suggesting different discrimination ability for the three complexes toward the entering groups.

Since the effectiveness of a substrate is due to its electrophilicity, which is dependent on the electron density at the reaction center, it is likely that the differences in discriminating ability of the complexes are due to different inductive effects of the aryl ligands.

In going from the protic to the dipolar aprotic solvent the reactivity for $SeCN^-$ and thiourea decreases while for CN^- it increases owing to the different solvation of these reagents in the two solvents.[20,21] The solvation effect on CN^- is large enough to cause a reversal in order of reagent reactivity. The sequence observed in methanol and dimethyl sulfoxide is $CN^- < SeCN^- <$ thiourea and $SeCN^- <$ thiourea $< CN^-$.

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The Tetracyanoplatinate(II)-Catalyzed Interconversion of *trans*-Dichloro- and *trans*-Dibromotetracyanoplatinate(IV) Anions

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The rates of chloride replacement in *trans*-$Pt(CN)_4Cl_2^{2-}$ and *trans*-$Pt(CN)_4ClBr^{2-}$ by bromide and bromide replacement in *trans*-$Pt(CN)_4ClBr^{2-}$ by chloride are catalyzed by $Pt(CN)_4^{2-}$. The kinetics of these reactions are described by a third-order rate law with rate dependence on entering halide, platinum(IV) substrate, and $Pt(CN)_4^{2-}$. Third-order rate constants at 25° and $\mu = 1.0\ M$ are 4.5, 4.2×10^3, and 0.020 $M^{-2}\ sec^{-1}$, respectively. The results are interpreted in terms of a bridged redox mechanism, and comparisons are made with previous work on corresponding ammine complexes of the type *trans*-$Pt(NH_3)_4XY^{2+}$ (X^-, Y^- = Cl^- or Br^-). The rate law for the reaction of *trans*-$Pt(CN)_4ClBr^{2-}$ with bromide also contained a second-order term independent of $Pt(CN)_4^{2-}$ ion concentration.

Introduction

As a result of a number of kinetic studies,[1-8] the platinum(II)-catalyzed reaction path has emerged as an important one for ligand replacements in platinum(IV) complexes. For example the first bromide replacement in *trans*-$Pt(CN)_4Br_2^{2-}$ by chloride ion to give *trans*-$Pt(CN)_4ClBr^{2-}$ is catalyzed[7] by $Pt(CN)_4^{2-}$. The kinetics are third order with rate dependence on *trans*-$Pt(CN)_4Br_2^{2-}$, Cl^-, and $Pt(CN)_4^{2-}$. A bridged inner-sphere redox mechanism outlined in eq 1–4 has been used to describe this reaction. The

$$Pt^{2-} + Cl^- \overset{\text{fast}}{\rightleftarrows} PtCl^{3-} \tag{1}$$

$$BrPtBr^{2-} + PtCl^{3-} \rightleftarrows BrPtBrPtCl^{5-} \tag{2}$$

$$BrPtBrPtCl^{5-} \rightleftarrows BrPt^{3-} + BrPtCl^{2-} \tag{3}$$

$$BrPt^{3-} \rightleftarrows Br^- + Pt^{2-} \tag{4}$$

four cyano ligands which lie in a plane about each platinum complex have been omitted for clarity. Such a mechanism is generally applicable to all platinum(II)-catalyzed reactions of platinum(IV) substrates.[1-8]

Previous work aimed at probing the details of the platinum(II)-catalyzed reaction path has largely involved cationic ammine complexes of the type *trans*-$Pt(NH_3)_4XY^{n+}$ (X, Y = ammonia, halide, or pseudohalide ligands)[2-5] or *trans*-$Pt(dien)ACl_2^{m+}$ (dien = diethylenetriamine and A = NH_3, Br^-, or NO_2^-).[8] However, the recent study of bromide replacement in the anionic *trans*-$Pt(CN)_4Br_2^{2-}$ and *trans*-$Pt(NO_2)_4Br_2^{2-}$ complexes by chloride[7] revealed that the four inert ligands lying in a plane about both substrate and catalyst complexes have a considerable influence on reactivity. In an effort to characterize further the influence of these four in-plane ligands and to extend data for reactivity correlations aimed at a detailed understanding of the bridged redox mechanism, the rates of halide replacement in three additional *trans*-dihalotetracyanoplatinate(IV) complexes have been investigated. The present paper reports kinetic studies on the forward and reverse reactions of eq 5 and the forward reaction of eq 6. Rate data

$$trans\text{-}Pt(CN)_4Cl_2^{2-} + Br^- \rightleftarrows trans\text{-}Pt(CN)_4ClBr^{2-} + Cl^- \tag{5}$$

$$trans\text{-}Pt(CN)_4ClBr^{2-} + Br^- \rightleftarrows trans\text{-}Pt(CN)_4Br_2^{2-} + Cl^- \tag{6}$$

