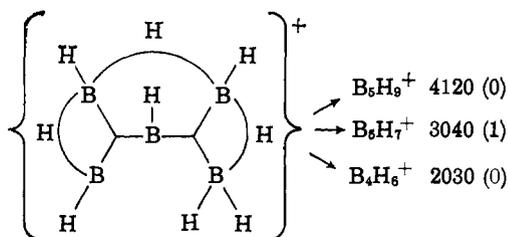
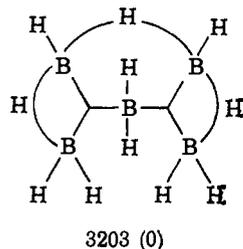


very favorable. This means that a terminal deuterium and a bridge proton are probably involved in the initial hydrogen loss.

In the case of B_6H_{11} it is thought that the $B_6H_9^+$ formed decomposes to $B_5H_7^+$ before it rearranges to normal $B_5H_9^+$. Structurally this would be



For convenience, Lipscomb's nomenclature is used to denote the structures.²⁴ In his topological theory the structural notation (*styx*) denotes a boron hydride with *s* hydrogen bridge bonds (B-H-B), *t* 3-center boron-boron bonds (B-B-B), *y* 2-center boron-boron bonds (B-B), and *x* BH_2 groups. In addition each boron atom has at least one BH terminal bond. The additional number in parentheses used here gives the number of borons without hydrogens.

Finally it is quite likely that hexaborane behaves in an analogous manner to pentaborane-9.

Using previously measured bond energies¹⁸ one can now calculate ionization potentials for some of the frag-

(24) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 118 (1959).

TABLE VIII

THE FRAGMENTATION PATTERN OF 1,2,3,4,5-PENTADEUTERIO-PENTABORANE

<i>m/e</i>	Relative intensity		Possible ions		
	$B_5^{11}H_9$	$B_5^{11}H_4D_5$ (75% D) 20% B^{10}	8.9	0% B^{10}	
69		8.9	8.9		$B_5H_4D_5^+$
68		25.1	-0.9		$B_5H_3D_5^+$
67		34.3	0.6		$B_5H_2D_5^+$
66		37.3	11.0		$B_5HD_5^+$
65		40.0			$B_5H_4D_4^+$
64	75	40.1			$B_5H_3D_4^+$
63	1				
62	75				
61	5				
60	100				

ment ions in the same manner as was done previously.² Ionization potentials along with the structure of the ion are given in Table IX. In general the agreement between ionization potentials of fragments from different molecules is good, lending consistency to the structures derived.

TABLE IX

IONIZATION POTENTIALS IN E.V. OF SELECTED FRAGMENT IONS

Ion	Structure	From			
		B_6H_{10}	B_6H_{11}	B_5H_9	B_4H_{10}
$B_6H_9^+$	3050 (1)	9.6			
$B_5H_9^+$	4120 (0)		10.6	10.5	
$B_5H_7^+$	3040 (1)	10.3	10.7	10.3	
$B_4H_6^+$	2030 (0)			10.3	10.0
$B_3H_5^+$	1021 (0)				10.1

Acknowledgments.—The mass spectrometer used in this study was obtained in part through a grant from the National Science Foundation. T. F. is indebted to the Kennecott Copper Corporation for its support through a graduate fellowship for 2 years.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

Olefin Exchange Reactions in Platinum(II) Complexes Containing Pyridine N-Oxides

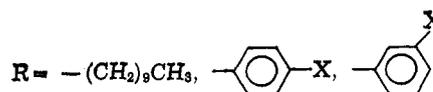
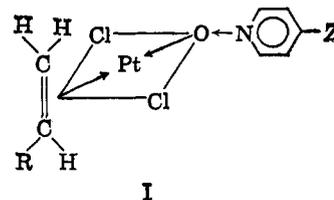
BY SAUL I. SHUPACK AND MILTON ORCHIN

RECEIVED SEPTEMBER 9, 1963

Some 66 new 1-(4-substituted pyridine N-oxide)-3-olefin-2,3-dichloroplatinum(II) complexes were prepared where the olefin is one of a series of 3- and 4-substituted styrenes. The styrene complexes were equilibrated with 1-dodecene and the equilibrium constants of the competitions for a site on the platinum were determined spectrophotometrically. The equilibrium is affected by the substituents on the styrene and to an even greater extent by the substituents on the pyridine N-oxide. The ratio of the two extreme equilibrium constants thus far determined is about 100,000.

