spectrometer at a probe temperature of ~36°. TMS was used as an internal reference, and chemical shifts were calibrated by the side-band method.

Nmr samples for contact shift measurements were prepared from a 1.0 *M* solution of the appropriate aniline in CCl_4 or CH_2Cl_2 with a trace of TMS by treating 1–5-ml portions of this solution with enough $Ni(acac)_2$ to give the desired concentration. The volume change resulting from the addition was assumed to be insignificant. For relative stability constant measurements, a solution containing both anilines at concentrations varying from 0.3 to 1.2 *M* was prepared and treated in a similar fashion.

Spectrograde solvents were distilled from CaH_2 before use. All anilines were freshly vacuum distilled or sublimed and the spectra were recorded immediately. Transfer of liquid anilines was made by syringe through rubber septa to minimize air oxidation, and solids were weighed under a stream of nitrogen. $Ni(acac)_2$ (J. T. Baker Chemical Co.) was dried in a vacuum oven just prior to use. Use of $Ni(acac)_2$ which was exposed to moist laboratory air for 1 day gave contact shifts which were nonreproducible and generally smaller than those obtained with freshly dried material.

A linear multiple regression analysis computer program provided in the IBM-1130 Scientific Subroutines Package was used for analysis of substituent effects.

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Kinetics and Mechanism of Substitution Reactions of *trans*-$Pt(P(C_2H_5)_3)_2RCl$

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The kinetic behavior of the complexes *trans*-$Pt(P(C_2H_5)_3)_2RCl$ (R = phenyl or *o*-tolyl) in substitution reactions with different entering groups in methanol and in dimethyl sulfoxide is examined. The substrates with *ortho*-substituted phenyl ligands show a discriminating ability toward the various entering groups, which distinguishes the biphilic reagents from the simple nucleophiles with respect to the possibility of associative attack. The influence of increasing steric hindrance on the central metal atom is estimated by comparing the kinetic data for the complexes with R = phenyl, *o*-tolyl, or mesityl.

Introduction

In a recent paper[1] we have reported the rates of substitution reactions of *trans*-$Pt(P(C_2H_5)_3)_2(ms)Cl$ (ms = mesityl) with various entering groups. The suggestion was made that in this sterically hindered complex the substitution proceeds by means of two competing paths, an associative one and a solvolytic one. When the latter is operative, the steric hindrance of two methyl groups on the metal atom seems sufficient to prevent a direct bimolecular attack by poor nucleophiles, especially in protic solvents which are very effective in assisting bond breakage in the rate-determining step. On the other hand an associative path is favored in dipolar aprotic solvents and in the reactions with good nucleophiles.

The analogous *o*-tolyl complex presents only one coordination position blocked by the *o*-methyl group of the aromatic ring, while the other is open to nucleophilic attack on the vacant p_z orbital of the metal.

In the present work kinetics data for substitution reactions of *trans*-$Pt(P(C_2H_5)_3)_2RCl$ (where R = phenyl, *o*-tolyl or mesityl) are reported. The object was to study the dependence of the reactivity and the reaction mechanism on an increasing steric hindrance at the reaction center.

Experimental Section

Materials.—The complexes used in this investigation, *trans*-$Pt(P(C_2H_5)_3)_2C_6H_5Cl$, *trans*-$Pt(P(C_2H_5)_3)_2(o\text{-tol})Cl$ (*o*-tol = *o*-tolyl), and *trans*-$Pt(P(C_2H_5)_3)_2(ms)Cl$, are all known compounds and were prepared by the methods reported in the literature.[2,3] Each one was characterized by elemental analysis and molecular weight determination.

Methanol was purified by distillation after refluxing over $Mg(OCH_3)_2$ to remove water.[4] Dimethyl sulfoxide was fractionated under reduced nitrogen pressure.[5] Other chemical products were all reagent grade commercial materials and were used without further purification.

