74. *The Stereochemistry of Metallic Derivatives of Pyrromethenes.*

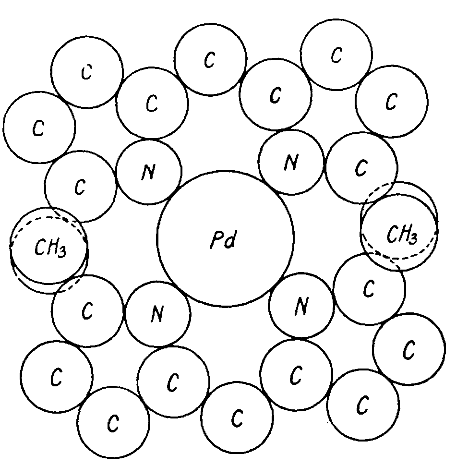
By Charles R. Porter.

The stereochemistry of the 4-covalent metallic derivatives of pyrromethenes is discussed, and it is shown on theoretical grounds that a planar configuration is impossible for simple salts of the type R_2M, where RH is the pyrromethene. Typical pyrromethene derivatives of cobalt, nickel, copper, zinc, cadmium, and palladium are described. These metals therefore must be able to take up a non-planar configuration. A number of other bivalent metals are shown not to form derivatives under similar conditions.

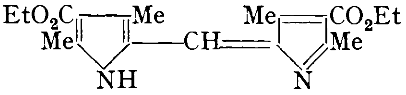
During the last few years, evidence in favour of a planar configuration of the valencies of the metallic atoms in 4-covalent compounds has been increasing, and the work of Linstead and his co-workers on the metallic derivatives of the phthalocyanines has shown that a large number of bivalent metals, many of which have normally a tetrahedral valency distribution, can take up a planar configuration when attached to the four nitrogen atoms of the phthalocyanine molecule. It was thought, however, that this molecule may impose a constraint on the valency distribution of the metals in question, and it would appear interesting to discover whether metals which normally give 4-covalent compounds of planar type could be constrained by the use of suitable chelate groups to give 4-covalent molecules of non-planar type.

The pyrromethenes afford such a chelate group, and have the advantage, for this comparison, of being very similar to the porphyrins and phthalocyanines except in their requirement of a tetrahedral symmetry on the part of the metallic atom. Inspection of a model or diagram of pyrromethene derivatives of bivalent metals shows that if all the α-positions of the base are substituted the molecule cannot have a planar configuration, so that such compounds should be resolvable, and a comparison of the rates of mutarotation of these substances with those of similar derivatives containing either or both of the α-positions unsubstituted should be of interest. A study of the pyrromethene derivatives of the metals has therefore been started with this end in view, and preliminary results are now described.

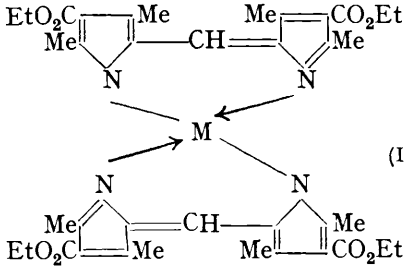
The palladium derivative of 5 : 5′-dimethylpyrromethene is shown in the diagram. The angles between the valencies of the metal have been made equal to 90°, and the sizes of the atoms are Pd = 1·37, N = 0·66, C in ring = 0·72, C in methyl group = 0·77A.; these values approximate to a mean of those found by Robertson and Woodward (J., 1937, **219**) for the phthalocyanines, except that the methyl groups have been given the dimensions usual for aliphatic carbon atoms. It will be seen that the methyl groups completely overlap, and in the case of a smaller metallic atom, such as nickel, the overlapping covers part of the nuclear carbon atom as well. The case is thus somewhat similar to that of the 2 : 2′-disubstituted diphenyl derivatives.



The most readily available pyrromethene is ethyl 3 : 3′ : 5 : 5′-tetramethylpyrromethene-4 : 4′-dicarboxylate (I). The ferrous salt of this base has been prepared by Fischer and Klarer (*Annalen*, 1926, **448**, 190), and the nickel, cobalt, copper, and zinc salts are described by Fischer and Schubert (*Ber.*, 1924, **57**, 611). The *cadmium* salt has now been prepared. The substances are readily obtained by the action of the acetates of the metals on the organic base, the reaction being always accompanied by a reddening of the colour of the solution. All these substances are of the type R_2M where RH is the base (II).



