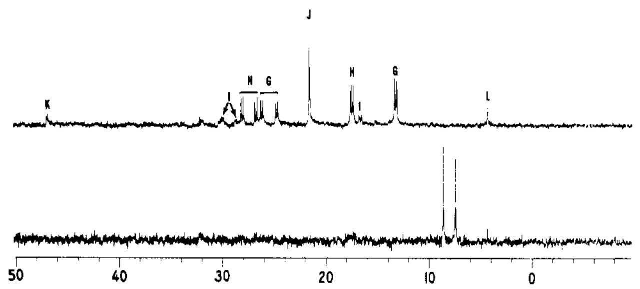
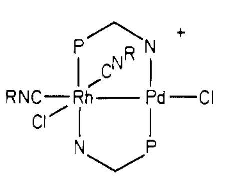


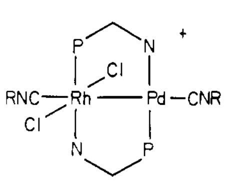
Figure 5. $^{31}P\{^1H\}$ NMR spectrum of $[RhPd(\mu\text{-}Ph_2Ppy)_2(CNCH_3)_2Cl_2][BPh_4]$ (*HH*(Rh)) at the bottom and the products obtained by heating this compound in boiling acetonitrile solution for 12 h at the top. After the mixture was heated, the solvent was removed by vacuum evaporation and the sample dissolved in $CDCl_3$ to record the spectrum.

$[Pt(Ph_2Ppy)_2Cl][Rh(CO)_2Cl_2]$, has been isolated and characterized by an X-ray crystal structure.[5]

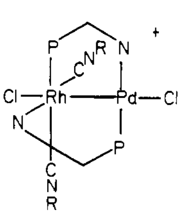
Thermolysis of $[RhPd(\mu\text{-}Ph_2Ppy)_2(CNCH_3)_2Cl_2]^+$ (*HH*(Rh)). The thermal interconversion of the *HH*(Rh), **7**, and *HT*, **6**, isomers of $[RhPd(\mu\text{-}Ph_2Ppy)_2(CNCH_3)_2Cl_2]^+$ has been examined. The *HT* isomer **6** is thermally inert. Heating complex **6** for 24 h in boiling acetonitrile results is no change in the ^{31}P NMR spectrum of the sample. However the *HH*(Rh), **7**, isomer is thermally reactive. The products produced by heating a sample of $[RhPd(\mu\text{-}Ph_2Ppy)_2(CNCH_3)_2Cl_2][BPh_4]$ (*HH*(Rh)) in boiling acetonitrile for 12 h can be partially identified from the ^{31}P NMR spectrum shown in Figure 5. During the reaction, the starting complex is completely consumed. The *HT* isomer **6** (peaks labeled H) is formed in appreciable yield as are several other products including $Pd_2(\mu\text{-}Ph_2Ppy)_2Cl_2$[3] (peak labeled L). The peaks labeled G and I appear to be due to other *HT* isomers since they contain the same basic spectral pattern as that of **5**. The spectral parameters for G are δ_1 12.98, δ_2 25.23, $^1J(Rh\text{-}P) = 118.4$ Hz, and $^3J(P\text{-}P) = 16.5$ Hz, and the corresponding values for I are δ_1 16.38, δ_2 29.1, $^1J(Rh\text{-}P) = 105.9$ Hz, and $^3J(P\text{-}P) = 17.6$ Hz. There are five structures, **10**–**14**, that are compatible with the available data for the species responsible for the resonances G and I. Less is known about the singlets labeled J and K. These are not associated with any known palladium complexes of 2-(diphenylphosphino)pyridine. The possibility exists that one is a *HH*(Pd) isomer, but until the species responsible for this spectrum are separated, identification remains incomplete.



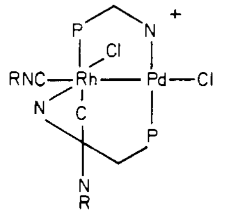
10



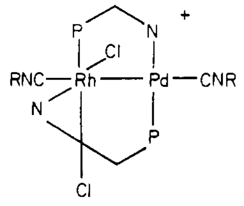
11



12



13



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Acknowledgment. We thank the National Science Foundation (Grant No. CHE 7924575) for support. J.P.F. was an Earl C. Anthony and University of California Regents Fellow.

Registry No. **1**, 75361-88-5; **5a**, 84695-82-9; **5b**, 84695-81-8; **6a**, 84695-86-3; **6b**, 84773-44-4; **7**, 84695-88-5; **8**, 84695-84-1; *trans*-$Pd(Ph_2Ppy)_2Cl_2$, 38255-46-8; *cis*-$Pd(Ph_2Ppy)_2Cl_2$, 84773-43-3; $[(CH_3N)_4Rh][BPh_4]$, 34742-53-5; $(PhCN)_2PdCl_2$, 14220-64-5; (1,5-COD)$PdCl_2$, 12107-56-1; *trans*-$Rh(CO)(Cl)(Ph_2Ppy)_2$, 75361-60-3; $Rh_2(\mu\text{-}Cl)_2(CO)_4$, 14523-22-9; $Pd(Ph_3P)_2Cl_2$, 13965-03-2; $Rh(Ph_3P)_2(CO)Cl$, 13938-94-8; $Rh(Ph_2Ppy)_2(CO)Br$, 84695-89-6; $[(CH_3NC)_2Rh(Ph_3P)_2][PF_6]$, 61160-81-4; $[(CH_3NC)_2Rh(Ph_3P)_2][BPh_4]$, 84695-90-9; $RhPd(\mu\text{-}Ph_2Ppy)_2(CO)Br_3$, 84695-91-0; Pd, 7440-05-3; Rh, 7440-16-6.

Supplementary Material Available: Table of structure factors for $RhPd(\mu\text{-}Ph_2Ppy)_2(CO)Cl_3$ (12 pages). Ordering information is given on any current masthead page.

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Kinetics of the Reversible Displacement of Chloride by Amines under the Trans Effect of Phosphines, Phosphites, and Arsines

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The rate and equilibrium constants are reported for the reaction $[Pt(L)Cl_3]^- + am \rightarrow$ *trans*-$[Pt(L)(am)Cl_2] + Cl^-$ (L = PMe_3, PEt_3, P-*n*-Bu_3, PPh_3, $P(OMe)_3$, $AsEt_3$; am is one of a series of amines and heterocyclic bases covering a wide range of basicity) in methanol at 30.0 °C, $\mu = 0.50$. The behavior patterns are discussed and compared with those of complexes where L is a sulfur donor ligand. The lability is strongly dependent upon the nature of the donor atom (P, As, or S) but far less sensitive to the nature of the substituents.

Introduction

As part of our study of the trans effects of ligands with second- and third-row donor atoms we have examined the kinetics and equilibria of the reactions associated with the reversible processes

$$[Pt(L)Cl_3]^- + am \rightarrow trans\text{-}[Pt(L)(am)Cl_2] + Cl^-$$

where L = Me_2SO,[1] Me_2S,[2] and Et_2S[3] and am is one of a series of amines and heterocyclic bases covering a wide range of basicity. Kinetically, these donors exert a moderately strong trans effect when compared to that of chloride and the nitrogen donors even though this is not accompanied by a similarly

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0020-1669/83/1322-1235$01.50/0

marked trans influence.[4] In order to see whether this simply reflects the much greater sensitivity of the reactivity probe (in the trans effect) when compared to the bond length or bond vibrational frequency probe (in the trans influence), we have extended our studies to L = phosphine, phosphite, and arsine, where very marked trans influences have been reported[5-7] and where it has long been known that the trans effect is large.[8] Part of our interest also lies in the extent to which it is possible to separate the contribution of the π-acceptor ability of the trans ligand, which should appear mainly as a stabilization of the five-coordinate intermediate and hence only be seen as a kinetic effect, from that of the σ-donor capacity, which leads, in part, to a destabilization of the ground state and should be observed as a trans influence as well as a trans effect. For this reason it is useful to compare a phosphine with a triphosphite. The effects of the organic substituents on the donor are also considered.

Experimental Section

Reagents. $Et_4N[Pt(PEt_3)Cl_3]$ was prepared in 67% yield from $Pt_2(PEt_3)_2Cl_4$ by the method of Bushnell et al.[6]

$Et_4N[Pt(P\text{-}n\text{-}Bu_3)Cl_3]$. $Et_4NCl{\cdot}H_2O$ (0.82 g, 4.5 mmol) was added to a solution of $Pt_2Cl_4(P\text{-}n\text{-}Bu_3)_2$ (2.04 g, 2.2 mmol; prepared from *cis*-$[Pt(P\text{-}n\text{-}Bu_3)_2Cl_2]$ by the method of Chatt and Venanzi[9]) in dichloromethane, and the solution was stirred overnight at room temperature. The crude product was precipitated by adding diethyl ether, filtered off, and recrystallized from a dichloromethane–diethyl ether mixture; yield 1.6 g.

$Et_4N[Pt(PPh_3)Cl_3]$. The starting material, $Pt_2Cl_4(PPh_3)_2$ (prepared from *cis*-$[Pt(PPh_3)_2Cl_2]$ by the method of Goodfellow and Venanzi[10]), was not, as expected, extractable by dichloromethane even though the elemental analyses were consistent with its formulation. A suspension of the orange solid (1.50 g, 1.4 mmol) in a solution of $Et_4NCl{\cdot}H_2O$ (0.56 g, 2.8 mmol) in dichloromethane (75 cm^3) was stirred overnight, during which time the solid dissolved almost completely to give a yellow solution. The reaction mixture was filtered and evaporated to dryness under reduced pressure, and the yellow solid obtained was recrystallized from CH_2Cl_2–Et_2O; yield 1.6 g.

