donation of electrons from the nickel to the phosphine will probably be partly compensated by π-donation from the halogen to the nickel. Such donation may be expected to decrease in the order I > Br > Cl leading to the prediction of the strongest phosphine π-bond in the iodide. This is in accord with the order of the labilities. It may be noted that consideration of the σ-bonding would lead to the opposite order since the phosphine donates to the nickel and the electronegativity decreases in the order Cl > Br > I. If these reasonings are correct, it would appear that the π-bonding is more important than the σ-bonding in determining the relative stability of these complexes. A very similar conclusion was reached by Allen and Cook,[21] who found that the relative stability of the complexes $(Ar_3P)_2Pt(ac)$ (where ac = acetylene) was increased by electron-withdrawing substituents on the acetylene and also by electron-donating substituents on the phosphine. This is in accord with predictions based on considerations of the π-bonding but contrary to those based on the σ-bonding.

(21) A. D. Allen and C. D. Cook, Can. J. Chem., 41, 1235 (1953).

Molecular Asymmetry in the Coordination of Olefins with Transition Metals. trans-Dichloro(olefin)(amine)platinum(II) Complexes[1]

BY GASTONE PAIARO AND ACHILLE PANUNZI

By crystallization of solutions of trans-dichloro(olefin)[(R or S)-α-phenethylamine]platinum(II), in which the olefin was propylene, styrene, or trans-2-butene, only one diastereoisomer was obtained. In the case of trans-2-butene, it was found that the type of diastereoisomer obtained depended upon the nature of the solvent. By removal of the amine ligand from the complex with trans-2-butene it was possible to obtain the corresponding enantiomeric anion as the $Pt(NH_3)_4{}^{+2}$ salt.

Introduction

An olefinic compound without substituent asymmetric groups, and which does not have symmetry planes perpendicular to the plane of the double bond, possesses two enantiomorphic (nonsuperimposable) faces.[2]

When, by any reaction, the double bond of an olefin is bound in a π-complex to whatever center, each of the unsaturated carbon atoms, if linked to two different substituent groups, $_{R'}^{R}>C=$, becomes asymmetric. Accordingly, if an olefinic compound with nonsuperimposable faces is π-bonded to a coordinative center (M), a pair of enantiomorphs is obtained.

If the center is asymmetric or is connected to an asymmetric environment, a diastereoisomeric pair is obtained.
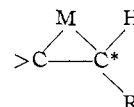
We can define the carbon atoms of the olefin bound to the coordination center as (R) or (S) according to the nomenclature proposed by Cahn, Ingold, and Prelog,[3] applied to the three-membered cyclic core
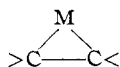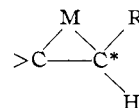

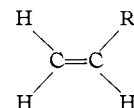The "sequence rule" states the order
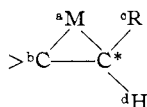
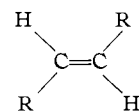and therefore in

the asymmetric atom C* is (R), while in

the atom C* is (S).[4]

Clearly, in the case of an olefinic compound of the type

(for example, styrene, propylene) (Fig. 1a and a'), only one asymmetric carbon is formed by coordination; in the case of an olefin of the type

(for example, trans-2-butene) (Fig. 1b and b'), two asymmetric carbon atoms having the same configura-

(1) For a preceding brief communication on this subject see G. Paiaro, P. Corradini, R. Palumbo, and A. Panunzi, Makromol. Chem., 71, 184 (1964).

(2) (a) G. Natta, M. Peraldo, M. Farina, and G. Bressan, ibid., 55, 139 (1962); (b) M. Farina and G. Bressan, ibid., 61, 79 (1963); (c) C. L. Arcus, J. Chem. Soc., 2801 (1955).

(3) R. S. Cahn, C. K. Ingold, and V. Prelog, Experientia, 12, 93 (1956).

(4) In a preceding work, ref. 1, the atoms C* were designated as r and s.

tion are formed; if the olefin is of the type

$$
\begin{array}{ccc}
\text{H} & & \text{H} \\
& \text{C}{=}\text{C} & \\
\text{R} & & \text{R}
\end{array}
$$
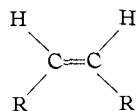
(for example, *cis*-2-butene) (Fig. 1c) the two asymmetric carbon atoms formed have opposite configurations, yielding a *meso* compound.

