the crude product by means of a rotary evaporator. Melting points were determined on a hot-stage microscope and are uncorrected. Benzene was dried over sodium and calcium hydride prior to use. Molecular weights were determined on a Hitachi Perkin-Elmer Model 115 osmometer as benzene solutions at 40.5°. Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. Infrared spectra were obtained as Nujol or hexachlorobutadiene mulls on a Perkin-Elmer Model 700 spectrometer. Nuclear magnetic resonance spectra were obtained as solutions in $CDCl_3$ on Varian A-60 or DP 60 spectrometers.

Method A.—Tetrakis(triphenylphosphine)platinum (415 mg) was dissolved in benzene ($\sim$20 ml) and succinimide (35 mg) was added. The yellow solution was refluxed for 24 hr and then allowed to stand for a further 24 hr, after which time it had become colorless. The solvent was removed and ether ($\sim$20 ml) was added. The suspension was stirred magnetically for several hours, filtered, washed with ether, and dried *in vacuo* to give the colorless complex; yield 230 mg.

A similar procedure was used for the preparation of complex II except that in this case phthalimide was used instead of succinimide.

Method B.—Tetrakis(triphenylphosphine)platinum (250 mg) was dissolved in benzene ($\sim$20 ml) and saccharin (52 mg) was added. Within a few minutes the color of the solution changed to a very pale yellow. The solvent was removed, and ether (30 ml) was added. The colorless precipitate was stirred for several hours, filtered, washed with ether, and dried *in vacuo* to give the colorless complex; yield 178 mg.

A similar procedure was used to prepare complex V, using parabanic acid instead of saccharin, although with this preparation it was several hours before the solution became pale yellow.

Method C.—Tetrakis(triphenylphosphine)platinum (325 mg) was dissolved in benzene (25 ml) and maleimide (29 mg) was added. The solution rapidly became pale yellow, and a microcrystalline precipitate slowly formed. After 12 hr the solid was filtered, washed with benzene, and dried *in vacuo* to give the complex; yield 224 mg.

A similar procedure was used for the preparation of complex VIII using tetrakis(triphenylarsine)platinum, complex IX using tetrakis(triphenylphosphine)palladium, and complex VI using tetrakis(triphenylphosphine)palladium and succinimide.

Method D.—Tetrakis(triphenylarsine)platinum (773 mg) as a suspension in benzene ($\sim$30 ml) was stirred with saccharin (104 mg) for 24 hr. The suspension was filtered to remove unchanged starting material and the solvent was removed from the solution of the complex. Ether was added and the resulting suspension was stirred for 2 hr. The solid was then filtered, washed with ether, and dried *in vacuo* to give the complex; yield 398 mg.

Complexes I–V can be recrystallized from a mixed chloroform–ether solvent.

Acknowledgments.—The author wished to thank Dr. J. A. Magnuson for assistance with the high-field-line ^1H nmr spectral work and Mr. Daniel M. Blake for many helpful discussions.

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Kinetics of Ligand Substitution Reactions for Platinum Complexes. Relative Influence of *cis*-Triethylphosphine and Amine Ligands upon the Isotopic Exchange between Chloride and Bromide Ions and the Halo Ligands[1]

By Giovanni Carturan and Don S. Martin, Jr.

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The kinetics of exchange for chloride and bromide ions with the corresponding halide ligands have been measured in methanol at 25 and 35° for the complexes *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$, *trans*-$Pt(P(C_2H_5)_3)(NH_3)Cl_2$, *trans*-$Pt(P(C_2H_5)_3)(N(C_2H_5)_2CH_2C_6H_5)Cl_2$, *trans*-$Pt(P(C_2H_5)_3)_2Br_2$, and *trans*-$Pt(P(C_2H_5)_3)(NH_3)Br_2$. For each complex the rate law was found to be: rate = $[Pt](k_1 + k_2[\text{halide}])$, where k_1 can be considered to characterize a solvation step. Exchange in the bromide systems is more rapid than for the corresponding chloride complexes. No systematic difference was evident between a phosphine or an amine in the *cis* position. However, in view of the trends observed the *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$ proved exceptionally inert.

