

been studied over such a large range in acidity as has that for $\text{Ru}(\text{NH}_3)_6^{+2}$ with $\text{Co}(\text{NH}_3)_6^{+3}$. In the pH range from 2 to 9, the rates of the two reactions are about equally sensitive (or insensitive) to pH, the rate increasing by only a factor of 4 or so in this pH range.

The reactions of $\text{Ru}(\text{NH}_3)_6^{+2}$ with $\text{Co}(\text{III})$ amines has given us an opportunity to study kinetic salt effects in dilute solution. One of the reactions, namely that in which $\text{Ru}(\text{NH}_3)_6^{+2}$ reduces $\text{Co}(\text{NH}_3)_5\text{Br}^{+2}$, is of the same charge type as (and in fact has a reactant in common with) a system which Olson and Simonson¹⁸ have investigated.

The data of Olson and Simonson for the reaction of Hg^{+2} with $\text{Co}(\text{NH}_3)_5\text{Br}^{+2}$ are shown together with our own in a plot of $\log k$ against $\sqrt{\mu}$ in Figure 4. Only those of Olson and Simonson's data which refer to a medium containing NaClO_4 as the predominant elec-

trolyte are included. From these latter data for ionic strengths less than 0.026 M , we estimate

$$\log k_7 = (2.5 \pm 0.3)\sqrt{\mu} + \log k_7^0$$

(where the error limits on the slope reflect the non-linearity of the dependence of $\log k_7$ on $\mu^{1/2}$). Our own data over the total range of ionic strengths less than 0.028 M fit the analogous equation with a slope of 4.4 ± 0.3 , which is somewhat more consistent with the Brønsted-Debye-Hückel equation. The Brønsted-Debye-Hückel equation thus seems applicable over a greater range of ionic strengths when $\text{Ru}(\text{NH}_3)_6^{+2}$ reacts with $\text{Co}(\text{NH}_3)_5\text{Br}^{+2}$ than when the reactant is Hg^{+2} .

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Ethylene Exchange in Zeise's Anion

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N.m.r. studies show that complexed ethylene in Zeise's anion, $[(\text{C}_2\text{H}_4)\text{PtCl}_3]^-$, exchanges at a rate $>70 \text{ sec.}^{-1}$ at temperatures as low as -75° . These results were qualitatively substantiated by tracer experiments. A description is given of a SnCl_2 -catalyzed synthesis of Zeise's salt.

Olefin displacement from complexes of platinum(II) is a rapid reaction. Thus, a number of analogs of Zeise's salt, $\text{K}[(\text{CH}_2=\text{CH}_2)\text{PtCl}_3]\text{H}_2\text{O}$, have been prepared by treating it with various olefins.¹ Reaction occurs readily, the volatility of ethylene tending to $[(\text{CH}_2=\text{CH}_2)\text{PtCl}_3]^- + \text{olefin} \rightarrow [(\text{olefin})\text{PtCl}_3]^- + \text{C}_2\text{H}_4$ (1)

drive it to completion. Also, in comparing the coordinating ability of various substituted styrenes by measuring the equilibrium constant of reaction 2, Joy and Orchin noted that, at 25° , equilibrium is attained in the $[(1\text{-dodecene})\text{PtCl}_3]^- + \text{XC}_6\text{H}_4\text{CH}=\text{CH}_2 \rightarrow [(\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2)\text{PtCl}_3]^- + 1\text{-dodecene}$ (2)

few minutes required to prepare the solution for study.² Further, C_2D_4 was found to equilibrate with coordinated C_2H_4 in the related platinum(II) complex, $[(\text{C}_2\text{-H}_4)\text{PtCl}_2]_2$, within 15 min. at temperatures as low as -15° .³ In order to define more precisely the rate of ethylene exchange we have examined the n.m.r. spectra

of solutions containing both $[(\text{C}_2\text{H}_4)\text{PtCl}_3]^-$ and free C_2H_4 .