Figure 1.

A method of resolving this kind of asymmetry is to form stable π-complexes, in which a transition metal atom is bonded both to an olefin having non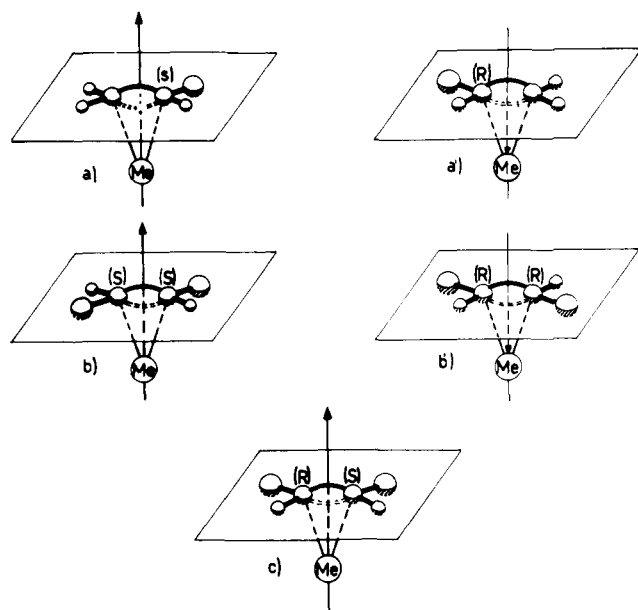superimposable faces and to an asymmetric ligand such as an optically active amine. Two diastereoisomers are possible (Fig. 2). The possible rotation of the coordinated olefin around the metal double-bond axis does not allow racemization.

We have prepared and resolved diastereoisomeric pairs of propylene, *trans*-2-butene, and styrene, coordinated to Pt(II)[5] and containing optically active (R or S)-α-phenethylamine of the general type *trans*-dichloro(olefin)(amine)platinum(II). The resolution is achieved by preferential crystallization from a suitable solvent or solvent mixture *via* second-order asymmetric transformation.[6] From each diastereoisomeric pair, it is possible to obtain one of the diastereoisomers in nearly quantitative yield. In the case of the *trans*-2-butene complex, according to the nature of the solvent or solvent mixture used in the crystallization, we were able to obtain, at will, one or the other of the two possible diastereoisomers. From these we obtained the resolved enantiomorph anions of type [PtCl₃–olefin]⁻ as tetraammineplatinum(II) salts. As was expected, we did not find any evidence of the formation of two different diastereoisomers in the case of *cis*-2-butene (Fig. 1c). In the preparation of the diastereo-

(5) For general reference, see "Gmelin's Handbuch der Anorganischen Chemie, Platin," Verlag Chemie, G.m.b.H., Weinheim, 1957, part D, No. 68.
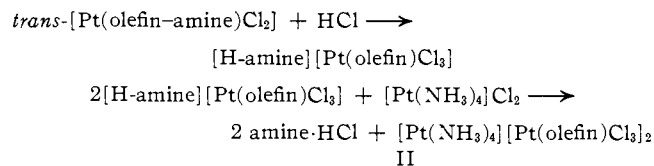
(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 63.

isomeric mixtures, we used the two schemes reported below.

Method A.—The exchange of ethylene with the corresponding olefinic compound, starting with *trans*-dichloro(ethylene)(amine)platinum(II).[7]

trans-Pt(C₂H₄–amine)Cl₂ + olefin ⟶

trans-Pt(olefin–amine)Cl₂ + C₂H₄
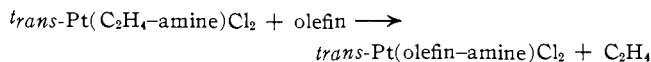
Method B.—The exchange of ethylene with the corresponding olefinic[8] compound, starting from bis-[chloro(ethylene)]-μ,μ'-dichlorodiplatinum(II) and the successive formation of the diastereoisomeric pairs with the optically active amine. The formation of complex anions of the type (PtCl₃–olefin)⁻, containing the resolved coordinated olefin, was realized by means of the following well-known reactions.

trans-[Pt(olefin–amine)Cl₂] + HCl ⟶

[H-amine][Pt(olefin)Cl₃]

2[H-amine][Pt(olefin)Cl₃] + [Pt(NH₃)₄]Cl₂ ⟶

2 amine·HCl + [Pt(NH₃)₄][Pt(olefin)Cl₃]₂

II

The salt (II) of the complex cation of Pt(II) is sparingly soluble and may be filtered off after a few minutes.