Introduction

Kinetics studies on the large variety of substitution-inert square-planar complexes of platinum(II) have provided much information about the mechanisms for the ligand substitution processes. Reviews of the relevant literature[2,3] have summarized the evidence for a *normal* type of mechanism which is believed to involve an associative type of process with a five-coordinate (approximately trigonal-bipyramidal) configuration. Also, in many instances the direct replacement of a ligand, X, by an entering group, Y, must compete with replacement of X by solvent. Although sometimes the intermediate may be characterized, frequently the solvent is rapidly displaced by Y. The result is a first-order term characterized by the rate constant k_1 in the rate law for substitution, *i.e.*

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

Evidence has been summarized[4] for a number of halide-exchange studies[5] in which an alternative mechanism must be operative. Also, it has been pointed out that some influences upon the kinetics which have

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(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2565.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 5.

(3) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 2.

(4) D. S. Martin, Jr., *Inorg. Chim. Acta Rev.*, **1**, 87 (1967).

(5) (a) J. E. Teggins and D. S. Martin, Jr., *Inorg. Chem.*, **6**, 1003 (1967); (b) D. G. McMane and D. S. Martin, Jr., *ibid.*, **7**, 1167 (1968).

long been attributed to the *trans* effect in reality reflect an influence of the *cis* neighbor in the square complex.[4,6]

The present work was undertaken to provide a careful characterization of isotopic exchange in methanol between the bromide or chloride ion with the corresponding halo ligand for a series of complexes *trans*-Pt(L)$_2$X$_2$ and *trans*-PtLAX$_2$ where X is either chloride or bromide, L is triethylphosphine, and A is either ammonia or diethylbenzylamine. It was planned in this way to compare the effect upon the kinetics of a phosphine in the *cis* position, which is a very strong *trans* director, to that of an amine which is a very weak *trans* director.

Experimental Section

Separation Method.—For the separation of free halide ions from the methanolic solution, an ion-exchange column with a 25-30 mesh Amberlite IRA-400 anion-exchange resin in the nitrate form was used. With the experimental conditions described in previous work[7] a reduction of the halide concentration to 0.1%, or less, was obtained, and the complexes were eluted with 100% of yield. Normally, the total time necessary to complete the separation was 2-3 min, but within 30 sec from the start of the separation, more than 30% of the complex was removed from the column. Therefore, only a negligible error in the time was introduced by the separation. In the case of Cl$^-$ exchange the effluent solutions, after reduction in volume by evaporation, were poured into plastic containers and brought to dryness. The residue obtained was dissolved in a constant and standard amount of scintillator solution and the counting rate of each sample was recorded with a Beckman Model LS200 liquid scintillation counting system. For the Br$^-$ exchange 1-ml aliquots from the samples were counted by a 3 in. × 3 in. NaI(Tl) scintillation crystal spectrometer, following the method of Teggins and Martin.[5a]

Procedure.—For all kinetics experiments, the complex and the reagent halide were dissolved in methanol to have a 50-ml volume. An ionic strength 0.03 *M* was obtained by the addition of the necessary quantity of salt (NaNO$_3$ or KNO$_3$). This solution was stored at a constant temperature in the dark. In some stability experiments, performed spectrophotometrically, no significant variations in the spectral range of 200-500 mμ were detectable for solutions stored without light for many hours. The isotopic exchange was initiated by the addition of 10 μl of H^{36}Cl (2.04 *M*) or 20 μl of NH$_4{}^{82}$Br (0.235 *M*) for the Cl$^-$ and the Br$^-$ exchanges, respectively. Changes in volume were therefore insignificant in this step, and the changes in the halide concentration were less than 1%. For the Br$^-$ exchange the infinity counting rates were measured after about 10 reaction half-times. For the Cl$^-$ case these values were calculated from the formula $C_\infty = (2[\text{complex}]A)/(2[\text{complex}] + [\text{Cl}^-])$, where A is the counting rate for a sample in which no chloride had been removed. Values calculated in this way were in satisfactory agreement with the observed values in several cases for which comparisons were performed.