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reported previously[7] for the reverse of eq 6 will be discussed in conjunction with the present results.

Experimental Section

Preparation of Compounds.—Potassium tetracyanoplatinate(II) hydrate, $K_2[Pt(CN)_4]\cdot 3H_2O$, was prepared by the published method[9] and potassium *trans*-dibromotetracyanoplatinate(IV), $K_2[Pt(CN)_4Br_2]$, was prepared previously.[7] These compounds served as starting materials for the other platinum(IV) complexes. All other chemicals were reagent grade. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Tetramethylammonium *trans*-Dichlorotetracyanoplatinate(IV), $[(CH_3)_4N]_2[Pt(CN)_4Cl_2]$.—The tetramethylammonium salt was prepared from $K_2[Pt(CN)_4Cl_2]$[10] which was prepared from $K_2[Pt(CN)_4]\cdot 3H_2O$. Solid $K_2[Pt(CN)_4]\cdot 3H_2O$ was dissolved in minimal 1 M HCl and chlorine gas bubbled through the solution on a steam bath for approximately 15 min. The solution was cooled to ice temperature and crystalline $K_2[Pt(CN)_4Cl_2]$ was collected. A concentrated aqueous solution of $K_2[Pt(CN)_4Cl_2]$ was heated with a concentrated aqueous solution of $(CH_3)_4NCl$ whereupon a precipitate formed immediately. This was collected and washed with a small amount of ice water and several portions of ether and dried under reduced pressure at room temperature. *Anal.* Calcd for $[(CH_3)_4N]_2[Pt(CN)_4Cl_2]$: Pt, 37.64; C, 27.80; H, 4.67; N, 16.21; Cl, 13.68. Found: Pt, 37.84; C, 27.57; H, 4.70; N, 16.16; Cl, 13.58.

Tetramethylammonium *trans*-Chlorobromotetracyanoplatinate(IV), $[(CH_3)_4N]_2[Pt(CN)_4ClBr]$.—Equimolar amounts of $K_2[Pt(CN)_4Cl_2]$ and $K_2[Pt(CN)_4Br_2]$ were dissolved together in a minimum amount of water at 80°.[11] After approximately 5 min the solution was cooled and a concentrated aqueous solution of $(CH_3)_4NCl$ was added with stirring. A fine yellow precipitate was formed immediately and was collected, washed with a small amount of ice water and several portions of ether, and dried under reduced pressure at room temperature. *Anal.* Calcd for $[(CH_3)_4N]_2[Pt(CN)_4ClBr]$: Pt, 34.66; C, 25.61; H, 4.29; N, 14.93; Cl, 6.30; Br, 14.20. Found: Pt, 34.88; C, 25.46; H, 4.39; N, 15.07; Cl, 6.44; Br, 14.20.

Kinetics.—The rates of halide replacements were measured spectrophotometrically by using a Cary 14 spectrophotometer equipped with a thermostated cell holder. The temperature was controlled to within ±0.1°, and except as noted the ionic strength was maintained at 1.01 M with $NaClO_4$. The reactions were initially characterized by scanning a portion of the spectrum at time intervals. Rate measurements were then made from data taken at a selected wavelength as a function of time. The infinite-time spectra were consistent in all cases with spectra of authentic samples of complexes prepared in our laboratory. Under the conditions used to study the forward reaction of eq 5 the replacement of the second chloride by bromide (forward reaction of eq 6) was nearly 10^3 times faster than the first. Therefore the product observed was *trans*-$Pt(CN)_4Br_2^{2-}$, but the rate for the overall replacement of the two chlorides in *trans*-$Pt(CN)_4Cl_2^{2-}$ corresponds to the limiting step of the first chloride replacement. Similarly under the conditions used to study the reverse reaction of eq 5, the reverse reaction of eq 6 was $>10^3$ times faster. Consequently identical rates corresponding to the reverse of eq 5 were obtained with *trans*-$Pt(CN)_4ClBr^{2-}$ and *trans*-$Pt(CN)_4Br_2^{2-}$ as the starting platinum(IV) complexes. Two distinct isosbestic points at 316 and 288 nm were observed for the forward reaction of eq 6. The former is identical with the isosbestic point at 316 nm observed[7] for the reverse reaction of eq 6.