Kinetics.—The rates of reaction were followed spectrophotometrically by measuring from time to time the changes in the optical density of the reaction mixture at some selected wavelength in the ultraviolet region. The instruments used were either a Beckman DU or an OPTICA CF 4 recording apparatus, with a cell compartment thermostated at the desired temperature.

All the reactions were carried out by using an excess of reagent with respect to the complex, in order to provide pseudo-first-order conditions. The substrate concentration in the reaction mixture was about 5×10^{-4} *M* and the reagent concentration varied from 5×10^{-3} to 10^{-1} *M*. The completeness of the reaction was checked by comparing the final spectra obtained at various reagent concentrations with those of the products independently prepared. In many cases the spectral changes during the reactions showed well-defined isosbestic points, indicating that only the substrate and the product are the absorbing species.

No significant ionic strength effect was found.

The pseudo-first-order constants were obtained graphically by means of the usual first-order plots. The experimental uncertainty in k_{obsd} values is about 10%.

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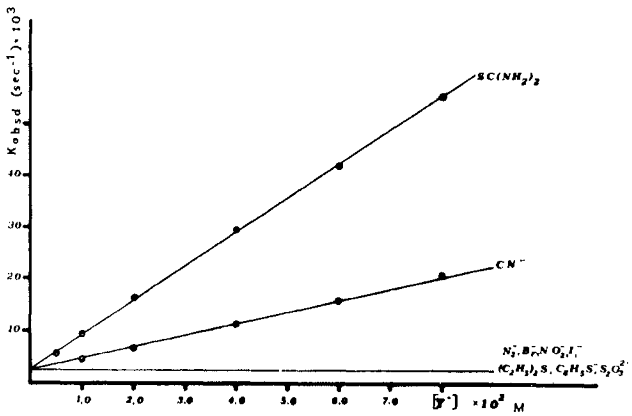

Figure 1.—Plot of k_{obsd} *vs.* reagent concentration for reactions of *trans*-Pt(P(C_2H_5)$_3$)$_2$(*o*-tol)Cl with various nucleophiles in methanol at 30°.

Results and Discussion

Figure 1 shows the dependence of the pseudo-first-order rate constants on the reagent concentration for reactions of *trans*-Pt(P(C_2H_5)$_3$)$_2$(*o*-tol)Cl with various entering groups in methanol. The data are consistent with the two-term rate law

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{Y}] \qquad (1)$$

A nonzero intercept is present as required by this rate law. It is noteworthy that the entry of many nucleophiles occurs with a rate independent of the nature and concentration of the reagent (in the range 10^{-3}–10^{-1} *M*). Thus the second-order term of eq 1 becomes inoperative even for such good nucleophiles as the anions $C_6H_5S^-$ and $S_2O_3^{2-}$, which show only first-order kinetics. A definite second-order contribution is present only with the reagents CN^- and thiourea, which are known to have biphilic properties.[6]

The same kinetic behavior was found in dimethyl sulfoxide. The k_1 value is greatly reduced with respect to that obtained in methanol (Table I) and the biphilic reagents CN^-, $SeCN^-$, and thiourea again exhibit a significant k_2 value.

As earlier described for the reactions of the analogous mesityl complex,[1] the two competing paths can be represented by eq 2. The second-order k_2 constant refers to a bimolecular attack by Y on the substrate. It is likely that the k_1 path can be described as a concerted process I_d,[7] occurring according to a dissociative interchange mechanism with the solvent, rather than one in which the solvent itself is acting as the nucleophile.

$$\begin{tikzcd}
trans\text{-Pt(P(C}_2\text{H}_5)_3)_2(o\text{-tol)Cl} + \text{Y} \arrow[rr, "k_2"] \arrow[dr, shift left, "k_1"', "\substack{+\text{solv}\\ \text{slow}}"] & & trans\text{-Pt(P(C}_2\text{H}_5)_3)_2(o\text{-tol)Y} + \text{Cl}^- \\
& \text{intermediate} \arrow[ul, shift left, "k_{-1}"'] \arrow[ur, "+\text{Y}"'] &
\end{tikzcd} \qquad (2)$$

Support for a dissociative mechanism rather than an associative one comes from the large decrease in the k_1 value in going from the protic to the dipolar aprotic solvent, in contrast with the higher nucleophilicity toward platinum(II) complexes[6,8–10] of dimethyl sulfoxide compared to methanol. Furthermore this substrate, owing to its low intrinsic reactivity,[11] should be able to discriminate between a very poor nucleophile such as the solvent and the anions used as entering groups.