Materials.—*trans*-Pt[P(C$_2$H$_5$)$_3$]$_2$Cl$_2$ was prepared by the method of Jensen[8] from H$_2$PtCl$_6$ and P(C$_2$H$_5$)$_3$ in water; mp 142-143°. *Anal.* Calcd: C, 28.69; H, 6.07. Found: C, 28.34; H, 5.98.

trans-Pt[P(C$_2$H$_5$)$_3$](NH$_3$)Cl$_2$ was obtained by the reaction of a stoichiometric amount of NH$_3$ with the chloro-bridged dimeric platinum complex *trans*-Pt$_2$(P(C$_2$H$_5$)$_3$)$_2$Cl$_4$, following the method used by Chatt and Venanzi[9] for similar compounds; mp 110-111° subl. *Anal.* Calcd: C, 17.96; H, 4.56. Found: C, 18.30; H, 4.53. This pale yellow compound was identified as a *trans* compound from the position of the Pt-Cl asymmetric stretching band (339.5 cm^{-1}), usual for the *trans* complexes of this type;[10] and from the similarity of the ν(N-H) of our complex (3365, 3305, 3248, 3213, 3170 cm^{-1}) with the ν(N-H) of *trans*-Pt(P(*n*-C$_3$H$_7$)$_3$)(NH$_3$)Cl$_2$ found by Chatt and coworkers[11] (3363, 3300, 3243, 3210, and 3167 cm^{-1}).

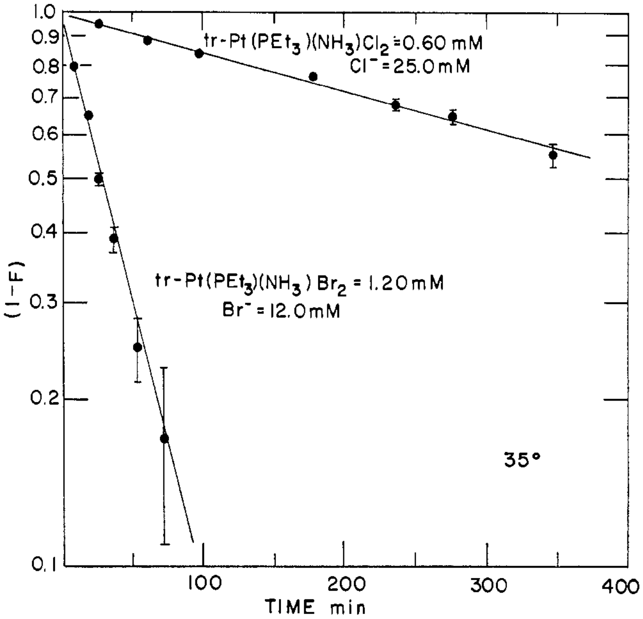

Figure 1.—Typical exchange reactions for Pt(P(C$_2$H$_5$)$_3$)(NH$_3$)X$_2$ in methanol, at 35° and μ = 0.030 *M*.

trans-Pt[P(C$_2$H$_5$)$_3$][(C$_2$H$_5$)$_2$NCH$_2$C$_6$H$_5$]Cl$_2$ was prepared under the same conditions as *trans*-Pt[P(C$_2$H$_5$)$_3$](NH$_3$)Cl$_2$; mp 101-102°. *Anal.* Calcd: C, 37.30; H, 5.89. Found: C, 36.48; H, 5.86. The ir spectrum of this compound shows ν(Pt-Cl) at 335 cm^{-1}.

