The two high-frequency bands may presumably be assigned to charge-transfer transitions. The 16-kK band is presumably due to an inverted electron-transfer transition[17] (*i.e.*, from the metal to the ligand). The ligand in fact has low-lying $\pi^*$ levels, as shown by the electronic spectrum, where the band in the region 33-39 kK has been attributed to $\pi$-$\pi^*$ transitions.[18] Such bands have been observed also in the present case, practically unshifted compared to the free ligand. It is possible then that napy acts similarly to other nitrogen heterocyclic ligands, such as phenanthroline and dipyridine, which are known to stabilize the low oxidation states of transition metal ions.[19] The single-crystal spectrum shows that the band at 16 kK is polarized perpendicularly, as would be expected for a charge-transfer transition involving the nickel and nitrogen atoms.[20] The 26-kK band could not be satisfactorily analyzed since it is at the limit of operation of our apparatus.

**Acknowledgment.** Thanks are due to Mr. G. Scapacci for technical assistance.

**Registry No.** Ni(napy)$_2$Br$_2$, 51425-51-5; Ni(napy)$_2$I$_2$, 51425-52-6; Ni(menapy)$_2$Br$_2$, 51464-62-1; Ni(menapy)$_2$(NCS)$_2$, 51425-21-9; Ni(napy)$_2$ClB(C$_6$H$_5$)$_4$, 51425-23-1; Ni(napy)$_2$BrB(C$_6$H$_5$)$_4$, 51425-25-3; [Ni$_2$(napy)$_4$Cl$_2$]B(C$_6$H$_5$)$_4$, 51518-88-8; [Ni$_2$(napy)$_4$Br$_2$]B(C$_6$H$_5$)$_4$, 39391-56-5; [Ni$_2$(napy)$_4$I$_2$]B(C$_6$H$_5$)$_4$, 51518-89-9; [Ni$_2$(napy)$_4$(NO$_3$)$_2$]B(C$_6$H$_5$)$_4$, 51518-90-2; [Ni$_2$(napy)$_4$(NCS)$_2$]B(C$_6$H$_5$)$_4$, 51518-91-3; [Ni$_2$(napy)$_4$Cl$_2$]PF$_6$, 51518-92-4; [Ni$_2$(napy)$_4$Br$_2$]PF$_6$, 51518-93-5; [Ni$_2$(napy)$_4$I$_2$]PF$_6$, 51518-94-6; [Ni$_2$menapy)$_4$Cl$_2$]B(C$_6$H$_5$)$_4$, 51518-95-7; [Ni$_2$(menapy)$_4$Br$_2$]B(C$_6$H$_5$)$_4$, 51518-96-8; [Ni$_2$(menapy)$_4$I$_2$]B(C$_6$H$_5$)$_4$, 51518-97-9; [Ni$_2$(menapy)$_4$(NCS)$_2$]B(C$_6$H$_5$)$_4$, 51518-98-0; [Ni$_2$(menapy)$_4$Cl$_2$]PF$_6$, 51518-99-1; [Ni$_2$(menapy)$_4$Br$_2$]PF$_6$, 51519-00-7; [Ni$_2$(menapy)$_4$I$_2$]PF$_6$, 51519-01-8.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1985.

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(18) B. Tinland, *Theoret. Chim. Acta*, **8**, 361 (1967).

(19) W. R. Mc Whinnie and J. D. Miller, *Advan. Inorg. Chem. Radiochem.*, **12**, 135 (1969).

(20) P. Day and N. Sanders, *J. Chem. Soc.*, 1536 (1967).

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# Kinetics of the Reversible Replacement of Amine by Chloride under the Trans Effect of Dimethyl Sulfoxide in Square-Planar Platinum(II) Complexes

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The rate constants for the forward and reverse steps of the reaction [PtCl$_3$(DMSO)]$^-$ + am $\rightleftarrows$ *trans*-[PtCl$_2$(DMSO)(am)] + Cl$^-$ (DMSO = S-bonded dimethyl sulfoxide; am is one of a number of amines covering a wide range of basicity) have been determined in methanol at 30.0° at constant ionic strength (0.50). The forward reaction goes mainly by way of the direct bimolecular attack of amine on the complex and the rate constant does not depend greatly upon the nature of the nucleophile, although small trends can be detected within the subgroups of amine used. The reverse reaction obeys the usual two-term rate law observed in square-planar substitution, and the nucleophile-independent, solvolytically controlled path carries a major part of the reaction. The first- and second-order rate constants decrease as the basicity of the leaving amine increases and plots of log $k^r{}_1$ and log $k^r{}_2$ against the p$K_a$ of the conjugate acids of the amines are parallel straight lines with a slope of −0.55. The equilibrium constants for these reactions have been determined from the ratio of the rate constants and a plot of log $K$ against the p$K_a$ of the amines is linear with a slope of 0.57.

## Introduction

In a recent paper,[2] we reported the kinetics of the reversible displacement, by chloride, of the amine ligand trans to dimethyl sulfoxide in complexes of the type *cis*-[Pt(am)$_2$(DMSO)Cl]Cl, the amines being members of a series of primary alicyclic amines ranging from cyclopropylamine to cyclooctylamine. Although the original intention was to examine the way in which the lability of the complex related to the basicity of the leaving group, it was found that the other amine ligand produced a very strong cis effect that followed the same dependence on basicity as the leaving group effect and was almost as large. Complexes of this type with less basic amines were not stable enough to allow a satisfactory investigation of the leaving group effect over a sufficiently wide range of amine basicity and so, in order to extend the range and to maintain a constant cis effect, we turned our attention to the forward and reverse steps of the reaction

$$[\mathrm{PtCl_3(DMSO)}]^- + \mathrm{am} \underset{k^r}{\overset{k^f}{\rightleftarrows}} trans\text{-}[\mathrm{PtCl_2(am)(DMSO)}] + \mathrm{Cl}^- \qquad (1)$$

It was possible to prepare, characterize, and study the complexes of a wide range of primary, secondary, and heterocyclic amines covering a range of basicity 2.84 < p$K_a$ < 8.66 and to measure the rates of the forward reaction for a similar range of amines but covering the range 2.84 < p$K_a$ < 11.12.