TABLE I

RATE DATA

trans-$Pt(CN)_4Cl_2^{2-} + 2Br^- \rightarrow$ *trans*-$Pt(CN)_4Br_2^{2-} + 2Cl^-$

$10^3[Pt(CN)_4^{2-}]$, M	10^3k_{obsd}, sec^{-1}	k_3, $M^{-2}\ sec^{-1}$	$10^3[Pt(CN)_4^{2-}]$, M	10^3k_{obsd}, sec^{-1}	k_3, $M^{-2}\ sec^{-1}$
25.0°[a]			35.0°[a]		
0.25	1.18	4.7	0.50	2.80	5.6
0.50	2.31	4.6	1.00	5.34	5.3
0.75	3.46	4.6	1.00	2.52[c]	5.0
1.00	4.60	4.6			
1.00	1.05[b]	4.2	45.0°[a]		
1.00	2.16[c]	4.3	0.50	3.20	6.4
1.00	3.35[d]	4.5	1.00	6.20	6.2
1.00	4.63[e]	4.6	1.00	2.92[c]	5.8
1.00	4.11[f]	8.2			
1.00	0.81[g]	1.6			
1.00	4.58[h]	4.6			
1.00	4.60[i]	4.6			

[a] [*trans*-$Pt(CN)_4Cl_2^{2-}$] = 1.00×10^{-3} M, [NaBr] = 1.00 M, [$HClO_4$] = 0.0100 M, μ = 1.01 M. [b] [NaBr] = 0.250 M. [c] [NaBr] = .0500 M. [d] [NaBr] = 0.75 M. [e] [Pt(IV)] = 5.0×10^{-4} M. [f] μ = 1.51 M. [g] μ = 0.51 M. [h] [$HClO_4$] = 0. [i] [$HClO_4$] = 0.0200 M.

TABLE II

RATE DATA

trans-$Pt(CN)_4ClBr^{2-} + Cl^- \rightarrow$ *trans*-$Pt(CN)_4Cl_2^{2-} + Br^-$

$10^2[Pt(CN)_4^{2-}]$, M	10^4k_{obsd}, sec^{-1}	10^2k_3, $M^{-2}\ sec^{-1}$	$10^2[Pt(CN)_4^{2-}]$, M	10^4k_{obsd}, sec^{-1}	10^2k_3, $M^{-2}\ sec^{-1}$
25.0°[a]			35.0°[a]		
1.40	2.63[b]	1.88	2.14	5.65[c]	2.64
2.04	3.82[c]	1.87	3.43	9.47[d]	2.76
3.01	6.37[d]	2.12			
3.98	8.22[e]	2.06	45.0°[a]		
2.04	2.18[c,f]	2.14	2.23	8.43[c]	3.78
2.06	4.11[c,g]	1.99	3.95	15.8[e]	4.00
2.03	1.15[f,h]	1.13			
0.58	1.37[i]	2.36			
2.14	4.27[c,j]	2.00			

[a] [*trans*-$Pt(CN)_4ClBr^{2-}$] = 5.1×10^{-4} M, [NaCl] = 1.00 M, [$HClO_4$] = 0.0100 M. [b] μ = 1.05 M. [c] μ = 1.07 M. [d] μ = 1.10 M. [e] μ = 1.13 M. [f] [NaCl] = 0.500 M. [g] [$HClO_4$] = 0.030 M. [h] μ = 0.57 M. [i] [Pt(IV)] = 1.86×10^{-3} M, μ = 1.03 M. [j] [*trans*-$Pt(CN)_4Br_2^{2-}$] = 4.98×10^{-4} M.