trans-Pt[P(C$_2$H$_5$)$_3$]$_2$Br$_2$ was prepared by action of a large excess of NaBr on *trans*-Pt[P(C$_2$H$_5$)$_3$]$_2$Cl$_2$ in a 50% H$_2$O-C$_2$H$_5$OH solution for about 100 hr. After evaporation, the product was extracted with ether and crystallized from methanol; mp 133-134°. *Anal.* Calcd: C, 24.38; H, 5.11. Found: C, 24.26; H, 5.05. The compound exhibits ν(Pt-Br) at 254 cm^{-1} in agreement with the published value.[9]

trans-Pt[P(C$_2$H$_5$)$_3$](NH$_3$)Br$_2$ was obtained similarly from *trans*-Pt[P(C$_2$H$_5$)$_3$](NH$_3$)Cl$_2$; mp 125-126°. *Anal.* Calcd: C, 14.50; H, 3.70. Found: C, 15.06; H, 3.87. In the ir spectrum were ν(Pt-Br) at 248 cm^{-1} and ν(N-H) at 3362, 3308, 3246, 3208, and 3170 cm^{-1}.

Bromine-82 was obtained by irradiating a solution of NH$_4$Br (0.235 *M*) in the Ames Laboratory research reactor. All the other materials were of Analytical Reagent grade.

Treatment of Data.—The counting rate of a sample, C_i, from the ion-exchange separation method, was taken proportional to the amount of the tagging nuclide which had replaced the halide ligand. From these values the fraction of exchange was calculated from the expression $F_i = C_i/C_\infty$. The exchange reaction half-life, $t_{1/2}$, was determined from the plot of log $(1 - F_i)$ *vs.* time by a least-squares method. With assigned 4 and 2% errors in the counting rate determinations, which appear realistic for the Cl$^-$ and Br$^-$ samples, respectively, the error in $t_{1/2}$ was evaluated in the least-squares calculation. Typical experiments are shown in Figure 1 for both a chloride and a bromide exchange of the corresponding triethylphosphine-ammonia complexes. From the $t_{1/2}$ data, the k_{obsd} values were calculated with the McKay[12] equation. The variation of the pseudo-first-order constants, k_{obsd}, with the initial halide concentration, [X$^-$], shows that the exchange rate is consistent with eq 1. Typical

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[6] C. B. Colvin, R. G. Gunther, L. D. Hunter, J. A. McLean, M. A. Tucker, and D. S. Martin, Jr., *Inorg. Chim. Acta*, **2**, 487 (1968).

[7] D. S. Martin, Jr., and E. L. Bahn, *Inorg. Chem.*, **6**, 1653 (1967).

[8] K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 225 (1936).

[9] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 3858 (1955).

[10] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *ibid.*, 734, (1964).

[11] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *ibid.*, **2712** (1956).

[12] H. McKay, *Nature*, **142**, 997 (1938).

examples of the resolution of k_{obsd} into the components k_1 and k_2 are shown in Figure 2. This figure illustrates the difference in rates between chloride and bromide exchange for the corresponding compounds. A tabulation of the values of the k_1's and k_2's with their activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, appears in Tables I and II.[13] The errors in these data were calculated by propagation of the errors from the counting to $t_{1/2}$ to k_{obsd} and from there to k_1 and k_2 using the weighted least-squares method. The weights were assigned proportional to $1/\sigma^2$, where σ is the standard deviation.

The uncertainties in the rate constants and activation parameters reflect moderate errors in evaluation of the counting rates for the various fractions. These uncertainties, as indicated by the sum of the squares, were statistically consistent with the assigned standard deviations for the counting measurements. It was apparent that the evaluation of bromide activities by scintillation counting of the ^{82}Br γ rays achieved a higher precision than the liquid scintillation counting of the ^{36}Cl β rays. Generally, a loss of precision in the log $(1 - F)$ function precluded significant evaluation of exchange beyond 1.5–2 half-times. Although the uncertainties in the rate constants may appear high in comparison to some methods for evaluating kinetics under more favorable circumstances, they are believed to represent fairly typical attainments for the isotopic exchange method which requires a chemical separation and the counting of a radioactive sample.

Since the intercepts of the plots of k_{obsd} *vs.* halide concentration were small, there was a rather large uncertainty in the values of k_1. In the case of $Pt(P(C_2H_5)_3)_2Cl_2$ the uncertainty was as large as the rate constant. With the other complexes, there was very definite evidence for the first-order reaction. However, the uncertainties were sufficiently high that it was not possible to reach meaningful conclusions concerning the activation parameters. However, the values of k_2 were given with much smaller fractional uncertainties.

