3)_3^{4+}$ is 0.16 V less positive than the $E_{1/2}$ value (+0.97 V) for $(NH_3)_3Ru(tppz)^{2+}$ and also demonstrates the communicative effectiveness of tppz by the addition of $\sigma$-donating $NH_3$ groups, via the coordination of the remote $(NH_3)_3Ru$ center.

The $E_{1/2}(2-1)$ values of the bimetallic complex allow for the calculation of $K_{com}$ according to the formula $\exp(\Delta E_{1/2}(2-1)/25.69)$, where $\Delta E_{1/2}$ is in millivolts and $T = 25$ °C; the comproportionation equilibrium is described by[24-26]

$$((NH_3)_3Ru)_2(tppz)^{4+} + ((NH_3)_3Ru)_2(tppz)^{6+} \rightarrow 2((NH_3)_3Ru)_2(tppz)^{5+}$$

The $K_{com} = 2.8 \times 10^8$ value is larger than the calculated value for the analogous tetraammineruthenium bpym- and dpp-bridged complexes.

Despite the high comproportionation constant, titration of the $((NH_3)_3Ru)_2(tppz)^{4+}$ [2+,2+] species with Ce(IV) produced a decrease and a broadening of the characteristic absorption at 585 nm without appearance of an intervalence band in the 700–1300-nm region. Throughout Ce(IV) addition, isobestic points at 720, 625, and 540 nm were observed as the 585-nm MLCT absorption decreased without a wavelength shift until the [3+,3+] equivalence point was reached. Attempted rereduction of the [2+,3+] and [3+,3+] samples with Sn(II) or by addition of Zn/Hg failed to regenerate the initial [2+,2+] spectrum, suggesting the 5+ and 6+ species decompose on the time scale of the experiment. Addition of excess Ce(IV) caused loss of the isobestic point, probably as a result of $NH_3$ oxidation to form NO, as has been reported for Ce(IV) oxidations of $(trpy)Ru(bpy)NH_3^{2+}$.[17]

## Conclusion

The transition energies, molar absorptivities, and visible-region photostability make this type of complex ideal in energy capture, storage, and conversion processes. Electrochemical results demonstrate the effective communication between the Ru(II) centers through the tppz bridging ligand. The impact of this new class of tppz-bridged complexes such as $(NH_3)_3Ru(tppz)Ru(NH_3)_3^{4+}$ is extensive, ranging from optical electron-transfer studies to potential intramolecular energy-transfer reactions.

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**Registry No.** $[((NH_3)_3Ru)_2tppz](ClO_4)_4$, 117828-26-9; $[(NH_3)_3Ru(tppz)](ClO_4)_2$, 117828-28-1; $[(NH_3)_5(H_2O)Ru](TFMS)_3$, 53195-18-9; $((NH_3)_3Ru)_2(tppz)^{6+}$, 117828-29-2; $((NH_3)_3Ru)_2(tppz)^{5+}$, 117860-18-1; $Ru(NH_3)_3(tppz)^+$, 117828-30-5.

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# Volume Profiles for Solvolysis Reactions of Sterically Hindered Diethylenetriamine Complexes of Palladium(II) in Aqueous Solution

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The intimate nature of solvolysis reactions of diethylenetriamine (dien) and substituted dien complexes of palladium(II) has interested us for quite some time[2-5] due to the general importance of this process in the substitution behavior of square-planar complexes. We and others have adopted high-pressure kinetic techniques to gain insight into the volume changes involved in such processes.[6] Our recent study[4] emphasized the importance of the nature of the leaving group in determining the volume of activation for the solvolysis process. It was reported that $\Delta V^*$ is significantly more negative for anionic leaving groups during the solvolysis of $Pd(R_5dien)X^{(2-n)+}$ ($R_5$dien = methyl- and ethyl-substituted diethylenetriamine). In fact, the correct analysis of such data calls for the construction of a volume profile on which basis the transition state of the process can be located with respect to the partial molar volumes of the reactant and product species.[7,8] Such analyses were not possible in our previous investigations due to a lack of either the required partial molar volume data or the overall reaction volume of the process.