Introduction

Previous work in this Laboratory has shown that pyridine N-oxide (PyO) can readily displace the *trans* chloride in Zeise's salt,¹ and a series of 4-substituted PyO moieties coordinated to Pt(II) were prepared² to study the substituent effect. The ethylene in these PyO complexes can be displaced by other olefins and the complexes containing styrene and various 4-substituted PyO moieties have been described.^{2,3} The present paper reports the preparation of a series of complexes of general structure I, in which both the styrene and the pyridine N-oxide are substituted by a



$X = OCH_3, CH_3, H, Cl, NO_2$

$Z = OCH_3, CH_3, H, Cl, CO_2CH_3, NO_2$

(1) L. Garcia and M. Orchin, *J. Chem. Soc.*, 2254 (1961).

(2) L. Garcia, S. I. Shupack, and M. Orchin, *Inorg. Chem.*, **1**, 863 (1962).

(3) S. I. Shupack and M. Orchin, *J. Am. Chem. Soc.*, **85**, 902 (1962).

variety of substituents X and Z, respectively, of differing electronic character.

Studies³ of the ethylene complexes (I, R = H) showed that the *para* substituent on PyO had a profound effect on the bonding in the complex, manifested by the change in C=C and the ⁺N—O⁻ stretching frequencies as a function of the substituent on the N-oxide. In still another earlier study,⁴ the competition between dodecene and a series of *para*-substituted styrenes for a site on Pt(II), where the *trans* ligand was chloride, was investigated. All of these studies are pertinent to an understanding of the nature of the olefin-Pt bond. The preparation of the sixty platinum complexes (I) has permitted us to extend this study, particularly with respect to the factors which influence the competition of olefins for a bonding site on platinum.

Experimental

The preparation of the pyridine N-oxides and ethylene complexes has been described previously.^{1,3}

1-(4-Z-Pyridine N-oxide)-3-(olefin)-2,4-dichloroplatinum(II) Complexes.—One mmole (about 0.400 g.) of 1-(4-Z-pyridine N-oxide)-3-ethylene-2,4-dichloroplatinum(II) was added to about 20 ml. of chloroform containing 2 mmoles of the appropriate styrene or dodecene. The solution was gently warmed until all the solid had dissolved. A few ml. of ether, in which the complexes are less soluble, was added and the solution was then concentrated while stirring, under reduced pressure, until a precipitate started to form. If no precipitate formed, more ether was added and the solution again concentrated. The precipitate was filtered and briefly air-dried until the solid was powdery. Recrystallization was performed in the same manner. In the synthesis of some of the compounds, namely when Z = CH₃O and NO₂, benzene was used in place of chloroform and hexane in place of ether. Usually, however, the benzene-hexane system tended to give gummy products.

All the styrenes were obtained from Columbia Organic Chemicals Co., Inc., and were used without further purification, except for the nitrostyrenes which were recrystallized.⁴ Table I lists the analyses and melting points of the complexes, all of which are new compounds.

Practically all sixty complexes were some shade of yellow. The color of each complex was determined according to the Munsell system.⁵

Determination of Equilibrium Constants.—Ultraviolet spectral measurements were made on a Cary 11 recording spectrophotometer using matched, 1 cm. quartz cells. Chloroform (spectral grade) was used exclusively as a solvent because all the compounds were soluble in it.

Weighed samples, 25 × 10⁻⁵ mole (0.01000–0.01400 g.), of the compound were dissolved in 25 ml. of chloroform, yielding 1.000 × 10⁻³ M solutions. Repurified nitrogen was bubbled through the solutions to expel air. The solutions were used immediately, as deposition of platinum occurs rather readily and becomes noticeable after 3 days.

Competition reactions were performed as follows: A 4 ml. aliquot from the 10⁻³ M styrene complex solution and a 2 ml. aliquot of a 10⁻² M 1-dodecene solution were pipetted into a 10 ml. volumetric flask; 4 ml. of chloroform was added to make a solution 4 × 10⁻⁴ M in styrene complex and 2 × 10⁻³ M in uncomplexed 1-dodecene at 25°.

The concentrations of the complexes were determined spectrophotometrically at wave lengths (Table II) at which the uncomplexed styrene generally did not absorb. When a NO₂-styrene was present, corrections had to be applied. The analysis was performed at three different wave lengths to improve the accuracy. The average of the concentrations determined at these wave lengths was used to calculate the K values. The appropriate method of calculation based on the Beer-Lambert law expression for a two and three component system may be found elsewhere.⁶ The equilibrium constants were evaluated from the equation

$$K_{eq} = \frac{C_{DC}C_S}{C_{SC}C_D}$$

where C_{DC} is the concentration of 1-dodecene complex; C_{SC} is the concentration of styrene complex; C_S is the concentration of uncomplexed styrene; C_D is the concentration of uncomplexed 1-dodecene. The poor precision which was observed for the values for the equilibrium constants can be attributed to a num-

(4) J. R. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 305 (1959).