A larger electron transfer from R^- toward platinum than from Cl^- accounts either for the high *trans* effect of an aryl carbanion as ligand[3] or for the Pt–Cl bond weakening,[12] shown by its very low stretching frequency value. [The ν(Pt–Cl) value found for the *o*-tolyl and mesityl complexes is the same (270 cm^{-1}) as those reported for the unhindered phenyl complex.] This lengthening and weakening of the platinum–halogen bond enhances the possibility of substitution by means of an interchange dissociative mechanism. Apart from the relative reactivity, the kinetic behavior of *o*-tolyl and mesityl complexes is the same, suggesting that it is not only steric factors that play an important role in determining the reaction mechanism. Moreover, if steric hindrance were the only discriminating factor between poor and good nucleophiles, the anions $C_6H_5S^-$ and $S_2O_3^{2-}$, which are known to have large nucleophilic reactivity constants,[13] should show a second-order contribution as do the biphilic reagents. In this regard it is noteworthy that a large contribution of k_1 to k_{obsd} has already been found[14] for the reactions in methanol of the unhindered complex *trans*-Pt(P(C_2H_5)$_3$)$_2$(C_6H_5)Cl with the entering groups NO_2^-, N_3^-, Br^-, and I^-, which behave as "poor" reagents toward the hindered systems. Moreover a bimolecular displacement is surely involved in the reactions of the complexes *trans*-Pt(P(C_2H_5)$_3$)$_2$RX (R = C_6H_5, *m*-FC_6H_4, or *p*-FC_6H_4; X = Cl, Br, N_3, NO_2) with thiourea in dimethyl sulfoxide, whereas no k_2 term was found with I^- as entering group.[15]

It is likely that the increase of electron density induced on the central metal atom by the strong σ-donor R^- ligand markedly hinders the attack by reagents whose nucleophilicity mainly depends on the polarizability of the donor atom.[16] On the other hand the attack of the biphilic reagents (which can delocalize negative charge by means of π interactions

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TABLE I[a]

FIRST-ORDER RATE CONSTANTS (k_1), SECOND-ORDER CONSTANTS (k_2), AND ACTIVATION PARAMETERS FOR THE REACTION *trans*-$Pt(P(C_2H_5)_3)_2(o\text{-tol})Cl + Y^- \rightarrow$ *trans*-$Pt(P(C_2H_5)_3)_2(o\text{-tol})Y + Cl^-$ AT 30 AND 45° IN METHANOL AND DIMETHYL SULFOXIDE

Entering group	Temp, °C	10^3k_1, sec^{-1}	ΔH_1^*, kcal/mol	ΔS_1^*, cal mol^{-1} deg^{-1}	10^2k_2, M^{-1} sec^{-1}	ΔH_2^*, kcal/mol	ΔS_2^*, cal mol^{-1} deg^{-1}
			Methanol Solvent				
N_3^-, Br^-, NO_2^-, I^-, $(C_2H_5)_2S$, $C_6H_5S^-$, $S_2O_3^{2-}$	30	2.29	13.5	−26.1			
	45	6.61					
CN^-	30				23.4	9.6	−29.7
	45				49.9		
$SC(NH_2)_2$	30				65.2	5.8	−40.4
	45				102.8		
			Dimethyl Sulfoxide Solvent				
N_3^-, I^-	30	0.046	15.1	−28.6			
	45	0.152					
$SeCN^-$	30				1.18	12.09	−27.6
	45				3.04		
$SC(NH_2)_2$	30				10.54	9.6	−31.4
	45				22.38		
CN^-	30				354	7.35	−31.8
	45				632		