$n\text{-}Bu_4N[Pt(P(OMe)_3)Cl_3]$ was prepared as an oil by the method of Crocker, Goggin, and Goodfellow[11] but could not be induced to crystallize. The carbon analysis is somewhat low, but the 60-MHz ^{1}H NMR spectrum agreed well with the literature values ($\tau_{Me} = 6.17$, lit.[11] $\tau_{Me} = 6.19$; $^3J(PH)/Hz = +12$, lit.[11] $J(PH)/Hz = +12.4$).

$Pt_2(PMe_3)_2Cl_4$. *cis*-$[Pt(PMe_3)_2Cl_2]$, prepared by the method of Evans et al.,[12] was converted to the required chloro-bridged dimer by the method of Goodfellow and Venanzi.[10] The crude yellow product was extracted with hot dichloromethane and recrystallized from the same solvent; yield (based on $Pt(PMe_3)_2Cl_2$) 30%.

$Pt_2(AsEt_3)_2Cl_4$. $Pt(AsEt_3)_2Cl_2$ was prepared by the method of Jensen[13] and converted to the chloro-bridged dimer by the method of Goodfellow and Venanzi.[10] The product was extracted with dichloromethane and recrystallized from the same solvent; yield (based on $Pt(AsEt_3)_2Cl_2$) 75%.

***trans*-$[Pt(PMe_3)(mor)Cl_2]$.** $Pt_2(PMe_3)_2Cl_4$ (0.094 g, 0.14 mmol) was dissolved in a 0.6 M solution of LiCl in methanol (1 cm^3). Morpholine (mor; 24 μL, 0.28 mmol) was added dropwise from a microsyringe to the stirred solution. The product precipitated immediately as a yellow solid, which was filtered off, washed with distilled water, and dried in vacuo; yield 0.040 g.

***trans*-$[Pt(PEt_3)(py)Cl_2]$.** Pyridine (py; 21 μL, 0.26 mmol) was added dropwise from a microsyringe to a stirred solution of $Pt_2(PEt_3)_2Cl_4$ (0.10 g, 0.13 mmol) in dichloromethane (15 cm^3). The yellow solution was filtered and the solvent removed in a rotary evaporator. The crude product was recrystallized from petroleum ether (bp 60–80 °C); yield 0.08 g.

***trans*-$[Pt(P\text{-}n\text{-}Bu_3)(c\text{-}HxNH_2)Cl_2]$** (35% yield) and ***trans*-$[Pt(PEt_3)(n\text{-}BuNH_2)Cl_2]$** (40% yield) were prepared in a similar way from the appropriate dimers.

***trans*-$[Pt(PPh_3)(c\text{-}HxNH_2)Cl_2]$.** Cyclohexylamine (c-$HxNH_2$; 14.9 μL, 0.124 mmol) was added dropwise to a solution of $Et_4N[Pt(PPh_3)Cl_3]$ (0.086 g, 0.124 mmol) in methanol (100 cm^3), the volume of the solution was reduced in a rotary evaporator, and the resulting solution was stored at −20 °C. After some time yellow crystals were deposited, and these were filtered off, washed with water, and dried in vacuo; yield 0.050 g.

***trans*-$[Pt(P(OMe)_3)(4\text{-}Mepy)Cl_2]$** was prepared in 10% yield by a similar method.

***trans*-$[Pt(AsEt_3)(pip)Cl_2]$.** Piperidine (pip; 20.8 μL, 0.210 mmol) was added drop by drop to a stirred solution of $Pt_2(AsEt_3)_2Cl_4$ (0.0898 g, 0.105 mmol) in dichloromethane (2 cm^3). Pentane was added to the solution, which was then placed in the freezer at −20 °C. The yellow solid that slowly precipitated was filtered off, washed with a little pentane, and dried in vacuo; yield 0.031 g.

***trans*-$[Pt(AsEt_3)(c\text{-}HxNH_2)Cl_2]$** was prepared in a similar way in 38% yield.

Amines were purchased from Aldrich Chemical Co. 4-Cyanopyridine and 3,5-dichloropyridine were recrystallized from diethyl ether. The liquid amines were refluxed over NaOH pellets and distilled. Stock solutions of the amines in methanol were made up by weight, and solutions of the more basic amines were titrated with standard hydrochloric acid. The concentrations of the solutions of the weaker amines could not conveniently be checked in this way, but the agreement between the two methods, where applied, indicated that the weight standardization method was satisfactory.

AR methanol was purchased from James Burrough Ltd. and used without further treatment.

"Anhydrous" lithium chloride (BDH) was extracted from a Soxhlet thimble with boiling methanol, and the solution was evaporated almost to dryness in a rotary evaporator. The wet substance was dried in an oven at 130 °C, and the white anhydrous salt, stored over P_2O_5, was found to be less hygroscopic than the untreated commercial material. Solutions in methanol were made up by weight and standardized by titration with silver nitrate.

"Dried" lithium perchlorate (BDH) has the approximate composition $LiClO_4{\cdot}H_2O$. The exact composition was determined by dissolving a known mass in water, passing the solution down an anion-exchange column in the hydroxide form, and titrating the effluent with standard acid. The material, stored over P_2O_5, maintained this composition. Methanolic solutions were made up by weight. All other reagents were AR where possible.

Kinetics. Reactions with half-lives greater than 20 s were followed spectrophotometrically with use of a Pye-Unicam SP 800 or SP 1750 spectrophotometer. In the studies of amine entry, methanolic solutions containing all reagents except the complex were placed in the sample and reference cells of the spectrophotometer and, when thermal equilibrium was reached, the reactions were initiated by adding 0.10 cm^3 of a stock solution of the complex in 0.50 M LiCl to the sample cell. Reactions with $t_{1/2} > 5$ m were followed by repetitive scanning of the spectra from 450 nm down to the "cutoff" wavelength with use of an SP 800 machine. Reactions with shorter half-lives were monitored at a suitable fixed wavelength. The reverse reaction was followed in a similar way unless the complex was insufficiently soluble in methanol. In these cases all reagents including the complex but excluding the acid were brought to thermal equilibrium and the reaction was initiated by adding a small volume of the acid. The cell blocks were maintained at a constant temperature (30.0 ± 0.1 °C) by circulating water from an external thermostat, and the temperature was monitored by a thermocouple inserted in the cell block.

Reactions with half-lives shorter than 20 s were studied with use of Durrum D110 stopped-flow spectrophotometer and its ancillary equipment as described elsewhere.[14] The reactions were initiated

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Table I. Analytical and Spectroscopic Data for the Complexes

compd[e]	empirical formula	microanal.[a] % C	microanal.[a] % H	microanal.[a] % N	electronic spectrum[b] λ_{max}/nm	electronic spectrum[b] λ_{min}/nm	IR spectrum ν_{Pt-Cl}/cm^{-1}
$[NEt_4][Pt(PEt_3)Cl_3]$	$C_{14}H_{35}Cl_3NPPt$	30.3 (30.6)	6.4 (6.4)	2.5 (2.5)	279 (700) 321 (460)	265 (510) 303 (313)	328 (s) 271 (s)
$[NEt_4][Pt(P\text{-}n\text{-}Bu_3)Cl_3]$	$C_{20}H_{47}Cl_3NPPt$	38.0 (37.9)	7.6 (7.5)	2.2 (2.2)	280 (721) 322 (478)	266 (486) 304 (327)	330 (s) 272 (s)
$[NEt_4][Pt(PPh_3)Cl_3]$	$C_{26}H_{35}Cl_3NPPt$	44.8 (45.0)	5.2 (5.1)	1.8 (2.0)	331 (522) 372 (231)	317 (451)	333 (s) 279 (s)
$[N\text{-}n\text{-}Bu_4][Pt(P(OMe)_3)Cl_3]$	$C_{19}H_{45}Cl_3NO_3PPt$	33.1 (34.2)	6.6 (6.8)	2.0 (2.1)	309 (615)	291 (448)	
$Pt_2(PMe_3)_2Cl_4$	$C_6H_{18}Cl_4P_2Pt_2$	10.5 (10.5)	2.7 (2.6)		278 (718)[c] 318 (526)	264 (521) 300 (366)	346 (s) 329 (m) 260 (s)
$Pt_2(AsEt_3)_2Cl_4$	$C_{12}H_{30}Cl_4As_2Pt_2$	17.0 (16.8)	3.7 (3.5)		291 (669)[d] 340 (455)	276 (466) 318 (244)	346 (s) 321 (s) 261 (s)
trans-$[Pt(PMe_3)(mor)Cl_2]$	$C_7H_{18}Cl_2NOPPt$	19.6 (19.6)	4.1 (4.2)	3.2 (3.3)			
trans-$[Pt(PEt_3)(py)Cl_2]$	$C_{11}H_{20}Cl_2NPPt$	28.6 (28.5)	4.4 (4.3)	3.0 (3.0)			
trans-$[Pt(PEt_3)(n\text{-}BuNH_2)Cl_2]$	$C_{10}H_{26}Cl_2NPPt$	26.6 (26.3)	5.7 (5.7)	2.9 (3.1)			
trans-$[Pt(P\text{-}n\text{-}Bu_3)(c\text{-}HxNH_2)Cl_2]$	$C_{18}H_{40}Cl_2NPPt$	38.2 (38.1)	6.9 (7.1)	2.4 (2.5)			
trans-$[Pt(PPh_3)(c\text{-}HxNH_2)Cl_2]$	$C_{24}H_{28}Cl_2NPPt$	45.6 (45.9)	4.8 (4.5)	2.5 (2.2)			340 (s)
trans-$[Pt(P(OMe)_3)(4\text{-}Mepy)Cl_2]$	$C_9H_{16}Cl_2NO_3PPt$	22.2 (22.4)	2.9 (3.3)	2.5 (2.9)			
trans-$[Pt(AsEt_3)(pip)Cl_2]$	$C_{11}H_{26}AsCl_2NPt$	26.1 (25.7)	5.3 (5.1)	2.6 (2.7)			
trans-$[Pt(AsEt_3)(c\text{-}HxNH_2)Cl_2]$	$C_{12}H_{28}AsCl_2NPt$	27.8 (27.3)	5.5 (5.4)	2.6 (2.7)			

[a] Calculated values in parentheses. [b] Molar extinction coefficients (M^{-1} cm^{-1}) in parentheses. Spectra were measured in methanol in the presence of 1.0 M LiCl. [c] Spectrum of $[Pt(PMe_3)Cl_3]^-$. [d] Spectrum of $[Pt(AsEt_3)Cl_3]^-$. [e] Abbreviations (for this and all subsequent tables): mor, morpholine; py, pyridine; c=Hx, cyclohexyl; pip, piperidine.

