Nmr spectra were obtained on the Varian A-60 nmr spectrometer, except for the high-field measurements which were made on the Varian HR-56.4, nmr spectrometer. Nmr tubes were sealed under $N_2$ to prevent contamination from air and moisture.

**Spectrum of $Fe(CO)_5$ in Pyrrolidine (5-$\mu$ Region).** $Fe(CO)_5$ (0.2 ml) was added to 10 ml of pyrrolidine and a spectrum taken within 2 min after mixing in a 0.015-mm cell. The results are shown in Figure 1.

**Concentrated Solutions of $Fe(CO)_5$ and Pyrrolidine.** $Fe(CO)_5$ (1.0 ml) was mixed with 3.0 ml of pyrrolidine and spectra taken between KBr plates within 2 min after mixing. An intense N-H stretching mode distinct from that of free pyrrolidine was found in these spectra (Figure 2). Nmr spectra were also obtained from these solutions, with the results shown in Figure 5.

**Hydrolysis of Species I. Pyrrolidine Case.** To a solution of 0.2 ml of $Fe(CO)_5$ in pyrrolidine was added 0.5 ml of water. The bands of $HFe(CO)_4^-$ appeared in the infrared spectrum of this solution within 5 min after addition of the water. Pyrrolidine carbamate was prepared by bubbling $CO_2$ through a solution of pyrrolidine and water in ether according to the method of Faurholt, *et al.*[14] It was possible to identify the infrared bands of the carbamate with those in solutions of species II described above, paralleling the identification in the piperidine case.[3] No attempt was made to isolate pyrrolidine carbamate from solutions of II.

**Preparation and Stoichiometry of Solid Species I. Pyrrolidine Case.** Pyrrolidine (10 ml) was frozen at liquid nitrogen temperatures in a tube sealed with a serum stopple. $Fe(CO)_5$ (3 ml) was added to the tube and frozen in another layer above the amine. The tube was then allowed to warm slowly to room temperature. As melting occurred, crystals formed in the tube, first at the interface, then throughout the sample. After about 1 hr the sample was almost completely crystalline, with only a small amount of excess liquid remaining. The reaction product was filtered under $N_2$. Although samples of the pale yellow-white crystals were stored in sealed tubes under $N_2$ and protected from light, after about 24 hr discoloration indicative of decomposition began to be apparent. The crystals could be easily purified immediately prior to use by vacuum sublimation. The stoichiometry of this solid was determined spectrophotometrically, making use of the fact that it dissociates completely to $Fe(CO)_5$ and pyrrolidine when dissolved in an inert solvent such as cyclohexane. The amounts of these two components in the compound were determined by comparing the intensities of the 1960-cm$^{-1}$ band of $Fe(CO)_5$ and the 784-cm$^{-1}$ band of pyrrolidine in a cyclohexane solution of the compound with those of solutions containing known amounts of the individual reagents in the same solvent. The molar ratio of pyrrolidine to $Fe(CO)_5$ in I was thus determined to be 2.2:1.[6]

**Spectra of Solid I in Various Solvents.** Solid I (0.2 g) was dissolved in 1 ml of *n*-heptane, in THF, and in DMSO. The spectrum of the *n*-heptane solution showed only the bands of $Fe(CO)_5$ in the 5-$\mu$ region, in THF the bands of I and of free $Fe(CO)_5$ were present, and in DMSO only the bands of I could be seen in the 5-$\mu$ region (see Figure 3).

**Conductance Measurements.** The conductance measurements were carried out using the instrument described in ref 3. To measure the concentration dependence of the conductance, 18 ml of pyrrolidine was placed in the cell, which had been previously flushed with $N_2$ and sealed with serum stopples. $Fe(CO)_5$ was added in small portions using Hamilton microliter syringes. In a typical pyrrolidine experiment (Figure 3) the amount of $Fe(CO)_5$ was increased from 0.001 to 0.20 ml.

**Dielectric Constant of Pyrrolidine.** The dielectric constant of pyrrolidine was measured using a Model DM01 Dipolmeter manufactured by the Kahl Scientific Instrument Co.[15] An MFL 1 cell was used, and gave a cell reading of 2702.6, which corresponded to a dielectric constant of 6.34.

**Preparation of Pyrrolidine Hydrochloride.** Pyrrolidine hydrochloride was prepared by slowly adding 12 *M* HCl to an aqueous solution of pyrrolidine in water. The water was then removed under vacuum, yielding the white, crystalline, hydroscopic amine hydrochloride.

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[14] C. Faurholt and A. Jensen, *Acta Chem. Scand.*, **6**, 1073 (1952).

[15] We thank Dr. M. Cefola for the use of this instrument.