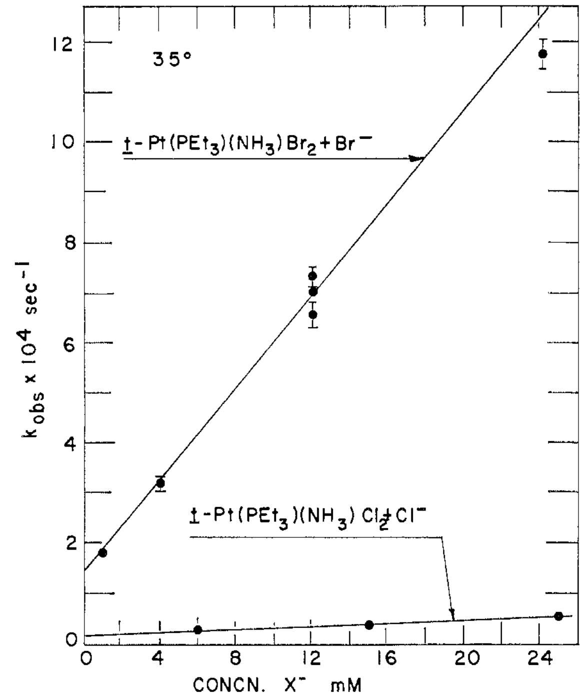

Figure 2.—Plots of the pseudo-first-order rate constants, k_{obsd}, *vs.* halide concentration for the triethylphosphine–ammonia complexes of platinum(II) in methanol at μ = 0.030 *M*.

TABLE I

FIRST-ORDER RATE CONSTANTS, k_1, FOR THE SOLVATION OF THE PLATINUM(II) COMPLEXES IN METHANOL (IONIC STRENGTH 0.030 *M*)

Complex	$10^5 k_1$, sec^{-1} 25°	$10^5 k_1$, sec^{-1} 35°	$\Delta H_1^{\ddagger}$ kcal/mol	$\Delta S_1^{\ddagger}$ cal/mol
trans-$Pt(P(C_2H_5)_3)_2Cl_2$		~0.01 ± 0.01		
trans-$Pt(P(C_2H_5)_3)(NH_3)Cl_2$	0.40 ± 0.12	1.26 ± 0.08	20 ± 6	−15 ± 20
trans-$Pt(P(C_2H_5)_3)(N(C_2H_5)_2CH_2C_6H_5)Cl_2$	0.53 ± 0.11	1.61 ± 0.41	19 ± 6	−20 ± 20
trans-$Pt(P(C_2H_5)_3)_2Br_2$	5.8 ± 3	16.4 ± 1.2	18 ± 1.6	−17 ± 5
trans-$Pt(P(C_2H_5)_3)(NH_3)Br_2$	3.6 ± 0.6	14.0 ± 1.4	23 ± 4	−2 ± 13
trans-$Pt(C_5H_{11}N)_2Cl_2$	21[a]			

[a] For 30°: L. Cattalini, U. Belluco, R. Ettore, and M. Martelli, *Gazz. Chim. Ital.*, 94, 356 (1964).

Results and Discussion

The specific rate constants and activation parameters given in Table I and especially Table II, despite the fairly large uncertainties, still provide a number of interesting comparisons for testing current theories and correlations for the kinetics of ligand substitution for platinum(II) square-planar complexes.

For example, the similarity in the values of k_1 and k_2 for *trans*-$Pt(P(C_2H_5)_3)_2Br_2$ and *trans*-$Pt(P(C_2H_5)_3)(NH_3)Br_2$ suggests only a small (30%) difference in the *cis* neighbor kinetics effect between NH_3 and $P(C_2H_5)_3$. The smaller k_2 for *trans*-$Pt(P(C_2H_5)_3)_2Br_2$ in part may reflect a steric difference. However, there is little difference in the k_2's between *trans*-$Pt(P(C_2H_5)_3)(NH_3)Cl_2$ and *trans*-$Pt(P(C_2H_5)_3)(N(C_2H_5)_2CH_2C_6H_5)Cl_2$. The two amines have similar basicities[14] so here the principal difference between the two should result from a steric effect. Again a difference of only 30% indicates that any such steric effect is rather minor.