(5) Recorded in Ph.D. Thesis of Saul I. Shupack, University of Cincinnati, 1963.

(6) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 556.

TABLE I
ANALYSES AND PROPERTIES OF 1-(4-Z-PYRIDINE N-OXIDE)-3-OLEFIN-2,4-DICHLOROPLATINUM(II) COMPLEXES

Z	Olefin	% Found			% Calcd.			M.p., °C. (dec.)
		C	H	Pt	C	H	Pt	
H	1-Dodecene	38.64	5.65	37.29	38.57	5.52	36.85	122
	Styrene							
H	4-CH ₃ O	34.65	2.89	38.40	33.96	3.05	39.41	118
H	3-CH ₃ O	34.10	2.99	37.52	33.96	3.05	39.41	134
H	4-CH ₃	34.40	2.92	37.28	35.09	3.16	40.72	90
H	3-CH ₃	34.92	3.33	40.40	35.09	3.16	40.72	119
H	H							
H	4-Cl	31.33	2.53	38.24	31.24	2.42	39.04	131
H	3-Cl	31.87	2.43	38.53	31.24	2.42	39.04	133
H	4-NO ₂	30.24	2.20	38.12	30.61	2.37	38.25	138
H	3-NO ₂	30.19	2.44	37.54	30.61	2.37	38.25	137
CH ₃ O	1-Dodecene	38.95	5.59	34.68	38.65	5.58	34.88	124
	Styrene							
CH ₃ O	4-CH ₃ O ^b	34.88	3.23	36.7	34.30	3.26	36.82	134
CH ₃ O	3-CH ₃ O	33.73	3.29	36.84	34.30	3.26	36.82	133
CH ₃ O	4-CH ₃	35.40	3.39	38.28	35.38	3.36	38.32	140
CH ₃ O	3-CH ₃	35.82	3.36	42.29	35.38	3.36	38.32	135
CH ₃ O	H	33.56	2.94	38.71	33.96	3.05	39.41	150
CH ₃ O	4-Cl	30.74	2.50	36.44	31.74	2.66	36.82	153
CH ₃ O	3-Cl	31.78	2.79	36.29	31.74	2.66	36.82	156
CH ₃ O	4-NO ₂	30.93	2.80	36.3	31.13	2.61	36.12	147
CH ₃ O	3-NO ₂	31.15	2.74	35.6	31.13	2.61	36.12	155
CH ₃	1-Dodecene	39.87	5.49	35.91	39.79	5.75	35.91	153
	Styrene							
CH ₃	4-CH ₃ O ^b	35.12	3.70	39.1	35.38	3.36	38.32	152
CH ₃	3-CH ₃ O	35.24	3.68	47.7	35.38	3.36	38.32	130
CH ₃	4-CH ₃	36.27	3.46	39.00	36.53	3.47	39.56	142
CH ₃	3-CH ₃	36.65	3.54	38.61	36.53	3.47	39.56	132
CH ₃	H	34.97	3.27	39.88	35.09	3.16	40.72	148
CH ₃	4-Cl	32.61	2.96	36.76	32.72	2.74	37.97	172
CH ₃	3-Cl	32.77	2.77	37.24	32.72	2.74	37.97	133
CH ₃	4-NO ₂	32.35	3.00	35.06	32.08	2.69	37.22	161
CH ₃	3-NO ₂ ^b	31.92	3.12	51.6	32.08	2.69	37.22	177
Cl	1-Dodecene	36.33	5.03	34.71	36.20	5.00	34.59	158
	Styrene							
Cl	4-CH ₃ O	31.88	2.72	36.80	31.74	2.66	36.82	142
Cl	3-CH ₃ O	31.65	2.68	36.03	31.74	2.66	36.82	134
Cl	4-CH ₃	31.95	2.73	37.31	32.72	2.74	37.97	142
Cl	3-CH ₃	32.72	2.76	37.11	32.72	2.74	37.97	146
Cl	H							
Cl	4-Cl	29.32	2.14	35.73	29.19	2.07	36.48	183
Cl	3-Cl	28.53	1.98	35.27	29.19	2.07	36.48	155
Cl	4-NO ₂	28.49	2.51	43.10	28.65	2.03	35.80	159
Cl	3-NO ₂	29.02	2.30	35.27	28.65	2.03	35.80	150
NO ₂	1-Dodecene	35.70	4.92	33.56	35.56	4.91	33.98	154
	Styrene							
NO ₂	4-CH ₃ O ^b	30.62	2.16	37.12	31.13	2.24	38.2	137
NO ₂	3-CH ₃ O ^b	31.15	2.91	36.3	31.13	2.24	38.2	140
NO ₂	4-CH ₃ ^b	32.46	2.73	35.02	32.0	2.69	37.22	133
NO ₂	3-CH ₃ ^b	32.08	2.85	37.2	32.0	2.69	37.22	140
NO ₂	H							
NO ₂	4-Cl	28.68	1.99	33.59	28.65	2.03	35.80	164
NO ₂	3-Cl	28.53	2.57	36.3	28.65	2.03	35.80	148
NO ₂	4-NO ₂ ^b	28.11	2.90	35.7	28.13	1.99	35.15	160
NO ₂	3-NO ₂	28.57	2.08	34.25	28.13	1.99	35.15	156
CO ₂ CH ₃	1-Dodecene	38.83	5.34	32.92	38.85	5.32	33.22	93
	Styrene							
CO ₂ CH ₃	4-CH ₃ O	35.05	3.27	34.71	34.74	3.09	35.27	154
CO ₂ CH ₃	3-CH ₃ O	34.19	3.21	34.94	34.74	3.09	35.27	158
CO ₂ CH ₃	4-CH ₃	35.76	3.11	35.66	35.77	3.19	36.32	145
CO ₂ CH ₃	3-CH ₃	35.43	3.21	35.29	35.77	3.19	36.32	158
CO ₂ CH ₃	H	34.83	2.89	34.83	34.44	2.89	37.29	150
CO ₂ CH ₃	4-Cl	32.29	2.53	34.39	32.31	2.53	34.99	170
CO ₂ CH ₃	3-Cl	32.41	2.66	34.88	32.31	2.53	34.99	148
CO ₂ CH ₃	4-NO ₂	32.07	2.57	34.18	31.71	2.48	34.34	156
CO ₂ CH ₃	3-NO ₂	32.18	2.63	33.37	31.71	2.48	34.34	162

