419. *Kinetics of the Reaction of Alkyl and Aryl Compounds of the Nickel Group with Pyridine.*

By F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw.

Kinetic studies are reported of the reaction in ethanol solution between pyridine and several planar platinum(II), palladium(II), and nickel(II) compounds of the general formula $[MClR(PR'_3)_2]$. The relative rates of attainment of equilibrium of *trans*-$[MCl(o\text{-tolyl})(PEt_3)_2]$ with pyridine are approximately 5,000,000 : 100,000 : 1 where M is Ni(II), Pd(II), and Pt(II) respectively. The effect on the rates of equilibration of different groups *trans* to the chloro-group undergoing replacement shows that the *trans*-labilizing abilities of these ligands decrease as follows: $PMe_3 > PEt_3 \gtrsim H > PPr_3 > Me >$ phenyl $\gtrsim$ *p*-methoxyphenyl $\gtrsim$ *p*-chlorophenyl $>$ biphenylyl $>$ *o*-tolyl $>$ mesityl $\gtrsim$ Cl. Both the electrostatic (polarization) and π-bonding theories of the *trans*-effect are needed to explain these results. Mesityl compounds always react more slowly than do analogous aryl derivatives. These observations are discussed in terms of probable mechanisms of planar substitution. Experimental details are also given for the synthesis of new compounds whose dipole moments are recorded.

Substitution (replacement) reactions of square-planar metal complexes have been studied kinetically, especially those of compounds of platinum(II) which react at rates suitable to be followed by ordinary techniques.[1] The results of these investigations indicate that solvent and/or reactant are involved in the rate-determining step. For reversible reactions of the type reported in this paper:

$$[MClR(PR'_3)_2] + py \rightleftharpoons [M(R)py(PR'_3)_2]^- + Cl^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

(where R = alkyl, aryl, or hydrogen; R′ = alkyl)

the general rate law for the attainment of equilibrium can be expressed by the equation

$$k_{obs} = k_1 + k_2[py] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where $k_{obs.}$ is a pseudo-first-order rate constant, k_1 is a first-order rate constant for solvent-controlled reaction, and k_2 is a second-order rate constant for reaction with pyridine.[2] This paper reports k_1 and k_2 values for a number of such reactions in ethyl alcohol solutions.

Neither k_1 nor k_2 is a simple rate constant since, for a reversible process, both forward and reverse reactions contribute to the attainment of equilibrium. It may then be expected that a part of k_1 and also of k_2 should depend on the chloride-ion concentration, which is certainly involved in the reverse reaction and increases markedly during the course of a kinetic study. Experimentally the effect of changing chloride concentration cannot be detected since a first-order course is followed throughout. This was also observed by Lamb[3] in his study of the reversible aquation of $[Rh(NH_3)_5Br]^{2+}$, and his explanation may be applicable here, namely, that changes in activity coefficients due to ionic-strength effects roughly cancel changes in concentration. Despite the complex nature of k_1 and k_2, they seem suitable for assessing the relative activating influence of substituents in a series of analogous compounds undergoing the same reaction, since they are independent of concentration over the ranges studied.

The results obtained permit (1) a comparison of rates of reaction of analogous nickel(II), palladium(II), and platinum(II) compounds; (2) an estimate of the *trans*-effect of different groups; (3) demonstration of a large steric effect on the rates of these reactions; and (4) comparison of rate constants and equilibrium constants.

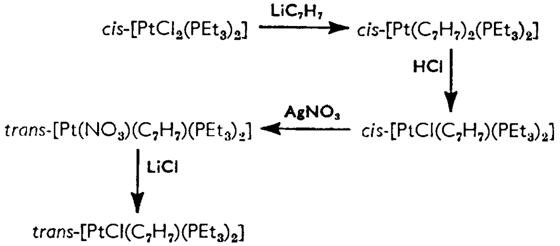
---

[1] (*a*) Grinberg, *Russ. J. Inorg. Chem.*, 1959, **4**, 683; (*b*) Basolo, Gray, and Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 4200; and references therein.

[2] Gray and Olcott, unpublished work.

[3] Lamb, *J. Amer. Chem. Soc.*, 1939, **61**, 699.

General Method of Preparation of the Organometallic Complexes.—Many of the alkyl-, aryl-, and hydrido-metal complexes studied in this work have been described previously;[4-7] and many of the remainder were prepared by analogous methods. A new method was used to prepare the chloro-complexes *trans*-$[PtClR(PEt_3)_2]$ (R = *o*-tolyl or mesityl). The reaction scheme is outlined below for the *o*-tolyl complexes.



The sterically hindered *cis*-$[PtCl(o\text{-tolyl})(PEt_3)_2]$ could not be converted into the *trans*-complex by treatment with a trace of triethylphosphine, in contrast with the complexes *cis*-$[PtClR(PEt_3)_2]$ (R = Me, Ph, or *p*-tolyl) which were readily isomerised by this treatment. However, *cis*-$[PtCl(o\text{-tolyl})(PEt_3)_2]$ on treatment with silver nitrate gave only the *trans*-nitrato-complex; presumably the *cis*-nitrato-complex is formed initially but this rapidly changes to the more stable *trans*-form. Mesitylplatinum complexes behaved similarly. The nitrate complexes *trans*-$[Pt(NO_3)R(PEt_3)_2]$ (R = *o*-tolyl, mesityl) were volatile, subliming slowly without decomposition above 160°/1 atm.