(S) or (R) Amine
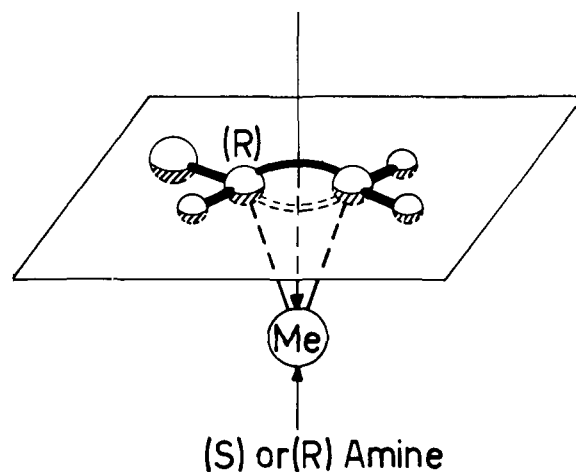
Figure 2.

Results

The crude diastereoisomeric pairs are viscous oils which can be converted by intensive drying under vacuum to glassy materials.

Analyses and infrared spectra of the crude mixtures of diastereoisomers are substantially identical with those of the corresponding crystalline pure diastereoisomers.

Treatment of the olefinic complexes with an aqueous solution of KCN yields the corresponding olefins unchanged, as was proved by means of infrared spectra and gas chromatographic analyses.

Pure diastereoisomers epimerize in solution, attaining at equilibrium values of rotation corresponding to that of the initial diastereoisomeric mixture. These

(7) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **85**, 3276 (1963).

(8) H. B. Jonassen and J. E. Field, *ibid.*, **79**, 1275 (1957).

TABLE I

OPTICAL ROTATION[a] OF THE DIFFERENT COORDINATION COMPOUNDS OF THE TYPE
trans-DICHLORO(OLEFIN)(α-PHENETHYLAMINE)PLATINUM(II)

Compounds	Abbreviation[b]	Crude products		Abbreviation[b]	Resolved diastereoisomers	
		$[\alpha]_D$	$[M]_D$		$[\alpha]_D$	$[M]_D$
(1) With (*S*)-amine and						
(A) Ethylene	(et,*S*)	−15.4	−63.9	...	...	....
(B) *cis*-2-Butene	(cb,*S*)	−14.3	−63.4	...	...	....
(C) Styrene	(st,*S*)	−13.1	−64.6	(st,+,*S*)	+292	+1440
(D) Propylene	(pr,*S*)	−14.7	−63.1	(pr,−,*S*)	−43.9	−188
(E) *trans*-2-Butene	(tb,*S*)	−14.5	−64.2	(tb,−,*S*)₁[c]	−76	−337
				(tb,−,*S*)₂[d]	−62.5	−329
				(tb,+,*S*)	+46.1	+204
(2) With (*R*)-amine and						
trans-2-Butene	(tb,*R*)	+13.4	+59.4[e]	(tb,+,*R*)₁[c]	+75.1	+332
				(tb,+,*R*)₂[d]	+61.8	+326
				(tb,−,*R*)	−44.6	−198

[a] The measurements were performed at 19° in methylene chloride (c 1/3.3). Concentrations are given in g./100 ml., lengths of polarimeter tubes in dm., $[\alpha]_D$ in α/(dm. g./ml.), and $[M]_D = [\alpha]_D \times$ mol. wt./100 (reading accuracy is ±0.02° with α not less than 0.35°). [b] The proposed abbreviations will be followed henceforth for the sake of simplicity in the course of the paper. [c] Compound having the formula $C_{12}H_{19}NCl_2Pt$. [d] Compound having the formula $C_{12}H_{19}NCl_2Pt \cdot C_6H_{12}$. [e] The lower values reported are due to lower optical purity of the (+)-amine.

values, expressed as molecular rotations [M] (see Table I), are nearly equal for all compounds investigated (including the ethylene and *cis*-2-butene complexes). This coincidence leads us to believe that (a) the contribution of the optically active amine to the molecular rotation of different complexes does not sensibly depend upon the nature of the *trans*-coordinated olefin, and (b) nearly equal quantities of the two possible diastereoisomers are present at equilibrium in solution.