Ethylene dissolved in 1 M methanolic HCl has a proton n.m.r. absorption at $\delta -5.37$ p.p.m. relative to tetramethylsilane (internal standard). In the same medium, coordinated ethylene in $[(\text{C}_2\text{H}_4)\text{PtCl}_3]^-$, Zeise's anion, absorbs at $\delta -4.83$ p.p.m.⁴ A solution containing both $[(\text{C}_2\text{H}_4)\text{PtCl}_3]^-$ and uncoordinated ethylene has a single n.m.r. proton absorption. The position of this absorption varies with the ratio *free* C_2H_4 /*coordinated* C_2H_4 and shifts toward -5.37 p.p.m. as the ratio increases. Since the spectra were measured using an oscillator frequency of 60 Mc. sec.^{-1} , the exchange rate ($>(\pi\delta_{AB}H)\sqrt{2}$) is faster than 70 sec.^{-1} .⁵ The n.m.r. spectra were recorded at temperatures down to -75° to find if the ethylene exchange rate would become so slow that absorptions due to free and coordinated ethylene would be separated. Although the n.m.r. signal broadened, it did not split but shifted

(4) This absorption is in fact the central line of a triplet. The satellites located 17 c.p.s. above and below the central peak are caused by spin-spin splitting by Pt^{111} (spin $1/2$ and natural abundance 34%). They were observed by B. D. Powell and N. Sheppard [*J. Chem. Soc.* 2519 (1960)].

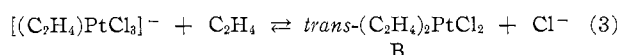
(5) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 63.

(1) J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).
(2) (a) J. R. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 305 (1959);
(b) J. R. Joy and M. Orchin, *ibid.*, **81**, 310 (1959).
(3) A. S. Gow, Jr., and H. Heinemann, *J. Phys. Chem.*, **64**, 1574 (1960).

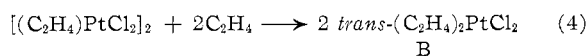
downfield corresponding to the increased solubility of ethylene in the reaction solution at lower temperatures.

To confirm qualitatively the conclusions reached from these n.m.r. experiments, an equivalent of C_2D_4 was stirred for 1 min. at -80° with a methanol solution of $[(C_2H_4)PtCl_3]^-$, then uncoordinated ethylene was distilled for mass spectrographic analysis. The recovered ethylene consisted of equal amounts of C_2H_4 and C_2D_4 , reflecting the rapid exchange of free and coordinated ethylene. In another confirmatory experiment, rapid exchange of ethylene between Zeise's anion and an ethylene complex of rhodium(I) was demonstrated. Earlier work⁸ had shown that coordinated ethylene in bis(ethylene)acetylacetonatorhodium(I) $[(acac)Rh(C_2H_4)_2]$ is very labile. When ethanol solutions of $K[(C_2D_4)PtCl_3] \cdot H_2O$ and $(acac)Rh(C_2H_4)_2$ are mixed, the coordinated C_2D_4 and C_2H_4 equilibrate within 1 min. at 25° .

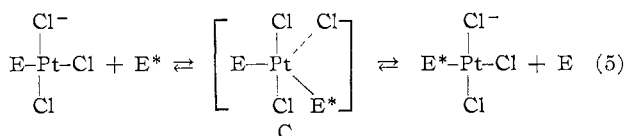
Ethylene exchange might occur through a series of *trans* displacements (eq. 3) with *trans*-bis(ethylene)-platinum(II) dichloride (B) as an intermediate. The



ability of ethylene to accelerate markedly the rate of displacement of ligands *trans* to it in Pt(II) complexes has been noted by several authors.⁷ Also Chatt and Wilkins were able to isolate B⁸ (from a Cl-bridged neutral complex derived from Zeise's anion), eq. 4, at -80° and found it lost ethylene readily at moderate temperatures.