Table II. Solvolytic Rate Constants, Chloride Anation Rate Constants, and Equilibrium Constants for the Reactions $[Pt(L)Cl_3]^- + MeOH \underset{k_{Cl}}{\overset{k_1^f}{\rightleftharpoons}}$ *trans*-$[Pt(L)(MeOH)Cl_2] + Cl^-$ [a]

L	k_1^f/s^{-1} [b]	k_{Cl}/M^{-1} s^{-1}	$k_1^f/k_{Cl} = K_s$/M	K_s/M [c]	% solvolysis in 0.48 M LiCl
PEt_3	6.6 ± 0.7	111 ± 4	0.059 ± 0.007	0.080	11
$P\text{-}n\text{-}Bu_3$	5.2 ± 0.6	93 ± 3	0.056 ± 0.009	0.083	10
PPh_3	3.1 ± 0.5	236 ± 3	0.013 ± 0.002	0.023	3
$P(OMe)_3$	10.3 ± 3.0	583 ± 18	0.018 ± 0.005	0.026	4
$AsEt_3$	0.63 ± 0.48	70 ± 3	0.009 ± 0.007	0.007	2
SMe_2 [d]	0.0015 ± 0.0003	1.07 ± 0.05	0.0014 ± 0.003		0.3
$OSMe_2$	0.0082 ± 0.0003	15.6 ± 1.3	0.00053 ± 0.00004		0.1
C_2H_4				0.000097	0.02

[a] In methanol at 30.0 °C; $[H^+] = 0.10$ M, [complex] $= 6.0 \times 10^{-4}$ M, and $\mu = 0.50$ ($LiClO_4$). [b] Determined from the reaction between $[Pt(L)Cl_3]^-$ and OH^- in methanol. [c] From a spectrophotometric analysis of the solution at equilibrium. Constant ionic strength was not maintained. [d] Data from ref 2.

by mixing equal volumes of solutions containing the platinum complex and the amine, respectively, in which the chloride ion concentration and the ionic strength were the same.

Results

(A) The Solvolytic Equilibrium. The spectrum of a solution of $Et_4N[Pt(PEt_3)Cl_3]$ in methanol (5.5×10^{-4} M) depends upon the amount of extra chloride that is present in solution. The changes are consistent with a rapidly established solvolytic equilibrium of the type

$$[Pt(L)Cl_3]^- + MeOH = \textit{trans}\text{-}[Pt(L)(MeOH)Cl_2] + Cl^- \quad K_s$$

which is common to all of the complexes studied in this work whether provided as the appropriate salt of the $[Pt(L)Cl_3]^-$ anion (L = PEt_3, $P\text{-}n\text{-}Bu_3$, PPh_3, $P(OMe)_3$) or the neutral chloro-bridged dimer $Pt_2L_2Cl_4$ (L = PMe_3, $AsEt_3$) which is rapidly cleaved in methanol. This trans-specific solvolysis has already been observed for L = Me_2SO,[1] Me_2S,[2] and Et_2S.[3] Any subsequent solvolysis is relatively slow and mainly suppressed in the presence of added chloride. The equilibrium constants were determined by a kinetic method in which a solution of the complex in methanol at 30.0 °C in the presence of a small amount of acid to suppress protolysis of the solvento complex was allowed to reach equilibrium and then was reacted with a solution of LiCl and the rate of approach to the new position of equilibrium measured. The chloride ion concentrations used, 0.090 M < $[Cl^-]$ < 0.25 M, were large enough to ensure first-order kinetics, and the first-order rate constants for approach to equilibrium, k_{obsd}, were determined in the usual way. Plots of k_{obsd} against $[Cl^-]$ were linear, with a finite intercept at $[Cl^-] = 0$, which is consistent with two opposed first-order processes approaching equilibrium, $k_{obsd} = k_1^f + k_{Cl}[Cl^-]$. Values of the slopes, k_{Cl}, intercepts, k_1^f, and the solvolytic equilibrium constants, $K_s = k_1^f/k_{Cl}$, are collected in Table II. To test further, and in order to include data for L = C_2H_4 where the rates of substitution were too fast even for the stopped-flow technique, the solvolytic equilibrium constants were also determined by a spectrophotometric analysis of the solution at equilibrium. In the case of L = PEt_3, $P\text{-}n\text{-}Bu_3$, PPh_3, and $P(OMe)_3$, where K_s is large enough for solvolysis to be complete in the absence of added chloride, use was made of the standard relationship $[Cl^-]^{-1} = C_0(\epsilon_a - \epsilon_b)/K_s(A - A_0) - K_s^{-1}$ (see Appendix) where C_0 is the total concentration of complex (which is held constant), ϵ_a and ϵ_b are the molar extinction coefficients of the $[Pt(L)Cl_3]^-$ and *trans*-$[Pt(L)(MeOH)Cl_2]$ complexes, and A and A_0 are the absorbances of solutions in the presence and in the absence of added chloride, respectively. The intercept of the linear plot of $[Cl^-]^{-1}$ against $(A - A_0)^{-1}$ is equal to K_s^{-1}. In the case of

L = $AsEt_3$ and C_2H_4, K_s is to small for this treatment and the alternative expression $[Cl^-] = K_sC_0(\epsilon_a - \epsilon_b)(A_\infty - A)^{-1} - K_s$ (see Appendix) was used. A_∞ is the limiting absorbance in the presence of a large excess of chloride, and the other symbols represent the same values as before. K_s was obtained from the intercept of the plot of $[Cl^-]$ against $(A_\infty - A)^{-1}$. All the values of K_s are collected in Table II and compared with those obtained from the kinetics of reversible solvolysis. Agreement is reasonable but not good. The problems of subsequent solvolysis and the fact that the direct measurements were made under conditions of variable ionic strength make the kinetically determined values more reliable.

(B) Reactions between $[Pt(L)Cl_3]^-$ and Amines. When an amine is added to a solution of $[Pt(L)Cl_3]^-$ in methanol, there is a very rapid change and the first product that can be identified by repetitive spectral scanning has a spectrum that is identical in all ways with that of the separately prepared and characterized *trans*-$[Pt(L)(am)Cl_2]$ species. The product was the same if this reaction was carried out in the presence of a large excess of chloride, and with the exception of experiments with low concentrations of the least basic amine (3,4-dichloropyridine), these reactions all go to completion under the conditions used for the kinetics. Since the rates of reaction are relatively fast and require the stopped-flow technique, the methanolic solution of the complex was always at solvolytic equilibrium when the two reagent solutions were mixed. Consequently, in order to minimize side effects arising from the separate reaction of the methanol complex, the reactions were studied in the presence of a considerable excess of chloride (0.48 M). Even so, in the case of the aliphatic phosphines, some 10% of the substrate was in the form of the solvento species. The concentrations of amine used were within the range 10^{-2} M < [am] < 0.15 M with [complex] $\approx 7 \times 10^{-4}$ M and so [am] and $[Cl^-]$ remained sensibly constant during any one kinetic run. In the reactions of the complexes with L = PPh_3, $P(OMe)_3$, and $AsEt_3$, the small concentrations of solvento complex present initially lead to no complications and a simple first-order change in absorbance is observed. The first-order rate constants, k_{obsd}, were obtained from the slopes of the plots of ln $(A_\infty - A_t)$ against time (A_t and A_∞ are the absorbances of the reacting solution at time t and after 10 half-lives, respectively). Good straight lines were obtained for at least 3 half-lives. In the reactions of the L = PMe_3, PEt_3, PEt_3, and P-*n*-Bu_3 complexes, when a significant amount of the substrate (~10%) was in the form of the more labile *trans*-$[Pt(L)(MeOH)Cl_2]$ complex at the beginning of the reaction, there was always a small, nonlinear, portion of the ln $(A_\infty - A_t)$ vs. time plot at the early stages of the reaction corresponding to the consumption of the solvento species. This never accounted for more than 20% of the reaction and was followed by a good linear relationship. The slopes of the linear portions were taken as k_{obsd}. As is usual in substitution reactions of d^8 metal complexes, k_{obsd} is dependent upon the concentration of the entering amine. In certain cases, namely, the reactions with the least basic substituted pyridines, e.g., 3,5-dichloropyridine, 3-chloropyridine, and 3-bromopyridine, and in the reactions of $[Pt(P(OMe)_3)Cl_3]^-$ with any heterocyclic amine, the plots of k_{obsd} against [am] were linear in accordance with the classic two-term rate law

$$k_{obsd} = k_1^f + k_2^f[am] \qquad (1)$$

with k_1^f independent of the nature of the amine. With the most basic amines these plots are curved, especially at the lower amine concentrations, and the data were analyzed with use of the more elaborate rate expression