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# Molecular Asymmetry in the Coordination of Olefins to Transition Metals. IV. *cis*-Dichloro(olefin)(amine)platinum(II) Complexes

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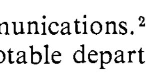
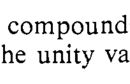
**Abstract:** Studies were extended on the molecular asymmetry that arises from the coordination of an olefin possessing symmetry differing from $C_{2v}$ or $D_{2h}$ to a transition metal. The stereochemical behavior of the Pt(II) complexes with an asymmetric amine *cis* coordinated to the olefinic ligand was examined. In this paper polarimetric behavior, preparation, and characterization are reported for complexes of this type with the olefins ethylene, propene, *cis*- and *trans*-butene, *t*-butylethylene, styrene, ethyl $\alpha$-chloroacrylate, *trans*-3-hexene, *trans*-1,4-dichloro-2-butene, and *trans*-cyclooctene.

Continuing our investigations concerning the molecular asymmetry of the complexes of the transition metals with olefins possessing symmetry differing from $C_{2v}$ or $D_{2h}$,[1] we have studied the diastereoisomeric compounds *cis*-dichloro(olefin)-(*S*)-($\alpha$-phenethylamine)platinum(II) (I). Some preliminary data concerning these compounds has already been reported in previous brief communications.[2] For *cis* compounds, we observed a notable departure from the unity value of the



$$\begin{array}{c} \text{Cl} \\ | \\ \text{Cl—Pt—NH}_2\text{R} \\ | \\ \text{olefin} \end{array}$$

I



$$\begin{array}{c} \text{NH}_2\text{R} \\ | \\ \text{Cl—Pt—Cl} \\ | \\ \text{olefin} \end{array}$$

II

[1] (a) G. Paiaro, P. Corradini, R. Palumbo, and A. Panunzi, *Makromol. Chem.*, 71, 184 (1964); (b) G. Paiaro and A. Panunzi, *J. Am. Chem. Soc.*, **86**, 5148 (1964).

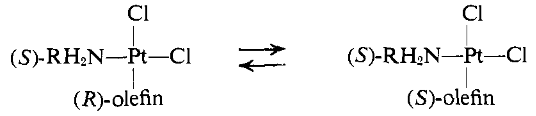
[2] (a) G. Paiaro and A. Panunzi, *Tetrahedron Letters*, **8**, 4411 (1965): (b) P. Corradini, S. F. Mason, G. Paiaro, A. Panunzi, and G. H. Searle, *J. Am. Chem. Soc.*, **88**, 2863 (1966).

**Table I.** Data of Optical Activity[a] of *cis*-Dichloro(olefin)-(*S*)-($\alpha$-phenethylamine)platinum(II) Complexes

| Olefinic compd | Complex abbreviation | Resolved diastereoisomers Mp, °C | $[\alpha]_D$ | $[M]_D$ | $[\alpha]_D$[b] | $[M]_D$[b] |
|---|---|---|---|---|---|---|
| Ethylene | (et, S) | 164 | | | −54.8 ± 2.2 | −228 ± 9 |
| *cis*-2-Butene | (cb, S) | 156 | | | −58.0 ± 1.6 | −257 ± 7 |
| Propylene | (pr, +, S) | 147–149 | +4.8 ± 2 | +206 ± 9 | −56.2 ± 2.3 | −241 ± 10 |
| Propylene | (pr, −, S) | 140 | −115 ± 6 | −493 ± 26 | | |
| *t*-Butylethylene | (tbe, +, S) | 135–141 | + 67 ± 4 | +316 ± 19 | −43.2 ± 6 | −203 ± 38 |
| *t*-Butylethylene | (tbe, −, S) | 139–145 | −148 ± 5 | −698 ± 24 | | |
| Styrene | (st, −, S) | 152 | −197 ± 10 | −971 ± 49 | −57.4 ± 5 | −283 ± 25 |
| *trans*-2-Butene | (tb, −, S) | 158–160 | −179 ± 5 | −793 ± 22 | −79.0 ± 3 | −351 ± 13 |
| *trans*-3-Hexene | (thx, −, S) | 148–149 | −142 ± 4 | −670 ± 19 | −77.9 ± 3 | −367 ± 14 |
| 1,4-Dichlorobutene | (dcb, −, S) | 132 | −104 ± 7 | −558 ± 38 | −73.0 ± 6 | −392 ± 32 |
| Ethyl $\alpha$-chloroacrylate | (eca, −, S) | 107 | −185 ± 6 | −965 ± 31 | −82.1 ± 3 | −428 ± 16 |

[a] In acetone at 25° (*c* 0.25–1.2) (deg). [b] Values at equilibrium (after epimerization) and values of nonresoluble complexes.

equilibrium constant of the reaction



$$(S)\text{-}RH_2N\text{—}\overset{\displaystyle Cl}{\underset{\displaystyle (R)\text{-olefin}}{Pt}}\text{—}Cl \rightleftharpoons (S)\text{-}RH_2N\text{—}\overset{\displaystyle Cl}{\underset{\displaystyle (S)\text{-olefin}}{Pt}}\text{—}Cl$$

whereas we could not detect any departure from unity for the corresponding constant for *trans* compounds II within the accuracy of the measurements.

The probable origin of the effect of asymmetric induction shown by *cis* complexes is the steric interaction between the amine and the *cis*-coordinated olefin. In fact, the optical data (see below) indicate that this effect is relevant only for 1,2-*trans*-disubstituted ethylenes. If an effect exists in the case of the monosubstituted olefins, it should be much less important. In this paper we report polarimetric behavior, preparation, and characterization of complexes of type I with various olefins.