The three reactions reported here were all studied using a large excess of entering halide ion. Under these conditions the reactions are pseudo first order in platinum(IV) complex. Rate data were evaluated by means of a Gauss–Newton fit to the equation $A = A_\infty + (A_0 - A_\infty)\exp(-k_{obsd}t)$.[12] Twenty data points spaced over approximately 3–5 half-lives were used for each kinetic run. The standard deviations in calculated values of k_{obsd} were less than 1% in almost all cases. Kinetic experiments generally could be reproduced to within ±5%, and the rate constants reported in this paper in many cases represent averages of several experiments. Third-order rate constants for the reactions of eq 5 were obtained by dividing k_{obsd} by $Pt(CN)_4^{2-}$ and halide concentrations. Values of k_3 were self-consistent to ±(5–7)%. For the forward reaction of eq 6 a substantial contribution to the rate was from a platinum(II)-independent reaction. Plots of $k_{obsd}/[Br^-]$ *vs.* [$Pt(CN)_4^{2-}$] were linear, however, and the slope corresponds to k_3 while the intercept corresponds to a second-order rate constant for the platinum(II)-independent reaction, k_2. Third-order constants for this reaction at any one temperature were self-consistent to ±10% while the value of k_2 is less precise.

Results

Rate constants for the three halide-replacement reactions investigated are given in Tables I–III. In

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

(10) Reference 9, p 206.

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

(12) The author is indebted to Dr. Ronald C. Johnson for the computer program used in calculating the rate constants.

Table III

Rate Data

trans-$Pt(CN)_4ClBr^{2-} + Br^- \rightarrow$ *trans*-$Pt(CN)_4Br_2^{2-} + Cl^-$

$10^5[Pt(CN)_4^{2-}]$, M	10^3k_{obsd}, sec^{-1}	10^3k_3, $M^{-2}\ sec^{-1}$	$10^5[Pt(CN)_4^{2-}]$, M	10^3k_{obsd}, sec^{-1}	$10^{-3}k_3$, $M^{-2}\ sec^{-1}$
25.0°[a]			15.3°[a,h]		
0	4.6	...	1.25	3.4	5.0
0	6.6[b]	...	2.50	4.9	5.5
0	9.4[c]	...	5.0	7.2	5.1
1.25	6.1	4.2	7.5	9.7	5.0
2.50	7.1	4.2	10.0	12.6	5.2
5.0	9.2	4.2	2.50	10.2[c]	5.9
7.5	11.1	4.0			
10.0	13.4	4.2	35.0°[a,i]		
2.5	14.3[c]	4.2	1.25	10.0	4.6
2.5	14.4[c,d]	4.3	2.50	11.8	5.9
2.5	10.0[e]	9.9	5.0	14.2	5.3
2.5	4.3[f]	1.4	7.5	16.8	5.3
2.5	6.9[g]	3.7	2.50	22.8[e]	5.1

[a] [*trans*-$Pt(CN)_4ClBr^{2-}$] = $7.5 \times 10^{-4}\ M$, [NaBr] = $0.0200\ M$, [$HClO_4$] = $0.0100\ M$, $\mu = 1.01\ M$, $k_2 = 0.25\ M^{-1}\ sec^{-1}$. [b] [NaBr] = $0.030\ M$. [c] [NaBr] = $0.040\ M$. [d] [Pt(IV)] = $1.50 \times 10^{-3}\ M$. [e] $\mu = 1.51\ M$. [f] $\mu = 0.51\ M$. [g] [$HClO_4$] = $0.0300\ M$. [h] $k_2 = 0.107\ M^{-1}\ sec^{-1}$. [i] $k_2 = 0.44\ M^{-1}$.

the absence of added $Pt(CN)_4^{2-}$ the reactions of eq 5 were too slow to measure under the conditions of this study, and the data for these reactions are consistent with the rate laws in eq 7 and 8. For the forward

$$-d[trans\text{-}Pt(CN)_4Cl_2^{2-}]/dt = d[trans\text{-}Pt(CN)_4Br_2^{2-}]/dt = k_3[Br^-][Pt(CN)_4^{2-}][trans\text{-}Pt(CN)_4Cl_2^{2-}] \quad (7)$$

$$-d[trans\text{-}Pt(CN)_4ClBr^{2-}]/dt = k_3[Cl^-][Pt(CN)_4^{2-}][trans\text{-}Pt(CN)_4ClBr^{2-}] \quad (8)$$