Epimerization rates are strongly increased by the presence of small amounts of impurities and chiefly by the presence of free olefins.[9] Accordingly, the preferential crystallization of one diastereoisomer is favored by the presence of a small amount of the corresponding olefin. In the absence of excess of olefin, the epimerization half-times in methylene chloride at 19° are measured in minutes for the diastereoisomers of propylene and styrene, and in hours for the diastereoisomeric complexes of *trans*-2-butene.

Suitable solvent–nonsolvent mixtures for the crystallization are mixtures of toluene and petroleum ether (b.p. 30–60°), toluene and *n*-heptane, and chloroform and cyclohexane, according to the directions given in the Experimental section. From the diastereoisomeric pair olefin-(*S*)-α-phenethylamine, we obtained from all solvents the (−)-(*S*) diastereoisomer in the case of propylene and the (+)-(*S*) diastereoisomer in the case of styrene. In the case of the *trans*-2-butene complex with (*S*)-α-phenethylamine we found that from solvent mixtures containing cyclohexane (in a ratio of 1:2 or greater), the diastereoisomer (−)-(*S*) is obtained, whereas from mixtures not containing cyclohexane the (+)-(*S*) diastereoisomer is obtained; with (*R*)-α-phenethylamine, (+)-(*R*) and (−)-(*R*) diastereoisomers are obtained, respectively, from solvent mixtures with or without cyclohexane. The interesting behavior of the *trans*-2-butene complexes from a solvent mixture containing cyclohexane is thought to be the formation of a 1:1 inclusion compound with cyclohexane.

(9) G. Paiaro and A. Panunzi, *Ric. Sci.*, to be published.

Table I provides a summary of the optical activities of the complexes in methylene chloride at 19°. Table II provides a more complete set of data on the molecular rotations of the different diastereoisomers (I) containing propylene and *trans*-2-butene and of the (+) enantiomer salt (II) with *trans*-2-butene, measured in various solvents. From the difference between the molecular rotation [M′] of the pure diastereoisomer and the molecular rotation [M″] of the corresponding diastereoisomeric mixture (at equilibrium), a mean contribution to the rotation per asymmetric carbon atom can be evaluated (last column). This contribution turns out to be fairly constant throughout the series with a mean value of 125° for each asymmetric carbon atom of the type[10]

$$>C \!\!-\!\! \overset{\displaystyle Pt}{\underset{\displaystyle H}{C^*}} \!\!-\!\! CH_3$$
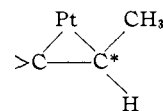
X-Ray studies are in progress in our laboratory to attribute the sign of rotation to the *R* or *S* configuration of the asymmetric olefinic carbon atoms.

The process of obtaining the pure diastereoisomers by recrystallization and epimerization can be repeated indefinitely as shown schematically in Table III for the *trans*-2-butene complex. This fact indicates that the process of epimerization does not allow any change in the positional distribution of ligands in the complexes of Pt(II) which were studied.

Experimental

All optical measurements were made with a Hilgher and Watts M412 polarimeter, with a reading accuracy of ±0.02°. Polarimeter tubes were maintained at constant temperature (±0.1°) by means of liquid circulation. Melting points were taken on a Kofler hot stage. Infrared spectra were recorded on a Beck-

(10) It may be of interest to note that the molecular rotation (calculated in the same way as for our complexes) per asymmetric carbon atom turns out to be of same order of magnitude (136°) for the Cope, ref. 7, fully resolved (+)-*trans*-dichloro(*trans*-cyclooctene)-(*R*)-(phenethylamine)platinum-(II).
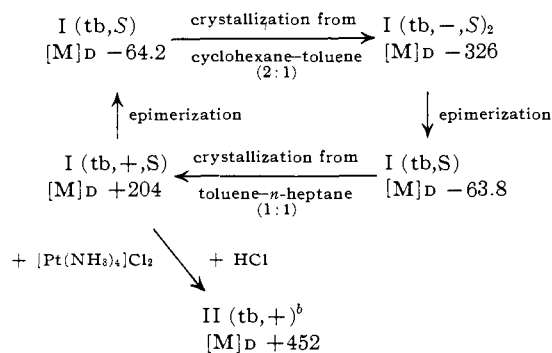
TABLE II