## Results

The diastereoisomeric nature of compounds I and II arises from the simultaneous presence of the asymmetric amine and one or two asymmetric centers in the complex generated after coordination of the olefin: the double-bonded carbon atoms of the olefin, if single-bonded, to two different substituents, become asymmetric[1b] upon coordination. The diastereoisomeric pairs of I can be resolved by fractional crystallization. In addition, one of the two possible diastereoisomers can be obtained with a nearly quantitative yield through a "*second-order asymmetric transformation*,"[3] as has already been shown for *trans* complexes.[1] Both possible diastereoisomers were obtained only in the case of the propylene and *t*-butylethylene complexes.

The olefinic complexes of the *cis* series were obtained by direct interaction of the olefin with the salt IV (scheme A), or, more advantageously, by exchange (method B) of the olefin with the ethylene complex obtained according to (A). The *cis* structure of I was

$$2(\text{amine}) + K_2PtCl_4 \longrightarrow \underset{\text{III}}{cis\text{-}[(\text{amine})_2PtCl_2]} + 2KCl \quad \text{(A)}$$

$$cis\text{-}[(\text{amine})_2PtCl_2] + HCl \xrightarrow[H_2O]{100°} \underset{\text{IV}}{[\text{H-amine}][(\text{amine})PtCl_3]}$$

$$[\text{H-amine}][(\text{amine})PtCl_3] + \text{olefin} \longrightarrow cis\text{-}[(\text{olefin})(\text{amine})PtCl_2] + \text{amine}\cdot HCl$$

$$cis\text{-}[(C_2H_4)(\text{amine})PtCl_2] + \text{olefin} \longrightarrow \underset{\text{I}}{cis\text{-}[(\text{olefin})(\text{amine})PtCl_2]} + \text{ethylene} \quad \text{(B)}$$

confirmed by dimensional X-ray analysis of the diastereoisomeric complexes with *trans*- and with *cis*-butene.[4]

Under the experimental conditions employed, we did not observe any isomerization of the *cis* complexes to *trans* complexes and, furthermore, the exchange between an olefin and the ethylene complex occurred with retention of configuration. The complexes of the *cis* series are generally more stable and less soluble in the common organic solvents than the corresponding *trans* series compounds. The resolved diastereoisomeric *cis* complexes undergo spontaneous mutarotation at a much lower rate than the corresponding *trans* complexes. For example, the half-time of mutarotation in the absence of free olefin in the case of the (−) diastereoisomer of the propylene complex was 4.5 hr in acetone at 25° (*c* 1.0 g/100 ml); under the same conditions for the (−) diastereoisomer of the propylene complex in the *trans* series, the half-time was of the order of minutes. Also in the case of *cis* complexes the rate of mutarotation is strongly affected by the presence of free olefin. Equilibrium rotation was obtained in a few minutes, with the resolved diastereoisomers of the *cis* complexes with propylene and styrene, in the presence of free olefin.

The *cis* complexes with olefins of the type *trans* R—CH═CH—R showed a slower mutarotation rate; in the presence of free olefin the equilibrium was attained only after several days at room temperature. The separation of one diastereoisomer in nearly quantitative yield (based on the equilibrium mixture) *via* "second-order asymmetric transformation" was thus conditioned by this slow step. A few attempts to remove the amine from the pure diastereoisomers I in order to isolate the enantiomeric anions containing the olefin (as was done in the case of the *trans* diastereoisomers) were unsuccessful. In Table I the values of optical rotation of the *cis* complexes are reported. The values of the optical rotation of diastereoisomeric pairs

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(3) E. E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 63.

(4) C. Pedone and P. Ganis, *Ric. Sci.*, in press.

at equilibrium are those obtained after mutarotation of the resolved pure diastereoisomers.[5]

The measurements of the optical rotations of diastereoisomeric mixtures as obtained after exchange of the ethylene complex with the corresponding olefin did not give generally reproducible values. The main reason for this was the peculiar tendency of the complex to crystallize from concentrated solutions preferentially in one of the two possible forms after local evaporation of the solvent on the walls of the container, or in removing the solvent, or in the precipitation with a "nonsolvent." Clearly, the complex with ethylene is not diastereoisomeric. In the complex with the *cis*-butene the two asymmetric carbon atoms formed upon coordination have opposite configurations yielding a *meso* compound.

As noted previously[2a] the deviation of the molecular rotation of an olefin complex I (as diastereoisomeric mixture at equilibrium) from that of the corresponding ethylene complex affords an indication that asymmetric induction occurs in the coordination of the olefin. These inferences were successively supported by the circular dichroism spectra of I,[2b] which suggested that the configuration of the olefin relative to the metal and the other ligands would be reflected in the sign of the circular dichroism band near 27,000 $\text{cm}^{-1}$ and that the composition of a mixture of diastereoisomers was given semiquantitatively by the magnitude of that dichroism. From these data it was possible to calculate that in the equilibrium mixture of the two diastereoisomers of the *trans*-butene complex, the (−) diastereoisomer predominated to the extent of 40% in ethanol solution at room temperature. This result is in accordance with the value that is obtained from the data of the optical activity of this complex, reported in Table I, if we suppose that the rotation of a mixture of equal amounts of the two possible diastereoisomers is near the rotation of the ethylene complex.