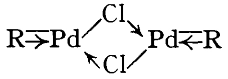
(I.)



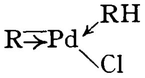
(II.)

With palladium, more complex results were obtained. In the presence of excess potassium chloropalladite, and sodium acetate in aqueous alcoholic solution, the pyrromethene gave a mixture of products from which was isolated the bimolecular compound, *bis-(4 : 4′-dicarbethoxy-3 : 3′ : 5 : 5′-tetramethylpyrromethene)dipalladous dichloride*, $R_2Pd_2Cl_2$, and the monopalladous *chloride*, R_2HPdCl. (The exact number of hydrogen atoms in this molecule is not determinable by elementary analysis, but a change of valency of palladium is unlikely.) The former substance was transformed into the latter on treatment in alcoholic solution with two molecular proportions of the base.

The bimolecular substance, $R_2Pd_2Cl_2$, presumably has the structure (III), and could possibly assume a planar configuration. The unimolecular compound might possibly be either (IV) or (V). The latter formulation is very unsatisfactory, for a co-ordination number of 3 is unlikely for palladium; in neither case could the palladium atom have a planar configuration unless neighbouring but not mutually attached carbon atoms approach



(III.)



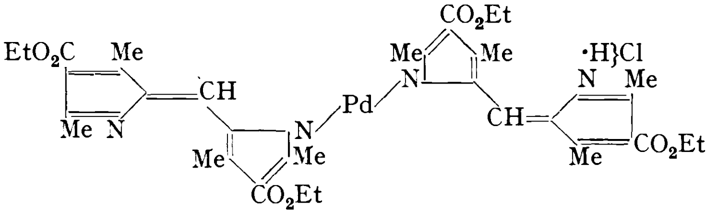
$$R{\rightarrow}Pd\begin{array}{l}\swarrow RH\\ \diagdown Cl\end{array}$$

(IV.)

$R{\rightarrow}Pd{-}RHCl$

(V.)

much closer than is usually supposed possible. In the formulation, R—Pd—RHCl, a planar configuration is possible if the pyrrole rings are rotated about the single bonds joining them to the bridge carbon atom (VI). The substance is not very stable, and



(VI.)

even on boiling with alcohol, the elements of hydrogen chloride are removed with the formation of *bis-(4 : 4′-dicarbethoxy-3 : 3′ : 5 : 5′-tetramethylpyrromethene)palladium*, R_2Pd. A good yield of this compound could also be obtained directly by the action of one equivalent of palladous nitrate on the base in the presence of sodium acetate. In distinction from the previously described derivatives of pyrromethenes, the palladium derivative is microcrystalline and almost insoluble in the common solvents except chloroform; it is, however, unimolecular and is therefore presumably of the non-planar type.

The difference in the reactions of palladium nitrate and potassium chloropalladite with this base is presumably due to the fact that Pd^{++} ions are not present to any appreciable extent in the latter case.

Somewhat similar results were observed when mercuric chloride was used. With excess of this, the pyrromethene gave an almost quantitative deposition of a *product* having the empirical formula, RHgCl. When the sulphate or nitrate was used, the result depended on the amount of reagent employed. With excess of either inorganic reagent dissolved in excess aqueous acetic acid, an alcoholic solution of the base gave an almost quantitative precipitation of a *compound* of the formula RHgOAc. When one molecular proportion of the pyrromethene was treated with one equivalent of mercuric nitrate, however, a *compound* of the normal type, R_2Hg, was obtained. On the other hand, when the pyrromethene was treated with one equivalent of mercuric chloride, only half of the base reacted, forming the chloro-compound previously mentioned.

The bivalent ions of beryllium, magnesium, chromium, manganese, and lead do not appear to form derivatives with this pyrromethene under similar conditions.

For comparison, metallic derivatives of the corresponding pyrromethene with free α-positions have been prepared. In compounds of this type, the α-carbon atoms should not touch, but should nevertheless approach closer, if a planar configuration be assumed, than is usual for carbon atoms not directly linked to one another. Ethyl 3 : 3′-dimethylpyrromethene-4 : 4′-dicarboxylate is distinctly less stable than the fully substituted substance, and metallic derivatives are best prepared by the addition of the calculated amount of the acetate to a cold alcoholic solution of the base. The salts are microcrystalline.