Alternatively, exchange might occur without formation of B according to the scheme summarized in eq. 5. Coordinated ethylene, E, and ethylene which may displace it, E*, would become equivalent in the trigonal bipyramidal activated complex (C). If ethylene is expelled from C, exchange will occur without the



intervention of *trans*-(C_2H_4)₂PtCl₂ as an intermediate.

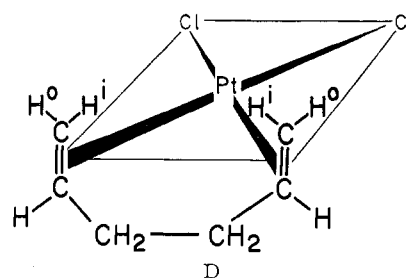
If it could be shown that *trans*-(C_2H_4)₂PtCl₂ existed in solutions of ethylene and $[(C_2H_4)PtCl_3]^-$, this might be taken as evidence of its participation as an intermediate in ethylene exchange. We have tried to detect the formation of B in solution at -37° through a pressure change corresponding to absorption of ethylene according to eq. 4 but did not succeed. While this result does not support the mechanism summarized by eq. 3, it does not disprove it since failure to detect absorption of ethylene does not preclude existence of B in low concentration.

(6) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(7) (a) A. D. Gel'man and E. F. Karandasheva, *Dokl. Akad. Nauk SSSR*, **87**, 597 (1952); (b) O. E. Zvyagintsev and E. F. Karandasheva, *ibid.*, **101**, 93 (1955); (c) I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

(8) J. Chatt and R. G. Wilkins, *Nature*, **165**, 859 (1950); *J. Chem. Soc.*, 2622 (1952).

Rapid exchange of ethylene may account for earlier failure to distinguish, in the n.m.r. spectrum, the two pairs of unsymmetrically disposed protons in the coordinated ethylene of the compound *cis*-[*p*-CH₃C₆H₄-NH₂(C₂H₄)PtCl₂].⁶ The protons on the terminal carbon atoms of 1,5-hexadiene coordinated to Pt(II) (Hⁱ and H^o of 1,5-hexadienedichloroplatinum(II) (D)) are clearly distinguishable in the n.m.r. spectrum. A doublet centered at -4.82 p.p.m. (tetramethylsilane, internal standard) is identified as Hⁱ because the separation of the absorptions is 14 c.p.s., as expected for splitting by *trans* protons on C₂ and C₅. Absorption of H^o is a doublet centered at -5.80 p.p.m., split 7 c.p.s. by C₂ and C₅ protons (*cis*). Exchange of chelate diene



would be expected to be slower than exchange of ethylene in its Pt(II) complexes.

Although coordinated ethylene in Zeise's anion exchanges quite rapidly, the formation of the anion from $[PtCl_4]^{2-}$ and ethylene is rather slow. It has been found that synthesis of $[(C_2H_4)PtCl_3]^-$ is catalyzed by stannous chloride.⁹ Under comparable conditions in an aqueous system the rate of ethylene absorption is about 15 times greater in the presence of 5 mole % of stannous chloride (based upon K_2PtCl_4) and directions are given in the Experimental section for the preparation of Zeise's salt in such a system.

Experimental

Materials.— $K[(C_2H_4)PtCl_3] \cdot H_2O$ and $[(C_2H_4)PtCl_2]_2$ were prepared from K_2PtCl_4 by the method of Chatt and Searle.¹⁰ $(CH_3COCHCOCH_3)Rh(C_2H_4)_2$ was prepared from "RhCl₃ · 3H₂O" in two steps.⁸ C_2D_4 was purchased from Merck of Canada. Other chemicals were commercial reagent grade and were used without further purification.