The differences between the k_2's for the bromide and chloride exchange in the system *trans*-$Pt(P(C_2H_5)_3)(NH_3)X_2$ can result from three factors: (1) a "leaving-group" effect, (2) an "entering-group" or nucleophilicity effect, and (3) a *trans* effect. For the clear-cut case of $Pt(dien)X^+$, where dien is diethylenetriamine, with which the leaving-group effect can be isolated, chloride is only a slightly poorer leaving group than bromide.[4] Also a comparison between bromide and chloride substitution for those complexes indicates that as an entering group Br^- reacts *ca.* ten times faster than Cl^-. The factor of 30 between the k_2's for the $Pt(P(C_2H_5)_3)(NH_3)X_2$ complexes suggests a factor of 3–5 for the *trans* effect of bromide over chloride. Such a factor is consistent with the accepted correlation that bromide is a slightly stronger *trans*-directing group than chloride.

Although they are not given precisely, it is apparent

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(13) For detailed experimental conditions order Document No. NAPS-00640 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10001, remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make check or money orders payable to: ASIS–NAPS.

(14) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957).

TABLE II

SECOND-ORDER RATE CONSTANTS, k_2, FOR THE REPLACEMENT OF A HALIDE LIGAND BY A HALIDE (IONIC STRENGTH 0.030 M)

Complex	Entering halide	$10^5 k_2$, M^{-1} sec^{-1}		$\Delta H_2^{\ddagger}$, kcal/mol	$\Delta S_2^{\ddagger}$, cal/mol
		25°	35°		
trans-$Pt(P(C_2H_5)_3)_2Cl_2$	Cl^-	4.2 ± 0.6	12.3 ± 5	19 ± 3	-15 ± 9
trans-$Pt(P(C_2H_5)_3)(NH_3)Cl_2$	Cl^-	81 ± 11	174 ± 8	13 ± 1.5	-27 ± 5
trans-$Pt(P(C_2H_5)_3)(N(C_2H_5)_2CH_2C_6H_5)Cl_2$	Cl^-	65 ± 10	140 ± 30	13 ± 3	-28 ± 9
trans-$Pt(P(C_2H_5)_3)_2Br_2$	Br^-	1740 ± 40	4090 ± 110	15 ± 1	-16 ± 3
trans-$Pt(P(C_2H_5)_3)(NH_3)Br_2$	Br^-	2300 ± 80	4600 ± 150	12 ± 1	-26 ± 3
trans-$Pt(P(C_2H_5)_3)_2Cl_2$	Br^-	93[a]			
trans-$Pt(C_5H_{11}N)_2Cl_2$	Cl	92.5[a]			
trans-$Pt(C_5H_{11}N)_2Cl_2$	Br^-	616[a]			

[a] See footnote *a* of Table I.

that the activation entropies for the majority of the reactions generally have moderately large negative values, which are typical for the square-planar platinum complexes.[15]

A striking consequence of the present results, which has not been recognized in previous work, is the inertness of *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$ which is badly out of line with the other complexes in view of the current systematics for the kinetics of square-planar complexes. In comparison of the k_2's for *trans*-$Pt(P(C_2H_5)_3)_2X_2$ and *trans*-$Pt(P(C_2H_5)_3)(NH_3)X_2$ there is only a 30% difference in the bromide system; there is an additional factor of 1:15 for the chlorides. Also while there is only a factor of 1:29 between the k_2's for chloride and bromide in the *trans*-$Pt(P(C_2H_5)_3)(NH_3)X_2$ complexes, the ratio is 1:410 for the *trans*-$Pt(P(C_2H_5)_3)_2X_2$'s, again an additional factor of nearly 1:15. The inertness is evident also in the value of k_1 for $Pt(P(C_2H_5)_3)_2Cl_2$ which cannot be determined with any real certainty, $(1 \pm 1) \times 10^{-7}$ M^{-1} sec^{-1} at 35°. Previous values of 2.9×10^{-7} M^{-1} sec^{-1} for 30°, which have been quoted in the literature, were based upon Arrhenius extrapolation from experiments above 55°.[16] This anomaly is especially important since the *trans*-dichlorobis(triethylphosphine)platinum(II) complex has served as the typical *trans* phosphine complex in series of complexes.[17] Thus, the very high nucleophilic discrimination factor for this compound, noted by Belluco, *et al.*,[16] may not be typical of other phosphine complexes.