^a See ref. 2. ^b Analyses performed by Galbraith Laboratories, Knoxville, Tennessee. All other analyses performed by Gulf Oil Corp., Pittsburgh, Pennsylvania.

TABLE II
WAVE LENGTHS USED FOR ANALYSIS

Styrene complex	λ, mμ	λ, mμ	λ, mμ
3- and 4-CH ₃ O	320	324	328
3- and 4-CH ₃	312	316	320
H	308	312	316
3- and 4-Cl	312	316	320
3- and 4-NO ₂	380 ^a	384 ^a	388 ^a

^a Uncomplexed 4-NO₂-styrene absorbs at these wave lengths.

TABLE III
 COMPETITION EXPERIMENTS

$$\text{Dod} + \text{XC}_6\text{H}_4\text{CH}=\text{CH}_2\text{Pt}(\text{Cl}_2)_4\text{-ZPyO} \rightleftharpoons \text{DodPt}(\text{Cl}_2)_4\text{-ZPyO} + \text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$$

Z	CH ₃ O	CH ₃	H	Cl	NO ₂
<i>m</i> -X					
CH ₃ O	3.8 ± 0.8	2.4 ± 0.5	6.6 ± 0.1	2.7 ± 0.4	0.6 ± 0.1
CH ₃	0.022 ± 0.004	0.08 ± 0.01	0.8 ± 0.2	0.09 ± 0.02	.0011 ± 0.0002
H	.029 ± 0.006	.055 ± 0.001	.052 ± 0.001	.14 ± 0.02	.0041 ± 0.0008
Cl	.0040 ± 0.0008	.023 ± 0.004	.10 ± 0.02	.10 ± 0.02	.033 ± 0.006
CO ₂ CH ₃	.026 ± 0.004	.20 ± 0.04	.13 ± 0.02	.043 ± 0.008	
NO ₂	.018 ± 0.003	.005 ± 0.001	3.3 ± 0.6	.05 ± 0.01	.013 ± 0.002
<i>p</i> -X					
CH ₃ O	9.5 ± 2	7.1 ± 1	6.6 ± 1	3.2 ± 0.6	.045 ± 0.009
CH ₃	0.30 ± 0.06	0.57 ± 0.01	.87 ± 0.2	0.099 ± 0.002	.0017 ± 0.0002
H	.26 ± 0.05	.016 ± 0.003	.052 ± 0.001	.071 ± 0.01	.00035 ± 0.0007
Cl	.18 ± 0.04	.51 ± 0.01	.10 ± 0.02	.11 ± 0.02	.010 ± 0.002
CO ₂ CH ₃	.25 ± 0.05	.016 ± 0.003	.13 ± 0.03	.22 ± 0.04	.077 ± 0.01
NO ₂	.0032 ± 0.0006	.078 ± 0.002	3.3 ± 0.7	.052 ± 0.001	.0015 ± 0.0003
<i>trans</i> -Cl	19.4	26	37		21

ber of factors. The error inherent in the instrument and method is probably about 5%. Difficulties in measuring the concentration of the reaction components stem mainly from the necessity of taking measurements on the slope of their absorption curves. The ultraviolet spectra of these complexes have many peaks and shoulders because of the types of ligands involved. Furthermore, the large extinction coefficients of the peaks of the complexes necessitated at least two dilutions of the solutions in order to carry out the measurements.

