

sulfate shows a somewhat bigger deviation from the expected curve than potassium sulfate and the difference between the two curves is apparent even at quite low concentrations. This is in contrast to the behavior of different metal sulfates in disulfuric acid which have identical conductivities up to at least 0.08 *m*. This is consistent with the fact that the molal conductivities of metal sulfates in H₂S₂O₇, λ_m = 10⁸κ/*m*, are of the order of 60 whereas Na₂SO₄ and K₂SO₄ in 65% oleum have λ_m ≈ 3. A considerable proportion of the conductivity of a metal sulfate in H₂S₂O₇ is proton-transfer conduction by the anions HS₃O₁₀⁻ and HS₂O₇⁻ but the much lower molal conductivity in 65% oleum strongly suggests that proton-transfer conduction is less effective in this medium and that cations therefore make a much larger contribution to the total conductance than they do in H₂S₂O₇. Consequently, differences between different cations are not surprising and the interpretation of conductivity results in terms of the number of conducting anions produced by a given solute must be correspondingly less certain. By comparison with the conductivity of KCl we see that the iodine compounds studied have the following γ values: I₂, 1; KI, 1.5, ICl, 0.6. These are the same values as were obtained for these solutes in H₂S₂O₇ and strongly suggest that they ionize according to exactly analogous equations in which H₂S₂O₇ is replaced by H₂S₄O₁₃, etc.

The conductivities of I₂ and KI solutions are in fact slightly greater than the reference curves and do not give any indication of the incomplete oxidation found in H₂S₂O₇ where the conductivities were slightly less than the reference curves. This is consistent with the absorption spectra measurements which showed essentially complete oxidation in 65% oleum. The fact that the conductivities in 65% oleum are slightly higher than the reference curves can perhaps be attributed to the fact that the I₂⁺ cation is much larger than the K⁺ ion. Conductivities of solutions were found to increase in H₂S₂O₇ with increasing cation size and from the single comparison of Na⁺ and K⁺ in 65% oleum this also appears to be the case in this solvent. Thus the conductivity measurements in 65% oleum provide further confirmation of the results obtained by cryoscopy and conductivity in H₂S₂O₇.

Experimental Section

The methods used for preparing the solvent and for the cryoscopic and conductometric measurements have been described previously.³ All solutes were carefully dried and stored in vacuum desiccators over phosphoric oxide. The absorption spectra measurements were made as described in part IV.¹

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Bromide Ion Replacement in the *trans*-Dibromotetracyanoplatinate(IV) and *trans*-Dibromotetranitroplatinate(IV) Ions by Chloride Ion

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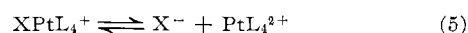
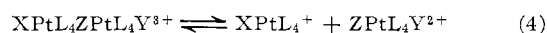
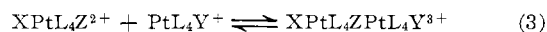
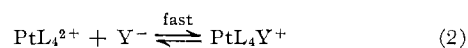
The first bromide replacement in the *trans*-PtL₄Br₂²⁻ (L⁻ = CN⁻ or NO₂⁻) ions by chloride is catalyzed by PtL₄²⁻. The kinetics of these reactions are described by a third-order rate law with rate dependence on chloride, platinum(IV) reactant, and PtL₄²⁻. The third-order rate constants at 25.0° and μ = 1.01 *M* are 72 and 0.76 *M*⁻² sec⁻¹ for L⁻ = CN⁻ and NO₂⁻, respectively. Activation parameters are reported for both reactions. The results are interpreted in terms of a bridged inner-sphere redox mechanism. The rate law for the reaction of *trans*-Pt(CN)₄Br₂²⁻ with chloride ion also contained a second-order term independent of chloride ion concentration. This result is interpreted in terms of solvent participation.

Introduction

A variety of ligand replacement reactions of platinum(IV) complexes of the type in eq 1 (L = ammonia or *trans*-PtL₄XZ²⁺ + Y⁻ → *trans*-PtL₄YZ²⁺ + X⁻ (1)

L₂ = ethylenediamine; X, Y = halide or pseudohalide ligands; and Z = halide or thiocyanate ligands) have been found¹⁻⁶ to be catalyzed by square-planar plati-

num(II) complexes of the type PtL₄²⁺. A mechanism for these catalyzed reactions was first postulated by Basolo, Pearson, and coworkers¹ and now seems well established. This mechanism is given in general terms for eq 1 in the eq 2-5. The ligands Y, Z, and X are



designated as the entering, bridging, and leaving ligands, respectively, while L is an inert ligand lying in a plane about the middle of each platinum complex.

