Anal. Calcd.: C, 23.1; H, 1.70; N, 3.37. Found: C, 23.7; H, 2.02; N, 3.15.

1,3-Bis-(4-nitrostyrene)-2,4-dichloro-μ-dichlorodiplatinum.—This compound was prepared in the same manner as the 3-nitrostyrene complex. The product was a yellow-orange powder which decomposed above 160°, without melting.

Anal. Calcd.: C, 23.1; H, 1.70; N, 3.37. Found: C, 22.4; H, 1.67; N, 2.81.

1,3-Bis-(3-chlorostyrene)-2,4-dichloro-μ-dichlorodiplatinum.—This complex was prepared in the same manner as the styrene complex. The product was a light orange powder which decomposed above 130°, without melting.

Anal. Calcd.: C, 23.8; H, 1.74. Found: C, 25.1; H, 2.08.

1,3-Bis-(4-methylstyrene)-2,4-dichloro-μ-dichlorodiplatinum.—This compound was prepared, in toluene solution, in the same manner as the 3-nitrostyrene complex. The product was an orange powder which decomposed above 165°, without melting.

Anal. Calcd.: C, 28.2; H, 2.62. Found: C, 28.2; H, 2.94.

1,3-Bis-(1-dodecene)-2,4-dichloro-μ-dichlorodiplatinum.—One millimole of ethylene platinous chloride was dissolved in the minimum volume of warm acetone. Two millimoles of 1-dodecene was added and the solution was warmed until evolution of ethylene stopped. A large volume of petroleum ether was added and the solution was boiled to reduce volume, after which it was cooled to promote crystallization. The product was filtered and recrystallized from petroleum ether, yielding a pink-orange material having a soapy consistency, m.p. 73–74°, with deepening of color but no apparent decomposition.

Anal. Calcd.: C, 33.2; H, 5.57. Found: C, 33.2; H, 5.42.

Ultraviolet Absorption Spectra.—The absorption spectra were obtained with a Beckman DU quartz spectrophotometer. Readings were taken at intervals of 2 mμ or less in the regions of the spectrum showing appreciable absorption. The spectra of some of the dimeric complexes were obtained in both chloroform and *t*-butyl alcohol. The spectra of the ionic complexes were obtained by dissolving the corresponding dimers in an acidic medium, either alcoholic or aqueous hydrochloric acid.

Spectrophotometric Evaluation of Equilibrium Constants.—Before the study of an equilibrium reaction was made, the spectra of the absorbing species involved were rechecked in 0.01 molar anhydrous alcoholic hydrochloric acid over the appropriate portion of the spectrum. A solution of the olefinic reagent in 0.01 molar alcoholic hydrochloric acid was made from freshly distilled material,[14] usually on the day before a run was made. No difficulties were encountered from polymerization of the styrenes. However, these solutions were checked to ensure that the absorbances were constant from the time that they were prepared until they were used.

A solution of the freshly crystallized complex, usually 4.0×10^{-3} molar, in 0.01 molar alcoholic hydrochloric acid, was made just before a run was started. Aliquots of 5 ml. of this solution were pipetted into five 50-ml. volumetric flasks. Aliquots of the olefin solution were added to the flasks in progressing volume. Thus, when the flasks were brought to volume, the total complex concentration was 4.0×10^{-4} molar in each case, whereas the total olefin concentration varied over a rather wide range. As soon as the volume in each flask had been brought to 50 ml. with 0.01 molar alcoholic hydrochloric acid, a sample was removed and its absorbance was measured in the spectrophotometer, thermostated at 25°. The flask was then suspended in a constant temperature bath at 25° for 1–2 hr. A second set of measurements then was recorded. These usually differed very slightly from the initial readings, indicating that equilibrium had been attained in the few minutes required to prepare the solutions. Absorbance measurements were taken at two or three wave lengths as a check, although it was necessary to use only one value to determine the concentrations of all components in equilibrium.