Seven reverse reactions were tried, but these gave only an approximate indication of the equilibrium constants. In these experiments further errors were introduced by contaminants in the styrenes. Gas chromatography and thin layer chromatography indicated that the styrenes were impure; these impurities were probably precursors in the synthesis or were polymers. The reaction system where Z = NO₂ and X = 4-Cl was amenable to analysis and gave a value for the equilibrium constant of 0.044, a 15% deviation from the value reported in Table III. The overall error in the equilibrium constants was considered to be ~20%.

Extensive solvation of all the species in solution occurs and this factor is difficult to evaluate. In each particular series where only one ligand is being changed, it might reasonably be assumed that changes in the solvation energy for the reactions should be relatively constant. Although the steric requirements of the 1-dodecene and styrene ligands are quite different, they probably do not play an important role in the relative stabilities of their respective complexes.

Results and Discussion

In the upper half of Table III are listed the equilibrium constants for the competition reaction between *meta*-substituted styrenes and dodecene and in the lower portion of the table are listed the results of the competition between *p*-substituted styrenes and dodecene. In general, the results with all the styrenes can be analyzed and interpreted in the same way. But because the trends, which are very difficult to interpret in any case, are very similar in the two series (except that differences in constants within the *m*-X-styrene series are not as extreme) all further discussion will be confined to the results and interpretation of the *para*-substituted styrenes.

In the discussion of results, it should be borne in mind that the larger the number for K_{eq} , the greater the concentration of dodecene complex, and the smallest K_{eq} represents the highest concentration of styrene complex. The words "more stable" are used in the loose sense of referring to the complex which is present in highest concentration in the competition reactions, and does not necessarily refer to either greater thermodynamic stability or to lesser reactivity.

Each row of constants in Table III represents the competition between dodecene and a 4-substituted styrene for a bonding site on platinum as a function of the 4-X substituent, since in each row the pyridine N-oxide is kept constant. The value for the most electron-withdrawing substituent (last column) is

smaller than the value for the most electron-releasing substituent (first column) in each of the six rows. However, the difference between these two extremes narrows as the substituent on the pyridine N-oxide is changed from the most electron-releasing to the most electron-withdrawing. Two values along a row are conveniently compared by their ratio; this ratio represents the competition between the two styrenes for a site on Pt. For the case where the CH₃O group is on PyO, the ratio of equilibrium values of the 4-methoxystyrene to the 4-nitrostyrene is 210, whereas when the NO₂ group is on PyO, this ratio is only about 2. This ratio is greatest, however, when the pyridine N-oxide is unsubstituted, *i.e.*, in the row where Z = H, the ratio OCH₃/NO₂ is 745. Examination of the row where Z is NO₂ reveals that, were these values to be plotted as a function of the σ -value of the X-substituent on styrene, an inverted U shape curve would result. Thus, when the parent styrene (X = H) is competing with dodecene, the dodecene complex is favored over the styrene complex; all substituents on styrene stabilize the styrene complex. Similar stabilization has been observed in the competition between dodecene and the series of styrenes when the ligand *trans* to the olefin is chloride; data for this case, taken from ref. 4, are given in the last row of Table III.

The values in the columns of Table III reflect the results of the competition between dodecene and a 4-substituted styrene for a bonding site on platinum as a function of the *para* substituent, Z, on pyridine N-oxide, since in each column the styrene is kept constant. In each column the most electron-releasing group has a significantly higher value than the electron-withdrawing substituent, and again the ratio of values decreases from CH₃O to NO₂. Thus with 4-methoxystyrene (X = CH₃O), the ratio of constants for the CH₃O-PyO as compared to the NO₂-PyO is 3000, whereas this ratio in the case of 4-nitrostyrene is only 30. Here the ratio of two column K values represents the competition between the two PyO moieties for a site on Pt. However, the value in each column is at a minimum when the parent unsubstituted PyO is the ligand. The U shape character of the column constants is most striking in the case where the parent styrene is the ligand; the values in this column of constants (X = H) as a function of the σ -value of the N-oxide substituent are shown in Fig. 1. Any substitution in the *para* position of the PyO destabilizes the styrene complex relative to the dodecene complex.