We have now completed a series of measurements in which volumes of activation were determined for solvolysis ($k_1$) and reverse anation ($k_{-1}$) reactions of some substituted dien complexes according to the overall process in (1), where R = $CH_3$ and $C_2H_5$.

$$Pd(R_5dien)X^{(2-n)+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd(R_5dien)H_2O^{2+} + X^{n-} \qquad (1)$$

These data enable us to construct volume profiles for a series of such reactions and to make quantitative correlations between the partial molar volumes of ground- and transition-state species.

## Experimental Section

Complexes of the type $Pd(R_5dien)X^{(2-n)+}$, where R = Me or Et and $X^{n-} = H_2O$, $Cl^-$, $Br^-$, $I^-$, $N_3^-$, or $C_2O_4^{2-}$, were prepared and characterized in the same way as previously reported for these or closely related complexes.[3,4,9-11] UV–vis absorption spectra were recorded on Shimadzu UV250 and Perkin-Elmer Lambda 5 spectrophotometers. All measurements were performed at 25 °C and 0.1 mol dm$^{-3}$ ionic strength ($NaClO_4$ medium). Kinetic experiments at ambient pressure were performed with a Durrum D110 stopped-flow instrument equipped with a data acquisition system,[12] whereas those at elevated pressure (up to 100 MPa) were performed with a high-pressure stopped-flow unit.[13] All reactions were studied under pseudo-first-order conditions, and the corresponding semilogarithmic plots were linear for at least 3 half-lives of the reaction. The reported rate constants are the mean values of at least six kinetic runs. UV–vis spectra at elevated pressure (up to 150 MPa) were re-

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**Table I.** Rate Constants and Volumes of Activation for Reactions of the Type $Pd(L)X^{(2-n)+} + H_2O \rightarrow Pd(L)H_2O^{2+} + X^{n-}$ ([Pd] = 0.001 mol dm$^{-3}$; [OH$^-$] = 0.01 mol dm$^{-3}$; $T$ = 25 °C; $\mu$ = 0.1 mol dm$^{-3}$)

| L | $p$/MPa | | $k_{obs}/s^{-1}$ | | | | |
|---|---|---|---|---|---|---|---|
| | | | $X^{n-} = Cl^-$ | $X^{n-} = Br^-$ | $X^{n-} = I^-$ | $X^{n-} = N_3^-$ | $X^{n-} = C_2O_4^{2-}$ |
| Me$_5$dien | 5 | | 0.27[a] | 0.374 ± 0.012 | 0.350 ± 0.005 | (2.57 ± 0.05) × 10$^{-2}$ | 0.366 ± 0.016 |
| | 25 | | | 0.431 ± 0.011 | 0.375 ± 0.004 | (2.95 ± 0.04) × 10$^{-2}$ | 0.382 ± 0.020 |
| | 50 | | | 0.468 ± 0.011 | 0.412 ± 0.004 | (3.29 ± 0.04) × 10$^{-2}$ | 0.430 ± 0.013 |
| | 75 | | | 0.530 ± 0.003 | 0.462 ± 0.003 | (3.60 ± 0.03) × 10$^{-2}$ | 0.480 ± 0.012 |
| | 100 | | | 0.588 ± 0.019 | 0.503 ± 0.002 | (4.04 ± 0.05) × 10$^{-2}$ | 0.539 ± 0.016 |
| | | $\Delta V^{\ddagger}$/cm$^3$ mol$^{-1}$ | −11.6 ± 0.5[a] | −11.4 ± 0.7 | −9.7 ± 0.3 | −11.4 ± 0.7 | −10.4 ± 0.6 |
| Et$_5$dien | 5 | | 7.0 × 10$^{-4}$ [b] | (1.41 ± 0.04) × 10$^{-3}$ | (5.40 ± 0.20) × 10$^{-4}$ | (2.22 ± 0.34) × 10$^{-4}$ | (5.86 ± 0.35) × 10$^{-3}$ |
| | 25 | | | (1.57 ± 0.04) × 10$^{-3}$ | (6.10 ± 0.05) × 10$^{-4}$ | (2.46 ± 0.22) × 10$^{-4}$ | (6.57 ± 0.24) × 10$^{-3}$ |
| | 50 | | | (1.72 ± 0.01) × 10$^{-3}$ | (6.32 ± 0.10) × 10$^{-4}$ | (2.68 ± 0.16) × 10$^{-4}$ | (7.00 ± 0.26) × 10$^{-3}$ |
| | 75 | | | (1.88 ± 0.06) × 10$^{-3}$ | (6.66 ± 0.02) × 10$^{-4}$ | (3.04 ± 0.27) × 10$^{-4}$ | (7.47 ± 0.21) × 10$^{-3}$ |
| | 100 | | | (2.16 ± 0.06) × 10$^{-3}$ | (7.13 ± 0.03) × 10$^{-4}$ | (3.39 ± 0.12) × 10$^{-4}$ | (7.96 ± 0.39) × 10$^{-3}$ |
| | | $\Delta V^{\ddagger}$/cm$^3$ mol$^{-1}$ | −11.6 ± 0.2[b] | −11.6 ± 0.5[c] | −6.8 ± 0.9[c] | −11.3 ± 0.4[c] | −7.6 ± 0.8 |