These indications are unambiguously supported by the exchange reaction of the ethylene complex I with racemic *trans*-cyclooctene (COT). When this exchange is effected using 2 moles of racemic olefin per mole of ethylene complex, there is preferential formation of diastereoisomer, and the unreacted olefin (levorotatory) is obtained with an optical purity of about 27%. Therefore, an approximate value of the equilibrium constant for the reaction

$$(+)\text{-}cis\text{-}[(\text{COT})(S\text{-amine})\text{PtCl}_2] + (+)\text{-COT} \rightleftarrows (-)\text{-}cis\ [(\text{COT})(S\text{-amine})\text{PtCl}_2] + (-)\text{-COT}$$

is 3 at 25° in methylene chloride and the ratio of the concentrations of the two possible diastereoisomers is near that of the concentrations of the two diastereoisomers of the *trans*-butene complex at equilibrium.

The levorotatory preferential diastereoisomer of the cyclooctene complex contains the (+) olefin, for which the (*S*) configuration was established.[6] When the double bond is coordinated to the metal the configuration becomes (*R*,*R*). It may be of interest to observe that this configuration is the same as that[7] of the two asymmetric carbon atoms formed in the coordination of *trans*-butene, in the preferential levorotatory diastereoisomer of the *cis* complex containing this olefin.

## Experimental Section

Melting points (with decomposition) were taken on a Kofler hot stage. Some of the analyses were performed in this laboratory and others by Mikroanalytisches Laboratorium of the Max-Planck Institut für Kohlenforschung, Mühleim. Optical rotations were determined with a Hilgher and Watts M412 polarimeter (accuracy 0.02) or a Perkin-Elmer M141 polarimeter; concentrations are given as g/100 ml. Polarimeter tubes were maintained at constant temperature (±0.1°) by means of liquid circulation.

Gas chromatographic analyses (vpc) were carried out by use of a 200-cm column packed with 15% polypropylene glycol (Ucon oil LB-500-X) on Chromosorb W (100–120 mesh). The samples were eluted with helium at 40 ml/m and thermal conductivity cells were used as detectors.

**Materials.** Commercial solvents of reagent grade were dried and fractionated. Ethylene, propylene, and *t*-butylethylene were kindly supplied by the Montecatini Co. of Milan and were 99.5% pure; the other olefins were of the same purity.

The *trans*-3-hexene ($n^{20}\text{D}$ 1.3936) was obtained by reduction of 3-hexyne as previously described;[8] the *trans*-cyclooctene was prepared by the procedure described by Cope.[9]

**(−)-*cis*-Dichloro(ethylene)-(*S*)-(α-phenethylamine)platinum(II), *cis*-(et,S).** (*S*)-α-phenethylamine, $[\alpha]^{25}\text{D}$ −40.2° (neat), was added (two portions of 1.63 g (0.00135 mole), the second 24 hr after the first) to a solution of 5.60 g (0.00135 mole) of $\text{K}_2\text{PtCl}_4$ in 175 ml of water. After 4 days at 5° a precipitate (5.37 g) was collected. This yellow powder was treated as crude *cis*-dichlorobis-(*S*)-(α-phenethylamine)platinum(II).[10] The material was suspended in 150 ml of 1 *N* HCl and refluxed for 2 hr with vigorous stirring.

The resulting yellow solution was separated by filtration from the black residue, cooled to 0°, and filtered again. It was then poured into a pressure flask and shaken with ethylene at 60 psi. After 2 days, 2.45 g (0.0059 mole, yield 43.7%) of crude *cis*-(et,S) was collected. By dissolving the crude product in acetone (25 ml), adding 50 ml of toluene, and removing the acetone *in vacuo*, nearly pure *cis*-(et,S) separated. A better purity can be achieved by recrystallization from a solution of equal amounts of acetone and *n*-heptane, $[\alpha]^{25}\text{D}$ −53.4°, (*c* 1.02, acetone).

*Anal.* Calcd for $\text{C}_{10}\text{H}_{15}\text{NCl}_2\text{Pt}$: N, 3.38; Pt, 47.00. Found: N, 3.36; Pt, 46.80.

The *cis*-dichloro(olefin)-(*S*)-(α-phenethylamine)platinum(II) in the preparation of the complexes of general formula *cis*-dichloro-(olefin)-(*S*)-(α-phenethylamine)platinum(II) by exchange of the ethylene with the corresponding olefin, was labeled with $\text{C}_2\text{H}_4\text{-C}^{14}$.