[a] The rate constants k_1 (sec^{-1}) are the mean of the k_{obsd} values, where no k_2 term is present. The mean error in k_1 values is about ±3%. The second-order rate constants k_2 (M^{-1} sec^{-1}) have been calculated by using the least-squares method. The error in ΔH^* is ±1 kcal/mol, estimated, and in ΔS^* it is ±2 cal mol^{-1} deg^{-1}.

with the metal) is enhanced. In this case the expanded 5d orbitals of platinum are more available for a direct overlap with the empty ligand orbitals, thus stabilizing the trigonal-bipyramidal transition state of the associative path.

Similar explanations have been given for the relative reactivities of NO_2^- and Cl^- toward some platinum(II) substrates.[11,17,18]

The low activation enthalpy values and the large entropy changes (Table I) are in agreement with the hypothesis of a bimolecular displacement for CN^-, $SeCN^-$, and thiourea.

An investigation[19] of how far the set of nucleophilic reactivity constants, n_{Pt}, could be applied to various platinum(II) complexes showed significant deviations from the simple linear free energy relationship for the reactions between biphilic reagents and charged substrates. The role of these hindered substrates is, therefore, very interesting because the effect of their different discriminating abilities is not limited to either reducing or enhancing reactivity but may actually cause a change in the reaction path. The possibility of distinguishing different reaction paths for "poor" and "good" nucleophiles provides further evidence for the hypothesis that the nucleophilic strength of a reagent toward platinum(II) depends on two different parameters related, respectively, to σ and π bonding.

The steric effect on the substitution rate can be illustrated by comparing (Table II) the kinetic data of the reactions where a bimolecular displacement is clearly involved.

TABLE II

SECOND-ORDER RATE CONSTANTS, 10^3k_2 (M^{-1} SEC^{-1}) FOR THE REACTIONS

trans-$Pt(P(C_2H_5)_3)_2RCl + Y^- \longrightarrow$ *trans*-$Pt(P(C_2H_5)_3)_2RY + Cl^-$

IN METHANOL AND DIMETHYL SULFOXIDE AT 30°

R	Entering groups: CN^-	$SeCN^-$	$SC(NH_2)_2$
	Methanol Solvent		
Phenyl	3610	. . .	6300[a]
o-Tolyl	234	. . .	652
Mesityl	8.49[b]	14.20[b]	49.40[b]
	Dimethyl Sulfoxide Solvent		
Phenyl	Very fast	65.0	532
o-Tolyl	3540	11.8	105.7
Mesityl	31.7	0.81[b]	9.52[b]

[a] U. Belluco, M. Graziani, and P. Rigo, *Inorg. Chem.*, **5**, 1123 (1966). [b] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *ibid.*, **8**, 2207 (1969).

The reactivity sequence phenyl > *o*-tolyl > mesityl due to increasing steric hindrance at the central metal atom is verified for all entering groups examined. The retardation for one coordination position blocked is such to suggest that the methyl group, besides shielding the platinum, can destabilize the transition state by limiting the freedom of movement of the leaving group.

Moreover, the relative reactivity of the various reagents is dependent upon the nature of the substrate,

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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 $M^{-2}\ \mathrm{sec}^{-1}$, 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 four cyano ligands which lie in a plane about each platinum complex have been omitted for clarity.

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

$$BrPtBr^{2-} + PtCl^{3-} \rightleftarrows BrPtBrPtCl^{5-} \qquad (2)$$

$$BrPtBrPtCl^{5-} \rightleftarrows BrPt^{3-} + BrPtCl^{2-} \qquad (3)$$

$$BrPt^{3-} \rightleftarrows Br^- + Pt^{2-} \qquad (4)$$

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

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

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

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