[a] Data taken from ref 2. [b] Data taken from ref 4. [c] Data determined at 34 °C.

**Table II.** Rate Constants and Volumes of Activation for Reactions of the Type $Pd(L)H_2O^{2+} + X^{n-} \rightarrow Pd(L)X^{(2-n)+} + H_2O$ ([Pd] = 0.001 mol dm$^{-3}$; [X$^{n-}$] = 0.01 mol dm$^{-3}$; $T$ = 25 °C; $\mu$ = 0.1 mol dm$^{-3}$)

| L | $p$/MPa | | $k_{obs}/s^{-1}$ | | | | |
|---|---|---|---|---|---|---|---|
| | | | $X^{n-} = Cl^-$ | $X^{n-} = Br^-$ | $X^{n-} = I^-$ | $X^{n-} = N_3^-$ | $X^{n-} = C_2O_4^{2-}$ [b] |
| Me$_5$dien | 5 | | 6.2 ± 0.1[a] | 10.1 ± 0.1[a] | 38.5 ± 1.4[a] | 50.3 ± 0.2 | 11.2 ± 0.5 |
| | 25 | | | | | 55.8 ± 0.4 | 11.9 ± 1.3 |
| | 50 | | | | | 60.9 ± 1.6 | 12.5 ± 0.9 |
| | 75 | | | | | 67.3 ± 0.8 | 13.5 ± 0.8 |
| | 100 | | | | | 74.7 ± 0.3 | 14.0 ± 1.2 |
| | | $\Delta V^{\ddagger}$/cm$^3$ mol$^{-1}$ | −4.9 ± 0.4[a] | −7.3 ± 0.4[a] | −9.9 ± 1.2[a] | −10.1 ± 0.3 | −5.9 ± 0.4 |
| Et$_5$dien | 5 | | (1.51 ± 0.02) × 10$^{-2}$ | (1.62 ± 0.06) × 10$^{-2}$ | (2.00 ± 0.04) × 10$^{-2}$ | (3.25 ± 0.08) × 10$^{-2}$ | (3.13 ± 0.06) × 10$^{-2}$ |
| | 25 | | (1.61 ± 0.03) × 10$^{-2}$ | (1.67 ± 0.01) × 10$^{-2}$ | (2.09 ± 0.03) × 10$^{-2}$ | (3.57 ± 0.05) × 10$^{-2}$ | (3.24 ± 0.09) × 10$^{-2}$ |
| | 50 | | (1.70 ± 0.02) × 10$^{-2}$ | (1.75 ± 0.03) × 10$^{-2}$ | (2.19 ± 0.02) × 10$^{-2}$ | (4.00 ± 0.15) × 10$^{-2}$ | (3.40 ± 0.06) × 10$^{-2}$ |
| | 75 | | (1.81 ± 0.01) × 10$^{-2}$ | (1.89 ± 0.03) × 10$^{-2}$ | (2.44 ± 0.02) × 10$^{-2}$ | (4.37 ± 0.08) × 10$^{-2}$ | (3.53 ± 0.11) × 10$^{-2}$ |
| | 100 | | (1.90 ± 0.02) × 10$^{-2}$ | (2.00 ± 0.02) × 10$^{-2}$ | (2.60 ± 0.01) × 10$^{-2}$ | (5.00 ± 0.24) × 10$^{-2}$ | (3.63 ± 0.17) × 10$^{-2}$ |
| | | $\Delta V^{\ddagger}$/cm$^3$ mol$^{-1}$ | −5.9 ± 0.3 | −5.8 ± 0.4 | −7.0 ± 0.6 | −11.0 ± 0.4 | −3.9 ± 0.2 |