It can be seen from the values of k_2 at 30° reported by Cattalini, *et al.*,[18] that the inertness of $Pt(P(C_2H_5)_3)_2Cl_2$ extends toward attack by bromide as well as by chloride. Also, the reactivity of a complex with a phosphine and an amine group in the *cis* positions is comparable to that of the complex with the two *cis*-piperidine ligands. This inertness of $Pt(P(C_2H_5)_3)_2Cl_2$ results from an activation enthalpy for k_2 which is about 4–5 kcal/mol higher than for reactions of the other complexes whose $\Delta H^{\ddagger}$ are all rather similar. Possibilities to be considered for explaining this inertness are the existence of a different coordination species, possibly one involving the solvent as a fifth ligand in equilibrium with the planar complex. However, there is no spectrophotometric evidence for such a species. Absorption spectra for solutions stored in the dark in 0.01 M halide showed no detectable changes for periods extending to several days from the few minutes required to dissolve the samples and introduce the solutions into the spectrophotometer. Possibly, there is a configuration with special stability for the small chloride ligands in the presence of the bulky phosphine groups. It was also clear from the spectra that there was no isomerization to form the *cis* complexes. The careful crystal structures of Messmer and Amma[19] for *trans*-$Pt(P(C_2H_5)_3)_2X_2$, with chloride and bromide have some interatomic distances which are indicative of fairly high strains in the ligands.

Attempts were made to prepare the complex $Pt(P(C_2H_5)_3)(N(C_2H_5)_2CH_2C_6H_5)Br_2$ by replacement of chloride by bromide in alcohol solutions. Similar methods served for the convenient preparations of *trans*-$Pt(P(C_2H_5)_3)_2Br_2$ and *trans*-$Pt(P(C_2H_5)_3)(NH_3)Br_2$. Two products were crystallized from these solutions but their analyses and infrared spectra proved them to be the dimeric complex *trans*-$Pt_2(P(C_2H_5)_3)_2Br_4$ and a monomeric species $Pt(P(C_2H_5)_3)Br_2(CH_3OH)$. Apparently, dibromo(triethylphosphine)(diethylbenzylamine)platinum(II) does not form in these solutions.

It is noted that the carbon analyses for *trans*-$Pt(P(C_2H_5)_3)((C_2H_5)_2NCH_2C_6H_5)Cl_2$ deviated from the calculated values by somewhat more than those for the other complexes. In view of the apparent instability of the corresponding bromo compound, it seems possible that a few per cent of the chloride compound had lost the amine to form perhaps the corresponding dimer or a solvated monomeric species which had not been eliminated by the fractional crystallization.

It seems clear that these studies indicate an interesting anomalous behavior for $Pt(P(C_2H_5)_3)_2Cl_2$ with respect to current mechanistic theories and that further careful study is needed for the kinetic behavior of these complexes.

Acknowledgment.—We wish to acknowledge the assistance of Mr. John Richards of the Ames Laboratory Analytical Services Group in performing the carbon–hydrogen analyses.

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[15] U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

[16] U. Belluco, L. Cattalini, and A. Orio, *Gazz. Chim. Ital.*, **93**, 1422 (1963).

[17] (a) L. Cattalini, U. Belluco, M. Martelli, and R. Ettore, *ibid.*, **95**, 567 (1965); (b) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

[18] L. Cattalini, U. Belluco, R. Ettore, and M. Martelli, *Gazz. Chim. Ital.*, **94**, 356 (1964).

[19] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).