added 2.86 g (8.49 mmol) of $Ba(ClO_4)_2$. To this solution was added a solution of 1.95 g (8.55 mmol) of $(NH_4)_2S_2O_8$. The 200 mL of solution had a pH of 1.3 and slight precipitate which was removed by filtration after 5 min. The pH of the filtrate was adjusted to 6 with NH_3 and the volume reduced to 50 mL under a vacuum. A slight precipitate was removed. The volume was then reduced to 20 mL and the product collected and dried under vacuum. The yield was 1.68 g (42%) of a white crystalline product. Anal. Calcd for $Pt(NH_3)_4OHSO_4ClO_4$: Pt, 41.01; N, 11.78; H, 2.76; S, 6.74; Cl, 7.45. Found: Pt, 41.0; N, 11.95; H, 2.81; S, 6.49; Cl, 7.62.

Analyses were done by Atlantic Microlab, Inc. Chemicals used in kinetic studies were reagent grade. Deionized water was used in all studies.

Kinetic Measurements. Kinetics were followed spectrophotometrically. The H_2O_2 reactions were monitored primarily at 260 nm with a Beckman DU instrument modified with a Gilford 220 absorbance indicator. The $S_2O_8^{2-}$ reactions were monitored at 240, 260, and 280 nm with a Durrum stopped-flow spectrometer. Reactions in which *trans*-$Pt(NH_3)_4Br_2^{2+}$ was a significant product were often studied at 318 nm. The temperature of the cell compartment varied less than ±0.02 °C. Reaction solutions were prepared in normal room light and no attempt was made to exclude air. Several studies at each set of conditions were generally made and average results are reported. Duplicate results reproduced well with deviations seldom being as large as 10%. Infinite-time absorbances of kinetic solutions were consistent with those expected for the reaction products; however $Pt(NH_3)_4OHSO_4^+$ and $Pt(NH_3)_4(OH)_2^{2+}$ do not have distinctive spectra.

Reactions were studied under pseudo-first-order conditions. Rate data were analyzed by a Gauss–Newton nonlinear least-squares fit to the equation $A = A_\infty + (A_0 - A_\infty)\exp(-kt)$. Absorbance vs. time data covering 3–4 half-lives were in general used and the fit to the equation was normally within the uncertainty of the absorbance measurements.

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Registry No. $Pt(NH_3)_4(SO_4)_2$, 62623-71-6; $[Pt(NH_3)_4OHSO_4]ClO_4$, 62571-46-4; *trans*-$Pt(NH_3)_4(OH)_2^{2+}$, 62623-70-5; $[Pt(NH_3)_4]Cl_2$, 13933-32-9; $S_2O_8^{2-}$, 15092-81-6; H_2O_2, 7722-84-1.

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Contribution from the William Ramsay and Ralph Forster Laboratories,
University College, Gower Street, London, W.C.1, England

Kinetics of the Displacement of Chloride by Amine under the Trans Effect of Dimethyl Sulfide in Square-Planar Platinum(II) Complexes

BRUCE P. KENNEDY, ROY GOSLING, and MARTIN L. TOBE*[1]

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The kinetics of the reaction $Pt(SMe_2)Cl_3^- + am \rightarrow$ *trans*-$Pt(SMe_2)(am)Cl_2 + Cl^-$ (am is one of a series of 15 amines covering a wide range of basicity) have been studied in methanol at 30.0 °C at $\mu = 0.505$ ($LiClO_4$). The reaction follows the usual two-term rate law $-d \ln [Pt(SMe_2)Cl_3^-]/dt = k^f_1 + k^f_2[am]$. k^f_1 ($=1.2 \times 10^{-3}\ s^{-1}$) is essentially independent of the nature of the amine, while k^f_2 is not very sensitive to the properties of the monofunctional amines. Bifunctional amines, such as morpholine, ethylenediamine, piperazine, and ethanolamine are considerably more reactive. The replacement of the amine in *trans*-$Pt(SMe_2)(am)Cl_2$ by chloride in the presence of acid is too slow to follow, except in the case of the weakest bases. The properties of the dimethyl sulfide system are compared with those previously reported for the analogous dimethyl sulfoxide system. Dimethyl sulfoxide is some 10–20 times more effective as a trans-labilizing ligand when chloride is being replaced by amine but the difference is much greater in the reverse reaction.

Introduction

Some time ago we reported the kinetics of a series of reactions involving the replacement of chloride by amines (and the reverse reaction) in complexes containing dimethyl sulfoxide.[2,3] Although our interest was directed toward the ways in which the nature of the amines affected the rates and equilibria, the strong trans-labilizing effect of S-bonded dimethyl sulfoxide was recognized and discussed. In an extension of these studies of the *trans effect* in complexes where steric effects are minimized, we wish to compare the sulfoxide with a thioether which we expect to exert a weaker transition-state *trans effect* (due to its lower π-acceptor capacity) perhaps coupled with a marginally increased ground-state *trans effect* (*trans influence*). To this end we report the kinetics of the reaction $Pt(Me_2S)Cl_3^- + am \rightarrow$ *trans*-$Pt(Me_2S)(am)Cl_2 + Cl^-$ where am represents an amine.