It was thus possible to test the completeness of the exchange by comparing the specific radioactivity of the starting material and that of the exchange product. The labeled ethylene complex was quickly obtained by shaking a solution of the ethylene complex in acetone with $\text{C}_2\text{H}_4\text{-C}^{14}$ for a few minutes.[11]

**(−)-*cis*-Dichloro-(*cis*-2-butene)-(*S*)-(α-phenethylamine)platinum(II), *cis*-(cb,S).** A 3.0-g (0.0072 mole) sample of *cis*-(et,S) was dissolved in 25 ml of acetone, *cis*-butene (5 ml) was condensed on the solution, and the mixture was gently refluxed for 4 hr in a condenser with Dry Ice–acetone as the cooling medium. After this time other 5 ml of *cis*-butene was added and the reflux was continued for 4 hr. The resulting solution was concentrated *in vacuo* to 15 ml with subsequent addition of heptane until clouding began; it was cleared with a few drops of acetone and kept at 0°. Within a period of a week two crops of pale yellow crystals were collected (2.3 g of *cis*-(cb,S), 0.00519 mole, yield 72%), $[\alpha]^{25}\text{D}$ −59.6° (*c* 1.0, acetone). The optical rotation of this compound did not change with time in solution, either spontaneously or upon addition of free *cis*-butene.

*Anal.* Calcd for $\text{C}_{12}\text{H}_{19}\text{NCl}_2\text{Pt}$; N, 3.16; Pt, 44.01. Found: N, 3.18; Pt, 44.41.

**(−)-*cis*-Dichloro(propylene)-(*S*)-(α-phenethylamine)platinum(II), *cis*-(pr,−,S).** A slow current of propylene was bubbled into a

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[5] The complexes were recrystallized to constant rotation and are considered in this paper as "pure diastereoisomers" according to this criterion.

[6] A. C. Cope and A. S. Mehta, *J. Am. Chem. Soc.*, **86**, 5626 (1964).

[7] P. Corradini and C. Pedone, *Chim. Ind.* (Milan), **47**, 664 (1965).

[8] K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216, 2683 (1941).

[9] A. C. Cope, R. A. Pike, and C. F. Spencer, *ibid.*, **75**, 3214 (1953).

[10] R. Kramer, *ibid.*, **86**, 217 (1964).

[11] G. Paiaro and A. Panunzi, *Ric. Sci.*, **34**, II-A, 601 (1964).

solution of 3.0 g (0.0072 mole) of *cis*-(et,S) in 25 ml of acetone for about 1 hr. After addition of 90 ml of toluene to the solution the acetone was removed *in vacuo*. After 12 hr of standing at −5° a jellylike mass formed. Filtration gave 1.05 g of *cis*-(pr,−,S) in the form of straw-colored crystals, The filtrate was stored at −5°, and two other crops of crystals were collected (total yield: 2.52 g, 0.00587 mole, 82%). After several recrystallizations from the same medium, $[\alpha]^{25}\mathrm{D}$ −113° (*c* 1.07, acetone), the rotation changed by spontaneous isomerization to $[\alpha]^{25}\mathrm{D}$ −55.3°.

*Anal.* Calcd for $C_{11}H_{17}NCl_2Pt$: N, 3.26; Pt, 45.45. Found: N, 3.29; Pt, 45.32.

**(+)-*cis*-Dichloro(propylene)-(*S*)-(α-phenethylamine)platinum(II), *cis*-(pr,+,S). A. Exchange of *cis*-(et,S) with Propylene.** The crude mixture of the two diastereoisomers was obtained in acetone solution by applying the procedure described for the preparation of the *cis*-(pr,−,S) to a sample of 3.0 g of *cis*-(et,S). The solution was concentrated *in vacuo* to 10 ml and diluted with heptane until clouding began, cleared with a few drops of acetone, and kept at 0°. Within a period of 10 days three crops of pale yellow needles were collected. The product was *cis*-(pr,+,S), total weight 2.27 g (0.00529 mole, total yield 74%): after several recrystallizations from the same medium, $[\alpha]^{25}\mathrm{D}$ 2.5° (*c* 1.34, acetone); after spontaneous epimerization, $[\alpha]^{25}\mathrm{D}$ −55.3°.

*Anal.* Calcd for $C_{11}H_{17}NCl_2PT$; N, 3.26; Pt, 45.45. Found: N, 3.29; Pt, 45.32.

**B. Preferential Formation of the *cis*-(pr,+,S).** A solution of IV obtained after hydrolysis of 2.0 g of III was shaken with propylene at 30 psi, in presence of 4 mg of solid *cis*-(pr,+,S). After 14 hr, 0.48 g of diastereoisomeric *cis*-(pr,+,S) having $[\alpha]^{25}\mathrm{D}$ 0.1°, (*c* 1.21, acetone) was obtained, after epimerization $[\alpha]^{25}\mathrm{D}$ −55.1°.

*Anal.* Calcd for $C_{11}H_{17}NCl_2Pt$; N, 3.26; Pt, 45.45. Found: N, 3.28; Pt, 45.31.