[a] Data reported in ref 10. [b] Measured at pH ~ 5.

corded on a Zeiss DMR 10 spectrophotometer equipped with a high-pressure optical cell.[14]

## Results and Discussion

Rate constants for the solvolysis reaction, $k_1$, were measured directly by treating complexes of the type $Pd(R_5dien)X^{(2-n)+}$ with $10^{-2}$ mol dm$^{-3}$ base. Under these conditions the hydrolysis goes to completion, solvolysis is the rate-determining step, and the observed rate constant exhibits no meaningful dependence on [OH$^-$]. The reverse anation reactions were studied by use of $Pd(R_5dien)H_2O^{2+}$ as reactant and by treatment with an excess of the anating ligand. In these cases $k_{obs}$ depends linearly on [X$^{n-}$] and the anation rate constant $k_{-1}$ can be calculated from $k_{obs}/[X^{n-}]$. Plots of ln $k_{obs}$ versus pressure were found to be linear in all cases, and the corresponding volumes of activation were calculated from the slope in the usual way.[7] The rate constants and volumes of activation for the solvolysis and anation reactions are summarized in Tables I and II, respectively. The overall reaction volume $\Delta \bar{V}$ can be calculated by using eq 2. These values are included in

$$\Delta \bar{V} = \Delta V^{\ddagger}(k_1) - \Delta V^{\ddagger}(k_{-1}) \qquad (2)$$

the volume profiles for the studied reactions, as summarized in Figure 1. The reaction volumes can also be determined from the pressure dependence of $K$ (= $k_1/k_{-1}$). This was done for the solvolysis of $Pd(Et_5dien)Cl^+$ ($Et_5dien$ = 1,1,4,7,7-$Et_5dien$) by use of the spectrophotometric method discussed previously.[3] At 25 °C, pH ≈ 3.5, and 0.1 mol dm$^{-3}$ ionic strength, $10^4K$ has values of 1.50, 1.70, 1.78, 1.82, and 2.09 at 5, 25, 50, 75, 100, and 150 MPa, respectively, which results in a $\Delta \bar{V}$ value of −4.9 ± 0.8 cm$^3$ mol$^{-1}$. The latter value is in close agreement with −5.7 ± 0.5 cm$^3$ mol$^{-1}$ calculated from the activation volumes by using eq 2—see Figure 1.

The values of $\Delta V^{\ddagger}$ for the solvolysis and anation reactions are in good agreement with those reported for closely related systems before.[2-4] $\Delta V^{\ddagger}$ values for the series of solvolysis (aquation) reactions in Table I are almost constant, with the only exception being the data for $Pd(Et_5dien)I^+$ and $Pd(Et_5dien)C_2O_4$. Many aquation reactions of Pd(II) dien complexes exhibit $\Delta V^{\ddagger}$ values between −10 and −12 cm$^3$ mol$^{-1}$. These are generally interpreted in terms of an associative reaction mode involving the formation of a five-coordinate species, which may be accompanied by an increase in electrostriction during the tetragonal-pyramidal to trigonal-bipyramidal conversion when the leaving group is anionic.[4] In comparison, values as small as −3 cm$^3$ mol$^{-1}$ were reported for the solvolysis of complexes with neutral leaving groups,[4,8,15] i.e., where solvational changes are presumably very small and the volume collapse due to bond formation is partially offset by a volume increase during the geometrical conversion. It follows that the values reported for $Pd(Et_5dien)I^+$ and $Pd(Et_5dien)C_2O_4$ in Table I lie between these extreme values, indicating a rather unique situation for such large anionic leaving groups on the most sterically hindered complex.