Experimental Section

Preparations. Tetraethylammonium trichloro(dimethyl sulfido)platinate(II) was prepared by a modification of the method of Goodfellow, Goggin, and Duddell[4] in which $Pt_2Cl_4(Me_2S)_2$, prepared by the method of Chatt and Venanzi[5] but not isolated, was treated with Et_4NCl. $Pt_2Cl_4(C_2H_4)_2$[6] (1.0 g, 1.7 mmol) was dissolved in dichloromethane (60 cm^3) and the solution cooled to −70 °C. Dimethyl sulfide (0.25 cm^3, 3.4 mmol) was added, and the solution was shaken and allowed to warm up to room temperature. $Et_4NCl \cdot H_2O$ (0.63 g, 3.4 mmol) was added, and the solution was stirred for 2 days and

Table I. Some Characteristic Peaks in the Far-Infrared (400–250 cm^{-1}) Region of the Spectra of Some Dimethyl Sulfide Complexes[a]

$Et_4N[Pt(Me_2S)Cl_3]$	*350* m, *328* s, *306* s, 302 s
$(n\text{-}Pr)_4N[Pt(Me_2S)Cl_3]$[b]	*344* sh, *330* sh, *325* s, *310* s, 283 w
$(n\text{-}Pr)_4N[Pd(Me_2S)Cl_3]$[b]	*344* s, *321* s, *307* s, 293 w, 283 w
trans-$Pt(Me_2S)(3,4\text{-}Me_2py)Cl_2$	*350* s, 339 m, 312 m, 302 m
trans-$Pt(Me_2S)(py)Cl_2$	*347* s, 335 m, 325 w
trans-$Pt(Me_2S)(3\text{-}Cl\text{-}py)Cl_2$	*348* s, 341 w, 334 w, 326 w, 323 w, 300 w

[a] Nujol mull spectra; wavenumber of major peaks; ν(M–Cl) in italics. [b] Data from ref 4; spectra of solutions in *cis*-1,2-dichloroethylene.

then evaporated to dryness. The residue was shaken with a mixture of $CHCl_3$–CCl_4 60:40 (10 cm^3) until all of the solid had dissolved and, on standing, the solution separated into two layers. The light yellow upper layer was discarded and the orange lower layer was evaporated to dryness. This process was repeated five to ten times until addition of the solvent mixture to the residue gave a crop of yellow, needle-shaped crystals. These were filtered off, washed with a little ice-cold solvent, and dried. If, on addition of solvent to the residue, separation of the solution into two layers did not occur and no crystals appeared, the compound could be crystallized by allowing the solution to stand in ice.

***trans*-Dichloro(3,4-dimethylpyridino)(dimethyl sulfido)platinum(II).** 3,4-Dimethylpyridine (13.9 μL, 0.13 mmol) was added slowly from a microsyringe to a solution of $Et_4N[Pt(Me_2S)Cl_3]$ (0.059 g, 0.13 mmol) in water (2 cm^3). The required compound precipitated rapidly and 2 cm^3 of acetone was added to coagulate the precipitate. After further stirring the solid was filtered off, washed with ethanol and ether, and air-dried. Anal. Calcd for $C_9H_{15}Cl_2NSPt$: C, 24.8; H, 3.48; N, 3.22. Found: C, 24.5; H, 3.59; N, 3.07.

***trans*-Dichloro(pyridino)(dimethyl sulfido)platinum(II).** This compound could also be prepared by the addition of an equimolar amount of pyridine to an aqueous solution of $Et_4N[Pt(Me_2S)Cl_3]$ using the above method. Equally conveniently, pyridine can be added to the trichloro complex prepared in situ by heating *trans*-$Pt(Me_2S)_2Cl_2$[7] with an equimolar amount of K_2PtCl_4 in aqueous solution. Since the reaction does not go to completion, the unreacted *trans*-$Pt(Me_2S)_2Cl_2$ must be filtered off from the cooled solution and the excess $PtCl_4^{2-}$ precipitated as green Magnus salt by the addition of $[Pt(NH_3)_4]Cl_2$ before the pyridine is added. Anal. Calcd for $C_7H_{11}Cl_2NSPt$: C, 20.6; H, 2.73; N, 3.44. Found: C, 20.3; H, 2.75; N, 3.67.

Alternative Method. *trans*-$Pt(Me_2S)_2Cl_2$[7] (0.1 g, 0.3 mmol) was dissolved in chloroform (2 cm^3) and pyridine (0.025 g, 0.3 mmol) was added. Yellow, needlelike crystals formed overnight and were filtered off, washed with ethanol and ether, and air-dried. Anal. Found: C, 20.5; H, 2.59; N, 3.45. The far-IR spectrum indicates varying amounts of the cis isomer characterized by the increase in the intensity of the peaks at 336.5 and 325 cm^{-1}. Thin-layer chromatography indicates that the amount of impurity is relatively small.

***trans*-Dichloro(3-chloropyridino)(dimethyl sulfido)platinum(II).** This compound could be prepared by the addition of an equimolar amount of 3-chloropyridine to an aqueous solution of $Et_4N[Pt(Me_2S)Cl_3]$ using the method described above. Alternatively, 3-chloropyridine (0.070 g, 0.60 mmol) was added drop by drop to a stirred solution of $Pt_2Cl_4(Me_2S)_2$ (0.20 g, 0.30 mmol) in dichloromethane and the stirring was continued overnight. The solvent was removed on a rotary evaporator and the crude product recrystallized from chloroform. The yellow trans product was always contaminated with white material (presumably the cis isomer) and was washed with ethanol and ether and air-dried. Anal. Calcd for $C_8H_{12}Cl_3NSPt$: C, 19.0; H, 2.29; N, 3.17. Found: C, 18.9; H, 2.30; N, 3.10.

Reagents. AR methanol was used without further purification. All liquid amines, whether purchased as the free amine or obtained from their hydrochlorides, were refluxed over NaOH pellets and then distilled. 4-Cyanopyridine and 3,5-dichloropyridine were recrystallized from ether, and piperazine was recrystallized from ethanol from which it was obtained as a material analyzing as a tetrahydrate. Methanolic solutions were made up by weight and, in the case of the more basic amines, standardized conductometrically against hydrochloric acid. The solutions of the less basic amines were monitored spectrophotometrically using molar extinction coefficients determined from more concentrated, weight-standardized solutions. "Dried" lithium perchlorate, purchased from BDH or Fisons or obtained by careful dehydration of the hydrated salt, is approximately $LiClO_4 \cdot H_2O$. The exact composition was determined by passing an aqueous solution of a known weight of the material down an anion-exchange resin in the hydroxide form and titrating the hydroxide in the effluent. If the material is stored in a desiccator over P_2O_5, the composition does not change. Standard methanol solutions were made up by weight. *Caution*! Although we have yet to encounter problems, there are many reports in the literature of serious explosions involving perchlorates and their solutions in organic solvents. Care should always be taking when drying, handling, and storing these materials.