COMPARISON BETWEEN MOLECULAR CONTRIBUTIONS[a] OF ASYMMETRIC CARBON ATOMS COORDINATED TO PLATINUM AT 19°

Compound	Abbreviation	Solvent	Resolved diastereoisomers $[\alpha]$D	Resolved diastereoisomers $[M]$D	Diastereoisomer pair $[\alpha]$D	Diastereoisomer pair $[M]$D	Δ $(M' - M'')$	Δ/n[b]
Propylene	(pr, −,S)	Methylene chloride	−43.9	−188	−14.7	−63.1	−125	−125
Propylene	(pr, −,S)	Acetone	−64.4	−276	−36.6	−157	−119	−119
trans-2-Butene	(tb, −,S)$_1$	Methylene chloride	−75.2	−334	−14.5	−64	−270	−135
trans-2-Butene	(tb, −,S)$_2$	Methylene chloride	−62.5	−329	−14.	−64	−265	−135
trans-2-Butene	(tb, +,S)	Methylene chloride	+46.1	+204	−14.5	−64	+268	+134
trans-2-Butene	(tb, +,S)	Acetone	+14.9	+66	−39.7	−176	+242	+121
trans-2-Butene[c]	(tb, +)	Hydrochloric acid (0.3 N)–acetone, 1:1 by volume	+47.3	+465	....	...	+465	+116

[a] See Table I.   [b] n is the number of asymmetric carbon atoms.   [c] Enantiomer partially racemized.

TABLE III

CYCLE OF CRYSTALLIZATION AND EPIMERIZATION OF
trans-DICHLORO(*trans*-2-BUTENE)-(S)-
(α-PHENETHYLAMINE)PLATINUM(II) (I)[a]

I (tb,S)   ——crystallization from——> I (tb, −,S)$_2$
[M]D −64.2   cyclohexane–toluene   [M]D −326
                    (2:1)

↑ epimerization   ↓ epimerization

I (tb,+,S) <——crystallization from—— I (tb,S)
[M]D +204   toluene–n-heptane   [M]D −63.8
                    (1:1)

+ [Pt(NH₃)₄]Cl₂ ⟍ + HCl

II (tb,+)[b]
[M]D +452

[a] At 19° in methylene chloride.   [b] At 19° in a mixture of HCl (0.3 N)–CH₃COCH₃ (1:1).

man IR9 spectrophotometer. Some of the analyses were performed in this laboratory and others by Mikroanalytisches Laboratorium of the Max Planck Institut für Kohlenforschung, Mülheim. Solvents were of Analar grade. Ethylene and propylene were kindly supplied by Montecatini Co. of Milano and were of 99.5% purity; *cis*-2-butene (99.87%) and *trans*-2-butene (99.47%) were purchased from Fluka; styrene was purified by distillation over KOH at 100 mm.

(−)-*trans*-**Dichloro(ethylene)-(S)-($α$-phenethylamine)platinum(II) (et,S).**[11]—To a solution of 20.0 g. of potassium trichloro(ethylene)platinate(II) in 300 ml. of water was added under cooling a solution of 6.25 g. of $α$-phenethylamine[12] ($[\alpha]^{19}$D −40.3°, using d^{25}_4 0.9531) in 80 ml. of 3% HCl. A cooled 3% potassium hydroxide solution was carefully added dropwise, under cooling and stirring, until a pH of 6 was reached.

The crude precipitate (et,S), weighing 18.1 g., was a viscous oil which showed a tendency to solidify on standing; the crystalline product was obtained as yellow prisms from a mixture of chloroform and cyclohexane (1:10), m.p. 74–75°, $[\alpha]^{19}$D −15.3° (c 2.3, methylene chloride).

Anal. Calcd. for C₁₀H₁₅NCl₂Pt: N, 3.38; Pt, 47.00. Found: N, 3.34; Pt, 46.83.