(1) F. Basolo, A. F. Messing, P. H. Wilks, R. G. Wilkins, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **8**, 203 (1958).

(2) F. Basolo, M. L. Morris, and R. G. Pearson, *Discussions Faraday Soc.*, **29**, 80 (1960).

(3) H. Ellison, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **83**, 3943 (1961).

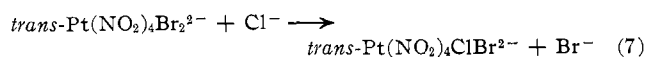
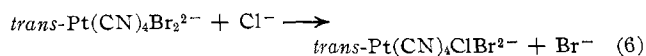
(4) W. R. Mason and R. C. Johnson, *Inorg. Chem.*, **4**, 1258 (1965).

(5) R. R. Rettew and R. C. Johnson, *ibid.*, **4**, 1565 (1965).

(6) W. R. Mason, E. R. Berger, and R. C. Johnson, *ibid.*, **6**, 248 (1967).

A number of studies aimed at probing the details of the reaction path described above have attempted to correlate reactivity with the nature of the ligands in the coordination sphere of the platinum(IV) complex and with the entering ligand. Effects on the rate due to the bridging ligand^{4,5} as well as those due to the entering and leaving ligands have been considered in detail.⁴⁻⁸ However, information as to the effect of the ligand L on reactivity is comparatively limited.^{2,3,9,10} Corresponding ammonia and ethylenediamine complexes are found^{2,3} to react at nearly the same rate—a fact that is not surprising in view of the similarity of donor type. Some steric effects have been observed for substituted ethylenediamine ligands,^{2,3} but electronic effects have not been considered. Furthermore, almost all studies have been concerned with cationic complexes, and there are few data available for platinum(IV) substrates of negative charge type.

To investigate the influence of the ligand L on reactivity and to extend data for reactivity correlations aimed at probing the details of the platinum(II)-catalyzed mechanism, the kinetics of reaction 6 and 7



have been studied and are reported in this paper. Both reactions involve platinum(IV) complexes of negative charge type, and the π -acceptor cyano and nitro ligands differ markedly from the σ -donor ammine ligands studied previously.

Experimental Section

Preparation of Compounds.—Potassium tetracyanoplatinate(II) hydrate, $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$, and potassium tetranitroplatinate(II) hydrate, $\text{K}_2[\text{Pt}(\text{NO}_2)_4] \cdot 2\text{H}_2\text{O}$, were prepared by published methods.^{11,12} These compounds served as starting materials for the platinum(IV) complexes. All other chemicals were reagent grade. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Potassium *trans*-Dibromotetracyanoplatinate(IV), $\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_2]$.¹³—Solid $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ was dissolved in a minimum amount of water with gentle warming on a steam bath. A saturated solution of bromine in methanol was added, and the resulting solution was evaporated until golden crystals were formed. The product was collected at ice-bath temperature and washed with a small amount of ice water, methanol, and finally several portions of anhydrous ether. The compound was dried under reduced pressure at room temperature and stored in the dark. *Anal.* Calcd for $\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_2]$: Br, 29.75; C, 8.94; N, 10.43. Found: Br, 29.72, 29.84; C, 8.98, 8.85; N, 10.44, 10.38.

Potassium *trans*-Dibromotetranitroplatinate(IV), $\text{K}_2[\text{Pt}(\text{NO}_2)_4\text{Br}_2]$.¹⁴—The preparation of this compound was very similar to that of $\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_2]$. Solid $\text{K}_2[\text{Pt}(\text{NO}_2)_4] \cdot 2\text{H}_2\text{O}$ was dissolved in water at room temperature and treated with a minimal amount

of a saturated solution of bromine in methanol. A yellow precipitate was formed almost immediately and was collected at ice-bath temperature. The product was then washed with a small amount of ice water, ethanol, and several portions of ether. After drying under reduced pressure at room temperature, the compound was stored in the dark. *Anal.* Calcd for $\text{K}_2[\text{Pt}(\text{NO}_2)_4\text{Br}_2]$: Br, 25.90; N, 9.08. Found: Br, 25.08, 25.25; N, 9.00, 8.86.