Commercial "anhydrous" lithium chloride was extracted from the thimble of a Soxhlet extractor by methanol, the solution was evaporated almost to dryness in a rotary evaporator, and the damp material was transferred to an oven at 130 °C where the drying process was completed. The material prepared in this way was anhydrous and could be stored unchanged in a desiccator. It proved to be less hygroscopic than the original material. Methanolic solutions were made up by weight.

Kinetics. In the reactions involving the entry of amine, solutions of the appropriate amount of amine, $LiClO_4$, and LiCl were placed in both cells of the spectrophotometer and allowed to reach thermal equilibrium. A stock solution of $Et_4N[Pt(SMe_2)Cl_3]$ (1.0×10^{-2} M) in methanol containing 0.50 M LiCl, which was stable for many days at room temperature in the dark, was prepared, and the reaction was started by adding 0.10 cm^3 of this to the reaction mixture. In the slower reactions, the spectrum was scanned repeatedly from 450 nm down to where absorption by the amine made readings meaningless; in the faster reactions the change in absorbance was recorded as a function of time at a single wavelength. Provided measurements were made far enough from the absorption cutoff of the amine, the rate constants, obtained from the slope of the plot of ln $(A - A_t)$ against time, were independent of wavelength. In most cases the isosbestic points were retained throughout and A_∞, the absorbance after 10 half-lives, could be obtained at any convenient wavelength. When there was a subsequent reaction, as evidenced by loss of the isosbestic points, A_∞ could only be determined at the wavelengths where the absorbance changes for the subsequent process were negligible. The reverse reaction was studied in a similar way. Spectrophotometric measurements were made with a Unicam SP 800 spectrophotometer equipped with a constant-temperature cell holder. The temperature was maintained at 30.0 ± 0.1 °C with water circulated from an ancillary thermostat and monitored by a thermocouple placed in the cell holder block.

Results

The $Pt(Me_2S)Cl_3^-$ anion was conveniently isolated, in a form that is sufficiently soluble in methanol for the kinetic studies, as its tetraethylammonium salt. The direct reaction between the $Pt_2Cl_4(Me_2S)_2$ dimer and Et_4NCl does not go to completion in chlorinated hydrocarbon solvents and the mixture, precipitated by the addition of ether or left after evaporation to dryness, is contaminated with Et_4NCl and the unreacted dimer. The pure material can be obtained by repeated extraction with a 60:40 $CHCl_3$–CCl_4 solvent mixture. The infrared spectrum of a Nujol mull of this complex in the region 400–250 cm^{-1} is simpler than that reported by Goodfellow et al.[4] for a mixture of $Pt_2Cl_4(SMe_2)_2$ and $(n\text{-}Pr)_4NCl$ in *cis*-1,2-dichloroethylene solution, Table I. There is, however, a much closer resemblance with the spectrum they reported for the analogous Pd(II) complex, which was actually isolated as a crystalline solid. Owing to the poor yield from the preparation of the $Pt(Me_2S)Cl_3^-$ complex and the difficulty in obtaining sufficiently large quantities of it, no systematic attempt was made to prepare and characterize all of the possible *trans*-$Pt(Me_2S)(am)Cl_2$ reaction products, as was done in the analogous dimethyl sulfoxide system.[3] Complexes with am = 3,4-dimethylpyridine, pyridine, and 3-chloropyridine were prepared by this method in small quantities. Alternative

Table II. Rate Constants for the Reaction $Pt(Me_2S)Cl_3^- + am \xrightarrow{k^f_1 + k^f_2[am]}$ *trans*-$Pt(Me_2S)(am)Cl_2 + Cl^-$ in Methanol[a-c]

am	pK_a[d]	Wavelength of cutoff/ nm	Isosbestic points/ nm	Wavelength for kinetics/ nm	$10^3k^f_1/s^{-1}$	$10^2k^f_2/M^{-1}\ s^{-1}$
Piperidine	11.12	250	265, 290, 324[e]	305	0.88 ± 0.07	15.8 ± 0.5
n-Butylamine	10.77	250	263, 289, 325[e]	305	0.89 ± 0.06	13.9 ± 0.4
Ethylenediamine	10.71	250	273, 286[e,f]	260	1.28 ± 0.03	45.6 ± 0.2
Cyclohexylamine	10.66	250	263, 289, 325[e]	305	1.01 ± 0.04	10.1 ± 0.2
Piperazine	9.83	255	266, 291[f]	305	1.98 ± 0.17	92.2 ± 2.1
Ethanolamine	9.50	250	287.5	305	1.16 ± 0.09	19.9 ± 0.7
Cyclopropylamine	8.66	250	267, 290, 324	305	1.21 ± 0.05	15.5 ± 0.3
Morpholine	8.33	250	267, 291, 325	260	1.07 ± 0.18	67.8 ± 1.6
3,4-Dimethylpyridine	6.50	280	301, 322, 337	290	1.25 ± 0.04	6.57 ± 0.26
4-Methylpyridine	6.02	280	301, 321[g]	290	1.21 ± 0.02	6.51 ± 0.11
Pyridine	5.25	285	307, 320[g]	290	1.18 ± 0.04	6.71 ± 0.27
3-Chloropyridine	2.84	290	342	299	1.14 ± 0.03	13.0 ± 0.2
3-Bromopyridine	2.84	295	None below 325	299	1.12 ± 0.02	14.2 ± 0.1
4-Cyanopyridine	1.86[h]	320	None below 360	340	1.12 ± 0.06	17.7 ± 0.4
3,5-Dichloropyridine	0.67[h]	300	350	310	1.26 ± 0.04	21.6 ± 0.3

[a] At 30.0 °C. [b] [LiCl] = 0.01 M, $\mu = 0.505$ ($LiClO_4$). [c] [Complex] = 1.6×10^{-4} M. [d] Reference 8. [e] Initial spectrum does not pass through the isosbestic points. [f] Did not scan >310 nm. [g] Did not scan >325 nm. [h] Reference 9.

methods were tried. The reactions between pyridine and *trans*-$Pt(Me_2S)_2Cl_2$ and between 3-chloropyridine and $Pt_2Cl_4(Me_2S)_2$ gave products of the correct analysis but the IR spectra in the 400–300-cm^{-1} region indicated the presence of variable but small amounts of the cis isomers.