$$k_{obsd} = k_1^f\left(1 + \frac{k_{Cl}[Cl^-]^{-1}}{k_{am}[am]} + k_2^f[am]\right) \qquad (2)$$

which takes account of the competition between chloride (k_{Cl}) and the amine (k_{am}) for the solvento complex, i.e., mass-law retardation of the solvolytic pathway.[2] The best fit values of the rate constants were obtained by the iterative nonlinear regression computer program BMDP3R. In the more favorable cases the values of k_1^f obtained in this were, for any particular substrate, independent of the nature of the entering amine and agreed with the values obtained by studying the solvolysis independently in the presence of hydroxide, but as has been observed previously,[1,2] in many of the reactions with the more basic amines the best fit of the experimental data by eq 2 yielded low values of k_1^f. This was particularly noticeable in the reactions of the complexes where L = PMe_3, PEt_3, and P-*n*-Bu_3, where the position of solvolytic equilibrium lies most in favor of the solvento complex, with the most basic amines. This effect has been observed in the other systems we have examined, namely, the reactions of the more basic amines with $[Pt(L)Cl_3]^-$ where L = Me_2SO,[1] Me_2S,[2] and Et_2S.[3] The rate constants for these systems were analyzed with use of a more elaborate expression whose derivation does not assume the steady-state approximation (see Appendix)

$$k_{obsd} = \left\{k_1^f\frac{k_{am}}{k_{Cl}} + k_2^f\left([Cl^-] + \frac{k_{am}[am]}{k_{Cl}}\right)\right\} \times \left\{\frac{K_s + [Cl^-]}{[am]} + \frac{k_2^fK_s}{k_1^f} + \frac{k_{am}}{k_{Cl}}\right\}^{-1} \qquad (3)$$

where the only new parameter introduced is the experimentally determined solvolytic equilibrium constant, K_s. The rate parameters k_1^f, k_2^f, and k_{am}/k_{Cl} were obtained from the variation of k_{obsd} with [am] at constant $[Cl^-]$ with use of the iterative, nonlinear regression computer program BMDP3R. The values are collected in Table III.

(C) Displacement of Amine from *trans*-$[Pt(L)(am)Cl_2]$ by Chloride. Under normal circumstances, the position of equilibrium for this reaction lies well over to the right-hand side even when little more than stoichiometric amounts of the amine are present; however, it can be shifted completely to the left by adding a sufficient excess of acid. Preliminary experiments showed that, when the amine was more basic than 3-chloropyridine, an acid concentration of 0.040 M was sufficient to make the final spectrum indistinguishable from that of a solution of $[Pt(L)Cl_3]^-$ in the same acid + chloride medium in the region where the amine or its conjugate acid did not absorb significantly. Higher acid concentrations were necessary for complexes with the less basic amines. Because of side reactions encountered when certain batches of perchloric acid were used at these concentrations, hydrochloric acid was employed even though this limited the range of chloride concentration that could be studied. The preliminary experiments also showed that the rate was independent of $[H^+]$. Because the product reached solvolytic equilibrium rapidly and the amount of unprotonated amine was negligible, the rate law was simple and no mass-law retardation of the solvolytic step was observed. In general the substrate was prepared in situ by mixing equimolar amounts of methanol solutions of $[Pt(L)Cl_3]^-$ and the amine and allowing the reaction to go to completion. Samples of this solution (0.10 cm^3, [complex] = 2.5×10^{-2} M) were added to the thermostated solution of the other reagents (HCl, LiCl, $LiClO_4$; 3.0 cm^3) in order to initiate the reaction, and the spectrum of the resulting solution was scanned repetitively over the range 290–350 nm. For the complexes of the less basic amines, where the reactions were too fast for this technique, equal volumes of solutions of the complex and of acid, respectively, in methanol with the same concentrations of LiCl and $LiClO_4$ were mixed in the stopped-flow spectrophotometer. When possible, the kinetics were repeated with solutions of the

Table III. Rate Constants for the Reactions of the Type $[Pt(L)Cl_3]^- + am \rightarrow$ *trans*-$[Pt(L)(am)Cl_2] + Cl^-$ [a]

L	am	k_1^f/s^{-1} [b]	$k_2^f/M^{-1}\,s^{-1}$ [b]	k_{am}/k_{Cl} [b]
PMe_3	pip	4.8 ± 0.2	35.6 ± 2.1	18.3 ± 1.9
	n-$BuNH_2$	4.6 ± 0.7	20.4 ± 3.9	16.9 ± 3.7
	c-$HxNH_2$	5.2 ± 0.1	9.5 ± 4.4	9.6 ± 2.0
	morpholine	6.4 ± 1.9	152 ± 14	54 ± 37
	4-Mepy	5.1 ± 0.4	8.7 ± 3.2	52 ± 8
	py	5.2 ± 0.3	10.6 ± 2.7	54 ± 8
	3-Clpy[c]	4.7 ± 0.3	58.7 ± 4.7	...
	3,5-Cl_2py[c]	4.5 ± 0.2	115 ± 4	...
PEt_3	pip	6.2 ± 0.3	28.5 ± 3.2	15.2 ± 1.9
	n-$BuNH_2$	6.3 ± 0.4	11.6 ± 2.2	15.9 ± 1.5
	c-$HxNH_2$	6.1 ± 0.1	10.5 ± 1.2	9.9 ± 0.5
	mor	6.5 ± 1.1	71.4 ± 4.6	65 ± 39
	3,5-Me_2py	5.8 ± 0.2	12.2 ± 1.8	48 ± 5
	4-Mepy	6.1 ± 0.4	10.0 ± 3.5	61 ± 10
	py	6.0 ± 0.4	8.4 ± 3.8	93 ± 20
	3-Brpy[c]	6.3 ± 0.5	48.3 ± 5.5	...
	4-CNpy[c]	4.7 ± 1.3	63 ± 9	...
	3,5-Cl_2py[c]	5.4 ± 0.7	90 ± 7	...
	OH^- [d]	6.6 ± 0.7		
H-n-Bu_3	pip	4.8 ± 0.1	26.3 ± 0.9	15.7 ± 1.3
	n-$BuNH_2$	4.6 ± 0.7	15.5 ± 3.4	19.5 ± 4.7
	c-$HxNH_2$	4.2 ± 1.1	14.0 ± 3.3	14.4 ± 6.2
	mor	4.4 ± 0.3	93.8 ± 2.5	121 ± 34
	3,5-Me_2py	4.6 ± 0.2	8.7 ± 2.0	87 ± 17
	4-Mepy	4.8 ± 0.2	8.7 ± 1.5	80 ± 13
	py	4.6 ± 0.3	13.5 ± 1.6	119 ± 26
	3-Clpy[c]	4.7 ± 0.2	48.6 ± 3.4	...
	3-Brpy	4.4 ± 0.3	51.2 ± 2.5	380 ± 150
	4-CNpy	5.1 ± 0.7	50.4 ± 7.4	190 ± 100
	3,5-Cl_2py[c]	4.5 ± 0.4	115 ± 7	...
	OH^- [d]	5.2 ± 0.6		
PPh_3	pip[e]	3.4 ± 0.2	34.8 ± 1.4	25 ± 7
	n-$BuNH_2$[e]	3.1 ± 1.3	47.0 ± 6.3	12 ± 6
	c-$HxNH_2$[e]	3.2 ± 0.2	26.6 ± 1.6	8 ± 2
	mor[e]	3.0 ± 0.6	184 ± 5	72 ± 40
	3,5-Me_2py[e]	3.1 ± 0.2	25.6 ± 1.1	60 ± 10
	4-Mepy[e]	3.1 ± 0.1	22.4 ± 0.6	85 ± 10
	py[e]	3.0 ± 0.2	34.1 ± 0.9	121 ± 27
	3-Clpy[e]	3.4 ± 0.3	103 ± 0.4	380 ± 560
	3-Brpy[e]	2.7 ± 0.6	94 ± 6	210 ± 340
	4-CNpy[e]	3.1 ± 0.3	110 ± 5	180 ± 100
	3,5-Cl_2py[c]	3.3 ± 0.2	149 ± 4	...
	OH^- [d]	3.1 ± 0.3		
$P(OMe)_3$	pip[e]	11.3 ± 1.2	232 ± 9	35 ± 8
	n-$BuNH_2$[e]	10.3 ± 1.5	198 ± 18	34 ± 17
	c-$HxNH_2$[e]	10.4 ± 2.0	82 ± 16	33 ± 11
	4-Mepy[c]	10.5 ± 0.8	161 ± 15	...
	py[c]	10.5 ± 0.4	190 ± 7	...
	3-Clpy[c]	14.3 ± 0.8	348 ± 16	...
	OH^- [d]	10.7 ± 1.0		
$AsEt_3$	pip[e]	0.58 ± 0.09	4.3 ± 0.6	23 ± 5
	n-$BuNH_2$[e]	0.44 ± 0.13	4.6 ± 0.9	27 ± 14
	c-$HxNH_2$[e]	0.71 ± 0.09	1.1 ± 0.3	10 ± 2
	4-Mepy[e]	0.72 ± 0.03	3.2 ± 0.3	81 ± 4
	py[e]	0.66 ± 0.04	4.4 ± 0.4	153 ± 47
	3-Clpy[c]	0.67 ± 0.03	12.6 ± 0.6	...