All the metallic derivatives described are insoluble in water, but are soluble in chloroform, those of smaller molecular weight being also soluble in benzene. The general properties of the substances suggest that the organic bases attach themselves to the metals as chelate groups, although the compound R_2HPdCl is difficult to formulate on this assumption. Schmitz and Dumont (*Ber.*, 1929, **62**, 226) obtained a compound of the type $RHSnCl_4$, and suggested that the pyrromethene occupies two co-ordination positions. The corresponding pyrromethanes neither form derivatives with metals nor readily form salts with acids.

The pyrromethene residues are not so firmly attached to the metals, except in the case of mercury and palladium, as are the porphyrins and phthalocyanines, the metal being eliminated in the case of nickel and copper by the action of 3N-hydrochloric acid. On being heated in air, the compounds decompose, leaving quantitative residues of the metals or their oxides.

EXPERIMENTAL.

Ethyl 3 : 3′ : 5 : 5′-tetramethylpyrromethene-4 : 4′-dicarboxylate was prepared by the method of Fischer, Werner, and Zerweck (*Ber.*, 1923, **56**, 526), and the 3 : 3′-dimethyl analogue by that of Fischer and Wiedemann (*Z. physiol. Chem.*, 1926, **155**, 52).

Metallic Derivatives of Ethyl Tetramethylpyrromethene-4 : 4′-dicarboxylate.—The cobalt, nickel, cupric, zinc, and cadmium compounds were prepared by warming an alcoholic solution of the base or its hydrochloride with excess of a concentrated aqueous solution of the acetate of the metal or the corresponding chloride mixed with sodium acetate. The solution reddened when the reagents were mixed, and after ½ hour the complex salts were precipitated by the addition of water. They were purified by recrystallisation from chloroform–petrol and from alcohol. They do not show sharp m. p.'s, but decompose over a range depending somewhat on the rate of heating.

The cobalt, nickel, copper, and zinc salts were prepared as described by Fischer and Schubert (*loc. cit.*). The cobalt salt had $M = 751$ in freezing benzene and the copper salt $M = 670$ in freezing bromoform (Calc.: $M = 745$ and 750 respectively). The *cadmium* derivative, brick red, sinters and decomposes at 235—245°; it is rather less soluble than the above compounds, being sparingly soluble except in chloroform, and was recrystallised from acetone (Found: Cd, 14·35. $C_{38}H_{46}O_8N_4Cd$ requires Cd, 14·1%).

Palladium derivatives. The pyrromethene (0·45 g., 1 mol.) and sodium acetate (1 mol.) were dissolved in alcohol, and potassium chloropalladite (1·6 mol.), dissolved in water, was added together with sufficient of the solvents to keep the reagents in solution in the cold. The colour gradually darkened, and after a day, 0·14 g. of reddish-brown crystalline powder (A) was removed. The alcoholic filtrate was treated with water, depositing a further 0·35 g. of product (B). The filtrate from this contained uncrystallisable material soluble in chloroform and containing palladium. (B) was left in contact with acetone for a day, and filtered, giving an insoluble portion (C), 0·18 g., and a soluble portion (D). The substance (C), recrystallised from chloroform–petrol, separated as brownish-red felted masses or as nearly black separate crystals decomposing at 235° [Found: C, 47·15; H, 5·1; Pd, 21·7; Cl, 7·55; *M* (cryoscopic in bromoform), 926. $C_{38}H_{46}O_8N_4Pd_2Cl_2$ requires C, 47·0; H, 4·8; Pd, 22·0; Cl, 7·3%; *M*, 971]. The material (A) was triturated with acetone, in which it was almost insoluble, and recrystallised in the cold from chloroform–petrol. This bright red *substance* was much more soluble than the previous compound, and decomposed indefinitely at 170—200°. It could be prepared from the compound $R_2Pd_2Cl_2$ by warming it in alcohol with two molecular proportions of the parent pyrromethene, and precipitating with petrol [Found: C, 54·7; H, 5·9; Pd, 12·85; Cl, 4·5; *M* (cryoscopic in benzene), 765. $C_{38}H_{47}O_8N_4PdCl$ requires C, 54·95; H, 5·7; Pd, 12·85; Cl, 4·3%; *M*, 830]. On prolonged boiling with alcohol, a less soluble substance separated, but this could be much more easily prepared by triturating in alcohol with silver carbonate or oxide, in which case a theoretical yield could be obtained. This derivative is a microcrystalline brick-red powder, decomposing at 322°, almost insoluble in the usual solvents except chloroform, from which it is best purified by precipitation with alcohol. It may also be prepared in 67% yield by the addition of palladous nitrate (1 mol.), dissolved in water, to the base (2 mols.) with excess of sodium acetate in alcohol [Found: C, 57·7; H, 6·1; Pd, 13·1, 13·5; *M* (cryoscopic in bromoform), 792. $C_{38}H_{46}O_8N_4Pd$ requires C, 57·5; H, 5·85; Pd, 13·45%; *M*, 793]. The *substance* may be precipitated unchanged by the dilution of its solution in concentrated sulphuric acid.