The kinetics of the reaction between $Pt(Me_2S)Cl_3^-$ and 3,4-dimethylpyridine were studied in detail in order to determine the best conditions for the general survey. In the presence of sufficient chloride to suppress solvolysis, the spectrum changes slowly to a fairly featureless tail of a strong peak in the far-ultraviolet region. The strong absorbance of the large excess of free ligand that is present prevents any study of this peak but, at wavelengths greater than 285 nm, there is close agreement between the molar extinction coefficients calculated for the "infinity" spectrum and those of a solution of an authentic sample of *trans*-$Pt(Me_2S)(3,4\text{-}Me_2py)Cl_2$. The changing spectrum is characterized by good isosbestic points at 301, 322, and 337 nm which are maintained throughout the reaction. The change in absorbance follows a first-order rate law and the first-order rate constants, determined graphically, are independent of the wavelength chosen provided this is not too close to the region where the absorption by the free amine is too strong. Those quoted were determined at 290 nm. Following the technique used in the analogous dimethyl sulfoxide system,[3] the reaction was studied in the presence of 0.50 M LiCl in order to ensure that the unreacted complex remained in the trichloro form. However, a plot of k_{obsd} vs. [amine] was not linear, the departure being most significant at the lower amine concentrations, Figure 1. The curvature is much less pronounced at [LiCl] = 0.10 M ($LiClO_4$ being added to maintain $\mu = 0.505$), and at [LiCl] = 0.015 M ($\mu = 0.505$) the normal linear relationship $k_{obsd} = k^f_1 + k^f_2[am]$ is obeyed. At this chloride concentration the bulk (91%) of the substrate is in the form of the trichloro complex and so a chloride concentration of 0.015 M was chosen as the optimum conditions for minimizing mass law retardation of the k^f_1 pathway without, at the same time, diverting significant quantities of the starting material to the more reactive solvento species.

The reactions with the other amines were studied at a single Cl^- concentration of 0.015 M. The behavior of pyridine and 4-methylpyridine closely resembles that of 3,4-dimethylpyridine. The halogeno- and cyanopyridines caused "cut out" at longer wavelengths and the reaction with 3-bromo- and 4-cyanopyridine had no isosbestic points within the range of wavelength scanned. The aliphatic amines absorb less strongly at the lower wavelengths and the scans could be extended to 250 nm, thereby revealing a new isosbestic point between 263 and 268 nm. The three isosbestic points were well defined, except for the reactions involving the four most basic amines where they did not develop until after the first two or three scans were complete. In the reaction with piperidine there was a further slow reaction after the main substitution was complete that was characterized by a general decrease in absorbance over the whole range of wavelength studied. This was not observed in the presence of 0.5 M LiCl. The wavelength of the first isosbestic point in the reaction with ethylenediamine differs sufficiently from the others to suggest that the first observed product is $Pt(Me_2S)(en)Cl^+$. The pseudo-first-order rate constants were determined in duplicate over a 15-fold range of amine concentration and the plots of k_{obsd} vs. [amine] were linear. The slopes, k^f_2, and intercepts, k^f_1, were evaluated by a linear least-squares analysis and are collected in Table II.

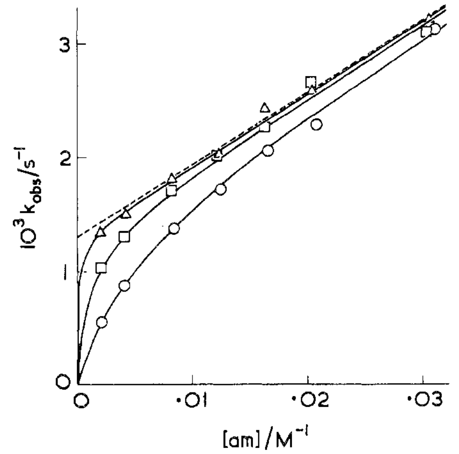

Figure 1. Pseudo-first-order rate constants for the reaction $Pt(Me_2S)Cl_3^- + 3,4\text{-}Me_2py \rightarrow$ *trans*-$Pt(Me_2S)(3,4\text{-}Me_2py)Cl_2 + Cl^-$ in methanol at 30.0 °C, $\mu = 0.505$, in the presence of (○) 0.505 M, (□) 0.105 M, and (△) 0.015 M LiCl, respectively. The curves are calculated from the expression $k_{obsd} = k^f_1 k^-_{am}[am](k^i_{Cl}[Cl^-] + k^i_{am}[am])^{-1} + k^f_2[am]$ with $k^f_1 = 1.30 \times 10^{-3}\ s^{-1}$, $k^f_2 = 6.35 \times 10^{-2}\ M^{-1}\ s^{-1}$, and $k^i_{am}/k^i_{am} = 115$. The line for $k_{obsd} = k^f_1 + k^f_2[am]$ is also shown.