reaction of eq 6 where a substantial rate was observed in the absence of added $Pt(CN)_4^{2-}$, the data are best described by the rate law given in eq 9. The value of

$$d[trans\text{-}Pt(CN)_4Br_2^{2-}]/dt = \{k_2 + k_3[Pt(CN)_4^{2-}]\}[Br^-][trans\text{-}Pt(CN)_4ClBr^{2-}] \quad (9)$$

k_2 in eq 9 was found to be 0.25 M^{-1} sec^{-1} at 25.0° and $\mu = 1.01\ M$. Under the conditions used to study the forward reaction of eq 6 the second-order path contributed 50% or more to the overall reaction. Consequently the third-order constants are less accurate than those of the reactions of eq 5 since they are derived from differences in large numbers. It should be pointed out that this platinum(II)-independent path may be due to a platinum(II) impurity in the platinum(IV) sample since only a few per cent $Pt(CN)_4^{2-}$ in *trans*-$Pt(CN)_4ClBr^{2-}$ can cause the observed rate. However, a true platinum(II)-independent path cannot be ruled out entirely since the temperature dependence of the intercepts of the $k_{obsd}/[Br^-]$ *vs.* [$Pt(CN)_4^{2-}$] plots is considerably greater than for the slopes. If the rate in the absence of added $Pt(CN)_4^{2-}$ were due to an impurity of $Pt(CN)_4^{2-}$, then comparable temperature dependencies should be observed. Furthermore similar platinum(II)-independent reactions were found for several halide replacements among cationic ammine complexes,[2-4] and in these cases rates at zero added platinum(II) concentration were too great to be explained by a platinum(II) impurity. Additional study is required to clarify this platinum(II)-independent path; a mechanistic interpretation at this point would be speculative.

The effect of [H^+] on the rates was negligible in the small range studied. The rates were somewhat sensitive to ionic strength, increasing as the ionic strength was raised. This behavior, which was also observed[7] for the reverse reaction of eq 6, is consistent with a primary salt effect for reactions between reagents of like charge.

The temperature dependence of the rates over a 20° range allowed calculation of activation parameters. Values of ΔH^* and ΔS^* are summarized in Table IV along with rate constants at 25°. Data for the reverse reaction[7] of eq 6 and also for the halide replacements of the related *trans*-$Pt(NH_3)_4XY^{2+}$ complexes[3] are included in Table IV for comparison. The values of ΔH^* and ΔS^* calculated for the forward reaction of eq 6 are somewhat less precise than those for the reactions of eq 5. This is undoubtedly a consequence of the relatively small change in slope of the $k_{obsd}/[Br^-]$ *vs.* [$Pt(CN)_4^{2-}$] plots compared with the substantial changes in the intercepts with temperature. Values of ΔH^* and ΔS^* calculated from the intercepts for the k_2 path are 12 ± 2.5 kcal mol^{-1} and −21 ± 7 cal deg^{-1} mol^{-1}, respectively.

Discussion

The third-order rate laws of eq 7 and 8 and the third-order term in eq 9 are consistent with a bridged redox mechanism of the type outlined in eq 1–4. Furthermore one of the remarkable and characteristic features of such a mechanism is the marked dependence of the rates on the bridging ligand. By comparing the relative rates of the forward reactions or the reverse reactions of eq 5 and 6, the influence of the bridging ligand may be observed since the reactions of eq 5 involve a bridging chlorine atom while those of eq 6 involve a bromine atom. It is important to note that these comparisons are valid since the entering bromide (or chloride for the reverse reactions) and leaving chloride (or bromide for the reverse reactions) are the same for both reactions. For both forward and reverse reactions the order of reactivity is Br > Cl. The same order of reactivity was found for replacements among cationic ammine complexes[2,3] and is generally characteristic of inner-sphere processes.