(−)-*trans*-**Dichloro(propylene)-(S)-($α$-phenethylamine)platinum(II) (pr, −,S).**[11]—A slow current of propylene was allowed to bubble for about 3 hr. into a solution of 6.10 g. of potassium trichloro(ethylene)platinate(II) in 30 ml. of water. Then 1.9 g. of (S)-$α$-phenethylamine, $[\alpha]^{19}$D −40.3°, in 35 ml. of 3% HCl was added. A cooled 3% potassium hydroxide solution was added until a pH of 6 was reached. Filtration gave 5.97 g. of the crude mixture of diastereoisomers, a viscous orange oil (pr,S). Treatment of a sample of this crude mixture with an aqueous solution of KCN resulted in the evolution of propylene, free of ethylene. The viscous oil, after extensive pumping at 0.2

mm., had $[\alpha]^{19}$D −14.5° (c 1.5, methylene chloride). The crude oil (pr,S) (2.52 g.) was dissolved in 20 ml. of cyclohexane and chloroform (1:10). After a few hours at 0°, it was possible to collect by filtration 1.75 g. of fine yellow needles (pr, −,S). A second fraction of 0.36 g. was collected after 2 days. The values of melting point and rotation were substantially the same for the two fractions. Another sample of 2.98 g. was crystallized from 10 ml. of a mixture of toluene and n-heptane (1:2). Fractions were collected (combined yield 2.42 g.) with values of optical activity and melting point identical with those of fractions obtained from a mixture of cyclohexane and chloroform.

Since the diastereoisomer had an epimerization half-time of the order of minutes, the value of specific rotation was determined, adding the solvent at a known temperature to the tube containing the weighed sample. The rotation was measured against time, and a value, $[\alpha]^{19}$D −43.3° (c 2.55, methylene chloride), was obtained by extrapolation to zero time. After about 2 hr., the specific rotation reached a constant value of $[\alpha]^{19}$D −14.9°.

Anal. Calcd. for C₁₁H₁₇NCl₂Pt: N, 3.26; Pt, 45.45. Found: N, 3.29; Pt, 45.32.

(+)-*trans*-**Dichloro(styrene)-(S)-($α$-phenethylamine)platinum(II) (st, +,S).**[11]—The crude mixture of two diastereoisomers was obtained in two ways.

A.—A solution of 4.00 g. of (et,S)[11] and 2 ml. of styrene in 15 ml. of CH₂Cl₂ was heated to the boiling point for 3 hr. The solvent was removed and the crude product washed twice with petroleum ether (b.p. 30–50°) and then dried *in vacuo*. After about 3 days under vacuum, the product was still a viscous orange oil (st,S), $[\alpha]^{19}$D −12.8°.

B.—The product was also prepared according to the procedure used by Andersen,[13] with a yield of 4.6 g. of potassium trichloro(styrene)platinate(II), by the action of styrene on 5.1 g. of potassium trichloro(ethylene)platinate(II) in 50 ml. of ethanol. Adding to a cooled solution of 3.6 g. of potassium trichloro(styrene)platinate(II) in 50 ml. of water a cooled solution of 1 g. of (S)-$α$-phenethylamine in 3% HCl, in the manner described for (et,S), we obtained by filtration 4.1 g. of the crude mixture of diastereoisomers (st,S). The oil crystallized from 25 ml. of toluene and cyclohexane (1:8); during a 10-day period, three crops were collected, 3.4 g. of orange needles (st, +,S) having a m.p. of 91–93°. The specific rotation was determined, as in the case of (pr, −,S), by extrapolating to zero time measurements taken against time, $[\alpha]^{19}$D +286° (c 1.3, methylene chloride). The constant value for rotation at equilibrium is $[\alpha]^{19}$D −13.2°.

Anal. Calcd. for C₁₆H₁₉NCl₂Pt: N, 2.85; Pt, 39.70. Found: N, 2.78; Pt, 40.02.