Attempts to examine the reverse reaction were unsuccessful except in the case of the complex of the weakly basic 3-chloropyridine. For example, the spectrum of a solution of *trans*-$Pt(Me_2S)(3,4\text{-}Me_2py)Cl_2$ in methanol in the presence of 0.50 M LiCl and 0.10 M $HClO_4$ did not change significantly

Table III. Displacement of 3-Chloropyridine from *trans*-$Pt(Me_2S)(3\text{-}Cl\text{-}py)Cl_2$ in Acidified Methanol[a-c]

$[Cl^-]/M$	0.051	0.10	0.144	0.30	0.40	0.40	0.50[h]
$10^5 k^r/s^{-1}$ [d]	4.12[e]	4.41[e,f]	4.31[e]	4.97[g]	5.57[g]	5.38[f]	6.03[g]

[a] At 29.5 °C. [b] $\mu = 0.50$ ($LiClO_4$). [c] [Complex] = 1.0×10^{-4} M. [d] Measured spectrophotometrically at 301 nm. $k^r = k^r{}_1 + k^r{}_2[Cl^-]$. From least-squares analysis $k^r{}_1 = (3.9 \pm 0.1) \times 10^{-5}$ s^{-1} and $k^r{}_2 = (4.1 \pm 0.3) \times 10^{-5}$ M$^-$ s^{-1}. [e] $[H^+] = 0.20$ M. [f] Complex prepared in situ by allowing 10^{-2} M solutions of $Et_4N[Pt(Me_2S)Cl_3]$ and 3-chloropyridine to equilibrate. Reaction started by adding 0.10 mL of equilibrated solution to 10.0 cm^3 of $LiCl/HClO_4/LiClO_4$ solution in the spectrophotometer cell. [g] $[H^+] =$ 0.10 M. [h] $\mu = 0.60$.

at 30 °C over a period of 24 h, and at much longer times there was a general increase in absorbance that did not match, in any way, the changes expected for the reverse reaction. However, with *trans*-$Pt(Me_2S)(3\text{-}Cl\text{-}py)Cl_2$ the spectra do retrace the path of the formation reaction but complications still arise from a process that leads to a general increase of absorbance over the whole range of wavelength scanned, probably due to oxidation to Pt(IV), but this is only serious at the lowest chloride concentrations. Because of the low basicity of 3-chloropyridine the rate of its displacement from the complex was not completely independent of the concentration of the added acid and, when the acid concentration was as low as 0.10 M, the reaction did not go to completion at the lowest chloride concentrations used. When necessary, calculated values for A_∞, based on the spectrum of an equimolar mixture of $Pt(Me_2S)Cl_3^-$ and $3\text{-}Cl\text{-}pyH^+$, were used in the calculation of k_{obsd}. In these cases the initial slope of the curved semilogarithmic plot was used. These rate constants are collected in Table III.

Discussion

Provided the amount of free chloride is less than ca. 0.015 M, the reaction between $Pt(Me_2S)Cl_3^-$ and amines follows the usual two-term rate law for substitution in four-coordinate planar d^8 complexes. Within the range of amine concentrations studied (0.002–0.03 M) the solvolytic path makes a significant contribution to the rate of reaction and, unlike the case of the analogous reaction with the dimethyl sulfoxide complex,[3] reasonably precise values could be obtained for both $k^f{}_1$ and $k^f{}_2$. Deviations from this simple rate law at higher chloride concentrations can be explained in terms of competition between chloride and amine for the reactive solvento intermediate.[10] For the reaction sequence

$$Pt(Me_2S)Cl_3^- + MeOH \underset{k^i{}_{Cl}}{\overset{k^f{}_1}{\rightleftharpoons}} trans\text{-}Pt(Me_2S)(MeOH)Cl_2 + Cl^-$$

$$trans\text{-}Pt(Me_2S)(MeOH)Cl_2 + am \xrightarrow{k^i{}_{am}} trans\text{-}Pt(Me_2S)(am)Cl_2 + MeOH$$

$$Pt(Me_2S)Cl_3^- + am \xrightarrow{k^f{}_2} trans\text{-}Pt(Me_2S)(am)Cl_2 + Cl^-$$

the observed first-order rate constant (assuming $[Cl^-]$ and [am] are large compared to [complex]) is given by the relationship

$$k_{obsd} = \frac{k^f{}_1 k^i{}_{am}[am]}{k^i{}_{Cl}[Cl^-] + k^i{}_{am}[am]} + k^f{}_2[am]$$

By plotting $(k_{obsd} - k^f{}_2[am])^{-1}$ against $[Cl^-]/[am]$ a straight line with slope $k^i{}_{Cl}/k^i{}_{am}k^f{}_1$ and intercept $1/k^f{}_1$ should be obtained. $k^f{}_2$ was varied to obtain the best fit and the derived values are $k^f{}_2 = (6.35 \pm 0.05) \times 10^{-2}$ M^{-1} s^{-1}, $k^f{}_1 = (1.30 \pm 0.02) \times 10^{-3}$ s^{-1}, and $k^i{}_{am}/k^i{}_{Cl} = 115 \pm 4$. These values are used to calculate the curves in Figure 1. A linear least-squares analysis of k_{obsd} vs. [am] gives $k^f{}_2 = (6.57 \pm 0.26) \times 10^{-2}$ M^{-1} s^{-1} and $k^f{}_1 = (1.25 \pm 0.04) \times 10^{-3}$ s^{-1}. The errors introduced by ignoring mass law retardation at $[Cl^-] = 0.015$ M are thus negligible. The analogous reaction with $Pt(Me_2SO)Cl_3^-$ was not carried out under conditions where mass law retardation could be examined in detail but the absence of detectable retardation at $[Cl^-] = 0.50$ M suggests that $k^i{}_{am}/k^i{}_{Cl}$ is probably greater than 150.[3] In the reaction between *trans*-$Pt(PEt_3)_2$(*o*-tol)Cl and heterocyclic amines in methanol at 30 °C the ratio $k^i{}_{am}/k^i{}_{Cl}$ is essentially independent of the basicity of the amine (but very sensitive to methyl substituents in the 2 and 6 positions) and is only about 1.5×10^{-3}; i.e., chloride is a much more effective scavenger for the methanolo complex than the amine.[12] Even taking into account the fact that this is a very sterically hindered system, it is clear that the relative nucleophilicities of chloride and amines for a methanoloplatinum(II) complex are extremely sensitive to the nature of the other ligands attached to the metal. In view of the similarity of the $n°_{Pt}$ values for chloride (3.04)[13] and pyridine (3.19)[13] these results serve as a reminder that a detailed study of the extent to which the concept of nucleophilicity scales applies to Pt(II) is long overdue.