## Experimental Section

**Preparations.** Potassium trichloro(dimethyl sulfoxide)platinate(II) was prepared by two of the three methods reported by Kukushkin,[3] namely, (i) the action of KCl upon a suspension of *cis*-[Pt(DMSO)$_2$Cl$_2$] in water[4] and (ii) the reaction between equimolar

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(2) P. D. Braddock, R. Romeo, and M. L. Tobe, *Inorg. Chem.*, 13, 1170 (1974).

(3) Y. N. Kukushkin, Y. E. Vyazmenskii, and L. I. Zorina, *Russ. J. Inorg. Chem.*, 13, 1573 (1968).

(4) The original preparation called for equimolar amounts of the two reagents but this leaves a considerable amount of unreacted starting material. We found that a fourfold excess of KCl gave a better product.

**Table I.** Analytical Data for Complexes of the Type *trans*-[$PtCl_2$(DMSO)(am)]

| am | Formula | % C |  | % H |  | % N |  |
|---|---|---|---|---|---|---|---|
|  |  | Calcd | Found | Calcd | Found | Calcd | Found |
| Piperidine[a] | $C_7H_{17}Cl_2NOSPt$ | 19.6 | 19.4 | 4.00 | 3.96 | 3.26 | 3.36 |
| *n*-Butylamine | $C_6H_{17}Cl_2NOSPt$ | 17.3 | 17.0 | 4.10 | 3.94 | 3.35 | 3.48 |
| Cyclohexylamine | $C_8H_{19}Cl_2NOSPt$ | 21.7 | 21.5 | 4.32 | 4.03 | 3.16 | 3.19 |
| Cyclopropylamine | $C_5H_{13}Cl_2NOSPt$ | 15.0 | 14.8 | 3.26 | 3.12 | 3.42 | 3.57 |
| Morpholine[a] | $C_6H_{15}Cl_2NO_2SPt$ | 16.7 | 16.1 | 3.50 | 3.42 | 3.24 | 3.23 |
| 3,4-Dimethylpyridine | $C_9H_{15}Cl_2NOSPt$ | 23.9 | 23.7 | 3.35 | 3.12 | 3.10 | 3.09 |
| 4-Methylpyridine[b] | $C_8H_{13}Cl_2NOSPt$ | 22.0 | 21.8 | 3.00 | 2.75 | 3.20 | 3.17 |
| Pyridine[c] | $C_7H_{11}Cl_2NOSPt$ | 19.9 | 19.8 | 2.62 | 2.47 | 3.31 | 3.49 |
| 3-Chloropyridine | $C_7H_{10}Cl_3NOSPt$ | 18.4 | 18.4 | 2.20 | 2.09 | 3.06 | 3.07 |
| Aniline | $C_8H_{13}Cl_2NOSPt$ | 22.0 | 22.4 | 3.00 | 2.90 | 3.20 | 3.33 |
| 4-Chloroaniline | $C_8H_{12}Cl_3NOSPt$ | 20.4 | 20.3 | 2.56 | 2.46 | 2.97 | 2.94 |
| 3-Chloroaniline | $C_8H_{12}Cl_3NOSPt$ | 20.4 | 20.4 | 2.56 | 2.44 | 2.97 | 3.02 |
| 3-Bromopyridine | $C_7H_{10}Cl_2BrNOSPt$ | 16.7 | 16.6 | 2.00 | 2.04 | 2.72 | 2.90 |

[a] Y. N. Kukushkin and V. A. Yurinov, *Russ. J. Inorg. Chem.*, 16, 601 (1971). [b] Y. N. Kukushkin and E. D. Ageeva, *ibid.*, 17, 767 (1972). [c] Reference 3.

amounts of $K_2PtCl_4$ and dimethyl sulfoxide. In our hands the second method was superior in many respects. As with many of these dimethyl sulfoxide complexes it was important to obtain the compound initially in as pure a form as possible since subsequent recrystallization served mainly to reduce the yield. *Anal.* Calcd for $C_2H_6Cl_3OSPt$: C, 5.74; H, 1.45; Cl, 25.40. Found: C, 5.57; H, 1.49; Cl, 25.43.

*trans*-Dichloro(pyridino)(dimethyl sulfoxide)platinum(II) was prepared by a modification of the method of Kukushkin[3] in which an equimolar amount of pyridine was added drop by drop to a stirred solution of K[$PtCl_3$(DMSO)] (0.2 g) in water (7 ml). The complex separated out and was filtered off, washed with water, ethanol, and ether and air-dried. The analytical data are reported in Table I.

All of the other complexes of the type *trans*-[$PtCl_2$(am)(DMSO)] were prepared in a similar way. The analytical data are collected in Table I.