Further insight into the details of the bridged redox mechanism and specifically the influence of the four nonlabile ligands in a plane about each platinum complex can be afforded from quantitative rate comparisons between eq 5 and 6 and the halide replacements of the corresponding ammine complexes,[3] eq 10 and 11. These latter reactions are catalyzed by $Pt(NH_3)_4^{2+}$.

$$trans\text{-}Pt(NH_3)_4Cl_2^{2+} + Br^- \rightleftarrows trans\text{-}Pt(NH_3)_4ClBr^{2+} + Cl^- \quad (10)$$

$$trans\text{-}Pt(NH_3)_4ClBr^{2+} + Br^- \rightleftarrows trans\text{-}Pt(NH_3)_4Br_2^{2+} + Cl^- \quad (11)$$

The pertinent data are summarized in Table IV. As noted previously[7] the rates of the cyano complexes

TABLE IV

THIRD-ORDER RATE CONSTANTS AT 25° AND ACTIVATION PARAMETERS

		L = NH_3[a]			L = CN^-[b]		
Substrate	Entering halide	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}	k_3, M^{-2} sec^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}	k_3, M^{-2} sec^{-1}
trans-$PtL_4Cl_2{}^{2\pm}$	Br^-	8	−24	108	2.3 ± 0.5	-48 ± 2	4.5
trans-$PtL_4ClBr^{2\pm}$	Br^-	3	−30	1.9×10^4	0 ± 4	-44 ± 10	4.2×10^3
trans-$PtL_4ClBr^{2\pm}$	Cl^-	11	−20	6.3	5.6 ± 1	-48 ± 3	0.020
trans-$PtL_4Br_2{}^{2\pm}$	Cl^-	6	−22	4.2×10^3	2.5	−42	72

[a] Data from ref 3; $\mu = 0.200\ M$. [b] This work and ref 7; $\mu = 1.01\ M$.

are slower than for corresponding ammine complexes. The large unfavorable ΔS^* values for the cyano complexes are responsible for their lower reactivity since ΔH^* values for the cyano complexes are actually more favorable. These facts may be rationalized in terms of solvation of the bridged activated complexes since the charge would be 5− for the cyano complexes but only 3+ for the ammine complexes. However closer inspection of the rate data shows that the nonlabile *cis* ligands also have marked influence on *relative* reactivity. Thus, after correction for the statistical advantage of two equivalent bridging sites in the dihalo complexes, relative rates at 25° for a bridging bromine atom compared to a chlorine atom for the respective forward (reverse) reactions of the ammine complexes of eq 10 and 11 and cyano complexes of eq 5 and 6 are 350:1 (335:1) at $\mu = 0.20\ M$ and 1880:1 (1800:1) at $\mu = 1.0\ M$. Since the pairs of reactions compared show similar ionic strength dependencies, differences between these ratios due to ionic strength effects are probably small. The greater sensitivity of rates to the nature of the bridging atom for the cyano complexes may be explained in terms of a more tightly bound, but not necessarily more stable, bridged activated complex. The binding of an anionic bridging ligand in the bridged complex is expected to be stronger because the π-acceptor CN^- ligands would tend to place a greater positive charge on the metal atoms of the substrate and catalyst compared to simple σ-donor ammonia ligands. A greater Pt–X–Pt bonding would certainly place more stringent requirements on the nature of the bridging X.

Relative stabilities of reactants and products for eq 5 and 6 may be estimated by calculating equilibrium constants from ratios of rate constants. These data along with the average equilibrium constants reported[3] for eq 10 and 11 are included in Table V.

TABLE V

EQUILIBRIUM CONSTANTS AT 25°

	L = NH_3[a]	L = CN^-[b]
$K_1 = \dfrac{[trans\text{-}PtL_4ClBr^{2\pm}][Cl^-]}{[trans\text{-}PtL_4Cl_2{}^{2\pm}][Br^-]}$	16	225
$K_2 = \dfrac{[trans\text{-}PtL_4Br_2{}^{2\pm}][Cl^-]}{[trans\text{-}PtL_4ClBr^{2\pm}][Br^-]}$	4.4	58

[a] Data from ref 3; $\mu = 0.20\ M$. [b] Calculated from ratios of rate constants; $\mu = 1.0\ M$.

The ratio of K_1 to K_2 is very nearly 4:1 expected on statistical grounds. The cyano complexes clearly favor the replacement of a chloride by bromide to a greater extent than the ammine complexes. This greater preference of platinum(IV) for a bromide ligand and the higher reactivity of the bromine atom bridge is interesting and may reflect an enhanced "softness" of the metal center by the presence of the plane of π-acceptor CN^- ligands.

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