The difference between the extreme values in the columns is greater than the difference between the

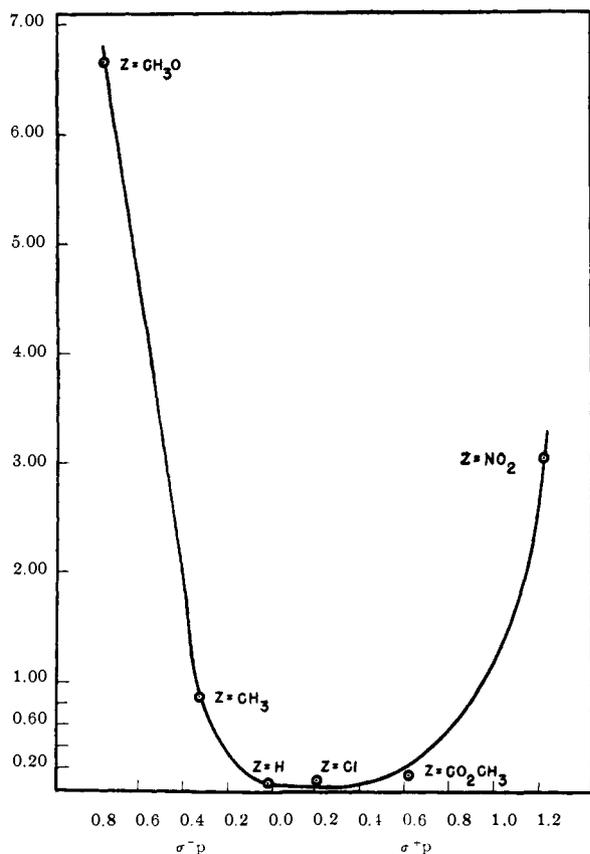


Fig. 1.— K_{eq} plotted against Hammett σ -values (Table III) for the 4-Z group on PyO.

extreme values in the rows, *i.e.*, the substituent effect in the pyridine N-oxide appears to be greater than the similar effect in the styrene. Previous work³ has shown that the substituent on the *para* position of the PyO has a large effect on the double bond character of the *trans* olefin. Accordingly, the large effects noted in the equilibrium constants are not unexpected, although it would be difficult *a priori* to predict the nature of these effects.

Another interesting fact which deserves emphasis is the difference in sensitivity of the equilibrium constants as a function of substituent. When methoxy is on either of the ligands, a change in the nature of the substituent on the other ligand causes a large change in the equilibrium value. However, when nitro is on either of the ligands, substitution on the other ligand produces only a relatively small change in equilibrium.

Finally, the data obtained in the present study show that the largest difference in equilibrium constants is between that observed for the complex $\text{X} = \text{OCH}_3$, $\text{Z} = \text{OCH}_3$ (the least stable styrene complex) and the value for the complex $\text{X} = \text{NO}_2$, $\text{Z} = \text{H}$ (the most stable styrene complex); the ratio of these values is 27,000. If the least stable styrene complex in the entire table (the one with styrene and chlorine *trans*) is compared to the most stable one (the one with pyridine N-oxide and *p*-nitrostyrene *trans*), the ratio is approximately 10^5 —truly a remarkable effect on relative stability as a function of appropriate substitution and an effect which offers enticing vistas for catalytic selectivity of platinum complexes.

Interpretation of Results

The relative stability of the olefin complexes depends principally upon (a) the energy matching of the highest bonding and lowest antibonding orbitals of the olefin with the corresponding platinum orbitals and (b) the

degree of overlap of these orbitals. Because of the extensive conjugation, the styrene π and π^* orbitals are more diffuse than those of dodecene, and it has been estimated that the overlap integrals of both σ - and π -bonds for dodecene with Pt are considerably more favorable than the corresponding overlap integrals for styrene and Pt.³

The energies of the relevant molecular orbitals are of great interest. We are not prepared at this time to do the necessary interpretations and calculations, but some numbers for the energy difference between the highest bonding and lowest antibonding orbitals can be approximated crudely by a qualitative consideration of some ultraviolet spectral data. Because the spectrum of K_2PtCl_4 has been thoroughly analyzed,⁷ this compound may be used as the starting point for an approach to the energy difference in the Pt orbitals.

In Fig. 2 are shown the d-orbital splitting for the D_{4h} , PtCl_4^{2-} , and the proposed splitting for Zeise's

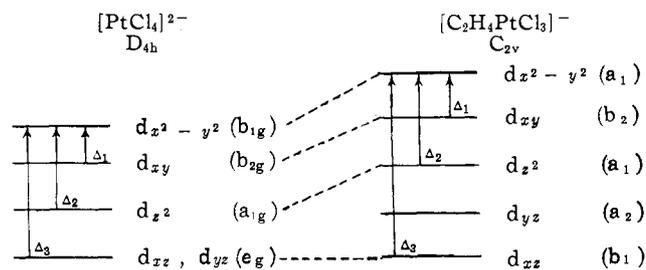


Fig. 2.—The d-orbital splittings in $[\text{PtCl}_4]^{2-}$ and Zeise's salt.