**(−)- and (+)-*cis*-Dichloro-(*t*-butylethylene)-(*S*)-(α-phenethylamine)platinum(II), *cis*-(tbe,−,S) and *cis*-(tbe,+,S).** A 2.0-g (0.0048 mole) sample of *cis*-(et,S) was dissolved in 15 ml of acetone. To this solution 3 ml of *t*-butylethylene was added, and the mixture was gently refluxed for 24 hr, with subsequent separation of a yellow precipitate. Upon addition of 7 ml of methylene chloride the precipitate dissolved and the reflux was then continued for 18 hr. The solution was concentrated *in vacuo* to about 10 ml. After 24 hr 0.966 g (0.00205 mole, yield 42.7%) of *cis*-(tbe,+,S) was obtained. This diastereoisomer very probably formed an inclusion compound with acetone. The product still contained about 5% acetone after extensive pumping. The acetone was removed by dissolving the product in methylene chloride and precipitating the product with heptane. After recrystallization the *cis* isomer (tbe,+,S) showed $[\alpha]^{25}\mathrm{D}$ +65° (*c* 0.90, acetone).

*Anal.* Calcd for $C_{14}H_{23}NCl_2Pt$: N, 2.97; Pt, 41.52. Found: N, 2.90; Pt, 41.37.

To the acetone mother liquor 30 ml of toluene was added and the acetone removed *in vacuo*. Within a period of a week 0.882 g (0.00187 mole, yield 39%) of *cis*-(tbe,−,S) was collected: after recrystallization, $[\alpha]^{25}\mathrm{D}$ −148° (*c* 0.95, acetone).

*Anal.* Calcd for $C_{14}H_{23}NCl_2Pt$: N, 2.97; Pt, 41.52. Found: N, 3.07; Pt, 39.01.

Both diastereoisomers changed their activity in acetone solution very slowly in the presence of free olefin. At equilibrium $[\alpha]^{25}\mathrm{D}$ −43° (*c* 1.05, acetone).

**(−)-*cis*-Dichloro(styrene)-(*S*)-(α-phenethylamine)platinum(II), *cis*-(st,−,S).** Three grams (0.0072 mole) of *cis*-(et,*S*) was dissolved in 25 ml of acetone; 25 ml of heptane containing 2 ml of styrene was added to this solution. The mixture was warmed to 40°; after a few minutes 3.05 g (0.0062 mole, yield 86%) of *cis*-(st,−,S) separated. The complex was recrystallized from methylene chloride–pentane at 0° until $[\alpha]^{25}\mathrm{D}$ −194° (*c* 0.95, acetone). The optical rotation changed spontaneously to $[\alpha]^{25}\mathrm{D}$ −61.8.°.

*Anal.* Calcd for $C_{16}H_{19}NCl_2Pt$: N, 2.85; Pt, 39.70. Found: N, 2.78; Pt, 40.10.

**(−)-*cis*-Dichloro(*trans*-1,4 dichlorobutene)-(*S*)-(α-phenethylamine)platinum(II), *cis*-(dcb,−,S).** A 1.5-g (0.0036 mole) sample of *cis*-(et,S) was dissolved in 12 ml of acetone, and 1.5 ml of *trans*-1,4-dichlorobutene was added. The mixture was left 3 days at room temperature; after this time the acetone was removed *in vacuo* and the yellow oil was treated with 1 ml of olefin and allowed to stand 24 hr.

The olefin was then removed by washing thoroughly with petroleum ether, and the residual, yellow oil was dissolved in 5 ml of toluene. After 3 days a crop (0.727 g, 0.00142 mole, yield 40%), of green-yellow needles was collected. After recrystallization from $CH_2Cl_2$–pentane, the product showed $[\alpha]^{25}\mathrm{D}$ −104.2° (*c* 1.12, acetone); after epimerization in presence of free olefin, $[\alpha]^{25}\mathrm{D}$ −74°.

*Anal.* Calcd for $C_{12}H_{17}NCl_4Pt$: N, 2.73; Pt, 38.11. Found: N, 2.71; Pt, 39.13.

**(−)-*cis*-Dichloro(*trans*-2-butene)-(*S*)-(α-phenethylamine)platinum(II), *cis*-(tb,−,S).** The crude mixture of the diastereoisomers was obtained by treating a sample of 3.0 g (0.0072 mole) of *cis*-(et,S) with *trans*-butene and applying the procedure described for the preparation of *cis*-(cb,S). The acetone solution of the diastereoisomeric pair was diluted with heptane until it clouded, then cleared with acetone, and kept at +5°. Within a period of 2 weeks three successive crops (3.08 g, 0.00682 mole, yield 94.8%) of pale yellow needles were obtained, after several crystallizations from the same medium: $[\alpha]^{25}\mathrm{D}$ −184° (*c* 0.91, acetone); at equilibrium in presence of free olefin, $[\alpha]^{25}\mathrm{D}$ −77.4.°

*Anal.* Calcd for $C_{12}H_{19}NCl_2Pt$: N, 3.16; Pt, 44.01. Found: N, 3.20; Pt, 44.33.