**Infrared spectra** of Nujol or hexachlorobutadiene mulls were measured with a Perkin-Elmer 225 instrument.

**Kinetics.** The techniques and equipment used are precisely the same as those described in the study of the reactions of the *cis*-[Pt(am)$_2$(DMSO)Cl]Cl complexes.[2]

## Results

### (a) Kinetics of the Displacement by Chloride of the Amine from *trans*-[PtCl$_2$(DMSO)(am)].

As in the case of the corresponding reaction of *cis*-[Pt(am)$_2$(DMSO)Cl]$^+$ the position of equilibrium strongly favors the amine coordination;[2] *i.e.*, the equilibrium in (1) lies well over to the right. However, in the presence of a small excess of acid, the protonation of the released amine forces the equilibrium well over to the left, even though the rate of reaction is independent of the concentration of acid. The displacement of amine was therefore studied in the presence of 0.01 *M* perchloric acid at constant ionic strength (0.50, $LiClO_4$) in methanol at 30.0° in the presence of excess chloride. In the reactions of the complexes containing the more labile amines the spectrum changes smoothly from that of the starting material to that of K[$PtCl_3$(DMSO)] together with that of amH$^+$ when this absorbs significantly in the region of spectrum studied. Under the experimental conditions the [$PtCl_3$(DMSO)]$^-$ anion undergoes further reaction at a rate that increases with the acid and chloride concentrations. This change is due, in part at least, to the oxidation of Pt(II) to Pt(IV) and the reduction of dimethyl sulfoxide to dimethyl sulfide.[2,5] While this reaction is too slow to interfere with the study of the displacement of the more labile amines, it does prevent the use of an experimental value for the infinity reading in the study of the displacement of the more strongly bound amines such as 3,4-dimethylpyridine and cyclopropylamine. The kinetics of the displacement of cyclohexylamine and the more basic amines could not be studied because the spectral changes were not consistent with the formation of [$PtCl_3$(DMSO)]$^-$ and it was not clear whether the redox process preceded or followed the displacement of the amine. The rates of the reactions were followed spectrophotometrically at 310 nm and the first-order rate constants determined graphically from the slope of the plot of log ($A_\infty - A_t$) against time, where $A_t$ and $A_\infty$ are the absorbances at time *t* and after 10 half-lives (except where the second stage interfered, in which case a value calculated from the spectrum of [$PtCl_3$(DMSO)]$^-$ was used). The reactions were carried out in the presence of sufficient excess of chloride to ensure first-order kinetics, at six separate concentrations in the range 0.05–0.5 *M*. The pseudo-first-order rate constants were plotted against [Cl$^-$] and the expected straight lines was observed, indicating a relationship of the form, $k^{r}{}_{obsd} = k^{r}{}_1 + k^{r}{}_2[Cl^-]$. Values of $k^{r}{}_1$ and $k^{r}{}_2$ are collected in Table II.

### (b) Kinetics of the Displacement of Chloride from [PtCl$_3$(DMSO)]$^-$ by Amine.

The reaction between [$PtCl_3$(DMSO)]$^-$ and amines in methanol at 30.0° is relatively fast and was conveniently followed with a Durrum-Gibson D110 stopped-flow-spectrophotometer. The reactions were slow enough for the output from the photonmultiplier to be displayed on a Servoscribe RE 511.20 potentiometric recorder as a function of time. The rate constants were determined in the usual way from the change in absorbance at a convenient wavelength within the region 330–340 nm.[6] In studying the reactions of [$PtCl_3$(DMSO)]$^-$ we were aware of the possibility of solvolysis. In aqueous solution, this complex rapidly loses the chloride trans to the dimethyl sulfoxide and an equilibrium is set up among the aquo complex, the hydroxo complex, and the chloro complex.[7] At 25° in aqueous solution, the equilibrium constant (neglecting the acid dissociation of the aquo complex) is $2.5 \times 10^{-3}$ *M*. It is likely that the solvolysis would be less pronounced in methanol but nevertheless the reactions were carried out in the presence of 0.50 *M* lithium chloride which served to maintain the same ionic strength as was used for the reverse reaction. At relatively high chloride concentrations the spectrum did not change with the amount of chloride present, indicating that solvolysis had been effectively prevented (or alternatively, but

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(5) Y. N. Kukushkin, Y. E. Vyazmenskii, L. I. Zorina, and Y. L. Pazukhina, *Russ. J. Inorg. Chem.*, 13, 835 (1968).

(6) The wavelength chosen depends upon the spectrum of the entering amine, now present in considerable excess, and does not necessarily correspond to the one used to follow the displacement of the amine.

(7) Y. N. Kukushkin and K. M. Trusova, *Russ. J. Inorg. Chem.*, 16, 139 (1971).

**Table II.** First- and Second-Order Rate Constants and Equilibrium Constants for the Reactions[a]

$$[PtCl_3(DMSO)]^- + am \underset{k^r_1 + k^r_2[Cl^-]}{\overset{k^f_1 + k^f_2[am]}{\rightleftharpoons}} trans\text{-}[PtCl_2(DMSO)(am)] + Cl^-$$

