

- 1 M. I. PRINCE AND K. WEISS, *J. Organometal. Chem.*, 2 (1964) 251.
- 2 I. RUIDISCH AND M. SCHMIDT, *J. Organometal. Chem.*, 1 (1964) 493.
- 3 E. WIBERG AND H. MICHAND, *Z. Naturforsch.*, 9b (1954) 495.
- 4 K. TERADA, A. J. ERBEL AND F. M. BROWER, *The Preparation of Some Novel Light Metal Azides*, Proc. of the Twelfth Basic Research Group, Contractors' Conference and Symposium, U.S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia, November 1963.
- 5 L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 2nd edn., 1958, Chapter 15.
- 6 J. I. JONES AND W. S. McDONALD, *Proc. Chem. Soc.*, (1962) 366, and earlier references cited therein.

Received October 15th, 1965

J. Organometal. Chem., 5 (1966) 584-586

Monochloro-amino-acid-olefin-platinum(II) complexes

Previous work¹⁻³ in this laboratory has shown that it is possible to resolve the diastereoisomers of a transition metal-olefin complex, containing π -bonded olefinic compounds with a symmetry lower than $2mm$, and an asymmetric ligand. The resolution was achieved using the (*S*)- or (*R*)- α -phenylethylamine as asymmetric ligand.

In examining some possibilities of change in the nature of the asymmetric center we have tried to prepare Pt(II) complexes, containing an olefin and an amino acid. We have not found any previous report on this kind of complex.

The reaction of three amino acids, (glycine, racemic alanine and β -phenylalanine) with some ethylenic complexes of Pt(II) gave yellow, stable, non-ionic complexes corresponding to general formula: chloro-ethylene-amino-acid-Platinum(II).

According to the amino acid used, one or more of the following procedures gives better yields: (a) Reaction at room temperature between aqueous solutions of an amino acid and of Zeise's salt. (b) Reaction between a saturated aqueous solution of the potassium salt of the amino acid and an ethanolic solution of Zeise's salt. (c) Neutralization with dilute aqueous potassium hydroxide of a mixture of aqueous solutions of the amino acid hydrochloride and Zeise's salt. (d) Reaction between an acetone solution of μ, μ' -dichloro-ethylene-platinum(II) and an aqueous solution of the potassium salt of the amino acid.

The complexes are insoluble in water, crystallize from ethanol, acetone, methanol, and are slightly soluble in toluene, chloroform, and methylene chloride.

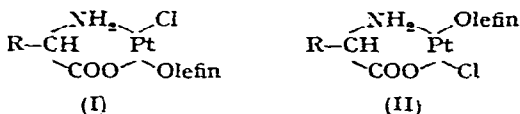
The ethylene in the complexes is readily exchanged in solution with ¹⁴C-labelled ethylene and with other olefins, and we obtained in this way the complexes containing *cis*-2-butene, *trans*-2-butene, styrene, polyene.

The general formula indicated by the analyses are consistent with monomeric or polymeric units, in relation to the double functionality of the amino acid. X-ray studies show that the complex containing ethylene and glycine is monomeric. X-ray data for the glycine complex gave: $a = 10.16 \pm 0.03$ Å; $b = 8.45 \pm 0.02$ Å; $c = 8.62 \pm 0.02$ Å; space group $P2_12_12_1$, $d_{RX} = 2.98$ g/cm³ ($d_{exp.} = 2.96$ g/cm³), and for

J. Organometal. Chem., 5 (1966) 586-588

the phenylalanine complex: $a = 12.04 \pm 0.05 \text{ \AA}$; $b = 8.27 \pm 0.03 \text{ \AA}$; $c = 12.30 \pm 0.03 \text{ \AA}$; space group $P2_1/c$, $d_{RX} = 2.21 \text{ g/cm}^3$ ($d_{exp.} = 2.26 \text{ g/cm}^3$).

For a non-ionic monomeric complex two stereoisomers are possible:



The complexes in acetone solution react with hydrochloric acid and the amino acid hydrochloride and a Zeise-like anion can be recovered from the solution. This behaviour, differing from the behaviour of *cis*-dichloro-olefin-amine-platinum(II) complexes, stable in the same medium, indicates that the complexes should have the structure (I).

The IR spectra are not in disagreement with this structure. The NH stretching region shows an absorption pattern very close to that of *trans*-dichloro-amine-olefin-platinum(II) complexes, with peaks shifted to lower wave lengths than in the *cis* series, and the carbonyl stretching is near 1650 cm^{-1} .

Investigations are currently under way in order to confirm by X-rays the molecular structure of the compounds and to achieve the resolution of the diastereoisomeric complexes containing L-alanine and L- β -phenylalanine and olefins with non-superimposable faces.

Experimental

Reaction of Zeise's salt with the potassium salt of the amino acid. To a cold solution of 2.0 g (5.2 mmole) of potassium trichloro(ethylene)platinate(II) in 60 ml of ethanol a solution of 0.39 g (5.2 mmole) of glycine in 5.2 ml of 1 N KOH was added dropwise with stirring. After 24 h standing at 0° , the solution was concentrated *in vacuo* to about 20 ml, without filtering off the precipitate.