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(14) 1-Dodecene was used directly as received from Humphrey-Wilkinson, Inc.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED SCIENCE AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Relative Stabilities of Isomeric *cis*- and *trans*-Olefin Complexes with Platinum(II)

BY JOHN R. JOY AND MILTON ORCHIN

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Styrene–platinum(II) complex was equilibrated successively with *cis*- and *trans*-4-methyl-2-pentene and the equilibrium constants measured spectrophotometrically. The data show that the *cis*-isomer is about twice as stable as the *trans*-isomer and slightly more stable than the analogous complex with *cis*-2-pentene.

Introduction

The unequivocal proof of the non-identity of the platinum–olefin complexes from *cis*- and *trans*-isomers of a particular olefin (2-butene) has only recently been reported.[1] We also succeeded some time ago in preparing different complexes from 4-methyl-*cis* and 4-methyl-*trans*-2-pentene and wish to report now our studies on the relative stabilities of these complexes.

In the present work, the equilibrium constants for the reaction of the olefin–platinum complexes with styrene were determined according to the reactions

$$(\mathrm{UnPtCl_3})_2 + 2\mathrm{HCl} \longrightarrow 2\mathrm{H(UnPtCl_3)} \quad (1)$$

$$\mathrm{PhCH{=}CH_2} + (\mathrm{UnPtCl_3})^- \rightleftharpoons \mathrm{Un} + [\mathrm{PhCH{=}CH_2PtCl_3}]^- \quad (2)$$

where Un represents the olefin under study. The expression for the equilibrium constant, which was evaluated spectrophotometrically according to the preceding paper,[2] is

$$K = \frac{[\mathrm{Un}][\mathrm{C_6H_5CH{=}CH_2PtCl_3}]}{[\mathrm{PhCH{=}CH_2}][(\mathrm{UnPtCl_3})^-]} \quad (3)$$

Experimental

1,3-Bis-(*cis*-2-pentene)-2,4-dichloro-μ-dichlorodiplatinum.—Four millimoles of cold *cis*-2-pentene[3] was stirred with one millimole of ethylene platinous chloride, $(\mathrm{C_2H_4PtCl_2})_2$, in about 15 ml. of cold chloroform. The mixture was allowed to come to room temperature, during which all solid material dissolved. The solution then was heated carefully to remove

(1) H. B. Jonassen and W. B. Kirsch, THIS JOURNAL, **79**, 1279 (1957).

(2) J. R. Joy and M. Orchin, *ibid.*, **81**, 304 (1959).

most of the solvent and excess olefin. Upon addition of petroleum ether, with vigorous stirring, extensive precipitation took place. The product was separated by filtration and washed with petroleum ether, yielding a light yellow-orange powder which melted with partial decomposition at 144–145°.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF IONIC COMPLEXES, H(UnPtCl$_3$)

Solvent, HCl in ethanol, 0.01 mole/l.

Un	Long wave length max. mμ	log ε	Short wave length max. mμ	log ε
cis-2-Pentene	342	2.23	248	3.70
4-Methyl-*cis*-2-pentene	341	2.25	248	3.70
4-Methyl-*trans*-2-pentene	340	2.24		

TABLE II

INFRARED ABSORPTION[a] SPECTRA OF COVALENT COMPLEXES, $(UnPtCl_2)_2$; Nujol mull

Un = *cis*-2-pentene μ	4-Methyl-*cis*-2-pentene μ	4-Methyl-*trans*-2-pentene μ
7.70m	7.76m	7.74m
8.65w	8.61m	7.88shoulder
9.30m	9.05m	8.03shoulder
9.57m	9.50shoulder	8.50m
9.80w	9.56m	8.64shoulder
10.04m	9.84m	9.04m
10.84m	9.97m	9.56m
11.23w	10.45shoulder	9.81m
11.80m	10.65vs	10.49vs
12.98m	10.80m	10.90s
	11.00m	11.25m
	11.40m	11.99m
	12.25m	

[a] w = weak intensity, m = medium intensity, s = strong intensity, vs = very strong intensity.