EXPERIMENTAL

Preparation of Organometallic Complexes.—The preparation and properties of the complexes studied in this paper and which have not been described previously [4-7] are given below. M. p.s were determined on a Kofler hot-stage and are corrected.

trans-*Di-*(o-*tolyl*)*bis*(*triethylphosphine*)*palladium*(II), $[Pd(o\text{-tolyl})_2(PEt_3)_2]$. A 1·75N-solution of *o*-tolyl-lithium in ether (9·0 c.c.) was added at *ca.* −10° to a solution of *trans*-dibromobis(triethylphosphine)palladium(II) (3·0 g.) in benzene (16 c.c.). After 15 min. at *ca.* 10° benzene (30 c.c.) and water were added and the product was isolated from the organic phase. After one recrystallization from methyl alcohol and one from light petroleum (b. p. 40—80°) trans-*di-*(o-*tolyl*)*bis*(*triethylphosphine*)*palladium*(II) was obtained as needles (1·29 g.), m. p. 123—127° (decomp.) (Found: C, 59·65; H, 8·6. $C_{26}H_{44}P_2Pd$ requires C, 59·5; H, 8·45%).

trans-*Chloro-*(o-*tolyl*)*bis*(*triethylphosphine*)*palladium*(II), $[PdCl(o\text{-tolyl})(PEt_3)_2]$. A solution of *trans*-di-(*o*-tolyl)bis(triethylphosphine)palladium(II) (0·84 g.) in benzene (5 c.c.) and ether (5 c.c.) was treated with a 1·00N-solution of hydrogen chloride in ether (1·61 c.c.). After 18 hr. at 20° the solution was evaporated to dryness and the residue recrystallized first from methyl alcohol, then from light petroleum (b. p. 40—60°), to give trans-*chloro-*(o-*tolyl*)*bis*(*triethylphosphine*)*palladium*(II) as prisms (0·67 g.), m. p. 86—88° (Found: C, 48·55; H, 7·95. $C_{19}H_{37}ClP_2Pd$ requires C, 48·65; H, 7·95%).

trans-*Nitrato-*(o-*tolyl*)*bis*(*triethylphosphine*)*platinum*(II), $[Pt(NO_3)(o\text{-tolyl})(PEt_3)_2]$. A mixture of *cis*-chloro-(*o*-tolyl)bis(triethylphosphine)platinum(II) (3·43 g.), silver nitrate (1·2 g.), and ethyl alcohol (40 c.c.) was shaken for 3 hr. at 20°. The precipitated silver chloride was then filtered off, the filtrate evaporated to dryness, and the residue extracted with boiling light petroleum (b. p. 60—100°). The light petroleum extracts, on cooling, gave trans-*nitrato-*(o-*tolyl*)*bis*(*triethylphosphine*)*platinum*(II) as needles (2·83 g.), m. p. 188—190° (with sublimation above 160°) (Found: C, 39·0; H, 6·45; N, 2·65. $C_{19}H_{37}NO_3P_2Pt$ requires C, 39·05; H, 6·4; N, 2·4%).

A mixture of this nitrate complex (0·290 g.), pyridine (0·04 g.), and ether (10 c.c.) was boiled

---

[4] Chatt and Shaw, *J.*, 1959, 705, 4020.
[5] Chatt and Shaw, *J.*, 1960, 1718.
[6] Adams, Chatt, and Shaw, *J.*, 1960, 2047.
[7] Chatt, Duncanson, and Shaw, *Proc. Chem. Soc.*, 1957, 343; *Chem. and Ind.*, 1958, 859.

for 5 min. Benzene (5 c.c.) was then added and after the mixture had been warmed to 40° an excess of light petroleum (b. p. 60—80°) was added. The precipitate was filtered off and washed with light petroleum (b. p. 60—80°), to give o-*tolyl*(*pyridine*)*bis*(*triethylphosphine*)*platinum*(II) *nitrate* (0·261 g.) as colourless prisms, m. p. 190—192° (decomp.) (Found: C, 43·5; H, 6·55. $C_{24}H_{42}N_2O_3P_2Pt$ requires C, 43·45; H, 6·4%). The product was soluble in benzene or water and had a molar conductivity in nitrobenzene at 25° of 29·3 mho corresponding to a univalent-univalent electrolyte.

trans-*Chloro-*(o-*tolyl*)*bis*(*triethylphosphine*)*platinum*(II), $[PtCl(o\text{-tolyl})(PEt_3)_2]$. The above-mentioned nitrate (0·70 g.) and lithium chloride (1·5 g.) in acetone (20 c.c.) were heated under reflux for 30 min., then evaporated to dryness, water was added, and the product was isolated with ether. trans-*Chloro-*(o-*tolyl*)*bis*(*triethylphosphine*)*platinum*(II) was obtained as prisms (0·305 g.), m. p. 104—105°, from light petroleum (b. p. 60—80°) (Found: C, 41·2; H, 6·85. $C_{19}H_{37}ClP_2Pt$ requires C, 40·9; H, 6·7%).