The compound appears to be stable indefinitely as a dry solid when stored in the dark, but the complex is slowly reduced in solutions exposed to laboratory lighting. Consequently, all kinetic measurements were made using fresh solutions carefully protected from light.

Kinetics.—The kinetics of the bromide replacement reactions were studied spectrophotometrically using a Cary 14 spectrophotometer equipped with a thermostated cell holder. Temperature was controlled to within $\pm 0.1^\circ$. The ionic strength was controlled at 1.01 M by NaClO_4 . Spectral changes during the course of the reactions were initially characterized by scanning a portion of the spectrum at time intervals. The reactions were then followed by measuring absorbance *vs.* time at a wavelength where products absorbed less than reactants. A well-defined isosbestic point was observed at 316 m μ for reaction 6. The infinite-time spectrum was consistent with a published spectrum¹⁵ for *trans*- $\text{Pt}(\text{CN})_4\text{BrCl}^{2-}$ and differed from an authentic sample of *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$ prepared in our laboratory. No isosbestic points were observed for reaction 7, but infinite-time spectra were consistent with the replacement of one bromide by chloride and differed from spectra of an authentic sample of *trans*- $\text{Pt}(\text{NO}_2)_4\text{Cl}_2^{2-}$.

Both reactions 6 and 7 were studied under conditions of a large excess of chloride ion. Under these circumstances the reactions are pseudo first order in the platinum(IV) complex. Rate data were evaluated by means of a Gauss-Newton fit to the equation: $A = A_\infty + (A_0 - A_\infty) \exp(-kt)$. Twenty data points spaced over approximately 5 half-lives were used for each kinetic run. The standard deviations in calculated values of k were less than 1% in almost all cases. Kinetic experiments could be reproduced generally to within $\pm 5\%$, and rate constants reported in this paper in many cases represent averages of several experiments.

Rate constants for reactions 6 and 7 were evaluated by subtracting the rates in the absence of added platinum(II) from the observed rates (k_{obsd}). For all but the slowest reactions studied, this correction was less than *ca.* 10% of the observed rate. Values of the rate constants corrected in this manner were used to construct least-squares plots of $k_{\text{obsd}}^{\text{corr}}/[\text{PtL}_4^{2-}]$ *vs.* $[\text{Cl}^-]$. For reaction 6, these plots were linear; the slope corresponds to a third-order constant, k_3 , and the intercept to a second-order constant k_2 . The values of k_3 were self-consistent to $\pm 5\%$ while the values of k_2 were less precise. Rate constants for reaction 7 were evaluated similarly except that plots of $k_{\text{obsd}}^{\text{corr}}/[\text{PtL}_4^{2-}]$ *vs.* $[\text{Cl}^-]$ gave a straight line passing through the origin. Third-order constants were self-consistent to $\pm 10\%$.

Results

Rate constants for reaction 6 and 7 are presented in Tables I and II. In the absence of added platinum(II) the rates of both reactions were very slow. Although the possibility of a platinum(II)-independent reaction cannot be ruled out entirely for these residual rates,¹⁶ it is probable that they are due to platinum(II) in the platinum(IV) samples. Less than 1% platinum(II) in the *trans*- $\text{Pt}(\text{CN})_4\text{Br}_2^{2-}$ sample can account for the observed residual rate in reaction 6. For reaction 7

(15) I. I. Chernyshev, A. V. Babkov, and N. N. Zheligorskaya, *Russ. J. Inorg. Chem.*, **8**, 1279 (1963).

(16) The rate law for reactions of several cationic ammine substrates showed second-order terms independent of platinum(II) concentration,⁴⁻⁶ but in these cases the rates at zero platinum(II) concentration were too great to be explained by a platinum(II) impurity.

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(9) (a) A. Peloso and G. Dolcetti, *Gazz. Chim. Ital.*, **97**, 120 (1967);

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(10) R. Dryer, *Z. Physik. Chem. (Frankfurt)*, **29**, 347 (1961).

(11) "Gmelins Handbuch der Anorganischen Chemie," 8th ed, Vol. 68C, Verlag Chemie, Weinheim/Bergstrasse, Germany, 1939, p 202.

(12) Reference 11, p 166.

(13) Reference 11, p 207.

(14) Reference 11, p 192.