The values of $k^f{}_1$ obtained from the intercept of the plot of k_{obsd} against [am] assuming that, at $[Cl^-] = 0.015$ M, the mass law retardation was negligible, are, for the most part, independent of the nature of the entering amine. Most lie within the range $(1.1\text{–}1.3) \times 10^{-3}$ s^{-1}. The rate constant for the $[OH^-]$- and $[Cl^-]$-independent base hydrolysis of $Pt(Me_2S)Cl_3^-$ is 1.38×10^{-3} s^{-1} suggesting that, even at 0.015 M Cl^-, there is a small amount of mass law retardation at the lower amine concentrations. The solvolytic reaction was also studied in the absence of both hydroxide and amine. A solution of the complex (6.0×10^{-4} M) in methanol ($\mu = 0.50$ ($LiClO_4$)) was allowed to come to solvolytic equilibrium at 30.0 °C and a small, accurately measured quantity of 1.00 M LiCl solution was added. The approach to the new position of equilibrium was followed spectrophotometrically and the first-order rate constant, k_{obsd}, determined in the usual way. For a reversible solvolysis of the form

$$Pt(Me_2S)Cl_3^- + MeOH \underset{k^i{}_{Cl}}{\overset{k^f{}_1}{\rightleftharpoons}} trans\text{-}Pt(Me_2S)(MeOH)Cl_2 + Cl^-$$

the specific rate constant for approach to equilibrium, k_{obsd}, obeys the relationship $k_{obsd} = k^f{}_1 + k^i{}_{Cl}[Cl^-]$. The plot of k_{obsd} against $[Cl^-]$ was linear with slope $k^i{}_{Cl} = 1.07 \pm 0.05$ M^{-1} s^{-1} and intercept, $k^f{}_1 = (1.54 \pm 0.28) \times 10^{-3}$ s^{-1}. It is thus possible to obtain the equilibrium constant for the solvolysis, $K = k^f{}_1/k^i{}_{Cl} = 1.4 \times 10^{-3}$ M. Therefore, at equilibrium in the presence of 0.015 M Cl^- (the conditions used in the study of amine entry) about 91% of the complex is present as the trichloro anion and the rest has been solvolyzed.

It is of interest to examine those nucleophiles that lead to $k^f{}_1$ values significantly different from the average. The most basic amines, piperidine, *n*-butylamine, and, to a lesser extent, cyclohexylamine, have smaller values for $k^f{}_1$ ($(0.9\text{–}1.0) \times 10^{-3}$ s^{-1}). In the reactions of the corresponding dimethyl sulfoxide complex,[3] the $k^f{}_1$ participation seemed to disappear completely with these amines, but the accuracy in determining $k^f{}_1$ was too low for any definite conclusion to be drawn. The unusual behavior at the beginning of the reactions between $Pt(Me_2S)Cl_3^-$ and the more basic amines is probably due to the consumption of the less labile deprotonated solvento species derived from the material present at equilibrium when the reaction started. The analogous reaction in the presence of the less basic amines, which would not deprotonate the solvento species, would be much faster and complete before the first spectrum was measured. It is also possible that deprotonation of the solvento species formed by the $k^f{}_1$ step interferes with this reaction pathway. A much more searching investigation of the system is required before this point can be settled. The other outstanding anomaly occurs in the reaction with piperazine, where k^f_1 is ca. 2×10^{-3} s^{-1}. The anomalously high reactivity of the bifunctional nucleophiles will be discussed below but, in general, the effect is confined to the k^f_2 pathway. This is the only example in this work where the k^f_1 term is also affected. It is possible that the anchiomeric assistance can arise from interaction between the N–H and the leaving chloride while the other end of the nucleophile is not committed to attacking the metal but hydrogen bonded to the entering solvent molecule; it is not clear why this behavior is confined to piperazine.

The second-order rate constants, k^f_2, demonstrate clearly the long known fact that proton basicity is not an important factor in determining the reactivity of amines toward platinum(II). The basicity of the amines examined covers the range $0.67 < pK_a < 11.12$ while the rate constants for the monofunctional amines are encompassed by a factor of 3. It is foolhardy to seek explanations for the small variations within this range and it is quite likely that the orderings might differ at different temperatures. Nevertheless it is of interest to note that, as in the reactions with $Pt(Me_2SO)Cl_3^-$, the least basic heterocyclic amine has the largest k^f_2 value and there is a rough linear relationship of the form $\log k^f_2 = -0.1pK_a(amH^+) + c$ for the substituted pyridines. This may arise from a small contribution toward the reactivity from the π-acceptor properties of the pyridine. Cattalini[14] has drawn attention to the possibility of such "biphilicity" (although not in connection with heterocyclic amines) and has suggested that its effectiveness increases as the effective nuclear charge of the reaction center decreases. Indeed, the departures from linear relationships between $\log k_2$ and $n°_{Pt}$ are most marked when the substrate is anionic, as in our case. In all of the other extensive studies of the entry of heterocyclic amines into four-coordinate planar substrates k_2 increases with increasing basicity of the amine. For example, in the reaction between $Pt(bpy)Cl_2$ and amines, all of the reagents studied, provided they did not generate steric hindrance, obeyed the relationship $\log k_2 = 0.057\ pK_a(amH^+) - 2.56$.[15] Thus, while the reactivity did not vary much from amine to amine, the least basic was the least reactive. A similar relationship was found with $AuCl_4^-$ [16] where the response to basicity was even more marked, the slope being 0.15. Although this is an anionic complex, the higher effective nuclear charge of Au(III) compared to that of Pt(II) is likely to reduce the importance of biphilic behavior. Cationic Au(III) complexes give even larger positive slopes.[17]

