reagent grade. Nitromethane was dried over calcium hydride and deoxygenated by passing dry nitrogen gas through the solution, followed by degassing under vacuum. The oxidation was carried out in an inverted U-tube, one arm of which was filled with anhydrous aluminum chloride and the compound to be oxidized (*ca.* 20 and 5 mg, respectively). This U-tube was connected to a vacuum line and nitromethane (1 ml) was distilled into the reaction mixture. The reaction proceeded at room temperature and the solution was subsequently transferred under vacuum into the capillary tube, which was then placed in the esr cavity.

The spectra were run on a JES-3BX spectrometer using a field-selector unit. Values of splitting constants are believed accurate to ±0.5%.

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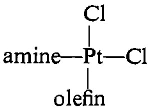
Received March 24, 1966

Induction of Asymmetry in *cis*-Dichloro(olefin)(amine)platinum(II) Complexes

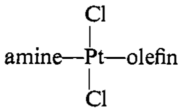
Sir:

In previous publications[1] we have described a number of platinum(II) complexes of olefins, containing a dissymmetric amine [(*R*)- or (*S*)-α-phenethylamine], *trans* or *cis* coordinated with respect to the olefin, of the general types I and II.



$$\begin{array}{c}\text{Cl}\\|\\\text{amine—Pt—Cl}\\|\\\text{olefin}\end{array}$$

I



$$\begin{array}{c}\text{Cl}\\|\\\text{amine—Pt—olefin}\\|\\\text{Cl}\end{array}$$

II

If the ethylene complex is allowed to equilibrate with an olefin having a symmetry different from C_{2v} or D_{2h}, two diastereoisomers are formed. For the *trans*-coordinated complexes no evidence has been found for the induction of asymmetry during the course of the exchange reaction.

For the *cis*-coordinated complexes we now report data showing that the equilibrium constant of the reaction

$$\begin{array}{c}\text{Cl}\\|\\\text{amine}(S)\text{—Pt—Cl}\\|\\\text{olefin}(R)\end{array} \rightleftharpoons \begin{array}{c}\text{Cl}\\|\\\text{amine}(S)\text{—Pt—Cl}\\|\\\text{olefin}(S)\end{array}$$

III IV

is generally different from unity.

As noted previously,[2] the deviation of the molecular rotation of an olefin complex (I) from that of the corresponding ethylene complex affords an indication that asymmetric induction occurs in the coordination of the olefin. A probable origin of the effect is a steric interaction between the amine and the *cis*-coordinated olefin. In fact, the deviation is particularly marked in the case of the complexes with olefins of the type *trans*-R—CH=CH—R.