For the anation reactions, however, $k_{-1}$ depends on the nucleophilicity of the entering ligand, and $\Delta V^{\ddagger}$ becomes more negative with increasing size of the entering ligand for the series of singly charged anions.[10] The values of $\Delta \bar{V}$ for reaction 1 (see Figure 1) vary between −6.7 and +0.2 cm$^3$ mol$^{-1}$. The transition state has a significantly smaller partial molar volume than either

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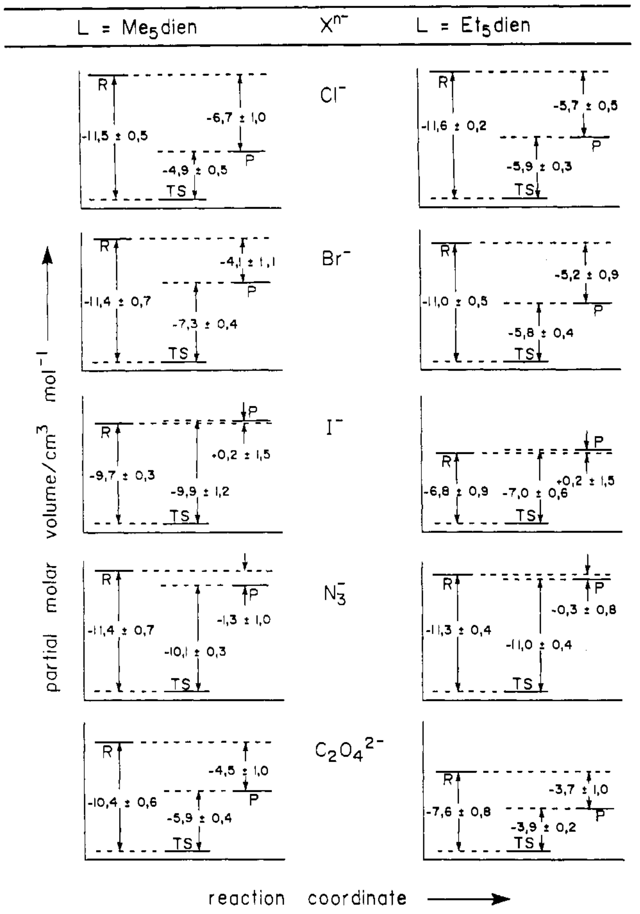

R = reactants; TS = transition state; P = products
Data taken from Table I and II

**Figure 1.** Volume profiles for the reaction $Pd(L)X^{(2-n)+} + H_2O \rightleftarrows Pd(L)H_2O^{2+} + X^{n-}$.

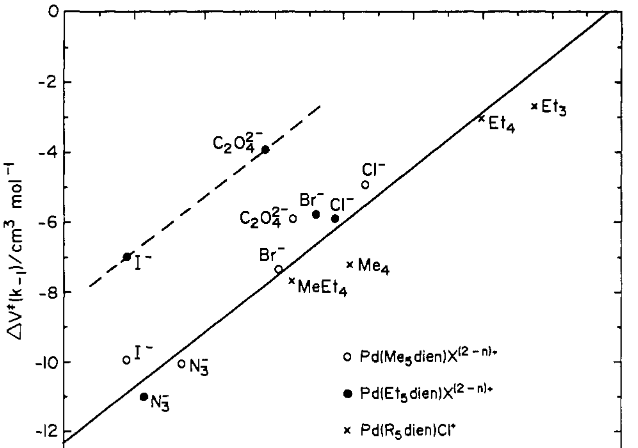

**Figure 2.** Plot of $\Delta V^{\ddagger}(k_{-1})$ versus $\Delta\bar{V}$ for a series of anation reactions of the type $Pd(R_5dien)H_2O^{2+} + X^{n-} \rightarrow Pd(R_5dien)X^{(2-n)+} + H_2O$ (data taken from Figure 1 and ref 6).