(−)-*trans*-**Dichloro(*cis*-2-butene)-(S)-($α$-phenethylamine)platinum(II)(cb,S).**[11]—Liquid *cis*-2-butene (10 ml.) was condensed on 3.27 g. of $μ,μ'$-dichloro-1,3-dichloro-2,4-bis(ethylene)diplatinum(II), (C₂H₄PtCl₂)₂,[14] in a one-neck flask equipped with an efficient condenser jacketed with a carbon dioxide–acetone mixture. The mixture in the flask was kept at the boiling point for about 30 min. The condenser was then removed and the residual *cis*-2-butene evaporated. The yellow residue was nearly pure $μ,μ'$-dichloro-1,3-dichloro-2,4-bis(*cis*-2-butene)diplatinum(II), (C₄H₈PtCl₂)₂.[9] To a solution of 3.02 g. of the crude compound

(11) Tables I and II denote abbreviations.
(12) W. Theilacker and H. G. Winkler, *Chem. Ber.*, **87**, 690 (1954).
(13) J. S. Andersen, *J. Chem. Soc.*, 1042 (1936).
(14) J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 210 (1957).

and 0.8 g. of KCl in 40 ml. of cold water, 1.19 g. of (S)-α-phen-ethylamine in 25 ml. of 3% HCl was added; to the cooled mixture a 3% potassium hydroxide solution was added until a pH of 6 was reached. The insoluble viscous oil was filtered, washed with water, and then dried with intensive pumping. The oil solidified on standing, m.p. 50–52°. By crystallizing 2.0 g. of the crude product from 10 ml. of chloroform and cyclohexane (1:10), 1.38 g. of fine pale yellow needles were obtained (cb,S), m.p. 59–60°, [α]^{19}D −14.3° (c 3.5, methylene chloride).

Crystallization of the crude material from several solvent mixtures (such as toluene and cyclohexane (1:5) and carbon tetrachloride and petroleum ether (1:6)) gave the same product.

Anal. Calcd. for C$_{12}$H$_{19}$NCl$_2$Pt: N, 3.16; Pt, 44.01. Found: N, 3.19; Pt, 44.35.

(−)-*trans*-Dichloro(*trans*-2-butene)-(S)-(α-phenethylamine)-platinum(II) (tb,−,S).[11]—The crude mixture of diastereoisomers (8.1 g.) was obtained by applying the procedure described for the preparation of (cb,S) to an 8.5-g. sample of (C$_2$H$_4$PtCl$_2$)$_2$. The crude product was a viscous orange-yellow oil after 1 day of pumping at 0.2 mm. The crude diastereoisomeric pair (2.73 g.) was dissolved at 40° in 10 ml. of a mixture of chloroform and cyclohexane (1:10). Yellow, well-formed needles separated immediately. After 24 hr. at 0°, the crystals were filtered off. The product (2.14 g.), melting at 70–71°, was collected (tb,−,S). After standing for 48 hr., a second crop of crystals separated (0.36 g.), melting at 70–72°. The product was washed with cyclohexane and petroleum ether (b.p. 30–60°) and dried for a few minutes in an air stream. The dried product was found to lose cyclohexane slowly at atmospheric pressure, and rapidly under vacuum. The specific activity of the pure diastereoisomer varied less with time than did (pr,−,S) and (st,+,S). It was therefore not necessary to extrapolate in order to obtain the specific rotation of the pure diastereoisomer, [α]^{19}D −61.7° (c 1.8, methylene chloride); after epimerization with free *trans*-2-butene, [α]^{19}D −11.2°.

Anal. Calcd. for C$_{12}$H$_{19}$NCl$_2$Pt·C$_6$H$_{12}$: N, 2.65; Pt, 37.00. Found: N, 2.69; Pt, 37.3.

X-Ray data gave a = 15.59 ± 0.07, b = 14.72 ± 0.07, c = 9.36 ± 0.05 Å.; space group P2$_1$2$_1$; d = 1.62 g./cm.^{3}. The molecular weight of the independent unit was 524; the molecular weight calculated for a 1:1 inclusion compound was 527. The evolution of cyclohexane after 2 days of pumping at 0.2 mm. was complete and the diastereoisomer has a m.p. of 93° and [α]^{19}D −75.6° (c 2.3, methylene chloride); after epimerization with free *trans*-2-butene, [α]^{19}D −14.6°.

Anal. Calcd. for C$_{12}$H$_{19}$NCl$_2$Pt: N, 3.16; Pt, 44.01. Found: N, 3.18; Pt, 44.45.

X-Ray data showed more intense lines of the powder spectrum: 2θ Cu Kα, 10.5, 14.4, 20.6, 28.4, 40.7.