The unusually high reactivity of the "bifunctional" amines is of considerable interest. The anomalous behavior of morpholine in its reactions with $Pt(Me_2SO)Cl_3^-$ has already been noted.[3] The effect is confirmed with the dimethyl sulfide complex and found to be more extensive. Piperazine, where the oxygen of morpholine is replaced by NH, is even more reactive, the effect even extending to the k^f_1 pathway. The same effect, but somewhat less pronounced, is found in the case of the more flexible molecules ethylenediamine and ethanolamine where, once again, the two-nitrogen reagent is more effective than the nitrogen–oxygen species. Cattalini et al.[18] reported enhanced reactivity of diamines with $Pt(bpy)Cl_2$ and discussed this in terms of an anchoring effect in which the nonattacking part of the nucleophile somehow attaches itself to the substrate, thereby enhancing the chances of the donor end to attack the platinum. In their case, however, the enhanced rate constants are never more than twice that for *n*-butylamine (enH^+ has the same reactivity as $n\text{-}BuNH_2$) suggesting that the effect is statistical. Piperazine, which in our system is very effective, is a poor nucleophile in comparison. Natile et al.[19] found clear evidence that the rate of ring closure in dien and tren complexes of Pt(II) (dien = bis(2-aminoethyl)amine and tren = tris(2-amionethyl)amine) is faster when a NH_3^+ group is present and suggested that ion pairing between this and the leaving chloride facilitates the reaction. In our case, such cationic groupings are not present and hydrogen bonding is not available for morpholine. The anchoring effect would seem to be the most plausible explanation, with the nonattacking end of the nucleophile "solvating" an axial site of the complex substrate. Apart from ethylenediamine, none of these nucleophiles undergo rapid subsequent ring closure under the experimental conditions used.

The systematic study of the reverse reaction was unsuccessful because the reactions were masked by other changes that slowly took place in solution. In the case of *trans*-$Pt(Me_2S)(3,4\text{-}Me_2py)Cl_2$ in 0.10 M $HClO_4$ in methanol at 30 °C, no change in spectrum was observed after 24 h, even in the presence of 0.5 M LiCl. At longer times the changes are not consistent with a simple replacement of amine by chloride. Since more than 5% reaction would easily be noticed, an upper limit can be set for $k^r < -(\ln 0.95)/24 \times 3600 < 5.9 \times 10^{-7}$ s^{-1}. It is possible to use this information to set a lower limit for the value of K, the equilibrium constant, by using the relationship $K = k^f_2/k^r_2 = k^f_1 k^i_{am}/k^r_1 k^i_{Cl}$ where $k^r = k^r_1 + k^r_2[Cl^-]$ and all the other constants have been discussed previously. Using $k^f_1 = 1.30 \times 10^{-3}$ s^{-1}, $k^f_2 = 6.35 \times 10^{-2}$ M^{-1} s^{-1}, and $k^i_{am}/k^i_{Cl} = 115$, for $[Cl^-] = 0.505$ M, $k^r_2 = (k^i_{Cl}k^f_2/k^i_{am}k^f_1)k^r_1 = 0.42k^r_1$. Since $k^r = k^r_1 + k^r_2[Cl^-] < 5.9 \times 10^{-7}$ s^{-1}, $k^r_1 < 5.0 \times 10^{-7}$ s^{-1} and $k^r_2 < 2.1 \times 10^{-7}$ M^{-1} s^{-1}. Therefore $K = k^f_2/k^r_2 > 6.6 \times 10^{-2}/2.1 \times 10^{-7} > 3.1 \times 10^5$. Only in the case of 3-chloropyridine was the study of the reverse reaction successful and k^r_1 ($(3.9 \pm 0.1) \times 10^{-5}$ s^{-1}) and k^r_2 ($(4.1 \pm 0.3) \times 10^{-5}$ M^{-1} s^{-1}) were evaluated. The equilibrium constant, K, was obtained from $k^f_2/k^r_2 = 1.3 \times 10^{-1}/4.1 \times 10^{-5} = 3.2 \times 10^3$.

It now remains to compare the trans-labilizing properties of dimethyl sulfide and dimethyl sulfoxide. It was predicted that the sulfide, by virtue of its poorer π-acceptor ability, would be a less effective stabilizer of the transition state, although this effect might be countered by a somewhat greater ground-state weakening of the trans metal–ligand bond.[3] However, there is no evidence for such a ground-state difference in ν(Pt–Cl) and the far-infrared spectra of the $Pt(Me_2S)Cl_3^-$ and $Pt(Me_2SO)Cl_3^-$ ions are remarkably similar. Where comparison can be made, it is found that all of the dimethyl sulfide complexes react more slowly than their dimethyl sulfoxide analogues but the extent of retardation depends upon the natures of the substrate and the reactions being studied. Thus, the values of k^f_2 for the reactions of the most basic amines (piperidine, *n*-butylamine, and cyclohexylamine) with $Pt(L)Cl_3^-$ are some 20 times smaller for L = Me_2S than for L = Me_2SO, whereas for the less basic amines the ratio is nearer 13. The ratio of the solvolysis rate constants k^f_1 is between 6 and 7. It would be of interest to study the reactions of these substrates with a range of stronger nucleophiles to see whether this is the consequence of a difference in the nucleophilic discrimination abilities of the two substrates. It has been suggested that the strong trans-effect ligands lead to a lower nucleophilic discrimination ability coupled with a greater intrinsic reactivity.[20] This would appear to operate in the opposite direction to our preliminary observations but the systems being compared are totally different. Belluco's examples are taken from the series *trans*-$Pt(PEt_3)_2(L)Cl$ in which there is considerable steric crowding and in which the high trans-labilizing power of L comes from a ground-state bond-weakening effect.