N.m.r. Experiments.—Spectra were measured at room temperature with a Varian A-60 instrument. A solution prepared from 0.5 ml. of 1 M methanolic HCl, 0.01 ml. of tetramethylsilane, and 25 ml. of gaseous ethylene in a 3×17 mm. n.m.r. tube had absorption peaks at -3.38 p.p.m. (methyl group of methanol), -5.37 p.p.m. (ethylene), and -5.59 p.p.m. (acidified methanol hydroxyl).

Solutions of $H[(C_2H_4)PtCl_3]$ were prepared by dissolving $[(C_2H_4)PtCl_2]_2$ in 1 M methanolic HCl containing 2% tetramethylsilane. A solution which was 0.25 M in $[(C_2H_4)PtCl_3]^-$ but with no added ethylene absorbed at -3.39 p.p.m. (methyl group of methanol), -4.83 p.p.m. (coordinated ethylene), and -5.60 p.p.m. (protonated methanol hydroxyl). Tubes containing 0.5 ml. of a 0.25 M solution of Zeise's anion and varying amounts of ethylene were examined, and the results are shown in Table I.

The n.m.r. absorption of 0.5 ml. of 1 M $H[(C_2H_4)PtCl_3]$ in 1 M methanolic HCl with 12 ml. of ethylene (gas) was measured at reduced temperatures with a Varian Associates HR 60 spec-

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(10) J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 210 (1957)

TABLE I

Ethylene, ml.	Ratio C ₂ H ₄ (free): C ₂ H ₄ (coord.)	Location of n.m.r. absorption of ethylene, p.p.m.
0	0	-4.83
2	0.6	-4.90
4	1.3	-5.00
6	1.9	-5.10
8	2.6	-5.15
25	∞	-5.37

trometer and a Varian Model V-4340 variable temperature probe accessory. As the temperature was reduced the location of the absorption ascribed to ethylene shifted downfield as follows: 0° (δ -4.82 p.p.m.); -25° (-4.85 p.p.m.); -50° (-4.93 p.p.m.); -75° (-5.13 p.p.m.).

Exchange Experiments. C₂D₄ and [(C₂H₄)PtCl₂]⁻.—A solution of 0.15 g. of [(C₂H₄)PtCl₂]₂ (0.5 mmole of coordinated ethylene) in 5 ml. of 1 M methanolic HCl was put in a flask containing a magnetic stirrer. The flask was chilled to -80° and evacuated. Then, 15 ml. of C₂D₄ (0.6 mmole) was admitted, and the mixture was stirred vigorously for 1 min. Ethylene was quickly distilled into an evacuated flask chilled in liquid nitrogen and analyzed by mass spectroscopy. The gas was 54% C₂D₄ and 46% C₂H₄.

K[(C₂D₄)PtCl₂] and (acac)Rh(C₂H₄)₂.—K[(C₂D₄)PtCl₂] was prepared by charging into a liquid nitrogen cooled, heavy-walled 4.5-ml. tube, 0.42 g. of K₂PtCl₄ (1 mmole), 2 ml. of H₂O, 0.25 ml. of concentrated HCl solution, and 25 ml. of gaseous C₂D₄ (1 mmole). The tube was sealed and agitated at 25° for 2 days during which time the color changed from red to yellow, corresponding to formation of Zeise's salt. About 1 ml. of water was removed by distillation at reduced pressure, and the residue cooled to give 0.3 g. (75% yield) of K[(C₂D₄)PtCl₂]·H₂O.

The exchange reaction was accomplished by mixing a solution of 0.1 g. of K[(C₂D₄)PtCl₂]·H₂O (0.26 mmole) in 3 ml. of ethanol with a solution of 0.035 g. of (acac)Rh(C₂H₄)₂ (0.13 mmole) in 2 ml. of ethanol. After 30 sec. the reaction mixture was divided

into two equal parts. One was immediately poured into 30 ml. of chloroform to precipitate the platinum complex, but hold the rhodium complex in solution. The other aliquot was diluted with 30 ml. of water to precipitate the rhodium complex. The complexes were recovered from the suspensions by centrifuge. Each was treated in an infrared gas cell with an ethylene glycol solution of sodium cyanide and both gave equal amounts of C₂D₄ and C₂H₄ as judged from the O.D. of the absorptions at 10.5 (C₂H₄) and 13.9 μ (C₂D₄).