1,3-Bis-(4-methyl-*cis*-2-pentene)-2,4-dichloro-μ-dichlorodiplatinum was prepared in the same manner as the *cis*-2-pentene complex. The product was a pale yellow powder which melted with partial decomposition at 157–158°.

Anal.[4] Calcd.: C, 20.6; H, 3.45. Found: C, 20.6 H, 3.53.

1,3-Bis-(4-methyl-*trans*-2-pentene)-2,4-dichloro-μ-dichlorodiplatinum also was prepared in the same manner as the *cis*-2-pentene complex. The product was a light yellow powder melting with partial decomposition at 139–140°.

Anal. Calcd.: C, 20.6; H, 3.45. Found: C, 20.3; H, 3.50.

Equilibrium Constants by Ultraviolet Spectroscopy.—The same method as employed previously[2] was used for the determination of equilibrium constants.

All ultraviolet spectra of the ionic complexes were obtained by dissolving the corresponding covalent complexes in 0.01 molar alcoholic hydrochloric acid and taking readings at intervals of 2 mμ or less, on a Beckman DU quartz spectrophotometer. The spectra are summarized in Table I.

Infrared Spectra.—All infrared spectra of complexes were obtained in Nujol mull, using a Baird Atomic Infrared Spectrophotometer with a sodium chloride prism. The spectra are summarized in Table II. The spectra of the isomeric olefin complexes are obviously different. The same conclusion had been reached previously in the case of the isomeric 2-butene complexes.[1]

Results and Discussion

The results of the equilibrium study are shown in Table III. It is apparent from the table that in the competition between styrene and the aliphatic olefin for coördination with the platinum(II), the simple olefin is the preferred ligand. If stoichiometric quantities of styrene and the aliphatic olefin complex are permitted to react, at equilibrium the ratio of 4-methyl-*cis*-2-pentene complex to styrene complex is 3.2. The similar ratio with 4-methyl-*trans*-2-pentene is 1.7. On this basis one can conclude that the *cis* complex is almost twice as stable as the corresponding *trans* isomer. Table III also shows that the unsubstituted *cis*-2-pentene gives a complex that is slightly less stable than the methyl substituted *cis*-2-pentene. Apparently substitution at the α-position to the double bond makes the pi electrons more available for complexing, and the steric factors, if any, are outweighed by this inductive effect. It is also of interest to note that the 1-dodecene complex[2] is approximately twice as stable as the most stable 2-pentene complex, probably because of steric factors.

TABLE III

EQUILIBRIUM CONSTANTS FOR THE REACTION OF PENTENE COMPLEXES WITH STYRENE

$$PhCH = CH_2 + (UnPtCl_3)^- \rightleftharpoons Un + (PhCH = CH_2PtCl_3)^-$$

Temp. = 25.0 ± 0.2°

Un	Concn. of HCl, mole/l.	Anal. wave length. mμ	K
cis-2-Pentene	0.0090	308	0.14 ± 0.002
4-Methyl-*cis*-2-pentene	.0092	308	.095 ± .001
4-Methyl-*trans*-2-pentene	.0099	310	.34 ± .004

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(3) All olefins were obtained from the Phillips Petroleum Company, Bartlesville, Oklahoma. The *cis*-2-pentene and 4-methyl-*cis*-2-pentene were 95 mole %. The 4-methyl-*trans*-2-pentene was 99.5 mole %. We are grateful to Dr. Fred E. Frey for his generous help in securing some of these materials.

(4) Analyses were performed by Geller Laboratories, Bardonia, New York.

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, UNIVERSITY OF SYDNEY]

Bidentate Chelate Compounds. II

BY HAROLD A. GOODWIN[1] AND FRANCIS LIONS

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α-Picolyldimethylarsine has been prepared and studies made of its ability to coördinate with the salts of certain metals Some features of its coördination chemistry are unusual.

Organic compounds are common whose molecules are capable of offering simultaneously to the same metal atom two donor nitrogen atoms. Less

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