o-Tolyl(pyridine)bis(triethylphosphine)platinum(II) nitrate (0·100 g.) in water (2 c.c.) was treated with sodium chloride (0·2 g.) and put aside. After 18 hr. at 20° *trans*-chloro-(*o*-tolyl)bis-(triethylphosphine)platinum(II) had crystallized as colourless needles (0·084 g.), m. p. 103—104°, identical with the preceding sample.

trans-*Nitrato*(*mesityl*)*bis*(*triethylphosphine*)*platinum*(II), $[PtNO_3(mesityl)(PEt_3)_2]$. A solution of *cis*-bromo(mesityl)bis(triethylphosphine)platinum(II) (1·89 g.) in benzene (30 c.c.) and ethyl alcohol (30 c.c.) was treated with a suspension of silver nitrate (0·61 g.) in ethyl alcohol (30 c.c.). The mixture was then shaken for 2 hr., after which the silver chloride was filtered off and the filtrate evaporated to dryness. The residue was recrystallized first from ethyl alcohol, then from light petroleum (b. p. 60—80°), to give trans-*nitrato*(*mesityl*)*bis*(*triethylphosphine*)*platinum*(II) as prisms (1·55 g.), m. p. 146—147° (Found: C, 41·25; H, 6·85; N, 2·4. $C_{21}H_{41}NO_3P_2Pt$ requires C, 41·15; H, 6·75; N, 2·3%).

trans-*Chloro*(*mesityl*)*bis*(*triethylphosphine*)*platinum*(II), $[PtCl(mesityl)(PEt_3)_2]$. A mixture of the last-mentioned nitrate (0·70 g.), lithium chloride (1·15 g.), and acetone (25 c.c.) was heated under reflux for 20 min., then evaporated to dryness, and water was added. The residue was dried and recrystallized from light petroleum (b. p. 60—80°), to give trans-*chloro*(*mesityl*)*bis*(*triethylphosphine*)*platinum*(II) as needles (0·43 g.), m. p. 196·5—197·5° (with sublimation into prisms) (Found: C, 43·1; H, 7·15. $C_{21}H_{41}ClP_2Pt$ requires C, 43·05; H, 7·05%).

cis- *and* trans-*Bromo*(*mesityl*)*bis*(*triethylphosphine*)*platinum*(II), $[PtBr(mesityl)(PEt_3)_2]$. *trans*-Dibromobis(triethylphosphine)platinum(II) (3·0 g.) and benzene (40 c.c.) were added to a Grignard reagent, prepared from magnesium (0·77 g.), a trace of iodine, 2-bromomesitylene (6·38 g.), and tetrahydrofuran (15 c.c.). The mixture was stirred at 20° for 50 min. and then heated under reflux for 20 min., cooled, and hydrolysed with dilute hydrobromic acid. The crude product isolated from the organic layer was extracted with hot light petroleum (b. p. 40—60°), leaving a residue of *cis*-bromo(mesityl)bis(triethylphosphine)platinum(II), which formed matted needles (0·51 g.), m. p. 184—186° from benzene–light petroleum (b. p. 60—80°) (Found: C, 39·65; H, 6·6. Calc. for $C_{21}H_{41}BrP_2Pt$: C, 40·0; H, 6·55%). The light petroleum (b. p. 40—60°) extract was evaporated to dryness and the residue recrystallized from light petroleum (b. p. 60—80°), to give trans-*bromo*(*mesityl*)*bis*(*triethylphosphine*)*platinum*(II) as needles (0·59 g.), m. p. 185·5—187° (with sublimation) (Found: C, 40·3; H, 6·6%).

Bromo(*mesityl*)-1,2-*bisdiethylphosphinoethanenickel*(II), $[NiBr(mesityl)(Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2)]$. Dibromo-1,2-bisdiethylphosphinoethanenickel(II) (0·80 g.) was added to the Grignard reagent, prepared from magnesium (0·24 g.), tetrahydrofuran (15 c.c.), and 2-bromomesitylene (1·99 g.). Benzene (15 c.c.) was added and the resultant dark brown solution stirred at 15° for 10 min., then cooled to *ca.* $-50°$ and hydrolysed by the slow addition of dilute hydrobromic acid. Ether was added and the product was isolated from the organic layer. *Bromo*(*mesityl*)-1,2-*bisdiethylphosphinoethanenickel*(II) was obtained as orange needles (0·69 g.), m. p. 172—174°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 49·4; H, 7·6. $C_{19}H_{35}BrNiP_2$ requires C, 49·2; H, 7·6%).

trans-*Di*-(4-*biphenylyl*)*bis*(*triethylphosphine*)*platinum*(II), $[Pt(C_6H_4{\cdot}C_6H_5)_2(PEt_3)_2]$. *trans*-Dichlorobis(triethylphosphine)platinum(II) (2·00 g.) was added to the Grignard reagent, prepared from magnesium (0·48 g.), 4-bromobiphenyl (4·66 g.), tetrahydrofuran (20 c.c.), and benzene (25 c.c.). After the mixture had been heated under reflux for $3\frac{1}{4}$ hr. it was cooled and hydrolysed with dilute hydrochloric acid, and the product was isolated from the benzene layer. trans-*Di*-(4-*biphenylyl*)*bis*(*triethylphosphine*)*platinum*(II) was obtained as prisms (1·45 g.), m. p. 209—