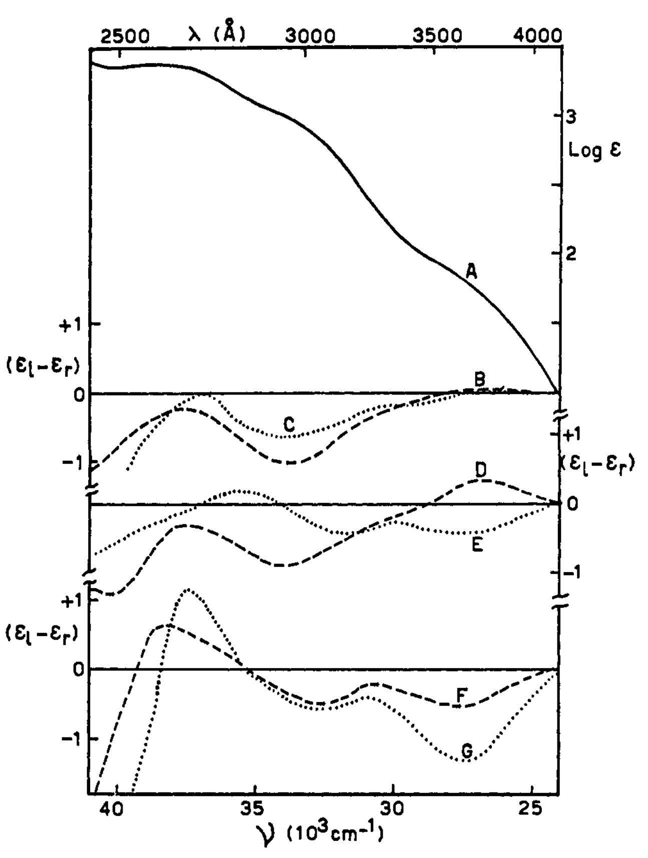


Figure 1. The electron absorption and circular dichroism spectra of *cis*-dichloroolefin-(*S*)-α-phenethylamineplatinum(II) complexes in ethanol solution: (A) the absorption spectrum, and (B) the circular dichroism spectrum of the ethylene complex; the circular dichroism spectra of (C) the *cis*-2-butene complex, (D) the (+) diastereoisomer and (E) the (−) diastereoisomers of the propylene complex, (F) the equilibrium mixture of diastereoisomers, and (G) the (−) diastereoisomer of the *trans*-2-butene complex.

The molecular rotations should indicate (Table I) that for the complexes with *trans*-2-butene, *trans*-3-hexene, and *trans*-1,4-dichlorobutene, there is a 25% or more excess of the (−) diastereoisomer in acetone solution at room temperature. Some deviation in the case of the *t*-butylethylene and propylene complexes, where both the (+) and the (−) diastereoisomers were isolated, was also found.

Table I.[a] Data of the Optical Activity[b] of *cis*-Dichloro(olefin)-(*S*)-a-phenethylamineplatinum(II) Complexes

Olefin	M_D[c]	M_D[d]
Ethylene	. . .	−226
(+) Propylene	+21	−238
(−) Propylene	−485	−238
(+) *t*-Butylethylene	−780	−197
(−) *t*-Butylethylene	+317	−197
(−) *trans*-2-Butene	−788	−365
(−) *trans*-3-Hexene	−675	−387
(−) *trans*-1,4-Dichloro-2-butene	−555	−394

[a] The reported data are average values. For the diastereoisomers the values are the maximum ones obtained after several recrystallizations. [b] In acetone at 25° (*c* 1.2–1.4). [c] Values for the pure diastereoisomers. [d] Values at equilibrium (after mutarotation) and values for the nonresolvable complexes.

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(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) G. Paiaro and A. Panunzi, *Tetrahedron Letters*, **8**, 441 (1965).

The circular dichroism spectra of I, previously described, are reported. Figure 1 gives the absorption spectrum of the *cis* complexes (I) (A), and the circular dichroism spectra of the ethylene complex (B), the pure *cis*-2-butene complex (C), the (+) (D) and (−) (E) diastereoisomers of the propylene complex, the equilibrium mixture of the diastereoisomers (F), and the pure (−) diastereoisomer (G) of the *trans*-2-butene complex. The curves show that the ethylene and the *cis*-2-butene complexes, which cannot form the diastereoisomers III and IV, give little or no circular dichroism in the region of the lowest energy d → d electronic transition of platinum(II) at 27,000 cm^{-1}, whereas the (+) and (−) diastereoisomers of the propylene complex give, respectively, a positive and a negative circular dichroism band in that region. The magnitude of the dichroism $(\epsilon_l - \epsilon_r)_{\max}$ is nearly the same for the two diastereoisomers. In general, the circular dichroism of the lowest energy d → d electronic excitation of transition metal complexes has been found[3] to be particularly sensitive to the absolute stereochemistry of the complex.

These observations suggest that the configuration of the olefin relative to the metal and the other ligands is reflected in the sign of the circular dichroism band near 27,000 cm^{-1} and that the composition of a mixture of diastereoisomers is given semiquantitatively by the magnitude of that dichroism. The comparison of the sign and the magnitude of the lowest energy circular dichroism band given by the equilibrium mixture of the diastereoisomers of the *cis* complex derived from *trans*-2-butene (Figure 1, F) with that of the corresponding pure (−) diastereoisomer (Figure 1, G) suggests that the latter predominates in the equilibrium mixture to the extent of 40% in ethanol solution at room temperature.

These inferences are unambiguously supported by the exchange reaction of the ethylene complex (I) with racemic *trans*-cyclooctene. This complex was allowed to react at room temperature with 2 moles of (*R*,*S*)-*trans*-cyclooctene in methylene chloride or acetone solution until complete exchange.