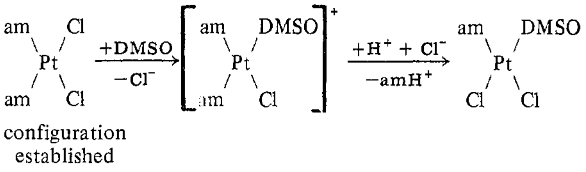
| am | $10^2k^f_1$, sec$^{-1}$ | $k^f_2$, $M^{-1}$ sec$^{-1}$ | $10^4k^r_1$, sec$^{-1}$ | $10^4k^r_2$, $M^{-1}$ sec$^{-1}$ | $10^{-3}K$ $(=k^f_2/k^r_2)$ | p$K_a$ of amH$^+$ |
|---|---|---|---|---|---|---|
| Piperidine | 0.0 ± 0.2 | 3.42 ± 0.05 | *b* | *b* | | 11.12 |
| *n*-Butylamine | 0.0 ± 0.2 | 2.77 ± 0.05 | *b* | *b* | | 10.77 |
| Cyclohexylamine | 0.0 ± 0.2 | 2.22 ± 0.05 | *b* | *b* | | 10.66 |
| Cyclopropylamine | 0.0 ± 0.2 | 2.02 ± 0.05 | 0.020 ± 0.002 | 0.10 ± 0.03 | 202 | 8.66 |
| Morpholine | 0.0 ± 0.2 | 9.18 ± 0.10 | 0.27 ± 0.01 | 0.92 ± 0.05 | 100 | 8.33 |
| 3,4-Dimethylpyridine | 1.0 ± 0.5 | 0.86 ± 0.02 | 0.37 ± 0.02 | 0.55 ± 0.05 | 15.6 | 6.50 |
| 4-Methylpyridine | 1.0 ± 0.5 | 0.95 ± 0.02 | 0.64 ± 0.02 | 1.21 ± 0.08 | 7.9 | 6.02 |
| Pyridine | 0.8 ± 0.3 | 0.96 ± 0.02 | 1.09 ± 0.03 | 1.96 ± 0.10 | 4.9 | 5.25 |
| Pyridine | 0.6 ± 0.3[c] | 0.84 ± 0.02[c] | | | | |
| Aniline | 0.5 ± 0.3 | 0.51 ± 0.02 | 3.8 ± 0.05 | 9.8 ± 0.30 | 0.52 | 4.63 |
| 4-Chloroaniline | 0.5 ± 0.4 | 0.38 ± 0.02 | 8.4 ± 0.08 | 15.1 ± 0.5 | 0.251 | 4.15 |
| 3-Chloroaniline | 0.5 ± 0.3 | 0.30 ± 0.02 | 14.2 ± 0.15 | 17.7 ± 1.0 | 0.169 | 3.46 |
| 3-Chloropyridine | 0.6 ± 0.3 | 1.62 ± 0.05 | 28.1 ± 0.3 | 52 ± 3.0 | 0.312 | 2.84 |
| 3-Bromopyridine | 0.5 ± 0.2 | 1.80 ± 0.05 | 31.3 ± 0.3 | 79 ± 4.0 | 0.227 | 2.84 |

[a] In methanol at 30.0°; $\mu = 0.50$ (LiCl) for forward reaction and 0.50 (LiClO$_4$) for the reverse reaction; [complex] = $2.0 \times 10^{-3}$ *M*; [H$^+$] = 0.010 *M* for the reverse reaction only. [b] Not measured. [c] [Cl$^-$] = 0.05 *M*; $\mu = 0.50$ (LiClO$_4$).

far less likely, that it was still complete). The spectral change associated with the substitution reaction was consistent with a single first-order process and there was no indication of any rapid previous change at short times after mixing. The reactions were studied in the presence of sufficient amine to ensure first-order kinetics and the rate constants were determined at six separate amine concentrations within the range 0.01–0.15 *M*, except in the case of am = morpholine when the range 0.0025–0.4 *M* was used and the concentration of the complex was reduced to $2.5 \times 10^{-4}$ *M*. The plots of $k_{obsd}$ against [am] are linear but only the less basic amines follow the usual behavior in having a finite intercept, $k^f_1$, that is independent of the nature of the nucleophile. The plots for the four most basic amines appear to pass through the origin. The slopes ($k^f_2$) and the intercepts obtained from a linear least-squares fit of these data are given in Table II.

## Discussion

The assignment of configuration to the complexes of the type [PtCl$_2$(am)(DMSO)] used in this work is of key importance in the subsequent discussion. Two isomeric forms of this type of complex were first obtained by Kukushkin for am = NH$_3$ and pyridine.[3] The assignment of configuration was based on chemical evidence which assumed a very high trans effect for S-bonded dimethyl sulfoxide, *i.e.*, K[PtCl$_3$(DMSO)] + NH$_3$ → *trans*-[PtCl$_2$(NH$_3$)(DMSO)] + KCl and K[PtCl$_3$(NH$_3$)] + DMSO → *cis*-[PtCl$_2$(NH$_3$)(DMSO)] + KCl. He also found that the yellow trans isomer changed to the off-white cis form on heating to its melting point. The isomeric pairs for am = 2-methyl-,[8] 3-methyl-,[8] and 4-methylpyridine,[8] morpholine,[9] and piperidine[9] were subsequently reported. We have prepared a series of pale yellow isomers of this type with am = C$_n$H$_{2n-1}$NH$_2$ ($n$ = 3–8) by treating *cis*-[Pt(am)$_2$(DMSO)Cl]Cl with 1 equiv of acid[2] and have assigned a cis configuration on the assumptions (i) that substitution proceeds with complete retention of configuration and (ii) that dimethyl sulfoxide has a strong trans effect, *i.e.*



The isomeric yellow complexes were prepared from K[PtCl$_3$(DMSO)] and assigned a trans configuration in accordance with Kukushkin's reasoning. All of these conclusions are internally consistent but rely on the assumption that S-bonded dimethyl sulfoxide has a strong trans effect. While this is an eminently reasonable hypothesis, independent evidence was sought to confirm the assignment of structure. Some important features of the infrared spectra are collected in Table III. The strong, sharp absorption assigned to the S–O stretch appears in the range 1108–1151 cm$^{-1}$ and is fully consistent with linkage to platinum through sulfur.[10] This sometimes appears as a pair of equally intense peaks separated by some 10–20 cm$^{-1}$ even though there is only one dimethyl sulfoxide per complex. The region of the spectrum from 500 to 300 cm$^{-1}$ can be quite rich in peaks. All the complexes reported in Table III have two strong peaks at 442 ± 8 and 377 ± 5 cm$^{-1}$ which probably arise from the dimethyl sulfoxide ligand. There is also a strong band at 345 ± 10 cm$^{-1}$ which is assigned to a Pt–Cl stretching mode. The yellow [PtCl$_2$(am)(DMSO)] species, which have been assigned a trans configuration, have no further strong absorptions in this region. Hartley[11] has pointed out that, in complexes of the type *trans*-[PtCl$_2$L$_2$], the Pt–Cl stretching frequency is remarkably insensitive to the nature of ligand L and is found at 340 ± 3 cm$^{-1}$ (the actual range is somewhat wider than this[12]). The off-white or pale yellow isomers that have been assigned a cis configuration also have a strong peak in this region together with at least one more strong band in the range 320 ± 10 cm$^{-1}$ and these two peaks have been assigned to Pt–Cl stretches. Some of the complexes have a third strong peak some 4–13 cm$^{-1}$ toward lower fre-

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(8) Y. N. Kukushkin and E. D. Ageeva, *Russ. J. Inorg. Chem.*, 17, 767 (1972).