215° (decomp.), from light petroleum (b. p. 80—100°) or ethyl methyl ketone (Found: C, 59·0; H, 6·65. $C_{36}H_{48}P_2Pt$ requires C, 58·6; H, 6·55%).

trans-*Chloro*-(4-*biphenylyl*)*bis*(*triethylphosphine*)*platinum*(II). A solution of *trans*-di-(4-biphenylyl)bis(triethylphosphine)platinum(II) (0·60 g.) in benzene (5 c.c.) and ether (10 c.c.) was treated with a 0·425N-solution of dry hydrogen chloride in ether (2·77 c.c.). After 3 hr. at 20° the solution was evaporated to dryness and the residue recrystallized from light petroleum (b. p. 60—80°), giving trans-*chloro*-(4-*biphenylyl*)*bis*(*triethylphosphine*)*platinum*(II) (0·395 g.) as prisms, m. p. 116—118° (Found: C, 46·55; H, 6·4. $C_{24}H_{39}ClP_2Pt$ requires C, 46·5; H, 6·35%).

trans-*Chloro*-(p-*chlorophenyl*)*bis*(*triethylphosphine*)*platinum*(II), [PtCl(*p*-chlorophenyl)(PEt$_3$)$_2$]. *trans*-Di-(*p*-chlorophenyl)bis(triethylphosphine)platinum(II) (1·67 g.) in methylene chloride (18 c.c.) was treated with a 0·935N-solution of dry hydrogen chloride in ether (3·0 c.c., 1 mol.).

TABLE 1. *Dipole moments of some arylplatinum*(II) *and palladium*(II) *complexes in benzene at* 25°

	$10^3\omega$	Δ/ω	$-\Delta v/\omega$	$_{\mathrm{T}}P$ *	$_{\mathrm{E}}P$	$_{\mathrm{O}}P$ *	μ * (D)
trans-[PdCl(*o*-tolyl)(PEt$_3$)$_2$]	4·362	2·597					
	6·229	2·600					
			(0·40)	334	(122)	194	3·1
trans-[PtNO$_3$(*o*-tolyl)(PEt$_3$)$_2$]	5·310	5·153					
	5·076	5·119					
			(0·55)	669	(114)	538	5·15
trans-[PtCl(*o*-tolyl)(PEt$_3$)$_2$]	3·990	1·348					
	7·202	1·335					
			(0·55)	240	(111)	112	2·35
trans-[PtNO$_3$(mesityl)(PEt$_3$)$_2$]	3·611	5·263					
	3·876	5·258					
			(0·55)	716	(123)	574	5·3
trans-[PtCl(mesityl)(PEt$_3$)$_2$]	4·436	1·430					
	5·301	1·434					
			(0·55)	262	(120)	124	2·45
trans-[PtBr(mesityl)(PEt$_3$)$_2$]	2·842	2·015					
	3·608	1·974					
			(0·58)	343	(123)	202	3·15
trans-[Pt(4-biphenylyl)$_2$(PEt$_3$)$_2$]	2·839	0·442					
			(0·45)	214	(186)	0	0
trans-[PtCl(4-biphenylyl)(PEt$_3$)$_2$]	3·582	1·833					
	4·454	1·879					
			(0·53)	330	(142)	167	2·85
trans-[PtCl(*p*-chlorophenyl)(PEt$_3$)$_2$]	4·542	0·482					
	7·466	0·462					
			(0·56)	152	(110)	26	1·1
trans-[Pt(*p*-methoxyphenyl)$_2$(PEt$_3$)$_2$]	4·106	1·058					
	4·864	1·044					
			(0·53)	245	(150)	73	1·9
cis-[Pt(*p*-methoxyphenyl)$_2$(PEt$_3$)$_2$]	5·193	8·503					
	6·433	8·524					
			(0·45)	1169	(150)	997	7·0
trans-[PtCl(*p*-methoxyphenyl)(PEt$_3$)$_2$]	4·037	2·072					
	4·452	2·067					
			(0·55)	326	(113)	196	3·1

* Calc. by using estimated values of densities and refractivities (see Chatt and Shaw [4]). Estimated values are given in parentheses.

After 1½ hr. the resultant solution was evaporated to dryness and the residue recrystallized from light petroleum (b. p. 40—60°), to give trans-*chloro*-(p-*chlorophenyl*)*bis*(*triethylphosphine*)-*platinum*(II) as prisms (1·28 g.), m. p. 110—111·5° (Found: C, 37·5; H, 5·95. $C_{18}H_{34}Cl_2P_2Pt$ requires C, 37·4; H, 5·95%).

cis- *and* trans-*Di*-(p-*methoxyphenyl*)*bis*(*triethylphosphine*)*platinum*(II), [Pt(C$_6$H$_4$OMe)$_2$(PEt$_3$)$_2$]. *trans*-Dichlorobis(triethylphosphine)platinum(II) (2·00 g.) in benzene (30 c.c.) was added to a Grignard reagent, prepared from magnesium (0·48 g.), *p*-bromoanisole (2·63 c.c.), a trace of iodine, and tetrahydrofuran (15 c.c.). The mixture was stirred at 20° for 50 min., then heated under reflux for 40 min., cooled, and hydrolysed with dilute hydrobromic acid. The crude product isolated from the organic layer was recrystallized from benzene–methyl alcohol, to give trans-*di*-(p-*methoxyphenyl*)*bis*(*triethylphosphine*)*platinum*(II) as prisms, m. p. 195—210° (decomp., with sublimation above 180°) (Found: C, 48·0; H, 7·0. $C_{26}H_{44}O_2P_2Pt$ requires C