TABLE I
RATE DATA
$$\text{trans-Pt}(\text{CN})_4\text{Br}_2^{2-} + \text{Cl}^- \longrightarrow \text{trans-Pt}(\text{CN})_4\text{BrCl}^{2-} + \text{Br}^-$$

$10^3[\text{Pt}(\text{CN})_4^{2-}]$, M	$10^3k_{\text{obsd}} (10^3k_{\text{obsd}}^{\text{cor}})$, sec^{-1}	k_3, M^{-2} sec^{-1}	$10^3[\text{Pt}(\text{CN})_4^{2-}]$, M	$10^3k_{\text{obsd}} (10^3k_{\text{obsd}}^{\text{cor}})$, sec^{-1}	k_3, M^{-2} sec^{-1}
25.0° ^a			35.0° ^a		
0	0.14	...	0.54	2.8 (2.7)	84
0.27	1.3 (1.2)	73	1.08	5.2 (5.1)	79
0.54	2.6 (2.4)	73	1.62	7.8 (7.7)	79
1.08	5.0 (4.9)	75	2.16	10.3 (10.2)	79
1.62	7.2 (7.1)	72	1.08	3.3 (3.2) ^b	87
2.16	9.5 (9.4)	71	0.54	4.1 (4.0) ^c	88
2.70	11.6 (11.5)	70	0.54	5.1 (5.0) ^d	85
1.62	4.2 (4.1) ^b	70	1.08	4.6 (4.5) ^m	68
1.08	6.8 (6.7) ^c	72	48.3° ^a		
0.54	4.4 (4.3) ^d	72	0.54	3.6 (3.5)	114
1.08	4.4 (4.3) ^e	64	1.08	6.5 (6.4)	103
1.08	4.4 (4.3) ^f	64	2.16	12.6 (12.5)	100
1.08	9.3 (9.2) ^g	154	1.08	3.8 (3.7) ^b	106
25.2	2.8 (2.8) ^{h,i}	9.8	0.54	4.8 (4.7) ^c	106
10.1	1.8 (1.8) ^{h,i}	11.6	0.54	6.3 (6.2) ^d	107
10.1	2.6 (2.6) ^{h,k}	9.8			
1.08	2.7 (2.7) ^{b,l}	65			
0.54	2.4 (2.3) ^l	70			
0.54	3.3 (3.2) ^{e,l}	69			
0.54	4.3 (4.1) ^{d,l}	68			

^a $[\text{Pt}(\text{IV})] = 1.57 \times 10^{-3} M$, $[\text{HClO}_4] = 0.010 M$, $\mu = 1.01 M$, $[\text{Cl}^-] = 0.50 M$, $k_2 = 7.8 M^{-1} \text{sec}^{-1}$. ^b $[\text{Cl}^-] = 0.250 M$. ^c $[\text{Cl}^-] = 0.750 M$. ^d $[\text{Cl}^-] = 1.00 M$. ^e $[\text{Pt}(\text{IV})] = 1.26 \times 10^{-3} M$. ^f $[\text{HClO}_4] = 0.113 M$. ^g $\mu = 1.51 M$. ^h $\mu = 0.21 M$, $k_2 = 0.62 M^{-1} \text{sec}^{-1}$. ⁱ $[\text{Cl}^-] = 0.050 M$. ^j $[\text{Cl}^-] = 0.100 M$. ^k $[\text{Cl}^-] = 0.200 M$. ^l $[\text{HClO}_4] = 0$, $\mu = 1.00 M$. ^m $[\text{Pt}(\text{IV})] = 7.9 \times 10^{-4} M$.

TABLE II
RATE DATA
$$\text{trans-Pt}(\text{NO}_2)_4\text{Br}_2^{2-} + \text{Cl}^- \longrightarrow \text{trans-Pt}(\text{NO}_2)_4\text{BrCl}^{2-} + \text{Br}^-$$