Attempt to Demonstrate the Formation of [(C₂H₄)₂PtCl₂] in Solution.—The apparatus consisted of a flask (with a side arm and magnetic stirrer) attached through a three-way T-stopcock to an open-end manometer made of capillary tubing. The apparatus was designed to minimize free space. The flask was charged with 2.00 ml. of acetone, and a magnetized tube holding 0.030 g. of [(C₂H₄)PtCl₂]₂ was inserted in the side arm. The acetone was frozen in liquid nitrogen and the apparatus evacuated. Next the flask was warmed to -36°, and the acetone was saturated with ethylene introduced through the stopcock (27 ml. (N.T.P.) of ethylene was required). The apparatus was closed and the [(C₂H₄)PtCl₂]₂ added to the acetone. The pressure of the system increased by 1 mm. Conversion of all the [(C₂H₄)PtCl₂]₂ into (C₂H₄)₂PtCl₂ would have led to absorption of 2.24 ml. of ethylene and a pressure drop of 63 mm.

Synthesis of Zeise's Salt.—A stirred flask was charged with 8.3 g. of K₂PtCl₄ (0.02 mole), 40 ml. of H₂O, and 5 ml. of concentrated HCl. The flask was swept free of air with ethylene, and 0.2 g. of SnCl₂·2H₂O was added. The mixture was stirred and ethylene was introduced at about 1.5 atm. Absorption of ethylene was nearly complete in 3 hr., and the reaction mixture was chilled to 0°. The reaction solution was siphoned from the product under nitrogen, and the crystals were washed with 10 ml. of methanol cooled to 0°. The yield was 5.4 g. (70% conversion).

The reaction solution from the first synthesis was used as the solvent for 8.3 g. of K₂PtCl₄ in a second synthesis conducted as the first. The yield of K[(C₂H₄)PtCl₂]·H₂O was 7.6 g. (98% conversion).

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Complexes of Chromium(II) with Diethylenetriamine and Triethylenetetramine¹

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The Cr(II)-dien and Cr(II)-trien systems have been studied using potentiometric, spectrophotometric, and magnetic methods. All pK values refer to concentration quotients obtained at an ionic strength of 0.1 F . Values of pK_H for dien and trien have been determined at 26°; dien: $pK_1 = 4.22$, $pK_2 = 8.95$, $pK_3 = 9.79$; trien: $pK_1 = 3.37$, $pK_2 = 6.62$, $pK_3 = 9.09$, $pK_4 = 9.69$. The pK_H values for trien have been redetermined at 20°: $pK_1 = 3.55$, $pK_2 = 6.76$, $pK_3 = 9.26$, $pK_4 = 9.80$. These studies indicate the existence of the complexes mono(dien)-Cr(II), bis(dien)-Cr(II), and mono(trien)-Cr(II) with respective $\log K_f$ values of 6.71, 2.69, and 7.71 at 20° and 6.78, 2.6, and 8.0 at 26°. Magnetic measurements using an n.m.r. technique indicate that the bis(dien)-Cr(II) and mono(trien)-Cr(II) complexes have four unpaired electrons. It is postulated that all of these complexes have distorted octahedral configurations with water molecules filling the remaining positions not occupied by the amine nitrogen atoms.

Introduction

In previous potentiometric and spectrophotometric studies of the complexes of chromium(II) with ethyl-

enediamine in aqueous solution, Pecsok and Bjerrum² established the existence of mono and bis complexes and determined the consecutive formation constants for these complexes. In the ethylenediamine study, it was suggested that chromium(II) forms planar com-

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