48·35; H, 6·85%). The mother-liquors from this crystallization were evaporated to dryness and the residue recrystallized from methyl alcohol and then light petroleum (b. p. 80—100°). Thus was obtained cis-*di*-(p-*methoxyphenyl*)*bis*(*triethylphosphine*)*platinum*(II) as prisms (0·72 g.), m. p. 129—132° (Found: C, 48·35; H, 6·85%).

trans-*Chloro*-(p-*methoxyphenyl*)*bis*(*triethylphosphine*)*platinum*(II), $[PtCl(C_6H_4OMe)(PEt_3)_2]$. *trans*-Di-(*p*-methoxyphenyl)bis(triethylphosphine)platinum(II) (0·890 g.) in benzene (10 c.c.) and ether (15 c.c.) was treated with a 1·17N-solution of hydrogen chloride in ether (1·19 c.c.). After 2 hr. the solution was evaporated to dryness and the residue recrystallized from light petroleum (b. p. 60—80°) to give trans-*chloro*-(p-*methoxyphenyl*)*bis*(*triethylphosphine*)*platinum*(II) as needles (0·582 g.), m. p. 131—133·5° (Found: C, 40·05; H, 6·6. $C_{19}H_{37}ClOP_2Pt$ requires C, 39·75; H, 6·5%).

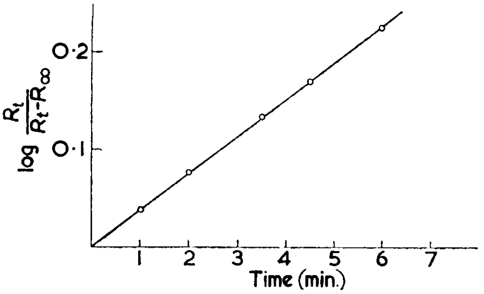


FIG. 1. *Pseudo-first-order rate analysis at 25°:* C_5H_5N, 0·0018M; *trans*-$[PtClMe(PEt_3)_2]$, 0·0002M. (*R_t and R_∞ are the electrical resistances of the solution at time t and equilibrium, respectively.*)

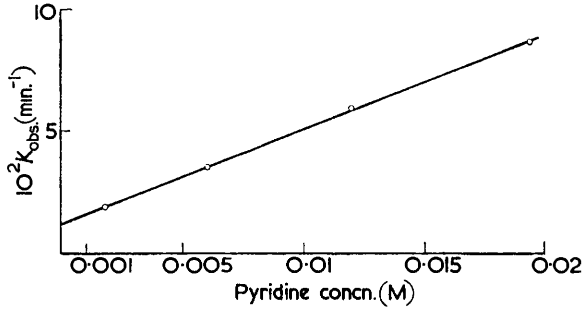


FIG. 2. *Dependence of k_{obs} on the concentration of pyridine in reaction with* 0·0002M-*trans*-$[PtClMe(PEt_3)_2]$ *at* 25°.

Determination of Dipole Moments.—These were determined as described previously;[4] the measurements and estimated values (shown in parentheses) are recorded in Table 1. The margin of error is less than +0·2 D for dipole moments between 5·5 and 2·5 D. For dipole moments <2·5 D the margin of error will be greater than this but is difficult to estimate. The errors in determining small dipole moments are largely due to the uncertainty in the magnitude of the atom polarization which has been assumed to be 15% of the electron polarization in Table 1 but may be higher than this in complex compounds.

TABLE 2. *Comparison of the rates of attainment of equilibrium of similar nickel*(II), *palladium*(II), *and platinum*(II) *complexes at* 25°.

Complex[a]	Range of initial 10^3[py] (M)	k_1 (min.$^{-1}$)
trans-[NiCl(*o*-tolyl)$(PEt_3)_2$]	1·24—6·2	2000[b]
trans-[PdCl(*o*-tolyl)$(PEt_3)_2$]	1·24—6·2	35[b]
trans-[PtCl(*o*-tolyl)$(PEt_3)_2$]	0·9—6·2	4×10^{-4}
trans-[NiCl(mesityl)$(PEt_3)_2$]	1·24—6·2	1·2
trans-[PtCl(mesityl)$(PEt_3)_2$]	0·9—6·2	7×10^{-5}
[NiBr(mesityl)$(PEt_2.CH_2{\cdot}CH_2{\cdot}PEt_2)$]	1·24—6·2	20[b]
cis-[PtBr(mesityl)$(PEt_3)_2$]	0·9—6·2	3×10^{-4}

[a] The initial concentration of complex was 0·0004M. [b] Rate constants estimated from data at temperatures ranging from −80° to 0°.