(9) Y. N. Kukushkin and V. A. Yurinov, *Russ. J. Inorg. Chem.*, 16, 601 (1971).

(10) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, 64, 1534 (1960).

(11) F. R. Hartley, "The Chemistry of Platinum and Palladium," Applied Science Publishers, Ltd., London, 1973, p 242.

(12) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

Table III. Some Strong Characteristic Absorptions for Platinum(II)–Dimethyl Sulfoxide Complexes

| Complex | $\nu_{S-O}$, cm$^{-1}$ | Significant peaks in range 500–300 cm$^{-1}$ [a] |
|---|---|---|
| K[PtCl$_3$(DMSO)] | 1102 s | 446 s, 382 s, *346 s, 331 m, 309 s* |
| *trans*-[PtCl$_2$(DMSO)(piperidine)] | 1142 s, 1114 s | 446 s, 377 s, *346 s*, 332 s |
| *trans*-[PtCl$_2$(DMSO)(*n*-butylamine)] | 1123 s | 436 s, 377 s, *339 s* |
| *trans*-[PtCl$_2$(DMSO)(morpholine)] | 1128 s, 1111 s | 438 s, 382 s, 362 s, *338 s* |
| *trans*-[PtCl$_2$(DMSO)(aniline)] | 1110 s | 452 s, 439 s, 380 s, 362 s, *346 s* 312 w |
| *trans*-[PtCl$_2$(DMSO)(*m*-Cl-aniline)] | 1119 s | 439 s, 377 m, *345 s*, 332 m |
| *trans*-[PtCl$_2$(DMSO)(*p*-Cl-aniline)] | 1120 s | 443 s, 401 m, 377 m, *344 s* |
| *trans*-[PtCl$_2$(DMSO)(3-Br-pyridine)] | 1135 s | 440 s, 382 m, *351 s*, 336 w |
| *trans*-[PtCl$_2$(DMSO)(3-Cl-pyridine)] | 1138 s, 1124 s | 441 s, 382 m, *353 s*, 336 w |
| *trans*-[PtCl$_2$(DMSO)(4-CH$_3$-pyridine)] | 1136 s | 441 s, 380 s, *347 s*, 304 w |
| *trans*-[PtCl$_2$(DMSO)(pyridine)] | 1151 s, 1136 s | 440 s, 379 s, *347 s*, 317 w |
| *trans*-[PtCl$_2$(DMSO)(cyclohexylamine)] | 1122 s, 1112 s | 439 s, 377 s, *346 s*, 317 w |
| *trans*-[PtCl$_2$(DMSO)(cyclopropylamine)] | 1108 s | 438 s, 401 m, 380 s, *346 s*, 305 w |
| *cis*-[PtCl$_2$(DMSO)(pyridine)] | 1151 s | 446 s, 379 s, *347 s, 320 s* |
| *cis*-[PtCl$_2$(DMSO)(cyclohexylamine)] | 1129 s, 1116 s | 443 s, 373 s, *342 s, 329 s*, 316 m |
| *cis*-[PtCl$_2$(DMSO)(cyclopropylamine)] | 1122 s | 444 s, 398 m, 376 s, *336 s, 311 s*, 303 s |
| *cis*-[PtCl$_2$(DMSO)(cyclobutylamine)] | 1132 s | 443 s, 414 w, 375 s, *345 s, 330 s*, 320 s |
| *cis*-[PtCl$_2$(DMSO)(cyclopentylamine)] | 1118 s | 442 s, 416 w, 373 s, *342 s, 318 s*, 312 s |
| *cis*-[PtCl$_2$(DMSO)(cyclohexylamine)] | 1129 s, 1116 s | 443 s, 373 s, *342 s, 329 s*, 316 m |
| *cis*-[PtCl$_2$(DMSO)(cycloheptylamine)] | 1118 s | 442 s, 402 w, 373 s, *341 s, 328 s*, 316 s |
| *cis*-[PtCl$_2$(DMSO)(cyclooctylamine)] | 1122 s | 444 s, 422 w, 373 s, *344 s, 322 s*, 318 s |

[a] $\nu_{Pt-Cl}$ in italic type.

quency. The complex anion $[PtCl_3(DMSO)]^-$ has three bands in this region and resembles the other complexes of the type $[PtCl_3L]^-$, L = $SMe_2$ and $SEt_2$,[13] and the bands have likewise been assigned to the symmetric and antisymmetric stretching modes of the mutually trans pair of chlorines (346 and 331 cm$^{-1}$) and the stretching of the Pt–Cl bond trans to S (309 cm$^{-1}$). This lowest frequency band is the one that is sensitive to the nature of the ligand L and the similarity to that for the $[PtCl_3(C_2H_4)]^-$ anion (309 cm$^{-1}$)[13] is further indication that the labilizing power of the dimethyl sulfoxide, like ethylene, does not arise from any ground-state weakening.