After a further period at 0° , the solvent was removed and the residue was washed with water and dried (0.76 g, 44%). The yellow solid was crystallized from methanol, decomp. 158° . (Found: C, 14.61; H, 2.60; N, 4.20; Pt, 58.28. $\text{C}_4\text{H}_3\text{ClNO}_2\text{Pt}$ calcd.: C, 14.44; H, 2.42; N, 4.21; Pt, 58.65%.)

Similarly were prepared, the complex with DL-alanine (47%), decomp. $162\text{--}166^\circ$ (Found: C, 17.16; H, 2.75; N, 4.16; Pt, 55.92. $\text{C}_5\text{H}_{10}\text{ClNO}_2\text{Pt}$ calcd.: C, 17.32; H, 2.90; N, 4.04; Pt, 56.27%.) and the complex with DL- β -phenylalanine (61%), decomp. $163\text{--}166^\circ$. (Found: C, 30.71; H, 3.45; N, 3.56; Pt, 46.50. $\text{C}_{11}\text{H}_{14}\text{ClNO}_2\text{Pt}$ calcd.: C, 31.25; H, 3.33; N, 3.31; Pt, 46.14%.)

Reaction of μ, μ' -dichloro-ethylene-platinum(II) with the potassium salt of an amino acid. To a cold solution of 1.7 g (2.9 mmole) of μ, μ' -dichloro-ethylene-platinum(II) in 70 ml of acetone was added dropwise with stirring a solution of 0.52 (5.8 mmole) of DL-alanine in 5.8 ml of 1 N KOH. The mixture was allowed to stand for 24 h at 0° , the white precipitate of KCl was filtered off, the solvent was removed *in vacuo* and the yellow residue was washed with water. After crystallization from acetone 1.5 g (74%) of the alanine complex was obtained. This procedure gave poor yields of the glycine complex and about 85% of the β -phenylalanine complex.

Neutralization of an aqueous solution of Zeise's salt in presence of amino acid hydrochloride. This method was useful only in the case of β -phenylalanine. To a cold solution of 2.1 g (5.4 mmole) of potassium trichloro(ethylene)platinum(II) in 12 ml of water was added a solution of 0.89 g (5.4 mmole) of DL- β -phenylalanine in 15 ml of 0.5 N HCl. Cooled 1 N KOH was added, under cooling and stirring, until a pH of 6.5 was reached. The temperature of the mixture was then raised to 45°. After a few minutes the complex separated, as well-formed yellow needles (2.11 g, 93%).

Reaction of Zeise's salt and the amino acid in water. In the conditions tried by us, this method was the least useful. As an example, a solution of 0.33 g (2 mmole) of DL- β -phenylalanine was added to a solution of 0.77 g (2 mmole) of potassium trichloro(ethylene)platinate(II) in 5 ml of the same solvent. After 3 h at room temperature 0.16 g (19%) of the complex separated.

Centro Nazionale di Chimica
delle Macromolecole del C.N.R.,
Sez. VII, Università di Napoli,
Via Mezzocannone 4, Napoli (Italy)

ACHILLE PANUNZI
ROSARIO PALUMBO
CARLO PEDONE
GASTONE PAIARO

- 1 G. PAIARO, P. CORRADINI, R. PALUMBO AND A. PANUNZI, *Makromol. Chem.*, 71 (1963) 184.
2 G. PAIARO AND A. PANUNZI, *J. Am. Chem. Soc.*, 86 (1964) 5148.
3 G. PAIARO AND A. PANUNZI, *Tetrahedron Letters*, (1965) 441.

Received October 10th, 1965

J. Organometal. Chem., 5 (1966) 586-588

A novel transition-metal silicon carbonyl, and the bonding in $\text{Co}_3(\text{CO})_9\text{R}$ molecules

The nature of the bonding within molecules containing a tetrahedron¹ or equilateral triangular array² of metal atoms has recently been discussed in terms of equivalent orbitals. In the present paper we use the same approach to discuss the electronic structure of a series of compounds which have structures intermediate between these two geometries. In molecules with the general formula $\text{Co}_3(\text{CO})_9\text{R}$ three cobalt atoms lie at the corners of an equilateral triangle and the R group completes the tetrahedron (Fig. 1). Compounds with a variety of substituent R have been prepared. Dent *et al.*³ prepared a number with $\text{R} = \text{CR}'$, we have reported elsewhere⁴ that with $\text{R} = \text{Si}-\text{CH}=\text{CH}_2$ and more recently the compound with $\text{R} = \text{Sn}-\text{Bu}$ has been described⁵.

It appears that there are generally nine metal-metal bonding molecular orbitals in an equilateral triangular array of transition metal ions. Three of these, of $A + E$ symmetry (in C_{3v}), are symmetric with respect to reflection in the plane of the triangle, the corresponding equivalent orbitals being metal-metal bent σ orbitals. The other six may also be considered to be derived from localized metal-metal bonds, three on either side of the metal triangle. In the case of $\text{Co}_3(\text{CO})_9\text{R}$ molecules the three

J. Organometal. Chem., 5 (1966) 588-590