Determination of Reaction Rates and Equilibrium Constants.—The reactions with pyridine were followed by measuring changes in the electrical conductivity of an ethanol solution of the reactants.[1a] The concentration of the complex was in the range 0·0002—0·002M and the pyridine concentration was varied between 0·001M and 0·02M. The conductance change corresponded to the reversible reaction:

$$[PtClR(PEt_3)_2] + py \rightleftharpoons [PtR(py)(PEt_3)_2]^+ + Cl^-$$

in which the equilibrium favours the left-hand side. The rate of attainment of equilibrium in all cases was of pseudo-first order, as shown in Fig. 1 for *trans*-$[PtCl(Me)(PEt_3)_2]$. The variation of the pseudo-first-order rate constants (k_{obs}) with initial pyridine concentration was consistent

TABLE 3. trans-*Effect: rates of attainment of equilibrium between pyridine and complexes of the types* A *and* B *in ethanol at* 25°.

trans-Ligand X	Range of initial 10^3[py] (M)	k_1 (min.$^{-1}$)	k_2 (mole^{-1} l. min.$^{-1}$)
(A) *cis*-$[PtCl_2X_2]$ [a]			
PMe_3	0·9—6·2	5 [b]	—
PEt_3	0·9—6·2	1 [b]	2·3 × 10^2 [b]
PPr_3	0·9—6·2	5 × 10^{-1} [b]	1 × 10^2 [b]
(B) *trans*-$[PtClX(PEt_3)_2]$ [a]			
H	1·24—6·2	1·1 [b]	2·5 × 10^2 [b]
Me [c]	1·24—37·2	1 × 10^{-2}	4
Ph	0·9—6·2	2 × 10^{-3}	9·5 × 10^{-1}
p-Chlorophenyl	0·9—6·2	2 × 10^{-3}	9 × 10^{-1}
p-Methoxyphenyl	0·9—6·2	1·7 × 10^{-3}	7·8 × 10^{-1}
4-Biphenylyl	0·9—6·2	1 × 10^{-3}	5·8 × 10^{-1}
o-Tolyl	0·9—6·2	4 × 10^{-4}	1 × 10^{-1}
Mesityl	0·9—6·2	7 × 10^{-5}	2·2 × 10^{-2}
Cl	0·9—6·2	6 × 10^{-5}	2·4 × 10^{-2}

[a] Initial concn. of complex, 0·0004M. [b] Rate at 0°; reaction is too fast to measure at 25°. [c] This complex was also examined for 0·0002—0·001M-solutions and the pyridine concentration varied from 0·062 to 0·124M.

TABLE 4. cis-*Effect: rates of attainment of equilibrium in the reaction of pyridine with complexes of the types* A, B, *and* C *in ethanol at* 0°.

cis-Ligand X	Range of initial 10^3[py] (M)	k_1 (min.$^{-1}$)
(A) *cis*-$[PtClX(PEt_3)_2]$ [a]		
Me	0·9—6·2	3·6
Ph	0·9—6·2	2·3
p-Tolyl	0·9—6·2	3
o-Tolyl [b]	0·9—18·6	5·2 × 10^{-3}
Mesityl [c]	0·9—6·2	2·5 × 10^{-5}
Cl	0·9—6·2	1

cis-Ligand X	Range of initial 10^3[py] (M)	k_1 (min.$^{-1}$)
(B) *trans*-$[PtHClX_2]$ [a]		
PEt_3	1·24—6·2	1·1
PEt_2Ph	1·24—6·2	0·8
$PEtPh_2$	1·24—6·2	2
PPh_3	1·24—6·2	*d*
(C) *trans*-$[PtClMeX_2]$ [a]		
PMe_3	0·9—6·2	1·5 × 10^{-1}
PEt_3 [b]	1·24—37·2	1 × 10^{-2}

[a] The initial concn. of complex was 0·0004M. [b] This complex was also examined in 0·0002—0·001M-solutions with pyridine concns. of 0·062—0·124M. [c] This complex was the bromide, *cis*-$[PtBr(mesityl)(PEt_3)_2]$. [d] Reaction is too fast to measure at 0°.

TABLE 5. *Comparison of rate constants and concentration equilibrium constants for the reaction with pyridine of some platinum*(II) *complexes in ethanol at* 25°.

Complexes	k_1 (min.$^{-1}$)	$K_{eq.}$
trans-$[PtHCl(PEt_3)_2]$	1·1 (at 0°)	0·03
trans-$[PtClMe(PEt_3)_2]$	1 × 10^{-2}	0·15
trans-$[PtClPh(PEt_3)_2]$	2 × 10^{-3}	0·02
cis-$[PtClMe(PEt_3)_2]$	3·6 (at 0°)	0·3

Complexes	k_1 (min.$^{-1}$)	$K_{eq.}$
cis-$[PtClPh(PEt_3)_2]$	2·3	0·15
cis-$[PtCl(o\text{-tolyl})(PEt_3)_2]$	3·8 × 10^{-2}	0·10
cis-$[PtBr(mesityl)(PEt_3)_2]$	3 × 10^{-4}	0·01

with the expression $k_{obs} = k_1 + k_2[py]$, since a plot of k_{obs} against pyridine concentration for *trans*-$[PtClMe(PEt_3)_2]$ gives a straight line with a non-zero intercept (Fig. 2). Similar plots were obtained for all the complexes studied and the rate constants k_1 and k_2 extracted are reported in Tables 2—4.