salt; these changes presumably result from the replacement of the rather symmetrically charged chlorine atom by the directional ethylene molecule. No change in the order of the orbitals in going from the PtCl_4^{2-} to Zeise's salt is expected. However, the ethylene, sitting perpendicular to the C_2 axis, has its electrons directed along the z -axis (the z -axis in PtCl_4^{2-} is the C_4 axis, and to facilitate comparison, the same coordinate system is used for Zeise's salt). The ethylene π -electrons extending along the z -axis and into the xy -plane would raise the $d_{x^2-y^2}$ level appreciably and the d_{z^2} level to a lesser extent. The d_{xy} orbital might be slightly lowered and the degenerate d_{xz} , d_{yz} are split in the less symmetrical Zeise's salt. The symmetry species assignment of the d-orbitals in Zeise's salt can be made by the technique of descending symmetry.⁸ In PtCl_4^{2-} the d-d electron promotions, Δ , are parity forbidden, but this forbiddenness is removed in Zeise's salt because of the loss of a center of symmetry. Considering then the energy levels and selection rules, it is to be expected that the one-electron transitions in Zeise's salt would be both hypsochromic and hyperchromic with respect to PtCl_4^{2-} . The data of Table IV are consistent with this interpretation. Figure 2 indicates that there should be a $d_{yz} \rightarrow d_{x^2-y^2}$ transition, but since this is an ${}^1A_1 \leftarrow {}^1A_2$ transition, it is forbidden by symmetry in C_{2v} . If this transition is assumed to have an energy intermediate between Δ_2 and Δ_3 , it should occur at about $34,900 \text{ cm}^{-1}$ ($286 \text{ m}\mu$). However, there is considerable absorption at this wave length and the contribution of the ${}^1A_1 \leftarrow {}^1A_2$ could not be determined.

Table IV shows that Δ_1 , the C.F.S.E. for Zeise's salt, is 8000 cm^{-1} greater than that for PtCl_4^{2-} , equivalent to about 9.75 Dq units (assuming 4.5 kcal./ Dq for Pt(II)),⁹ which helps to explain the stability of $\text{C}_2\text{H}_4\text{PtCl}_3^-$ and its ease of formation from PtCl_4^{2-} .

(7) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

(8) E. B. Wilson, T. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, p. 336.

(9) F. Basolo and R. G. Pearson, *Prog. Inorg. Chem.*, **4**, 424 (1962).

TABLE IV
 SPECTRAL DATA FOR Pt(II) COMPLEXES

Compound	ν_{\max} , cm. ⁻¹	ϵ	Assignment	Energy, kcal.
PtCl ₄ ²⁻ ^a	21,000	15	b _{2g} → b _{1g}	Δ ₁ , 60
	25,500	59	a _{1g} → b _{1g}	Δ ₂ , 73
	30,200	64	e _g → b _{1g}	Δ ₃ , 87
	46,000	9580	C.t.	
C ₂ H ₄ PtCl ₃ ^{-b}	29,800	235	b ₂ → a ₁	Δ ₁ , 85
	33,700	725	a ₁ → a ₁	Δ ₂ , 96
	38,000	1905 ^c	b ₁ → a ₁	Δ ₃ , 103
	42,000	3390	C.t.	

^a Ref. 7. ^b From the Ph.D. thesis of John R. Joy, University of Cincinnati (1958). ^c The intensity is too large for this to be wholly a d-d band and charge transfer probably adds considerably to the intensity here (see ref. 7).

There is of course a substantial contribution to stability by the π -bond between Pt and C₂H₄.

The $\pi \rightarrow \pi^*$ transitions for ethylene and styrene occur at 165 and 292 m μ , corresponding to an energy spread of 173 and 98 kcal., respectively. With this information, the crude level diagram of Fig. 3 may be constructed. The broken lines in the platinum atomic

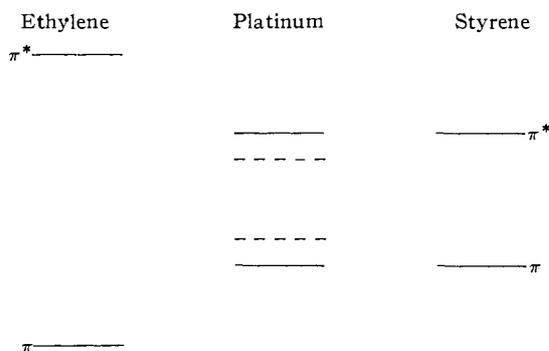


Fig. 3.—Energy levels of orbitals.