[a] In methanol at 30.0 °C; [complex] = 4×10^{-4} M, [LiCl] = 0.48 M, and $\mu = 0.48$. Rate constants were analyzed with use of eq 3. [b] See text for significance of rate constants. [c] From the slopes and intercepts of the plot of k_{obsd} vs. [am]. [d] First-order rate constant for the displacement of Cl^- in the presence of excess hydroxide. [e] Data analyzed with use of eq 2.

characterized, authentic samples of the *trans*-$[Pt(L)(am)Cl_2]$ complex. In all cases the observed rate constants were in close agreement. The change in absorbance followed a first-order rate law, and the rate constant, k_{obsd}, was determined in the usual way. These rate constants generally obey the simple two-term rate law $k_{obsd} = k_1^r + k_2^r[Cl^-]$ although the contribution from the chloride-dependent pathway is not large and, in some cases, too small to be detected within the limits of random variation. The values of k_1^r and k_2^r obtained by a linear regression analysis of the plot of k_{obsd} vs. $[Cl^-]$ are collected in Table IV.

(D) Equilibrium Constants for the Reaction $[Pt(L)Cl_3]^-$ + am = *trans*-$[Pt(L)(am)Cl_2]$ + Cl^- (K_{am}). In principle, the equilibrium constants for the above process can be determined by a direct spectrophotometric analysis of the system at equilibrium or else evaluated from the measured rate constants for the forward and reverse reactions. For amines more basic than 3-chloropyridine the equilibrium constants are too large for the direct analysis to be useful. A method in which the free amine concentration is controlled by adding small amounts of acid required a knowledge of the pK_a of the amine in methanol, and this value is very sensitive to the concentration of the small amount of water that was always present and that we could not control.

The kinetic evaluation makes use of the relationship $K_{am} = k_2^f/k_2^r = (k_1^f/k_1^r)(k_{am}/k_{Cl})$. Although it might be thought that the ratios of the rate constants for the direct substitution might give rise to the least error, the contribution of $k_2^r[Cl^-]$

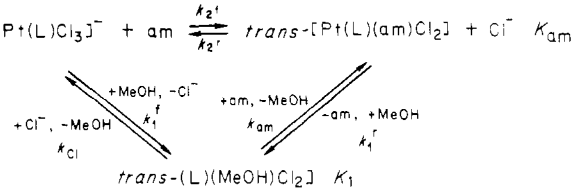
Table IV. Rate Constants for the Reactions of the Type $trans\text{-}[Pt(L)(am)Cl_2] + Cl^- + H^+ \xrightarrow{k_1^r + k_2^r[Cl^-]} [Pt(L)Cl_3]^- + amH^+$ [a]

L	am	$10^3k_1^r/s^{-1}$	$10^3k_2^r/M^{-1}\ s^{-1}$
PMe_3	mor	5.2 ± 0.1	2.5 ± 0.5
	$n\text{-}BuNH_2$	0.127 ± 0.002	0.033 ± 0.007
	$c\text{-}HxNH_2$	0.164 ± 0.002	0.038 ± 0.008
	4-Mepy	7.1 ± 0.4	0.23 ± 0.10
	py	15.4 ± 0.9	0.58 ± 0.18
	3-Clpy	275 ± 13	*b*
	3-Brpy	277 ± 15	*b*
PEt_3	pip	0.380 ± 0.025	0.18 ± 0.07
	$n\text{-}BuNH_2$	0.143 ± 0.002	0.018 ± 0.009
	$c\text{-}HxNH_2$	0.136 ± 0.006	0.028 ± 0.024
	$c\text{-}PrNH_2$	0.969 ± 0.020	0.47 ± 0.06
	3,5 Me_2py	10.8 ± 0.7	0.47 ± 0.09
	4-Mepy	11.5 ± 0.6	0.31 ± 0.15
	py	25.7 ± 1.1	0.39 ± 0.26
	3-Clpy	495 ± 20	*b*
	3-Brpy	275 ± 10	*b*
P-*n*-Bu_3 [c]	pip	0.33 ± 0.01	0.16 ± 0.01
	$n\text{-}BuNH_2$	0.13 ± 0.01	0.034 ± 0.018
	$c\text{-}HxNH_2$	0.126 ± 0.003	0.043 ± 0.010
	mor	4.78 ± 0.08	1.36 ± 0.33
	$c\text{-}PrNH_2$	0.84 ± 0.04	0.42 ± 0.16
	3,5-Me_2py	10.2 ± 0.7	0.22 ± 0.07
	4-Mepy	10.9 ± 0.2	0.25 ± 0.06
	py	23.2 ± 1.2	0.58 ± 0.15
	3-Clpy	376 ± 25	*b*
	3-Brpy	454 ± 17	*b*
PPh_3	pip	0.21 ± 0.01	0.095 ± 0.020
	$n\text{-}BuNH_2$	0.070 ± 0.002	0.035 ± 0.005
	$c\text{-}HxNH_2$	0.069 ± 0.006	0.057 ± 0.025
	mor	2.88 ± 0.11	2.33 ± 0.41
	$c\text{-}PrNH_2$	0.48 ± 0.01	0.21 ± 0.06
	3,5-Me_2py	10.6 ± 0.2	1.5 ± 0.3
	4-Mepy	11.0 ± 0.4	0.93 ± 0.13
	py	27.4 ± 0.8	2.6 ± 0.6
	3-Clpy	335 ± 25	*b*
	3-Brpy	444 ± 23	*b*
$P(OMe)_3$ [c]	$n\text{-}BuNH_2$	0.92 ± 0.04	0.53 ± 0.11
	$c\text{-}HxNH_2$	0.91 ± 0.03	0.48 ± 0.08
	4-Mepy	179 ± 13	*b*
	py	365 ± 27	*b*
	3-Clpy	5240 ± 230	*b*
$AsEt_3$ [d]	4-Mepy	0.82 ± 0.03	0.046 ± 0.011
	py	1.74 ± 0.11	0.076 ± 0.025
	3-Clpy	39.3 ± 2.2	*b*
	3-Brpy	34.8 ± 1.2	*b*

[a] In methanol at 30.0 °C; [complex] = 8 × 10^{-4} M. [b] Too small to measure. [c] [complex] = 5 × 10^{-4} M. [d] [complex] = 4 × 10^{-4} M.

to the rate of the reverse reaction was always very small and so, even in the most favorable cases, the accuracy of k_2^r was poor. We therefore used the second relationship $K_{am} = (k_1^f/k_1^r)(k_{am}/k_{Cl})$ even though the errors in the determination of k_{am}/k_{Cl} were unacceptably large in some cases. With the least basic amines it was not possible to obtain a value for this ratio from the kinetic analysis of mass-law retardation of the forward step but fortunately K_{am} was small enough for the equilibrium to be capable of spectrophotometric examination without the need to add acid. With use of a constant concentration of chloride (0.40 M), large compared to that of the complex, the absorbance at the wavelength where the spectra of *trans*-$[Pt(L)(MeOH)Cl_2]$ and $[Pt(L)Cl_3]^-$ cross was measured as a function of the total amine concentration, $[am]_{tot}$. If the equilibrium coefficient K' is defined by $K' = [t\text{-}Pt(L)(am)Cl_2][Cl^-]/([Pt(L)Cl_3^-] + [t\text{-}Pt(L)(MeOH)Cl_2])[am]$, it can be shown that (see Appendix) $(A - A_\infty)^{-1} = K'[am]_{tot}(A_0 - A)[Cl^-] - K'/(\epsilon_a - \epsilon_c)[Cl^-]$, where A_0 and A are the absorbances of the solution at equilibrium with the concentration of added amine equal to 0 and $[am]_{tot}$, respectively, A_∞ is the absorbance of a solution with the same total concentration of complex in the presence of a considerable excess of amine and no added chloride, and ϵ_a and ϵ_c are the molar extinction coefficients of $[Pt(L)Cl_3]^-$ (or *trans*-$[Pt(L)(MeOH)Cl_2]$) and *trans*-$[Pt(L)(am)Cl_2]$, respectively. K' was determined from the slope of the linear plot of $(A - A_\infty)^{-1}$ against $[am]_{tot}/(A_0 - A)$, and K_{am} was obtained from the relationship (see Appendix) $K_{am} = K'(1 + K_s/[Cl^-])$. The values of the equilibrium constants are collected in Table V.

Scheme I



Discussion

The reactions of the complexes are summarized in Scheme I. The rate constants, k_1^f, k_2^f, k_1^r, k_2^r, k_{Cl}, and k_{am}, and the equilibrium constants, K_{am} and K_{Cl}, were all determined either by direct measurement or by suitable combinations of the other constants. The expected trans effect sequence is found in all cases, the rate constants in a series of comparable reactions increasing in the order L = thioether < sulfoxide < arsine < phosphine < phosphite. Where examined, the substituent effects are small and, for the phosphines, the order depends upon the nature of the reaction being studied. A similar effect has been observed in the case of the thioethers.[2,3] The quantitative trans effect depends upon the nature of the reaction being studied, and relative rate constants for a selection of the reactions are collected in Table VI. Although the rate constant for the least reactive species in this study (L = SMe_2) is represented as 1.0, it should be remembered that a thioether exerts a moderate trans effect. Although there are no comparable data for reactions in methanol for complexes of the type $[Pt(L)Cl_3]^-$, where L has a weaker trans effect than SMe_2, some studies in aqueous solution have been reported. For the weakest, L = H_2O, k_1^f for the displacement of the trans chloride is 8 × 10^{-8} s^{-1} at 25 °C,[15] and for L = NH_3, k_1^f = 6.3 × 10^{-6} s^{-1} at 25 °C.[16] The dimethyl sulfide complex has not been examined in water, but if k_1^f for L = Me_2SO is taken as 9.8 × 10^{-2} s^{-1} at 25 °C in water[17] and it is assumed that the change of solvent and temperature does not seriously affect the relative magnitudes of the rate constants, H_2O and NH_3 on the scale Me_2S = 1 would have the relative magnitudes 5 × 10^{-6} and 4 × 10^{-4}, respectively.