Equilibrium concentrations of products were calculated from conductance measurements and the concentration equilibrium constants resulting are reported in Table 5. Conductance was directly related to concentration only in the case of the isolable compound

[Pt(*o*-tolyl)(py)$(PEt_3)_2$]NO_3 which gave a molar conductance of 34 cm.^{2} mole^{-1} ohm^{-1} in the concentration range used in the kinetic studies. This value of the molar conductance was used as equal to that of [PtR(py)$(PEt_3)_2$]Cl in calculating the equilibrium constants. The constancy of these equilibrium constants over a range of pyridine concentrations was taken to justify the proportionality between conductance and concentration for the non-isolable chloride salts.

DISCUSSION

The kinetic data in Table 2 afford a unique quantitative comparison of rates of reaction of analogous nickel(II), palladium(II), and platinum(II) compounds. The ratio of rates for *trans*-[MCl(*o*-tolyl)$(PEt_3)_2$] compounds is approximately 5,000,000 : 100,000 : 1 where M is Ni, Pd, and Pt respectively. The large difference in lability between platinum(II) and nickel(II) is consistent with a mechanism in which groups above and below the plane move in to displace the halide ion,[8] since nickel(II) is known to expand its co-ordination number more easily than platinum(II). It is also consistent that *trans*-[NiCl(mesityl)$(PEt_3)_2$] reacts only about 20,000 times faster than *trans*-[PtCl(mesityl)$(PEt_3)_2$]. Thus by blocking the positions above and below the plane of the complex with a mesityl group,[5] nickel(II) is made much less labile than platinum(II), and in fact the rate differences then resemble those between octahedral cobalt(III) and iridium(III) complexes. For example, the relative rates of acid-hydrolysis of $[M(NH_3)_5Br]^{2+}$ complexes are about 4000 : 1 when M = Co and Ir respectively.[9]

Table 3 summarizes data showing how k_1 and k_2 depend on the ligand in *trans*-position to the chlorine atom. By using either k_1 or k_2 as a measure, the *trans*-labilizing ability (*trans*-effect) of the ligands in this particular equilibration reaction is found to decrease in the order: $PMe_3 > PEt_3 \approx H > PPr_3 > Me >$ phenyl $\approx$ *p*-methoxyphenyl $\approx$ *p*-chlorophenyl $>$ biphenyl $>$ *o*-tolyl $>$ mesityl $\approx$ Cl.

There are two main hypotheses on the nature of the *trans*-effect.

Grinberg and others of the Russian school consider it to be mainly electrostatic in origin,[10] and to depend on the polarizability of the ligand. Thus the more polarizable the ligand the greater the *trans*-effect.

The second hypothesis suggests that large *trans*-effects are produced by ligands capable of dative π-bonding to the metal.[11,12] The large *trans*-effects of the trialkylphosphines are well known and have been attributed to this π-bonding which enhances nucleophilic attack and/or stabilizes a five-co-ordinated transition state.

The relative rates of reaction of complexes with *trans*-groups H, Me, phenyl, and Cl are approximately 100,000 : 200 : 30 : 1. Since π-bonding is not expected to be very important in binding these groups to the metal, this rapid decrease in rate must be mainly electrostatic in orgin. This is supported by the rapid decrease in dipole moment along the series of compounds *trans*-[PtClR$(PEt_3)_2$] whose moment are R = H (4·2 D), Me (3·4 D), Ph (2·6 D), and Cl (0 D).

It is of interest that hydrogen (or hydride ion) has such a high *trans*-effect. Indeed it causes more rapid substitution in the position *trans* to itself than any other anionic ligand we have studied. The hydride ion, because of its substantial polarizability, may induce a strong polarization of the positive platinous ion which causes the repulsion of the *trans*-ligand according to the mechanism suggested by Grinberg.[10] We would expect that the large electrostatic effect of the hydride ion would be apparent as a large ligand field strength. Recent work[13] has confirmed this: both hydride ion and methide ion cause large ligand field splittings of the *d*-energy levels in ruthenium(II) complexes. The

---

[8] Basolo and Pearson, " Mechanism of Inorganic Reactions," Wiley and Sons, New York, 1958, pp. 186—190.

[9] Ref. 8, p. 122.

[10] Grinberg, *Ann. Inst. Platine U.S.S.R.*, 1932, **10**, 58; see ref. 8, p. 177.

[11] Chatt, Duncanson, and Venanzi, *Chem. and Ind.*, 1955, 749; *J.*, 1955, 4456.

[12] Orgel, *J. Inorg. Nuclear Chem.*, 1956, **2**, 137.

[13] Chatt and Hayter, *J.*, 1961, 772.

development of negative charge on the side of the platinous ion *trans* to the hydride ion should also lead to long bonds of considerable ionic character between the metal and the *trans*-ligand. This has been observed in *trans*-$[PtHBr(PEt_3)_2]$ where the distance Pt–Br is 2·56 Å, to be compared with the radius sum of 2·43 Å.[14]

Data in Table 4 show that the reactivity of *cis*-$[PtClR(PEt_3)_2]$ varies only slightly with changes in R. Thus for R = Cl, Ph, and Me the relative rates are 1, 2·3, and 3·6, increasing in the same sequence but very much more slowly than in the *trans*-series of complexes. This shows clearly the directional nature of this activating effect for groups such as H, Me, Ph, and Cl which must act almost entirely by induction.