The entry of amine into $[PtCl_3(DMSO)]^-$ goes mainly through the pathway of direct bimolecular attack. The plots of $k_{obsd}$ against [am] have small finite intercepts, listed as $k^f_1$ in Table II. A direct measure of this rate constant was made by treating $[PtCl_3(DMSO)]^-$ with hydroxide in the presence of 0.50 *M* chloride. The rate of spectrophotometric change and the final spectrum was independent of the hydroxide concentration, and the first-order rate constant, $(8.15 \pm 0.3) \times 10^{-3}$ sec$^{-1}$, is identified as $k^f_1$. This agrees well with the values recorded for the reactions with the less basic amines but the apparent disappearance of the $k^f_1$ term in the reactions with the more basic amines may be significant. The second-order rate constants, $k^f_2$, show only a slight dependence upon the nature of the amine. A plot of log $k^f_2$ against the p$K_a$ of amH$^+$ (a measure of the basicity of am) is reasonably scattered but a least-squares fit gives a straight line of slope +0.15. However, a glance at Figure 1 will show that this relationship may be totally illusory and that, had the study been restricted to any of the narrower ranges of structurally similar amines, completely different conclusions would have been drawn. If the subgroup had consisted of pyridine and its substituted derivatives, a favorite group for studying basicity-nucleophilicity relationships,[14-16] it might have been concluded that the reactivity actually decreased with the increasing basicity of the nucleophile. The reactivity of the alicyclic primary amines does not seem to vary with basicity. Of course, it should be realized that the vertical scale in Figure 1 is greatly expanded when compared to the horizontal scale and the most valid conclusion is the long known one that the nucleophilicity of amines toward Pt(II) substrates is not particularly dependent upon their basicity. Morpholine appears to be an unusually reactive amine and it is possible that, in this particular reaction, the oxygen at the other end of the ligand assists in some way the departure of the chloride.

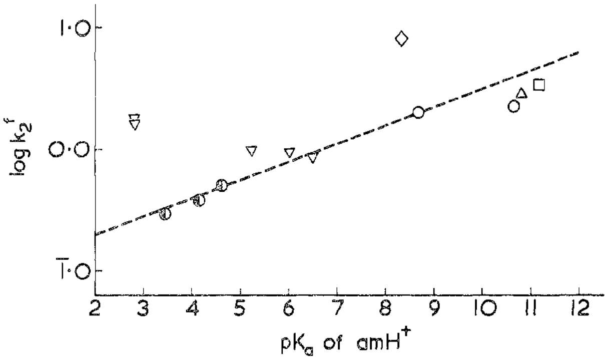

Figure 1. log $k^f_2$ for the reaction $PtCl_3(DMSO)^-$ + am → *trans*-$[PtCl_2(am)(DMSO)]$ + $Cl^-$ plotted against p$K_a$ of amH$^+$: ⊕, aniline and substituted derivatives; ▽, pyridine and substituted derivatives; ○, cycloalkylamines; ◇, morpholine; △, *n*-butylamine; □, piperidine.

The displacement of amine by chloride presents at least two significant features, especially when the results are compared with the corresponding reactions of the cationic *cis*-$[Pt(am)_2(DMSO)Cl]^+$ species reported in a previous paper.[2] The nucleophile-independent ($k^r_1$) pathway constitutes the major part of the reaction, the rate constant is very sensitive to the basicity of the leaving group, and a plot of log $k^r_1$ against the p$K_a$ of amH$^+$ is linear with a slope of −0.55, Figure 2. The $k^r_1$ pathway for the corresponding reaction of the cationic diamine complex provides such a small fraction of the reaction that its dependence upon the nature of am could not be determined; nevertheless $k^r_1$ for the least basic leaving group, cyclopropylamine, is at least 5 times greater than that for cyclopentylamine. These results are in

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(13) R. J. Goodfellow, P. L. Goggin, and D. M. Duddell, *J. Chem. Soc. A*, 504 (1968).

(14) L. Cattalini, A. Orio, and A. Doni, *Inorg. Chem.*, 5, 1517 (1966).

(15) L. Cattalini, M. Nicolini, and A. Orio, *Inorg. Chem.*, 5, 1674 (1966).

(16) L. Cattalini, A. Doni, and A. Orio, *Inorg. Chem.*, 6, 280 (1967).

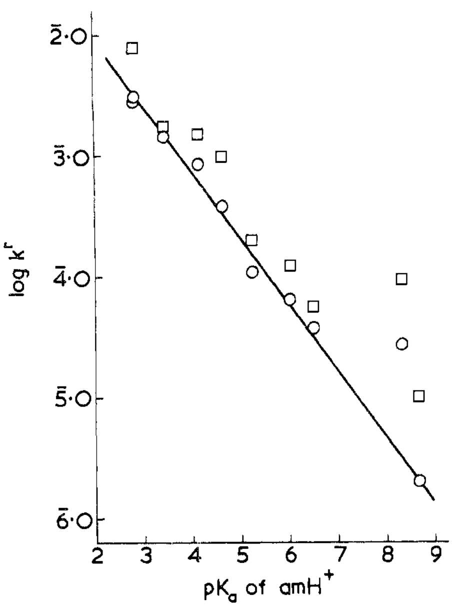

**Figure 2.** log $k^r_1$ (○) and log $k^r_2$ (□) for the reaction *trans*-[PtCl$_2$(am)(DMSO)] + H$^+$ + Cl$^-$ → [PtCl$_3$(DMSO)]$^-$ + amH$^+$ plotted against p$K_a$ of amH$^+$.