$10^3[\text{Pt}(\text{NO}_2)_4^{2-}]$, M	$10^3k_{\text{obsd}} (10^3k_{\text{obsd}}^{\text{cor}})$, sec^{-1}	$10k_3, M^{-2}$ sec^{-1}	$10^3[\text{Pt}(\text{NO}_2)_4^{2-}]$, M	$10^3k_{\text{obsd}} (10^3k_{\text{obsd}}^{\text{cor}})$, sec^{-1}	$10k_3, M^{-2}$ sec^{-1}
25.0° ^a			15.8° ^a		
0	0.23	...	1.19	1.2 (1.0)	7.5
0.50	0.59 (0.36)	7.2	2.44	2.2 (2.0)	7.8
1.30	1.2 (1.0)	7.5	5.09	4.7 (4.5)	8.8
2.51	2.2 (2.0)	7.8	4.98	2.6 (2.5) ^e	8.4
5.10	4.4 (4.2)	8.2	35.0° ^a		
5.07	3.2 (3.0) ^b	7.3	1.40	1.3 (1.1)	7.6
5.03	2.4 (2.2) ^c	7.6	2.50	2.1 (1.9)	7.5
5.10	1.8 (1.7) ^d	8.3	5.13	4.3 (4.1)	7.9
5.34	1.0 (0.9) ^e	8.4	5.28	3.2 (3.0) ^b	7.1
5.00	0.15 ^{e,f}	1.5	5.09	2.4 (2.3) ^c	7.5
5.00	9.7 (9.5) ^g	18.9			
5.10	4.7 (4.5) ^h	8.8			

^a $[\text{Pt}(\text{IV})] = 5.0 \times 10^{-3} M$, $[\text{NaCl}] = 1.00 M$, $[\text{HClO}_4] = 0.010 M$, $\mu = 1.01 M$. ^b $[\text{NaCl}] = 0.80 M$. ^c $[\text{NaCl}] = 0.60 M$. ^d $[\text{NaCl}] = 0.40 M$. ^e $[\text{NaCl}] = 0.20 M$. ^f $\mu = 0.21 M$; no correction was made for residual Pt(II) in calculating k_3 . ^g $\mu = 1.64 M$. ^h $[\text{HClO}_4] = 0$.

about 6% platinum(II) in the *trans*-Pt(NO₂)₄Br₂²⁻ sample would be required. However, in view of the method of preparation of the platinum(IV) complex and its sensitivity toward reduction on exposure to light, the comparatively greater residual rate is not surprising. Therefore, for both reactions observed rates were corrected for the residual rate in the absence of added platinum(II). Data treated in this way are consistent with the rate laws given in eq 8 and 9. The

$$-d[\text{trans-Pt}(\text{CN})_4\text{Br}_2^{2-}]/dt = \{k_2 + k_3[\text{Cl}^-]\} \times [\text{Pt}(\text{CN})_4^{2-}][\text{trans-Pt}(\text{CN})_4\text{Br}_2^{2-}] \quad (8)$$

$$-d[\text{trans-Pt}(\text{NO}_2)_4\text{Br}_2^{2-}]/dt = k_3[\text{Cl}^-][\text{Pt}(\text{NO}_2)_4^{2-}][\text{trans-Pt}(\text{NO}_2)_4\text{Br}_2^{2-}] \quad (9)$$

value of k_2 in eq 8 was found to be $7.8 \pm 1 M^{-1} \text{sec}^{-1}$ at 25° and $\mu = 1.01 M$. Under the reaction conditions used in the study of reaction 6 the contribution of the second-order path to the over-all rate was always less than 35% and was usually less than 15%.

Both reactions were essentially independent of $[\text{H}^+]$ over the limited range studied. Ionic strength effects were fairly substantial; a 10–15-fold rate increase was observed on increasing the ionic strength from 0.2 to 1.5 M . The increase in rate with ionic strength is consistent with a primary salt effect for reactions between reagents of like charge.

The temperature dependence of the rates over ap-

proximately a 30° temperature range is quite small. Values of k_2 for reaction 6 were found to be independent of temperature within experimental error over the range 25–45°. Values of ΔH^* and ΔS^* calculated for this path are: $\Delta H^* = -0.5 \pm 1$ kcal mol⁻¹ and $\Delta S^* = -56 \pm 4$ cal deg⁻¹ mol⁻¹. At temperatures higher than 35°, reaction 7 showed slight deviation from pseudo-first-order behavior. Therefore, studies were confined to lower temperatures where satisfactory first-order behavior was observed. Activation parameters were calculated for the third-order path for reactions 6 and 7 and are presented in Table III along with rate constants at 25°; data for the related *trans*-Pt(NH₃)₄-Br₂²⁺ complex⁵ are included for comparison.