(+)-*trans*-Dichloro(*trans*-2-butene)-(S)-(α-phenethylamine)-platinum(II) (tb,+,S).—The crude material (tb,S) (4.27 g.) was dissolved at 40° in 11 ml. of a mixture of toluene and n-heptane (1:2). The pure diastereoisomer separated in the form of small blades. Two identical fractions were filtered off (3.45 g.).

The diastereoisomer melted at 110°, [α]^{19}D +45.9° (c 1.9, methylene chloride). Epimerization, in the presence of free olefin, led to a value of [α]^{19}D −14.4°.

Anal. Calcd. for C$_{12}$H$_{19}$NCl$_2$Pt: N, 3.16; Pt, 44.01. Found: N, 3.13; Pt, 43.95.

X-Ray data gave a = 8.87 ± 0.04, b = 12.21 ± 0.05, c = 6.92 ± 0.04 Å.; β = 99 ± 1°; d = 2.02; space group P2$_1$. The molecular weight of the independent unit was 449, mol. wt. (calcd.) 443.

(+)-*trans*-Dichloro(*trans*-2-butene)-(R)-(α-phenethylamine)-platinum(II) (tb,+,R).—The diastereoisomeric mixture was obtained by the procedure used for (cb,S). In this case (+)-(R)-α-phenethylamine, [α]^{19}D +38.4°, was used. The crude product (12.8 g.) was obtained from 9.2 g. of (C$_4$H$_8$PtCl$_2$)$_2$ and 3.5 g. of amine. The product, dried by intensive pumping, was a viscous orange-yellow oil, [α]^{19}D +13.2° (c 2.6, methylene chloride). The pure diastereoisomer (3.1 g.) separated from a solution of 4.5 g. of crude mixture in 10 ml. of chloroform and cyclohexane (1:10). The product contained cyclohexane, as did (tb,−,S). By removing the cyclohexane with pumping, a product was obtained with m.p. 92–93° and [α]^{19}D +75.3° (c 1.6, methylene chloride); after epimerization with free olefin, [α]^{19}D +13.3°.

Anal. Calcd. for C$_{12}$H$_{19}$NCl$_2$Pt: N, 3.16; Pt, 44.01. Found: N, 3.18; Pt, 43.96.

(−)-*trans*-Dichloro(*trans*-2-butene)-(R)-(α-phenethylamine)-platinum(II) (tb,−,R).—The crude product (tb,R) (1.39 g.) was dissolved in 3 ml. of a mixture of toluene and n-heptane (1:2). The levorotatory complex separated in the form of small blades. Two fractions (0.97 g.) were collected from solution, having a m.p. of 105–106° and [α]^{19}D −45.1° (c 2.1, methylene chloride); after epimerization with free olefin, [α]^{19}D +13.6°.

Anal. Calcd. for C$_{12}$H$_{19}$NCl$_2$Pt: N, 3.16; Cl, 16.00; Pt, 44.01. Found: N, 3.13; Cl, 16.06; Pt, 44.1.

(+)-Tetraammineplatinum(II)–Trichloro(*trans*-2-butene)platinum(II), [Pt(NH$_3$)$_4$][C$_4$H$_8$PtCl$_3$]$_2$ (tb,+).—Pure (tb,+,S) (0.85 g.) was dissolved in 2 ml. of acetone. To this solution, maintained at 0°, was added slowly 6 ml. of 1 N HCl, after which the acetone was removed *in vacuo.* To this aqueous solution was added a solution of 0.6 g. of [(NH$_3$)$_4$Pt]Cl$_2$ in 2 ml. of water. At once a crop of bright yellow crystals was obtained, and the yield of solid increased by keeping the solution at 0°. The precipitate was washed twice with 1 ml. of water, then with 1 ml. of acetone. After drying, 0.42 g. of (tb,+) was obtained. An infrared spectrum did not show the presence of amine in the complex. The product was fairly soluble in a mixture of 0.2 N HCl and acetone (1:1), [α]^{19}D +45.6°. The product isomerized slowly until [α] was zero.

Anal. Calcd. for C$_8$H$_{25}$N$_4$Cl$_8$Pt$_2$: Cl, 21.75; Pt, 59.82. Found: Cl, 21.32; Pt, 59.67.