Mercuric derivatives. On the addition of excess mercuric chloride to the base with sodium acetate in alcohol, an almost quantitative yield of an orange microcrystalline halogen-containing substance is precipitated. With only one equivalent of mercuric chloride, only half the base is precipitated. The *product* is almost insoluble in the usual solvents, sparingly soluble in chloroform, and was recrystallised from bromoform; it sinters and melts at 214—216° (Found: C, 39·0; H, 4·2; Hg, 34·0; Cl, 6·2. $C_{19}H_{23}O_4N_2HgCl$ requires C, 39·35; H, 4·0; Hg, 34·6; Cl, 6·1%).

When excess mercuric nitrate or sulphate dissolved in hot dilute aqueous acetic acid was added to an alcoholic solution of the pyrromethene under similar conditions, an almost quantitative amount of orange microcrystalline material was precipitated after a few moments. This *substance* is more soluble than the above, and may be recrystallised from acetone or chloroform–petrol. Although individual crystals are minute, the substance on crystallising appears to fill the whole volume of the solution until pressed down; m. p. 217—220° (decomp.) (Found: C, 41·6; H, 4·5; Hg, 32·9, 32·85. $C_{21}H_{26}O_6N_2Hg$ requires C, 41·8; H, 4·35; Hg, 33·3%).

Mercuric nitrate (1 equiv.), dissolved in water containing the minimal amount of nitric or acetic acid necessary for solution, was added to an alcoholic solution of the pyrromethene. The solution darkened, and a quantitative precipitation of an orange *product* was formed; recrystallised from acetone and chloroform–petrol, this had m. p. 227—230° (decomp.) (Found: C, 51·2; H, 5·4; Hg, 22·2. $C_{38}H_{46}O_8N_4Hg$ requires C, 51·4; H, 5·2; Hg, 22·6%).

The action of other bivalent metals on this pyrromethene was investigated by treating it in alcoholic solution with beryllium, magnesium, chromous, manganous, and plumbous acetates. No change in colour was observed on mixing the reagents, and the base could be recovered unchanged after the reaction. Neither were complex salts formed by the action of the pyrromethene on the freshly precipitated hydroxides or carbonates of these metals. On prolonged boiling with these reagents the colour darkened owing to deomposition of the pyrromethene.

Metallic Derivatives of Ethyl 3 : 3'-*Dimethylpyrromethene*-4 : 4'-*dicarboxylate*.—The cobalt, nickel, copper, zinc, and cadmium compounds were prepared by the addition of the acetates of these metals in very slight excess to a cold alcoholic solution of the base. The products were more unstable and less soluble than those of the fully methylated compound. *Cobalt* salt, m. p. 340° (decomp.) (Found: Co, 8·3. $C_{34}H_{38}O_8N_4Co$ requires Co, 8·55%). *Nickel* salt, m. p. 315° (decomp.) (Found: Ni, 8·4. $C_{34}H_{38}O_8N_4Ni$ requires Ni, 8·5%). *Copper* salt, m. p. 305° (decomp.) (Found: Cu, 9·05. $C_{34}H_{38}O_8N_4Cu$ requires Cu, 9·15%). *Zinc* salt, m. p. 302° (decomp.) (Found: Zn, 9·3. $C_{34}H_{38}O_8N_4Zn$ requires Zn, 9·4%). *Cadmium* salt, m. p. 316° (decomp.) (Found: Cd, 15·35. $C_{34}H_{38}O_8N_4Cd$ requires Cd, 15·15%).

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