the reactant or product states, in agreement with the associative reaction mode. Similar volume profiles can be constructed for the solvolysis of $Pd(R_5dien)Cl^+$, where $R_n$ = 1,1,7,7-$Me_4$, 1,1,4-$Et_3$, 1,1,7,7-$Et_4$, and 4-Me-1,1,7,7-$Et_4$, and the corresponding reaction volumes, calculated as the difference in activation volumes, are −6.2, −11.5, −10.0, and −4.5 $cm^3\ mol^{-1}$, respectively.[6] A plot of $\Delta V^{\ddagger}(k_{-1})$ versus $-\Delta\bar{V}$ (i.e. $\Delta\bar{V}$ for the reverse anation process) in Figure 2 demonstrates that for most of the available data there is a linear correlation between these parameters with a slope of 0.79. This means that an increase in $\Delta V^{\ddagger}(k_{-1})$ is accompanied by an increase in $\Delta\bar{V}$ for the anation process (i.e. a decrease in $\Delta\bar{V}$ for the aquation process). Only the data points for $Pd(Et_5dien)X^{(2-n)+}$ ($X^{n-}$ = $I^-$, $C_2O_4^{2-}$) deviate from this correlation, although they do exhibit the same trend. $\Delta V^{\ddagger}(k_{-1})$ should be significantly more negative for these two points to fall on the line. In terms of eq 2, a plot of $\Delta V^{\ddagger}(k_{-1})$ versus $-\Delta\bar{V}$ should for closely related systems exhibit a slope of 1 and a common intercept of $\Delta V^{\ddagger}(k_{-1})$. Although the slope of the plot is slightly smaller than 1, the intercept for 12 systems is ca. −11 $cm^3\ mol^{-1}$, in agreement with the constant volume of activation found for the solvolysis reactions. The substantially higher intercept of ca. −7 $cm^3\ mol^{-1}$ for the two deviating systems results from the significantly different solvolysis activation volume found for these complexes (see earlier discussion).

The main correlation in Figure 2 means that there is a linear relationship between the partial molar volumes of $Pd(Et_5dien)X^{(2-n)+}$ and the transition state for the anation process, since $H_2O$ is the common leaving ligand. Thus, intrinsic and solvational volume contributions[7] affect the partial molar volume of the transition and product states in a similar way and will be governed by the nature of $R_5dien$ and $X^{n-}$. Similar correlations have been used to interpret the nature of the mechanism for series of aquation and base hydrolysis reactions of octahedral complexes.[16-19]

The exact nature of the transition state has been discussed in much detail before.[4,6,8] Volume changes during the activation process involve not only those associated with the entrance of a fifth ligand into the square-planar coordination sphere but also subsequent changes associated with a tetragonal-pyramidal to trigonal-bipyramidal transition. The extent of bond lengthening in the latter case will partially balance the volume decrease due to bond formation during the associative process. We thoroughly believe that the type of activation volumes reported in this and some of our other papers[2-6] are typical of limiting associative substitution reactions. The volume profiles not only underline our earlier conclusions but also clearly demonstrate the compact nature of the transition state on a volume basis.

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**Registry No.** $Pd(Me_5dien)Cl^+$, 21007-58-9; $Pd(Me_5dien)Br^+$, 118141-56-3; $Pd(Me_5dien)I^+$, 118141-57-4; $Pd(Me_5dien)N_3^+$, 118141-58-5; $Pd(Me_5dien)C_2O_4$, 118141-59-6; $Pd(Me_5dien)OH_2^{2+}$, 85344-11-2; $Pd(Et_5dien)Cl^+$, 70472-44-5; $Pd(Et_5dien)Br^+$, 118141-60-9; $Pd(Et_5dien)I^+$, 88056-32-0; $Pb(Et_5dien)N_3^+$, 118141-61-0; $Pd(Et_5dien)C_2O_4$, 118141-62-1; $Pd(Et_5dien)OH_2^{2+}$, 118169-65-6; $Cl^-$, 16887-00-6; $Br^-$, 24959-67-9; $I^-$, 20461-54-5; $N_3^-$, 14343-69-2; $C_2H_4^{2-}$, 338-70-5; $H_2O$, 7732-18-5.

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# Pulse Radiolysis Studies on Pertechnetate and Perrhenate in Aqueous Media. Decay of the Technetium(VI) Transient[1]

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The radiolysis of Tc(VII) and Re(VII) in aqueous media, and especially the nature and reactivity of the unstable M(VI) species