The excess olefin was then removed *in vacuo* at 10°, leaving as an oil the crude mixture of the diastereoisomers of the *trans*-cyclooctene complex (I).

Anal. Calcd for $C_{16}H_{25}Cl_2NPt$: C, 38.62; H, 5.06; Pt, 39.27. Found: C, 39.03; H, 4.89; Pt, 38.71.

The unreacted olefin was the (−) olefin with enantiomeric purity of about 30%. The treatment of the crude mixture (a solid after washing with petroleum ether and extensive pumping) of diastereoisomers with KCN in ethylene glycol–methanol yielded the (+) olefin with the same degree of optical purity.

Further work is in progress to check the above interpretation of the optical rotation data by means of CD measurements on a more extended range of olefin complexes (I).

[3] (a) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965); (b) A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, 5094 (1965).

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Received March 21, 1966

Oxidation, Reduction, and Electrochemiluminescence of Aryl-Substituted Isobenzofurans and Isoindoles

Sir:

Recent investigations have shown[1–6] that a number of fluorescent aromatic hydrocarbons luminesce in conducting aprotic media under an applied ac voltage. We wish to report that certain heterocyclic compounds also luminesce or electrochemiluminesce (ECL) under these conditions. Because some of these heterocyclics ECL brightly, they have been used in studies designed to provide mechanistic information regarding the ECL process. The latter will be reported in a separate paper. We report here only on the ECL and related properties of 1,3,4,7-tetraphenylisobenzofuran[7] (I) and on the effect of structural modifications on these properties.

The cell used in these studies consisted of two 1-cm^2 80-mesh platinum gauze electrodes spaced 2 mm apart in a 15-ml glass container. The fluorescer was examined in a conducting medium consisting of 0.1 *M* tetra-*n*-butylammonium perchlorate in dry, deaerated N,N-dimethylformamide (DMF). Upon imposing 8 v peak to peak (60 cps) with a square wave generator on this solution,[8] the intensity of light emitted from the region of the electrodes[9] increased from 1.9 ft-lamberts to 20 ft-lamberts (*cf.* Figure 1) as the concentration of I was increased from 1 m*M* to almost 6 m*M* (saturated). The intensity of the ECL emission of the saturated solution remained at or above 18 ft-lamberts in the 50–3000-cps range with a maximum of 22 ft-lamberts being measured at 120–130 cps.

Compound I exhibits an intense green fluorescence in DMF solution (fluorescence efficiency [Φ] = 0.51) with a maximum at 530 mμ. The ECL emission is *identical* spectrally with the fluorescence emission. Oxidation (rotating platinum electrode) and reduction (dropping mercury electrode) of I in DMF occurs by one-electron changes at $E_{1/2} = +0.98$ and -1.86 v *vs.* sce, respectively. A second one-electron reduction wave presumably due to dianion formation can be seen at $E_{1/2} = -2.11$ v and a third wave at $E_{1/2} = -2.38$ v can also be detected. Cyclic voltammetry in the same solvent shows that the first reduction product is stable (lifetime > 15 sec), while the first oxidation product and the second reduction products are both unstable under these conditions. By varying the voltage scan rate lifetimes of 1 sec are indicated for both the cation and dianion.

Substitution of the *para* positions of the phenyl substituents on the furan ring with methoxy groups to give

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[1] Technical Report No. 4 to the Office of Naval Research and Advanced Research Projects Agency, Contract Nonr 4200(00), July 1964.

[2] E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

[3] R. E. Visco and E. A. Chandross, *ibid.*, **86**, 5350 (1964).

[4] D. M. Hercules, *Science*, **145**, 808 (1964).

[5] K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **87**, 139 (1965).

[6] E. A. Chandross, J. W. Longworth, and R. E. Visco, *ibid.*, **87**, 3259 (1965).

[7] E. D. Bergmann, S. Blumberg, P. Brasha, and S. Epstein, *Tetrahedron*, **20**, 195 (1964).

[8] Square wave input was provided by a 2 Trygon Electronics HR20-5A DC power supply and a transistorized switch which alternated between the positive and negative outputs of the two power supplies at 60 cps.

[9] Brightness measurements were obtained with a Photo Research Corporation Model UB 1/2 spectral brightness meter which could be focused on the cell electrodes.