The span of reactivity for the replacement of the weakly bound MeOH by Cl^- (measured by k_{Cl}) on going from L = Me_2S to L = $P(OMe)_3$ is a factor of 500; for replacement of chloride by MeOH (k_1^f) or by pyridine (k_2^f) it is a factor of 3 × 10^3 and 7 × 10^3, respectively, while for the replacement of the most tightly bound amine that could be studied systematically (3-chloropyridine, k_1^r) it is a factor of 1.3 × 10^5. Thus, as the leaving group becomes more tightly bound, the magnitude of the kinetic trans effect (in terms of relative reactivity) increases. Because of the inertness of the *trans*-$[Pt(R_2S)(am)Cl_2]$ complexes it has been possible to examine complete sequences for the displacement of more tightly bound amines. However, the value of k_1^r increase from L = Me_2SO to L = $P(OMe)_3$ by a factor of 3.3 × 10^3 when pyridine is displaced (cf. 2.0 × 10^3 for the displacement of 3-chloropyridine). Although the value of k_1^r for the displacement of the most tightly bound amine, $n\text{-}BuNH_2$, trans to Me_2SO was

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Table V. Equilibrium Constants ($10^{-4} K$) for the Reaction $[Pt(L)Cl_3]^- + am \overset{K}{\rightleftharpoons} trans\text{-}[Pt(L)(am)Cl_2] + Cl^-$ [a]

	L						
am	PMe_3	PEt_3	P-*n*-Bu_3	PPh_3	$P(OMe)_3$	$AsEt_3$	method[b]
pip	. . .	25 ± 4	23 ± 2	40 ± 11	. . .	. . .	k
		(16 ± 7)	(16 ± 1)	(37 ± 7)			
n-$BuNH_2$	61 ± 16	70 ± 8	69 ± 20	53 ± 34	38 ± 20	. . .	k
	(62 ± 13)	(64 ± 30)	(46 ± 20)	(134 ± 20)	(38 ± 16)		
c-$HxNH_2$	30 ± 3	44 ± 3	47 ± 23	36 ± 11	38 ± 15	. . .	k
	(25 ± 10)		(33 ± 8)	(47 ± 24)	(17 ± 6)		
mor	6.6 ± 4.9	. . .	11 ± 3	7.5 ± 4.4	. . .	. . .	k
	(6.1 ± 1.2)		(6.9 ± 1.8)	(7.9 ± 1.6)			
3,5-Me_2py	. . .	2.3 ± 0.3	3.9 ± 0.8	1.8 ± 0.5	. . .	. . .	k
		(2.6 ± 0.5)	(4.0 ± 1.3)	(1.7 ± 0.4)			
4-Mepy	3.7 ± 0.7	3.2 ± 0.8	(3.5 ± 0.6)	(2.4 ± 0.3)	. . .	7.1 ± 1.3	k
	(3.8 ± 1.2)	(3.2 ± 1.6)	(3.5 ± 0.9)	(2.4 ± 0.5)		(7.0 ± 1.7)	
py	1.8 ± 0.3	2.2 ± 0.3	2.4 ± 0.6	1.3 ± 0.3	. . .	5.8 ± 1.9	k
	(1.8 ± 0.5)		(2.3 ± 0.6)	(1.3 ± 0.3)			
3-Clpy	0.45	0.45	0.47	. . .	0.23	0.72	d
4-CNpy	. . .	0.48	0.41	0.15	0.095	0.49	d
3,5-Cl_2py	. . .	. . .	0.068	0.040	. . .	0.13	d

[a] In methanol at 30.0 °C. [b] k denotes constants determined from kinetic data, with use of $K = k_1^f k_{am}/k_1^r k_{Cl}$. Values in parentheses use the relationship $K = k_2^f/k_2^r$ ($\mu = 0.48$). d denotes constants determined from a direct spectrophotometric analysis ($\mu = 0.40$).

Table VI. Effect of the Nature of the Reaction upon the Relative Trans Effects[a]

	L								
reacn	Me_2S	Et_2S	$S(O)Me_2$	$AsEt_3$	PPh_3	PMe_3	PEt_3	P-*n*-Bu_3	$P(OMe)_3$
$Pt(L)Cl_3^- + MeOH$ (k_1^f)	1	1.6	5.5	420	2100	3500	4400	3500	6900
trans-$[Pt(L)(MeOH)Cl_2] + Cl^-$ (k_{Cl})	1		15	65	220		104	87	545
$Pt(L)Cl_3^- + py$ (k_2^f)	1	1.6	15	71	550	170	140	220	3100
trans-$[Pt(L)(3\text{-}Clpy)Cl_2] + MeOH$ (k_1^r)	1	3.2	67	1000	8600	7100	13000	9600	134000

[a] k/k_{SMe_2} at 30.0 °C in MeOH ($\mu \approx 0.5$).

too small to be measured directly, extrapolation of the data in Figure 2 in ref 1 would suggest a value of 1×10^{-7} s^{-1}, which is nearly 10^4 times smaller than the corresponding value for the $P(OMe)_3$ complex.

The small contribution made by the direct pathway for the entry of chloride into *trans*-$[Pt(PR_3)(am)Cl_2]$ and *trans*-$[Pt(P(OMe)_3)(am)Cl_2]$ only permits approximate values for k_2^r to be determined, but it is of interest to note that the importance of this contribution increases as the basicity of the leaving amine increases. Thus the ratio $k_2^r:k_1^r$ decreases from 0.5 for the displacement of the most basic amines to 0.1 for the displacement of pyridine. The ratio must decrease still further because no systematic dependence of the rate of displacement of the less basic amines on the concentration of chloride could be observed over the range of concentrations studied. When L = Me_2SO, the ratio is 2.0 and appears to remain independent of the basicity of the leaving amine,[1] while for L = Me_2S, where only the displacement of 3-chloropyridine has been studied, the ratio is 1.0.[2]

This behavior pattern indicates that the trans effect of phosphorus donors becomes more important when the leaving group is strongly bound. This suggests that the role of phosphorus is mainly to weaken the bond with the leaving group. Although we have only examined weak nucleophiles, there is an indication that the nucleophilic discrimination is also least when the leaving group is less strongly bound, a further indication of a fairly open transition state.

It has long been accepted that at least two factors contribute to the trans effect in the substitution reactions of d^8 metal complexes. There is a bond-weakening effect that arises from competition between a pair of trans ligands whereby the stronger σ-bonding donor improves its bonding at the expense of the bond between the trans partner and the metal. This will be observed as a nonkinetic trans influence, and since this competition is reduced in the transition state, it will also lead to an increase in lability. There is also a transition-state-strengthening effect that occurs when the ligand trans to the leaving group can act as a π-acceptor, thereby facilitating five-coordination by withdrawing charge from the metal. This is mainly observed as a kinetic effect. The two processes can work in concert. The ligands in this and the previous studies in the series have S, P, and As donors and, in principle, can act as π-acceptors in addition to being moderate to strong σ-donors. The aim of this work has been to assess the relative contributions of the ground-state-weakening and transition-state-strengthening effects. We had hoped to determine the characteristic behavior patterns of model complexes where the contribution of one of the two effects predominates. C_2H_4 and CO are relatively strong π-acceptor ligands but fairly weak σ-donors, and the complexes $[Pt(C_2H_4)Cl_3]^-$ and $[Pt(CO)Cl_3]^-$ are well-defined and readily prepared species that can serve as models. Unfortunately, the substitution reactions of these complexes, even with weak nucleophiles, are too fast for the techniques available to us (although we hope to examine them shortly at low temperature) and there can be ambiguity about the initial site of nucleophilic attack. Therefore, the characteristic patterns of the π-acceptor labilization have not yet been determined. Nevertheless, it is reasonable to predict that, since the reactivity of the system will be dominated by the energy of the transition state and therefore, in part, by the bonding with the incoming group these reagents will exhibit very marked nucleophilic discrimination. But how, other than by the high reactivity, can this behavior be distinguished from that of a complex where the trans ligand provides little assistance in the labilization of the complex, whatever the mode of action?

Pure σ-donor ligands such as H, CH_3, C_2H_5, etc. have been examined extensively but in complexes of the type *trans*-$[Pt(PR_3)_2(L)X]$, where the phosphines are generally bulky enough to exert steric inhibition. In general, these complexes have a very high intrinsic reactivity (measured by the solvolytic rate constant) and very poor nucleophilic discrimination.

Table VII. Slopes of the Plots of log k_2^{f} against pK_a of amH^{+} [a] (Where am Is a Pyridine Derivative) for the Reaction Pt(L)Cl$_3^-$ + am → *trans*-[Pt(L)(am)Cl$_2$] + Cl$^-$

L	slope	L	slope	L	slope
PMe$_3$	−0.224 ± 0.027	AsEt$_3$	−0.178 ± 0.005	P(OMe)$_3$	−0.106 ± 0.003
P-*n*-Bu$_3$	−0.204 ± 0.014	PPh$_3$	−0.156 ± 0.013	SMe$_2$ [c]	−0.098 ± 0.009
PEt$_3$	−0.189 ± 0.026	SEt$_2$ [b]	−0.121 ± 0.008	S(O)Me$_2$ [d]	−0.070 ± 0.008

[a] Values from Table III. [b] From ref 3. [c] From ref 2. [d] From ref 1.