It is interesting that in *trans*-$[PtCl_2(C_2H_4)(NHMe_2)]$ the dimethylamine is very readily replaced by other groups owing to the high *trans*-effect of the ethylene, yet in contrast to the bromohydride mentioned above the Pt–N bond is of normal length {2·02 Å,[15] very similar to the distance 2·06 Å in Magnus's green salt $[Pt(NH_3)_4][PtCl_4]$}.[16] In this case we consider the rapid substitution to be mainly an effect of dative π-bonding by the ethylene.[11,12]

We can thus distinguish two electronic mechanisms of the *trans*-effect; (1) polarization of the metal ion by electrostatic forces resulting from electron release by the ligand *via* the σ-bond; (2) polarization of the metal ion by dative π-bonding to a suitable ligand, *i.e.*, electron release by the metal *via* the π-bond. Hydride ion and ethylene are examples of ligands with high *trans*-effects promoted mainly by mechanisms (1) and (2) respectively. There is also the possibility that both effects may operate with some ligands (*e.g.*, iodide ion) and in combination give a strong *trans*-effect.

It is interesting that *para*-substituents, X in *trans*-$[PtCl(p\text{-}C_6H_4X)(PEt_3)_2]$ (X = H, Ph, OMe, Cl), hardly affect the rate of displacement of chloride ion. This supports the above observation that hydrogen and hydrocarbon radicals must exert their *trans*-effects mainly through induction. The inductive effects of the groups X should be very weak when they reach the platinum atom and so have little effect on the rate. On the other hand, if dative π-bonding were essential to a high *trans*-effect the *para*-substituent, X, would affect the rates considerably, because dative π-bonding would be very sensitive to the widely different and strongly transmitted mesomeric effects of the groups X.

In contrast, substituents in the *ortho*-position of the phenyl group do markedly affect the rate of reaction. Molecular models indicate that this is largely due to shielding of the central metal. For example, with the mesityl compound the aromatic ring is forced out of the plane of the complex so that two methyl groups occupy positions above and below the plane.[5] This will hinder the approach of a nucleophilic reagent and thus retard the rate of displacement. Since the results show that both k_1 and k_2 are affected, this supports the view that k_1 is a solvent displacement process and not just a bond-cleavage dissociation path. It is of interest that the steric effect is greater for *cis*- than for *trans*-isomers. Thus, for $[PtClR(PEt_3)_2]$ where R = phenyl, *o*-tolyl, and mesityl, the relative rates of reaction for the *cis*-isomers are 100,000 : 200 : 1 whilst for the *trans*-isomers they are 30 : 6 : 1 respectively.* Scale molecular models suggest that the formation of a square-pyramidal intermediate by the approach of nucleophilic groups along the *z*-axis of either isomer is extremely difficult, if not impossible. Further, the same steric effect would be expected for both isomers. However, a nucleophilic approach at a slight angle in the direction of the chloro-group leading to a trigonal bipyramidal intermediate is possible in both cases and the steric hindrance would be much larger for the *cis*- than for the *trans*-isomer. The results therefore suggest a displacement process *via* a trigonal bipyramidal intermediate for these hindered complexes.

---

* When R was mesityl the *cis*-compound was a bromide, but kinetically there is little difference between the reactivities of chlorides and bromides of this type.

[14] Owston, Partridge, and J. M. Rowe, *Acta Cryst.*, 1960, **13**, 246.

[15] Alderman, Owston, and J. M. Rowe, *Acta Cryst.*, 1960, **13**, 149.

[16] Atoji, Richardson, and Rundle, *J. Amer. Chem. Soc.*, 1957, **79**, 3017.

The decrease in *trans*-effect of trialkylphosphines with increasing chain length of the alkyl groups is probably due to increased steric hindrance, because similarly a slightly larger effect is found in the compounds where both trialkylphosphine ligands are in the *cis*-position to the chloride ion being replaced (compare the last two compounds in Table 3 with the last two in Table 4).

The replacement of a halide by pyridine in these complexes is reversible in ethyl alcohol solution. It was not possible to isolate complexes of the type $[PtR(py)(PEt_3)_2]Cl$ from the reaction mixtures since the equilibrium favours the non-ionic compound. With nitrato-complexes, however, the reaction with pyridine goes to completion and salts $[PtR(py)(PEt_3)_2]NO_3$ can be isolated. This can be converted into the non-ionic chloro-complex by adding chloride ion.

It can be seen from Table 5 that the equilibrium constants for the reaction of pyridine with several platinum complexes vary very much less than the rate constants.

This investigation was partly supported by a grant from the U.S. Atomic Energy Commission under Contract AT (11-1)-89-project No. 2. We thank Miss I. Bates for assistance in measuring the dipole moments, and A. E. Field and M. L. Searle for other experimental assistance. One of us (H. B. G.) also thanks the National Science Foundation for a fellowship.

NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS, U.S.A.
AKERS RESEARCH LABORATORIES, IMPERIAL CHEMICAL INDUSTRIES LIMITED,
THE FRYTHE, WELWYN, HERTS.

[*Received, September 20th*, 1960.]