**(−)-*cis*-Dichloro(*trans*-3-hexene)-(*S*)-(α-phenethylamine)platinum(II), (hex,−,S).** The crude mixture of diastereoisomers was obtained by applying the procedure described for the preparation of *cis*-(cb,S) to a 3.0-g sample of *cis*-(et,S). To the solution containing the diastereoisomeric pair, a half-volume of pentane was added; pale yellow needles separated almost immediately at room temperature. Within a period of 10 days three fractions were collected: 2.65 g (0.00562 mole, yield 78%); after recrystallization, $[\alpha]^{25}\mathrm{D}$ −142° (*c* 0.50, acetone). The rotation changed very slowly with time as in the case of the *trans*-butene complex: at equilibrium, in the presence of free olefin, $[\alpha]^{25}\mathrm{D}$ −79.4.°

*Anal.* Calcd for $C_{14}H_{23}NCl_2Pt$: N, 2.97; Pt, 41.52. Found: N, 3.01; Pt, 41.38.

**(−)-*cis*-Dichloro(ethyl α-chloroacrylate)-(*S*)-(α-phenethylamine)-platinum(II), *cis*-(eca,−,S).** A 3.0-g sample of *cis*-(et,S) was suspended in a solution of 2 ml of ethyl α-chloroacrylate in 5 ml of methylene chloride. After 48 hr of stirring the *cis*-(et,S) was completely dissolved. Removal of the solvent *in vacuo* gave an oil. After several washings with *n*-heptane, the oil dissolved in 15 ml of toluene. Within a period of 1 week three crops (3.15 g, 0.00604 mole, yield 84%) of yellow needles were collected: after recrystallization, $[\alpha]^{25}\mathrm{D}$ −186° (*c* 1.1, acetone); at equilibrium, after epimerization, $[\alpha]^{25}\mathrm{D}$ −81.2.°

*Anal.* Calcd for $C_{13}H_{18}O_2NCl_3Pt$: N, 2.68; Pt, 37.40. Found: N, 2.72; Pt, 37.70.

**Exchange Reaction between *dl*-*trans*-Cyclooctene and *cis*-(et,S).** To 2.655 g (0.00639 mole) of *cis*-(et,S) dissolved in 180 ml of methylene chloride, a solution containing 0.772 g (0.007 mole) of *dl*-*trans*-cyclooctene in 5 ml of the same solvent was added at 25°. The resulting solution was left at 25° for 2 hr. A portion was then introduced into a 10-ml polarimetric cell kept at 25°: the rotation, $[\alpha]^{25}\mathrm{D}$ −0.479°, did not change during a 2-hr period. This sample was added to the residual solution with 0.637 g (0.00578 mole) of *dl*-*trans*-cyclooctene.

The rotation of this solution was $[\alpha]^{25}\mathrm{D}$ −1.228°, and did not change after 2 hr at 25°. A portion of this solution was evaporated *in vacuo* at 25°; the residual yellow pale oil solidified when washed thoroughly with petroleum ether.

*Anal.* Calcd for $C_{16}H_{25}NCl_2Pt$; N, 2.81; Pt, 39.27. Found: N, 2.68; Pt, 36.86.

The crude mixture of diastereoisomers (530 mg) was treated by the sodium cyanide method used by Cope and co-workers[12] to recover the olefin. The recovered *trans*-cyclooctene, after distillation, had $[\alpha]^{25}\mathrm{D}$ −115° (*c* 0.47, methylene chloride, determined by vpc analysis). The retention time and the infrared spectrum were identical with those of authentic *trans*-cyclooctene. By comparing, the rotation of the recovered olefin to that of the pure enantiomers the optical purity of the sample appeared to be about 27%. When the unreacted dextrorotatory olefin was separated from the complex either by precipitating this complex with pentane, or by distilling and collecting the solvent and the olefin, it showed an optical purity near that found for the olefin recovered from the diastereoisomeric mixture.

In another run 1.0 g of the crude mixture of diastereoisomers was dissolved in acetone solution (5 ml); after 2 days of standing at 5°, pale yellow crystals (378 mg) of (+)-*cis*-dichloro(*trans*-cyclooctene)-(*S*)-(α-phenethylamine)platinum(II) were formed. After addition of 15 ml of toluene to the mother solution, the acetone was removed *in vacuo*, and the resulting toluene solution was kept

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[12] A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **87**, 3644 (1965).

1 week at 5° producing three crops (410 mg) of (−)-*cis*-dichloro-(*trans*-cyclooctene)-(*S*)-(α-phenethylamine)platinum(II). When the olefin was recovered from the recrystallized levorotatory diastereoisomer, (+)-COT was obtained, with an optical purity of more than 95%.

**Chemical Properties of the Complexes I.** From all the complexes I, the olefin can be removed by reaction with cyanide aqueous solutions, or triphenylphosphine, or α,α′-bipyridine. By reduction with $H_2$ of the complexes I and II, either in solution or in the absence of solvents we obtained platinum metal and the saturated hydrocarbon corresponding to the olefin within a short period of time. Treatment of the (−) diastereoisomer of the ethyl α-chloroacrylate in acetone solution with $H_2$ at 50 psi led to the formation of racemic ethyl α-chloropropionate. This behavior supports the observation that the hydrogenation,[13] even if occurring with a stereospecific mechanism, is followed by a rapid racemization process with a rate of the same order as that of the hydrogenation reaction. With regard to this argument other experiments are in progress.