TABLE III
THIRD-ORDER RATE CONSTANTS AT 25° AND
ACTIVATION PARAMETERS FOR THE REACTION
trans-PtL₄Br₂ⁿ + Cl⁻ → *trans*-PtL₄BrClⁿ + Br⁻

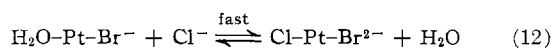
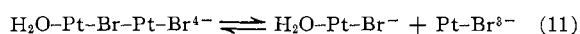
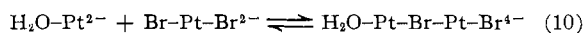
L	ΔH^* , kcal mol ⁻¹	ΔS^* , cal mol ⁻¹ deg ⁻¹	k_2 , ^b M ⁻² sec ⁻¹ (25°)
NH ₃ ^a	6	-22	4200
CN ⁻	2.5 ± 1	-42 ± 2	72 (10.4)
NO ₂ ⁻	-1.6 ± 1	-64 ± 2	0.76 (0.15)

^a Data from ref 5; $\mu = 0.20$ M. ^b Values in parentheses are for $\mu = 0.21$ M; main entries for CN⁻ and NO₂⁻ refer to $\mu = 1.01$ M.

Discussion

The third-order term in the rate laws eq 8 and 9 can be readily interpreted within the framework of the mechanism presented in eq 2–5. A first-order dependence on entering ligand, platinum(IV) substrate, and platinum(II) catalyst is predicted, provided the equilibrium in eq 2 is rapidly established and lies far to the left. Either eq 3 or eq 4 may be rate determining. Thus the present study confirms the generality of the platinum(II)-catalyzed mechanism for anionic platinum(IV) substrates as well as cationic ones.

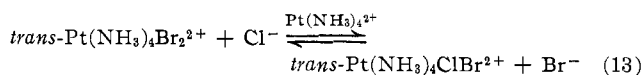
The appearance in the rate law for reaction 6 of a second-order term, which is independent of the entering ligand, is a new feature for reactions of the general type in eq 1. This term can be explained, however, by assuming solvent participation as an entering ligand. A rapid replacement by chloride following the rate-determining step would lead to the observed product. Equations 10–12 outline this process; the cyano ligands



have been omitted from the platinum complexes for clarity. The rapid replacement step in eq 12 cannot be specified in detail from the present data. However, it is clear from the observed product that the replacement must proceed with retention of the *trans* geometry. It is possible that this process involves another platinum(II)-catalyzed step with the formation of the bridged complex H₂O-Pt-Br-Pt-Cl⁴⁻, but confirmation of this suggestion must await further study.

A chloride-independent path for the reaction of the anionic cyano complexes is perhaps not surprising in view of the electrostatic repulsion developed in an activated complex involving not only an anionic entering ligand but anionic substrate and catalyst as well. A neutral water molecule would tend to compete more effectively with chloride as an entering nucleophile since an activated complex of lower charge would result. Similarly the absence of a solvent path for cationic ammine complexes studied previously can be rationalized; a negative entering ligand would be strongly favored since the positive charge on the activated complex would be reduced. Perhaps more surprising is the absence of a chloride-independent path for the anionic nitro complex.

Additional insight into the mechanism can be afforded from the rate data for reactions 6 and 7. These data in conjunction with those reported⁶ for the analogous reaction of the *trans*-Pt(NH₃)₄Br₂²⁺ cation, eq 13, permit a



direct assessment of the dependence of the rates on the in-plane ligands, L. The pertinent data summarized in Table III show that the dependence on L is striking; the order of reactivity is NH₃ > CN⁻ > NO₂⁻ with relative rates of approximately 28,000:70:1 (25° and $\mu = 0.2$ M), respectively. The order of decreasing reactivity results primarily from the unfavorable activation entropy for the cyano and nitro complexes; the activation enthalpy is actually more favorable in these cases than for the ammine complex. The larger negative values of ΔS^* for the anionic complexes are not surprising since the assembly of the reactants results in an activated complex with a 5- charge compared to 3+ for the ammine complex. There would undoubtedly be greater solvation requirements for the activated complex in the former case. However, ΔS^* for the nitro complex is about 20 cal deg⁻¹ mol⁻¹ more negative than for the cyano complex. It seems unlikely that differences in solvation alone can account for such an effect. Consequently, the result may be interpreted as arising from enhanced bonding in the activated complex for the nitro complex. Since NO₂⁻ is a weaker σ donor than CN⁻ (both are strong π -acceptor ligands and participate in metal → ligand π bonding), it is likely that the platinum centers in the bridged complex with nitro ligands are more positive, leading to a more tightly bound activated complex. Consistent with this point of view is the negative ΔH^* for the reaction of *trans*-Pt(NO₂)₄Br₂²⁻. Thus the present results suggest that bond-making is an important feature of the activation process for these anionic complexes.

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