complete contrast to those obtained for the displacement of am from [AuCl$_3$am], where $k_1$ shows no systematic dependence upon the basicity of am.[17] The second-order rate constants ($k^r_2$) are also dependent on the basicity of the leaving amine and, although the scatter is greater, the relationship (log $k^r_2$ *vs.* p$K_a$) can be represented by a line of similar slope to that relating to the log $k^r_1$ values, Figure 2. The leaving group effect in the replacement of am from *cis*-[Pt(am)$_2$(DMSO)Cl]$^+$ was not examined in isolation of the cis effect of the other amine and the plot of log $k^r_2$ against p$K_a$ was linear with slope of −0.91. A similar treatment in which the leaving group was held constant and the cis amine varied give a linear relationship with slope −0.43, and, if the two effects were additive in this treatment, one might expect to find that the leaving group effect should produce a slope in the region of −0.50, which is close to that observed for the monoamine series. The major difference in the behavior of the neutral *trans*-[PtCl$_2$(am)(DMSO)] and the cationic *cis*-[Pt(am)$_2$(DMSO)Cl]$^+$ species is the relative importances of the direct attack and the solvolytically mediated pathway. The removal of the cationic charge and the replacement of the cis amine by a chloride reduces $k^r_1$ by a factor of 20–40 (the values can be directly compared when am = cyclopropylamine, when $k^r_1 = 5 \times 10^{-5}$ sec$^{-1}$ for the diamine complex and $2 \times 10^{-6}$ sec$^{-1}$ for the monoamine complex at 30.0°), whereas the second-order rate constant, $k^r_2$, is reduced by factors of 1000–2000 (again for cyclopropylamine, $k^r_2$ decreases from $1.48 \times 10^{-2}$ to $1.0 \times 10^{-5}$ sec$^{-1}$). The difference in lability and, as will be seen, the difference in the equilibrium constants had made it impossible to overlap the two series more extensively than this. With amines of lower basicity than cyclopropylamine the diamine complexes could not easily be prepared, and with the amines of greater basicity, the decomposition of the monoamine complex was too slow to follow. These results suggest that charge effects are more important than has hitherto been believed although it would be necessary to extend this type of study over a much wider range of nucleophile before any firm conclusions could be drawn.

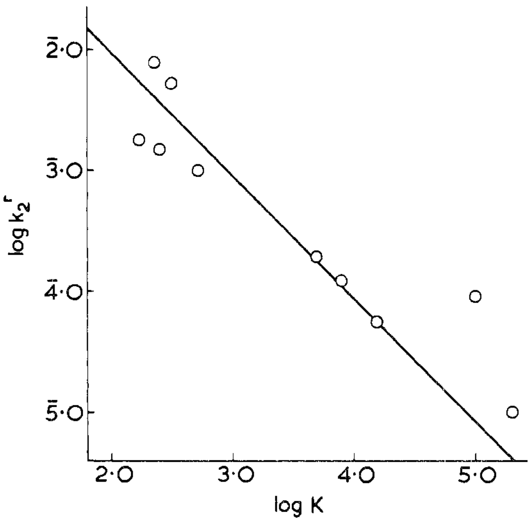

**Figure 3.** The relationship between log $k^r_2$ and $K$.

The equilibrium constants for reaction 1 can be conveniently calculated from the relationship $K = k^r_2/k^r_2$.[18] These are also collected in Table II. A plot of log $K$ against the p$K_a$ of amH$^+$ indicates that there is a slightly scattered linear free-energy relationship. The best straight line through the unweighted points has a slope of +0.57. This is possibly the first systematic determination of the relationship between stability constants and basicity for amine complexes of platinum(II). The dependence on basicity seems somewhat less than in the case of Ag(I), where a plot of $\beta_2$ against p$K_a$ of a series of substituted pyridines in ethanol has a slope of +0.73,[19] or even in the case of Au(III), where the plot of log $K$ for the equilibrium AuCl$_4^-$ + am = [AuCl$_3$am] + Cl$^-$ against the p$K_a$ of amH$^+$ (a series of unhindered substituted pyridines) has a slope of +0.78.[15] It is of interest to note that a similar plot for the equilibrium *cis*-[PtCl$_2$(DMSO)am] + am = *cis*-[Pt(am)$_2$(DMSO)Cl]$^+$ + Cl$^-$ has a slope of +0.65, although this is complicated by steric hindrance that appears with the larger ring alicyclic amines.[2] A major point of contrast between the trans monoamine complexes and the cis diamine complexes is that the stabilities of the former are nearly $10^3$ times greater than those of the latter type (for am = cyclopentylamine, $K_{\text{mono}} = 2.02 \times 10^5$, $K_{\text{bis}} = 3.05 \times 10^2$). This difference in stability is apparently the reason for the lack of success in the attempts to make the chlorides of *cis*-[Pt(am)$_2$(DMSO)Cl]$^+$ with amines significantly less basic than cyclopropylamine.

If log $k^r_2$ is plotted against −log $K$, the best straight line to fit the points (ignoring the anomalous morpholine reaction) has a slope of 1.0 (Figure 3). This follows from the great similarity of the dependence of the equilibrium constant and of $k^r_2$ on the basicity of the amine and on the lack of serious dependence of $k^f_2$ on the nature of the amine. This relationship indicates that the energy of the rate-determining transition state is not greatly affected by the nature of the amine

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[17] L. Cattalini and M. L. Tobe, *Inorg. Chem.*, 5, 1145 (1966).

[18] In a process involving parallel reaction pathways, as occurs in this case, the condition that, at equilibrium, the rate of transfer of material in the forward direction must be equal to that in the reverse direction must hold independently for each pathway. It is easy to see that $K = k^f_2/k^r_2$ for the direct-attack pathway and it can easily be shown the $K = k^f_1 k_3/k_1{}^r k_{-1}$ ($k_{-1}$ and $k_3$ are defined in (2) for the solvolytic pathway). Since the values for the competition rate constants $k_{-1}$ and $k_3$ were not determined and there were ambiguities in the determination of $k^f_1$, the equilibrium constant was determined from the second-order rate constants.