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(13) J. H. Flynn and H. M. Hulburt, *J. Am. Chem. Soc.*, **76**, 3393 (1954).

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# Structure of the Hexapyridineiron(II) Salt of the Tetranuclear Iron Carbonyl Anion, $[Fe_4(CO)_{13}]^{-2}$, with Comments Concerning the Nonisolation of the Corresponding Neutral Tetranuclear Iron Carbonyl, $Fe_4(CO)_{14}$

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**Abstract:** A three-dimensional single-crystal X-ray examination of the salt $[Fe(C_5H_5N)_6]^{2+}[Fe_4(CO)_{13}]^{2-}$ not only has shown a new type of molecular configuration for the diamagnetic tetrameric anion, $[Fe_4(CO)_{13}]^{2-}$, but also has produced definite stereochemical information concerning the nonexistence of the corresponding neutral iron carbonyl, $Fe_4(CO)_{14}$. The triclinic crystals of $[Fe(C_5H_5N)_6][Fe_4(CO)_{13}]$ contain two formula species in a unit cell of symmetry $P\bar{1}$ and of reduced-cell parameters $a = 10.09$, $b = 14.86$, $c = 15.61$ A, $\alpha = 90°\ 00'$, $\beta = 90°\ 00'$, $\gamma = 103°\ 12'$. Isotropic least-squares refinement carried out with a specially written full-matrix rigid-body program, in which the six pyridine rings were constrained to a fixed geometry, yielded final discrepancy factors of $R_1 = 10.9\%$ and $R_2 = 12.7\%$. The $[Fe_4(CO)_{13}]^{2-}$ anion of pseudo-threefold symmetry consists of four tetrahedrally oriented iron atoms in which an apical $Fe(CO)_3$ group is symmetrically coordinated by only iron–iron bonds to a basal $Fe_3(CO)_9$ fragment containing three identical $Fe(CO)_3$ groups located at the corners of an equilateral triangle and bonded to one another by iron–iron bonds. The thirteenth carbonyl group triply bridges the three basal iron atoms. As a result of weak interactions with neighboring basal iron atoms, three of the essentially terminal basal iron carbonyl groups are slightly deformed toward a doubly bridging carbonyl configuration. The chemical significance of these highly unsymmetrical doubly bridging groups is indicated. To a first approximation the carbonyl carbon atoms lie at the vertices of a polyhedral fragment which is related to an icosahedron. The criteria necessary for the possible formation of the polynuclear metal carbonyls and their derivatives are discussed, and the little appreciated importance of the stereochemical compatibility requirements of the ligands about the metal cluster in determining the compound's stoichiometry is stressed. The hexapyridineiron(II) cation, which has a regular octahedral array of six nitrogen atoms about the central iron(II) with the pyridine molecules oriented in three mutually perpendicular planes such that each pair of *trans* pyridine rings is coplanar, is one of the few known species belonging to the centosymmetric cubic point group $T_h$.

While no neutral tetranuclear carbonyl of iron has been prepared, the anion $[Fe_4(CO)_{13}]^{2-}$ is well known, having first been synthesized by Hieber and co-workers[2,3] in 1930. Initially, the products of the reactions of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ with pyridine were formulated as $Fe_2(CO)_4(C_5H_5N)_3$[2] and $Fe(CO)_3(C_5H_5N)$,[3] respectively; Hieber and Werner[4] later recognized that only one product of stoichiometry $Fe_5(CO)_{13}(C_5H_5N)_6$ is formed from either of these two reactions. Their formulation of this complex as $[Fe(C_5H_5N)_6]^{2+}[Fe_4(CO)_{13}]^{2-}$ was based on conductance measurements which established its ionic character and on identification of one of the five iron atoms per formula unit as an iron(II) by its precipitation as $Fe(OH)_2$. The magnetic moment of 5.47 BM for this salt was of the magnitude expected for a single high-spin iron(II), thereby indicating that the anion is diamagnetic.[4] Reactions of the iron carbonyls with other bases have yielded a large number of additional salts containing the tetrameric anion.[4–8] All of the salts containing this anion are air sensitive, and many are

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(1) National Science Foundation Predoctoral Fellow, 1961–1964; this article is based in part on a dissertation by R. J. Doedens in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin, 1965.

(2) W. Hieber, F. Sonnekalb, and E. Becker, *Chem. Ber.*, **63**, 973 (1930).

(3) W. Hieber and E. Becker, *ibid.*, **63**, 1405 (1930).

(4) W. Hieber and R. Werner, *ibid.*, **90**, 286, 1116 (1957).

(5) W. Hieber and J. G. Floss, *ibid.*, **90**, 1617 (1957).

(6) W. Hieber and N. Kahlen, *ibid.*, **91**, 2223 (1958).

(7) W. Hieber and A. Lipp, *ibid.*, **92**, 2075 (1959).

(8) W. Hieber and A. Lipp, *ibid.*, **92**, 2085 (1959).