In the only case where we have been able to measure rate constants for the reverse reaction, k^r_2 for the replacement of 3-chloropyridine from *trans*-$Pt(Me_2S)(3\text{-}Cl\text{-}py)Cl_2$ by chloride is 4.1×10^{-5} M^{-1} s^{-1} and is some 130 times smaller than the corresponding value for the dimethyl sulfoxide complex;[3] k^f_1 is some 75 times smaller. This significant difference of the trans effect on the forward and the backward reaction means that a change from dimethyl sulfoxide to dimethyl sulfide strongly affects the equilibrium constant which increases from 3.1×10^2 to 3.2×10^3. This is not an isolated observation and it is clear that the minimum value for the equilibrium constant for the analogous reaction with the 3,4-dimethylpyridine complex, 5.1×10^5, is considerably greater than that measured for the corresponding dimethyl sulfoxide complex (1.6×10^4).[3] It is therefore not possible to explain the difference in the trans effects of Me_2S and Me_2SO solely in terms of transition-state effects.

It would now be of interest to compare the trans effects of Me_2S and Me_2SO in the reaction *cis*-$Pt(L)(am)Cl_2 + am =$ *cis*-$Pt(L)(am)_2Cl^+ + Cl^-$ to see whether the difference between sulfides and sulfoxides is even more marked in cationic substrates.

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Registry No. $Et_4N[Pt(Me_2S)Cl_3]$, 62571-71-5; *trans*-$Pt(Me_2S)(3,4\text{-}Me_2py)Cl_2$, 62571-72-6; *trans*-$Pt(Me_2S)(py)Cl_2$, 31203-93-7; *trans*-$Pt(Me_2S)(3\text{-}Cl\text{-}py)Cl_2$, 62571-73-7; *trans*-$Pt(Me_2S)_2Cl_2$, 17457-51-1; $Pt_2Cl_4(C_2H_4)_2$, 15905-87-0; piperidine, 110-89-4; *n*-butylamine, 109-73-9; ethylenediamine, 107-15-3; cyclohexylamine, 108-91-8; piperazine, 110-85-0; ethanolamine, 75-39-8; cyclopropylamine, 765-30-0; morpholine, 110-91-8; 3,4-dimethylpyridine, 583-58-4; 4-methylpyridine, 108-89-4; pyridine, 110-86-1; 3-chloropyridine, 626-60-8; 3-bromopyridine, 626-55-1; 4-cyanopyridine, 100-48-1; 3,5-dichloropyridine, 2457-47-8.

Supplementary Material Available: A table of observed first-order rate constants, k_{obsd}, for the reaction $Pt(Me_2S)Cl_3^- + am =$ *trans*-$Pt(Me_2S)(am)Cl_2 + Cl^-$ in methanol at 30.0 °C, $[LiCl] = 0.015$ M, and $\mu = 0.505$ and a table of specific rate constants for the approach to equilibrium for the process $Pt(Me_2S)Cl_3^- + MeOH = Pt(Me_2S)(MeOH)Cl_2 + Cl^-$ at $\mu = 0.50$ ($LiClO_4$ in methanol), 30.0 °C, and [complex] $= 6.0 \times 10^{-4}$ M (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
State University of New York at Albany, Albany, New York 12222

N-Organotin Aziridines and Other Cyclic Amines and Their Adducts

M. E. BISHOP and J. J. ZUCKERMAN*[1]

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N-Trimethyltin aziridine is shown to possess an associated solid-state structure involving nitrogen→tin coordination on the basis of its crystalline state at ambient temperature and larger ^{119m}Sn Mössbauer quadrupole splitting (QS), a dimeric structure in benzene from osmometry and the identical QS in frozen *n*-butylbenzene, and the retention of these structures in the gas phase from the observation of 12 ditin fragments larger than the parent molecular ion in the mass spectrum. 2-Methyl and 2,2-dimethyl substitution or use of cyclic amines with rings of four to seven members disrupts the association. *N*-Trimethyltin aziridine is synthesized by trans- and lithioamination reactions and undergoes hydrolysis, methanolysis, carbonylation, acid cleavage with hydrogen chloride and cyclopentadiene, and transamination reactions with higher amines as well as insertion reactions with the dipolar, unsaturated substrates carbon dioxide and disulfide, phenyl isocyanate and isothiocyanate, acetone, and diethylacetylene dicarboxylate and with tetrasulfur tetranitride. Boron trifluoride is removed from its etherate as a 1:1 complex which is inert to refluxing triethylamine. The 1:1 carbon dioxide insertion product has the aziridine ring intact in an axially associated, trigonal-bipyramidal structure, but 2 mol of carbon disulfide reacts to form a solid thiazolidone which is associated through sulfur→tin axial bridging. The carbon dioxide adduct is converted to the carbon disulfide adduct by treatment with CS_2. Heating the 1:1 adduct with phenyl isocyanate which is bonded through nitrogen yields the corresponding imidazolin-2-one, while the analogous 1:1 thio adduct is bonded through sulfur, the acetone adduct is bonded through oxygen, and the acetylene adduct contains a cis tin enamine. Reaction with tetrasulfur tetranitride yields bis(1-aziridinyl) sulfide and *N*,*N*′-bis(trimethylstannyl)sulfur diimide. Complete infrared and ^1H and ^{13}C NMR assignments are made. The absence of the two-bond $|^2J(^{119}Sn\text{–}N\text{–}^{13}C)|$ couplings in all but the *N*-trimethyltin cyclic amines with ring sizes of greater than five is interpreted in terms of bimolecular exchange of NR_2 groups in the concentrated solutions studied.

Introduction

Aziridine (ethylenimine) holds an especial place among amines[2] because of its small steric bulk and the exceptional electrical properties of its three-membered ring. Aziridine is a weaker base than dimethylamine, and the possibility of ring opening provides another dimension to its chemistry. The poorer proton-acceptor ability reflects the diminished availability of the lone electron pair on nitrogen owing to its interaction with the ring. The order of pK_a and hydrogen-bonding values among the cyclic imines $(CH_2)_nNH$ and $(CH_2)_nNCH_3$ is $n = 3 << 6 < 5 < 4$.[2]

N-Trimethyltin aziridine has been synthesized by transamination,[3] and the germanium analogue, by lithioamination.[4] The triethylgermyl analogue[5] and over 30 triorganosilyl-