[19] W. J. Peard and R. T. Pflaum, *J. Amer. Chem. Soc.*, 80, 1593 (1958).

and implies that, in this transition state, the bond between platinum and nitrogen is almost completely broken. This is a restatement of the conclusion of Leffler and Grunwald that a slope of 1.0 in such a relationship indicates that the transition state resembles the products of the reaction (use of $-\log K$ in this plot considers the change in the direction of amine loss and chloride gain).[20] It does not necessarily imply a dissociative intimate mechanism (except insofar as the reactive intermediate is dissociating), and in this case, the first-order dependence upon chloride ion concentration indicates clearly an A mechanism. Yet the behavior closely resembles that encountered in the aquation of the $[Co(NH_3)_5X]^{2+}$ complexes where the plot of log $k$ against log $K$ has a slope of 1.0;[21] in this case there is a great deal of other evidence to suggest that the intimate mechanism is essentially dissociative although the intermediate of lower coordination number may not be free enough for the assignment of a D mechanism. This is a further reminder that rate constants or equilibrium constants or any quantity that is derived from them do not provide direct evidence quantifying the molecularity of solvent participation and that an unquestioning use of LFER relationships of this sort to determine the molecularity of substitution reactions in which a molecule of the solvent is either the entering or the leaving group is dangerous and can be misleading.

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**Registry No.** *trans*-$[PtCl_2(DMSO)(piperidine)]$, 32370-20-0; *trans*-$[PtCl_2(DMSO)(n\text{-butylamine})]$, 51425-26-4; *trans*-$[PtCl_2(DMSO)(morpholine)]$, 32458-43-8; *trans*-$[PtCl_2(DMSO)(aniline)]$, 51425-27-5; *trans*-$[PtCl_2(DMSO)(m\text{-Cl-aniline})]$, 51425-28-6; *trans*-$[PtCl_2(DMSO)(p\text{-Cl-aniline})]$, 51425-29-7; *trans*-$[PtCl_2(DMSO)(3\text{-Br-pyridine})]$, 51472-50-5; *trans*-$[PtCl_2(DMSO)(3\text{-Cl-pyridine})]$, 51425-30-0; *trans*-$[PtCl_2(DMSO)(4\text{-}CH_3\text{-pyridine})]$, 51425-31-1; *trans*-$[PtCl_2(DMSO)(pyridine)]$, 51425-32-2; *trans*-$[PtCl_2(DMSO)(cyclohexylamine)]$, 51425-33-3; *trans*-$[PtCl_2(DMSO)(cyclopropylamine)]$, 51425-34-4; *trans*-$[PtCl_2(DMSO)(3,4\text{-dimethylpyridine})]$, 51425-35-5; *cis*-$[PtCl_2(DMSO)(pyridine)]$, 20647-45-4; *cis*-$[PtCl_2(DMSO)(cyclohexylamine)]$, 50830-89-2; *cis*-$[PtCl_2(DMSO)(cyclopropylamine)]$, 50830-86-9; *cis*-$[PtCl_2(DMSO)(cyclobutylamine)]$, 50830-87-0; *cis*-$[PtCl_2(DMSO)(cyclopentylamine)]$, 50830-88-1; *cis*-$[PtCl_2(DMSO)(cyclohexylamine)]$, 50830-89-2; *cis*-$[PtCl_2(DMSO)(cycloheptylamine)]$, 50830-90-5; *cis*-$[PtCl_2(DMSO)(cyclooctylamine)]$, 50830-91-6; $K[PtCl_3(DMSO)]$, 31168-86-2; piperidine, 110-89-4; *n*-butylamine, 109-73-9; cyclohexylamine, 108-91-8; cyclopropylamine, 765-30-0; morpholine, 110-91-8; 3,4-dimethylpyridine, 583-58-4; 4-methylpyridine, 108-89-4; pyridine, 110-86-1; aniline, 62-53-3; 4-chloroaniline, 106-47-8; 3-chloroaniline, 108-42-9; 3-chloropyridine, 626-60-8; 3-bromopyridine, 626-55-1; chlorine, 7782-50-5.

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[20] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 156.

[21] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 61.

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# Stabilization of Five-Coordinate Platinum(II) Olefin and Allene Complexes by the Hydrotris(1-pyrazolyl)borate Ligand

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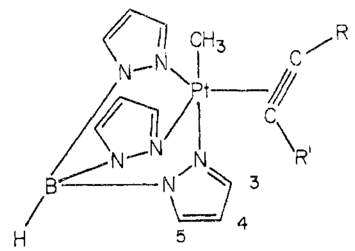
The hydrotris(1-pyrazolyl)borate ligand has been shown to stablize five-coordinate olefin, allene, and carbonyl complexes of platinum(II). Nuclear magnetic resonance measurements suggest a trigonal-bipyramidal configuration with the olefin and allene contained within the trigonal plane of the platinum and two equatorial nitrogen atoms. When more than one geometrical isomer is possible for the olefin complexes, the ratio of isomers is dependent upon the steric requirements of the olefin substituents. An unusual hydrogen–fluorine through-space coupling interaction has been observed between the platinum methyl hydrogens or the axial pyrazolyl 3-H proton and the fluorine atoms on several fluoroolefin complexes. The olefin and allene complexes are stereochemically rigid at room temperature while the carbonyl complexes are fluxional.

## Introduction

Poly(pyrazolyl)borate ligands have been shown to confer considerable stability on organometallic complexes[2-5] apparently because of the favorable electronic and geometrical properties of the ligand. For example, five-coordinate acetylene complexes of platinum(II) are relatively unstable with respect to insertion and dissociation;[6-7] however, by using the poly(1-pyrazolyl)borate ligands we have been able to stabilize a number of five-coordinate methylplatinum(II) acetylene complexes 1, where R and R′ are either electron-donating or electron-withdrawing substituents. The acetylene is constrained within the trigonal plane of the platinum



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[1] Address correspondence to this author.

[2] S. Trofimenko, *Accounts Chem. Res.*, 4, 17 (1971); *Chem. Rev.*, 72, 497 (1972).

[3] M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Chem. Commun.*, 1124 (1972).

[4] H. C. Clark and L. E. Manzer, *J. Amer. Chem. Soc.*, 95, 3812 (1973).

[5] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 13, 1291 (1974).

[6] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 10, 18 (1971).

[7] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 9, 2670 (1970).