Romeo et al.[18] have shown that, in the reaction *trans*-[Pt(PEt$_3$)$_2$(L)X] + Y^{n-} → *trans*-[Pt(PEt$_3$)$_2$(L)Y]$^{(1-n)+}$ + X$^-$ (X = Cl, Br, I), the strong trans effect observed when L = H or C$_2$H$_5$ is associated with a high intrinsic reactivity (k_1) coupled with a very low nucleophilic discrimination. However, when the entering group is biphilic[19] (i.e., it also possesses π-acceptor properties), e.g., CN$^-$, SC(NH$_2$)$_2$, the k_2 contribution becomes considerable. The importance of this effect was ascribed to the enhancement of the π-basicity of platinum by the inductive effect of the strong σ-donor.[20]

If the ground-state bond weakening dominates the trans effect, we might expect to find a relationship between the trans effect and and the trans influence. McWeeny et al.[23] suggested some time ago that the most readily interpretable measure of trans influence would be the trans-metal–ligand and assuming of course that this is related to bond strength. The amount of information now available is considerable, and consequently the more indirect parameters such as force constant, stretching frequency, and even NMR coupling constants have been somewhat eclipsed. They showed that the length of the Pt–Cl bond increases as the Pauling electronegativity of the trans ligand decreases, but Kaduk and Ibers[24] consider this to be an oversimplification. Trans-Pt–Cl bond lengths have now been determined for a number of members of the [Pt(L)Cl$_3$]$^-$ series and can be compared to the known reactivity. The trans influence increases along the sequence L = Me$_2$SO (2.318)[4] < NH$_3$ (2.321)[25] < C$_2$H$_4$ (2.327)[26] < PEt$_3$ (2.382)[6] (trans-Pt–Cl bond length/Å). It is generally considered that the differences between the first three Pt–Cl bond lengths are not particularly significant and that the trans influence of C$_2$H$_4$ and Me$_2$SO is negligible. Ethene, nevertheless, has an extremely large trans effect, while that of Me$_2$SO is not inconsiderable. It has been suggested that, since S and P can, in principle, use their 3d orbitals to function as π-acceptors, their trans influence will be reduced by this contrary electron drift and the maximum trans influence will be found where the donors do not possess π-acceptor properties, e.g., H and CH$_3$.[23] In the absence of supporting evidence it is rarely satisfactory to postulate a pair of canceling interactions and, in any case, there is reason to believe that π-acidity makes a negligible contribution to the bonding of phosphorus to platinum(II) in a four-coordinate planar complex.[27] The absence of π-bonding in the substrate does not preclude a significant contribution in the five-coordinate transition state.

In order to resolve this difficulty, it is necessary to examine the reactivity patterns reported in this and previous papers. If, as suggested by McWeeny,[23] the trans influence should follow the effective σ-interaction as measured by the calculated Pt(II) pσ–ligand hybrid-σ overlap, the sequence P > As ≈ S > O is predicted. Within a series of ligands with the same donor atom one might expect a contribution to the overall σ-donor strength from the electron displacement effects of the substituents attached to the donor, so that PR$_3$ > PPh$_3$ > P(OR)$_3$ and SR$_2$ > S(O)R$_2$. This prediction should be treated with some caution since photoelectron spectroscopy suggests the order PPh$_3$ > PMe$_3$,[28] but it still seems reasonable to expect that phosphites are weakerσ-donors than phosphines and sulfoxides are poorer than thioethers. π-acceptor sequences are more contentious. If one uses as a criterion the ease with which the 18-electron valence shell is attained by five-coordination, then the sequence As > P >> N is predicted.[29] From an analysis of the C–O stretching frequencies of Ni(CO)$_3$L, Tolman[30] has suggested that the π-acceptor capacity of L increases along the sequence PR$_3$ < PPh$_3$ < P(OR)$_3$, and a similar study with Co(CO)$_2$(NO)L suggested the sequence NH$_3$ < pyridine < PR$_3$ < SR$_2$ < PPh$_3$ < P(OR)$_3$.[31] The presence of the oxygen atom in the sulfoxide would increase its π-acceptor ability relative to that of the corresponding thioether, and it has been suggested that certain similarities between dimethyl sulfoxide and ethene might be due to the former having significant π-acceptor properties.[32]

Returning to the question of the kinetic evaluation of the trans effect, we shall take the view that, as in the case of the labilization by a pure σ-donor,[18] the ground-state bond-weakening effect is characterized by a low nucleophilic discrimination ability and in the absence of more extensive studies will take the ratio of the rate constants for the direct and the solvolytic pathway (k_2/k_1) as a crude measure of the nucleophilic discrimination. The phosphine complexes afford the smallest ratios, and together with the conclusions drawn above about the open nature of the transition state, it is concluded that, as expected, the phosphine trans effect comes mainly from its σ-donor ground-state weakening and parallels its trans influence. Triethylarsine has a smaller trans effect, paralleling its trans influence, and a mainly ground-state bond-weakening effect is indicated. The enhanced trans effect of P(OMe)$_3$ runs counter to its weaker σ-donor capacity, and it must therefore receive a significant contribution from the transition-state-stabilizing π-acceptor interaction. The relatively greater contributions from the k_2 pathways are consistent with this conclusion. The absence of any large trans influence from the sulfur donor ligands in spite of their moderate trans effects

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(20) Although it is eminently reasonable to expect that the presence of a strong σ-donor would lead to poor nucleophilic discrimination, it is cautionary to note that the steric hindrance itself could be the cause of the low nucleophilic discrimination. The reaction of the sterically hindered [M(Et$_4$dien)Cl]$^+$ cation (M = Pd, Pt; Et$_4$dien = 1,5-bis(diethylamino)-3-azapentane) with nucleophiles goes almost entirely through the nucleophile-independent solvolytic pathway, except for a small biphilic contribution from some biphilic entering groups.[21,22] If suitable non sterically hindered complexes containing H or CH$_3$ trans to the leaving group could be prepared and studied, this uncertainty could be resolved.

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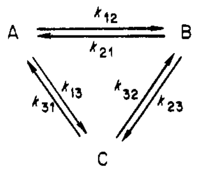
Scheme II



suggests that these ligands, especially dimethyl sulfoxide, owe much of their trans effects to their role as π-acceptors.

Although the variation of the nature of the entering group in the displacement of chloride has been confined to a series of amines and heterocyclic nitrogen bases, the inverse dependence of k_2^f on the basicity of the heterocyclic base, which was first commented on when L = Me_2S,[2] deserves further discussion. In general, the nucleophilicity of amines with respect to four-coordinate planar d^8 metal complexes either is independent of or increases with increasing amine basicity.[33] However, in the reactions of $Pt(L)Cl_3^-$, where L is a moderate or strong trans-effect ligand, the plot of $\log_{10} k_2^f$ against the pK_a of the entering heterocyclic base has a negative slope, the magnitude of which is greatest when L has the strongest trans influence (Table VII). The suggestion that biphilicity (the enhancement of the reactivity of nucleophiles with potential π-acidity, e.g., CN^-, $SC(NH_2)_2$) increases as the π-basicity of the reaction center increases[19] (and strong σ-donor trans ligands are one way of ensuring this[18]) would provide an explanation of this observation. The presence of a LUMO of π symmetry in these heterocyclic bases would allow them to exhibit biphilicity under the appropriate circumstances. Anionic Pt(II) complexes, especially those containing strong σ-donor ligands, provide these circumstances.

The various equilibrium constants also depend upon the nature of the trans ligands, but the variation, which must represent a trans influence, is a great deal less than the trans effect and does not necessarily follow the same sequence. The solvolytic equilibrium $Pt(L)Cl_3^- + MeOH = trans\text{-}[Pt(L)(MeOH)Cl_2] + Cl^-$ (Table II) followed the equilibrium constant sequence L = $C_2H_4 < S(O)Me_2 < SMe_2 < AsEt_3 < PPh_3 < P(OMe)_3 < P\text{-}n\text{-}Bu_3 < PEt_3$. It is easy to confuse this with evidence for bond weakening, but this is not a dissociative equilibrium. The chloride is replaced by coordinated methanol, and the same sequence can be observed for the replacement of the chloride by the much more strongly bound amine ligands.

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Appendix

For the reversible and parallel first-order processes displayed in Scheme II, it can be shown that the concentrations of the species A, B, and C at time t can be written as

$$c_i = \sum_{r=1}^{3} B_{ir} Q_r^0 \exp(-\gamma_r t)$$

where B_{ir} and Q_r^0 are constants depending upon the individual rate constants and the concentrations of the species A, B, and C when $t = 0$.[34]

If we simplify the scheme by treating the formation of C as irreversible, i.e., k_{31} and $k_{32} = 0$, then the solution can be handled by the transformation method of Rodiguin and Rodiguina.[35] The rate equations take the form

$$dc_a/dt = k_{21}c_b - k_{12}c_a - k_{13}c_a$$

$$dc_b/dt = k_{12}c_c - k_{21}c_b - k_{23}c_b \qquad dc_c/dt = k_{13}c_a + k_{23}c_b$$

where c_a, c_b, and c_c are the concentrations of A, B, and C at time t. If we apply the boundary conditions that A and B are at equilibrium when the reaction starts, $c_a = c_a^0$ and $c_b = c_b^0$ when $t = 0$ and $c_c = 0$. If we make the transformations

$$Pc_a - Pc_a^0 = k_{21}c_b - k_{12}c_a - k_{13}c_a$$

$$Pc_b - Pc_b^0 = k_{12}c_a - k_{21}c_b - k_{23}c_b \qquad Pc_c = k_{13}c_a + k_{23}c_b$$

and solve the equations

$$c_a = \frac{P[(P + k_{23})c_a^0 + k_{21}(c_a^0 + c_b^0)]}{(P + \gamma_1)(P + \gamma_2)}$$

$$c_b = \frac{P[(P + k_{13})c_b^0 + k_{12}(c_a^0 + c_b^0)]}{(P + \gamma_1)(P + \gamma_2)}$$

$$c_c = P[P(k_{13}c_a^0 + k_{23}c_b^0) + (k_{13}k_{23} + k_{13}k_{21} + k_{12}k_{23}) \times (c_a^0 + c_b^0)]/[(P + \gamma_1)(P + \gamma_2)]$$

where γ_1 and γ_2 are the roots, with signs inverted, of the quadratic expression $P^2 + (k_{12} + k_{13} + k_{21} + k_{23})P + k_{12}k_{23} + k_{13}(k_{21} + k_{23})$, all three concentrations can be represented as

$$c_i = \frac{P(P + b_i)}{(P + \gamma_1)(P + \gamma_2)}$$

where b_i depends upon the rate constants and the initial concentrations. All these will lead to originals of the form

$$c_i = \frac{b_i - \gamma_1}{\gamma_2 - \gamma_1} \exp(-\gamma_1 t) + \frac{b_i - \gamma_2}{\gamma_1 - \gamma_2} \exp(-\gamma_2 t)$$