orbital diagram represent the d splitting in C₂H₄PtCl₃⁻ where the long wave length b₂ → a₁ band is at 336 m μ . It is important to report that the long wave length band in the spectrum of 1-(pyridine N-oxide)-3-ethylene-2,4-dichloroplatinum(II) occurs at 339 m μ

(ϵ 580), and thus in this compound the d splitting may be assumed to be similar to that in Zeise's salt. However, if this similarity exists, it is difficult to explain on the basis of Fig. 3 why in the competition of styrene and dodecene for a site in UnPtCl₃⁻, the dodecene is favored ($K = 37$), whereas in UnPtCl₂PyO the styrene is favored ($K = 0.052$, Table III). It may be that the PyO with its strong dipole in the direction of the Pt¹⁰ increases the overlap with the diffuse orbitals of styrene very effectively, whereas the overlap increase with the orbitals of dodecene is not as effective.

The "U" shape character of Fig. 1 is probably additional evidence for the double bond character of the UnPt bond and implies that all substituents on PyO favor dodecene in its competition with styrene ($X = H$). Substitution by the electron-releasing CH₃O group ($Z = CH_3O$ as compared to H) probably improves the energy matching of the dodecene-Pt orbitals, whereas the principal effect of $Z = NO_2$ is to encourage back donation from the styrene. When PyO is substituted by any group other than CH₃O, the styrene is favored regardless of the nature of the substituent on styrene (with the exception of $X = H$, $Z = NO_2$).

The effect of substitution on styrene is to compress the styrene levels and on this basis to improve the energy matching with the Pt orbitals. When $X = NO_2$, the styrene complex is always more favored than the dodecene complex. Perhaps solvation effects are important and operate to stabilize the styrene. The most stable styrene complex of all those reported here is the *p*-nitrostyrene complex with the parent PyO as partner.

All attempts at a Hammett σ - ρ correlation to fit all the data were unsuccessful. The work is being continued in an attempt to arrive at a consistent explanation.

Acknowledgment.—The authors wish to thank the Gulf Oil Company for a fellowship which made this work possible and Engelhard Industries for a generous supply of platinum.

(10) A. R. Katritzky, E. W. Randall, and L. E. Sutton, *J. Chem. Soc.*, 1769 (1957).

[A CONTRIBUTION FROM THE BIOLOGICAL INORGANIC CHEMISTRY UNIT, THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, THE AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, AUSTRALIA]

Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. IX. The Equilibrium Ratios and Isolation of Some of the Isomers in the Mixture Tris-((\pm) -propylenediamine)-cobalt(III) Chloride

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The optical isomers D-bis($(+)$ -propylenediamine)-($-$)-propylenediaminecobalt(III) iodide and L-bis($(-)$ -propylenediamine)-($+$)-propylenediaminecobalt(III) iodide have been isolated and characterized. The equilibrium constants $D[Co(+)pn_3]^{3+} / L[Co(-)pn_3]^{3+} / D[Co(+)pn_2(-)pn]^{3+} / L[Co(-)pn_2(+)pn]^{3+} = 1.0$,^{1b} $D[Co(+)pn_2(-)pn]^{3+} / L[Co(+)pn_2(-)pn]^{3+} = 2.4$, and $D[Co(+)pn(-)pn_2] / L[Co(-)pn(+)pn_2]^{3+} / D[Co(-)pn_3]^{3+} / L[Co(+)pn_3]^{3+} = 6.1$ were determined and the stabilities of the isomers have been rationalized with respect to the possible conformations which may be adopted by the propylenediamine rings.

Introduction

A previous paper in this series dealt with the conformational effects and the stabilities of the optical

(1) (a) Deceased. (b) *Notation for Optical Isomers:* D refers to the absolute configuration of the isomer relative to the $D(+)[Co(en)_3]^{2+}$ ion, (+) refers to the sign of rotation of the optically active entity (either the base or the complex) in the Na D line. If the rotation is recorded at another wave length the latter appears as a subscript, *i.e.*, $[\alpha]_{578}$. The literature associated with stereospecificity in metal complexes has denoted $D(+)[Co(+)pn_3]I_3$ as *Dddd* in the past; in this paper *Dddd* and $D[(+)(+)(+)]$ are equivalent.

isomers of "tris"-cobalt(III) complexes containing ethylenediamine (en) and ($-$)-propylenediamine ($(-)$ -pn). It was pointed out that both ethylenediamine

In the usage exemplified by *Dddd*, D referred to the sign of rotation in the Na D line of the complex and *d* was the sign of rotation of the base in the same wave length. Fortunately, in the cobalt(III) propylenediamine complexes the dextrorotatory isomers have the absolute configuration D so that $D[ddd]$ is equivalent to $D[d[ddd]]$, or $D[(+)(+)(+)]$ or $D[(+)(+)(+)]$.

(2) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 2913 (1963).