The fact that the change in absorbance takes on a simple first-order form after less than 20% of the reaction has occurred indicates that $\gamma_2 << \gamma_1$ and the slope of the linear portion of the semilogarithmic plot, k_{obsd}, is to be equated with γ_2. Consequently, it is not necessary to evaluate the preexponential parts of the expression for c_i nor to know the molar extinction coefficients of the species concerned. The roots of the quadratic equation γ_1 and γ_2 are given by $\gamma_1 = (p + q)/2$ and $\gamma_2 = (p - q)/2$, where $p = k_{12} + k_{21} + k_{13} + k_{23}$ and $q = \{p^2 - 4[k_{12}k_{23} + k_{13}(k_{21} + k_{23})]\}^{1/2}$. In order that γ_2 be much less than γ_1, it is necessary that $p \approx q$. Now $k_{obsd} = \gamma_2 = (p - q)/2 = [p - p(1 - 4\alpha/p^2)^{1/2}]/2$, where $\alpha = k_{12}k_{23} + k_{13}(k_{21} + k_{23})$. This expression can be expanded to give $k_{obsd} = [p - p(1 - 2\alpha/p^2 - 2\alpha^2/p^4 \cdots)]/2$, and since in order to meet the conditions laid down above, $p^2 >> 4\alpha$, this series will be convergent and can be terminated at $k_{obsd} = [p - p(1 - 2\alpha/p^2)]/2$; i.e., $k_{obsd} = \alpha/p$.

Transcribing the rate constants used above to those relevant to the system under examination, i.e., $k_{12} = k_1^f$, $k_{21} = k_{Cl}[Cl^-]$, $k_{13} = k_2^f[am]$, and $k_{23} = k_{am}[am]$ we obtain

$$k_{obsd} = \frac{k_1^f k_{am}[am] + k_2^f[am](k_{Cl}[Cl^-] + k_{am}[am])}{k_1^f + k_{Cl}[Cl^-] + k_2^f[am] + k_{am}[am]}$$

which reduces to the simpler stationary-state expression if $k_1^f + k_2[am]$ is small enough compared to $k_{Cl}[Cl^-] + k_{am}[am]$ for the former to be ignored in the denominator. With use of the relationship $k_1^f/k_{Cl} = K_s$ this expression can be rearranged to give the more convenient expression

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$$k_{\mathrm{obsd}} = \left\{k_1{}^{\mathrm{f}}\frac{k_{\mathrm{am}}}{k_{\mathrm{Cl}}} + k_2{}^{\mathrm{f}}\left([\mathrm{Cl}^-] + \frac{k_{\mathrm{am}}[\mathrm{am}]}{k_{\mathrm{Cl}}}\right)\right\} \left\{\frac{K_{\mathrm{s}} + [\mathrm{Cl}^-]}{[\mathrm{am}]} + \frac{k_2{}^{\mathrm{f}}K_{\mathrm{s}}}{k_1{}^{\mathrm{f}}} + \frac{k_{\mathrm{am}}}{k_{\mathrm{Cl}}}\right\}^{-1}$$

For the processes $Pt(L)Cl_3^-$ + MeOH = *trans*-[Pt(L)-(MeOH)Cl_2] + Cl^- (K_s) or $Pt(L)Cl_3^-$ + am = *trans*-[Pt-(L)(am)Cl_2] + Cl^- (K_{am}) at equilibrium, let $[Pt(L)Cl_3^-] = c_a$, [*trans*-Pt(L)(MeOH)Cl_2] = c_b, and [*trans*-Pt(L)(am)Cl_2] = c_c and ϵ_a, ϵ_b, and ϵ_c represent their molar extinctions at the wavelength used in the measurement. Then

$$K_s = \frac{c_b[\mathrm{Cl}^-]}{c_a} \tag{4}$$

and

$$K_{am} = \frac{c_c[\mathrm{Cl}^-]}{c_a[\mathrm{am}]} \tag{5}$$

Let a "pseudo equilibrium quotient" be defined as

$$K' = \frac{c_c[\mathrm{Cl}^-]}{(c_a + c_b)[\mathrm{am}]} \tag{6}$$

In the absence of added amine, the absorbance at equilibrium is

$$A = \epsilon_a c_a + \epsilon_b c_b \tag{7}$$

(for a 1-cm light path) and

$$c_a + c_b = C_0 \tag{8}$$

gives the total concentration of Pt(II) species. Eliminating c_b from (4) and (8) gives, after rearrangement

$$[\mathrm{Cl}^-]^{-1} = C_0/K_s c_a - 1/K_s \tag{9}$$

If K_s is large enough, the complex will be fully solvolyzed in the absence of added chloride so that

$$A_0 = \epsilon_b C_0 \tag{10}$$

where A_0 is the absorbance of the solution in the absence of added chloride (and amine). Combining (7), (8), and (10) gives

$$c_a = (A - A_0)/(\epsilon_a) \tag{11}$$

and combining (9) with (11) gives

$$[\mathrm{Cl}^-]^{-1} = C_0(\epsilon_a - \epsilon_b)/K_s(A - A_0) - K_s^{-1} \tag{12}$$

Thus, plotting $[Cl^-]^{-1}$ against $(A - A_0)^{-1}$ should give a straight line with intercept K_s^{-1}.

If the complex is not fully dissociated in the absence of added chloride, then K_s will be small enough for it to be possible to reach a limit at high chloride concentration, where very little of the complex remains in the methanol form. The absorbance will then be independent of $[Cl^-]$ when the concentration is high enough. If the limiting absorbance is designated as A_∞, then

$$A_\infty = \epsilon_a c_a \tag{13}$$

Eliminating c_a from (4) and (8) gives

$$[\mathrm{Cl}^-] = C_0 K_s/c_b - K_s \tag{14}$$

and replacing c_b with use of (7), (8), and (13) gives

$$[\mathrm{Cl}^-] = C_0(\epsilon_a - \epsilon_b)K_s/(A_\infty - A) - K_s \tag{15}$$

so that a plot of $[Cl^-]$ against $(A_\infty - A)^{-1}$ should be a straight line with intercept $-K_s$.

In the presence of added amine it is necessary to combine the two equilibria. Equation 3 can be rewritten as

$$K' = [C_0 - (c_a + c_b)][\mathrm{Cl}^-]/(c_a + c_b)\{[\mathrm{am}]_T - [C_0 - (c_a + c_b)]\} \tag{16}$$

where $[am]_T$ is the total amount of amine present. If measurements are made at a wavelength where $\epsilon_a = \epsilon_b$ and where the free amine does not absorb significantly

$$A = \epsilon_a(c_a + c_b) + \epsilon_c[C_0 - (c_a + c_b)] \tag{17}$$

Let the absorbance equal A_0 when no amine is present and A_∞ when all the platinum is in the form of the amine complex; then $A_0 = C_0\epsilon_a$ and $A_\infty = C_0\epsilon_c$. Combining these with (16) and (17) gives $K' = (A_0 - A)[Cl^-]/(A - A_\infty)\{[am]_T - (A_0 - A)/(\epsilon_a - \epsilon_c)$, which on rearrangement gives

$$(A - A_\infty)^{-1} = K'[\mathrm{am}]_T/(A_0 - A)[\mathrm{Cl}^-] - K'/(\epsilon_a - \epsilon_c)[\mathrm{Cl}^-] \tag{18}$$

Combining (4), (5), and (6) gives $K_{am} = K'(1 + K_s/[Cl^-])$.

Registry No. $[Pt(PMe_3)Cl_3]^-$, 44630-63-9; $Et_4N[Pt(PEt_3)Cl_3]$, 56544-60-6; $Et_4N[Pt(P(n\text{-}Bu)_3)Cl_3]$, 84835-91-6; $Et_4N[Pt(PPh_3)Cl_3]$, 84835-92-7; $Bu_4N[Pt(P(OMe)_3)Cl_3]$, 62428-87-9; $[Pt(AsEt_3)Cl_3]^-$, 44968-34-5; *n*-$BuNH_2$, 109-73-9; pip, 110-89-4; c-$HxNH_2$, 108-91-8; mor, 110-91-8; 3,5-Me_2py, 591-22-0; 4-Mepy, 108-89-4; py, 110-86-1; 3-Clpy, 626-60-8; 4-CNpy, 100-48-1; 3,5-Cl_2py, 2457-47-8.

Notes

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Mössbauer Spectroscopy of Mixed-Metal Bimetallic Complexes Containing the Pentacyanoferrate(II) Metal Center

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There have been numerous studies on the thermal[1-6] and photochemical[7] reactions of unsaturated, nitrogen heterocyclic ligands (L) bound to the pentacyanoferrate(II) metal center. The near-ultraviolet and visible spectra of these complexes are dominated by an intense metal-to-ligand charge-transfer (MLCT) band assigned as $d_\pi(M) \rightarrow p_{\pi^*}(L)$ in character.[2] The energy of the MLCT band maxima is very sensitive to substituent changes on L (i.e., the energy of the π^* orbitals of free L), with more electron-withdrawing substituents causing red shifts in the MLCT maximum as well as greater

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