

171. *Studies in Co-ordination Chemistry. Part II. Trisarsine Complexes of Bivalent Platinum and Palladium.*

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The compounds $\text{PtBr}_2, 3\text{AsR}_3$ and $\text{PdBr}_2, 3\text{AsR}_3$ (where AsR_3 is diphenylmethylarsine) have been isolated and their properties investigated. Although their solubility in organic solvents suggested that they were non-ionic covalent complexes, it was found that they dissolved in these solvents with dissociation. Electrical-conductivity measurements in acetone solution on the palladium compound support the view that they are salts of the triammine type, *i.e.*, $[\text{Pd}(\text{AsR}_3)_3\text{Br}]^+\text{Br}^-$.

DURING an investigation of the tertiary arsine complexes of metal salts, two new complexes of bivalent platinum and palladium have been isolated of a type not previously described, and their properties were carefully investigated because their behaviour at first suggested that they might be examples of five-covalency similar to that observed by Jensen and Nygaard (*Acta Chem. Scand.*, 1949, **3**, 474) in the nickel compound $\text{NiBr}_2, 2\text{PEt}_3$. When preparing the compound $\text{PtBr}_2, 2\text{AsMePh}_2$ by the action of diphenylmethylarsine on chloroplatinic acid in the presence of excess of sodium bromide, it was observed that excess of the arsine led to the formation of an orange crystalline compound of empirical formula $\text{PtBr}_2, 3\text{AsMePh}_2$. Further investigation showed that this orange compound could be obtained readily by heating the bisarsine compound ($\text{PtBr}_2, 2\text{AsMePh}_2$) with excess of arsine in alcohol solution under reflux, the trisarsine compound crystallising out on cooling. This complex dissolved readily in chloroform or benzene on shaking and was fairly soluble in acetone and warm alcohol. From the alcoholic solution the bisarsine compound was precipitated on cooling unless excess of arsine was present. The trisarsine compound melted at 151° as compared with 201° for the yellow bisarsine complex.

The corresponding *palladium* compound was prepared in a similar manner, starting with the orange compound $\text{PdBr}_2, 2\text{AsMePh}_2$ and using a greater excess of arsine. Conditions were found to be more critical than in the case of the platinum compound, for the trisarsine complex dissociated very readily. It forms almost black crystals which melt at 109° , the colour changing to light orange; the bisarsine complex melts at 178° . The trisarsine compound dissolved very readily in organic solvents such as acetone, benzene, and chloroform, and was fairly soluble in alcohol, the black crystals giving an orange solution.

The molecular weights of both of these compounds were measured in a variety of solvents, benzene, bromoform, ethylene dibromide, and acetone being used; in the first three the determinations were cryoscopic, in the last ebullioscopic. In every case a molecular weight corresponding to half of the formula weight $\text{MBr}_2, 3\text{AsMePh}_2$ ($\text{M} = \text{Pd}$ or Pt) was observed because the compounds dissociated into one molecule each of arsine and the bisarsine compound; from benzene solution the bisarsine complexes were precipitated at the freezing point.

There are four obvious ways in which these compounds might be formulated: (a) as a molecular (lattice) compound of arsine and the bisarsine complex; (b) as a bridged complex of two octahedrally co-ordinated bivalent metal atoms, requiring a molecular formula $(\text{MBr}_2, 3\text{AsMePh}_2)_2$; (c) as a salt of the type $[\text{M}(\text{AsR}_3)_3\text{Br}]^+\text{Br}^-$; (d) as a five-covalent complex in which the extra molecule of arsine forms a very weak bond to the metal atom by using the remaining *5p* or *6p* orbital. Since a solution of the compound shows some properties different from those expected of a mixture of its constituents, (a) is excluded; (b) is readily disposed of since neither molecular weight nor solubility lends any support, and in any case six-covalent complexes of bivalent palladium and platinum are very rare. Solubility in organic solvents and low melting point and the fact that such a complex should dissociate readily lent some support to (d), but the salt-like structure (c) has been finally accepted from studies on the conductivity of the palladium complex in acetone. The higher solubility of the palladium compound, particularly at low temperatures, made it preferable to the platinum complex for this purpose.

trialkylstibines similar to those isolated by Jensen. It is noteworthy that the iodide and bromide corresponding to the compounds described in this paper could not be obtained, and attempts to use trialkylarsines were unsuccessful; triphenylarsine also gave no trisarsine complex. Phenyl dimethylarsine may be used instead of diphenylmethylarsine but the complexes are unsuitable for study because the arsine is very readily oxidised in air. The isolation of the compounds described in this paper must be ascribed to peculiarly favourable conditions of solubility not found with the other arsines or anions.

Like all bivalent complexes of palladium and platinum which have been measured, these trisarsine compounds are diamagnetic.

EXPERIMENTAL.

Bisdiphenylmethylarsinedibromopalladium(II).—Anhydrous palladous chloride (0.66 g.), dissolved in distilled water (33 ml.) containing a few drops of 10*N*-hydrochloric acid, was treated with sodium bromide (10 g.) in water (30 ml.) and diphenylmethylarsine (1.45 g.) in alcohol (150 ml.), and the solution heated on the water-bath. The initial yellow precipitate slowly redissolved on heating to form a reddish solution. After about $\frac{1}{2}$ hour an orange precipitate gradually formed which was filtered off (2.1 g.) after several hours' heating on the water-bath, washed with cold aqueous alcohol and finally with water, and recrystallised from alcohol; m. p. 178° (Found: C, 41.2; H, 3.4; Pd, 14.0. $C_{26}H_{26}Br_2As_2Pd$ requires C, 41.3; H, 3.4; Pd, 14.1%). The compound crystallises as sparkling orange plates, readily soluble in chloroform or benzene, fairly soluble in acetone, but only slightly soluble in cold alcohol. Like all similar bisarsine compounds of palladium it is undoubtedly the *trans*-isomer.

Trisdiphenylmethylarsinemonobromopalladium(II) Monobromide.—The foregoing compound (0.34 g.) was treated with diphenylmethylarsine (3.0 g.) in alcohol (40 ml.) and heated to boiling. All dissolved to an orange solution, but on cooling, the original bisarsine complex crystallised out. (It is necessary to get concentrations just correct, otherwise the trisarsine complex is not obtained.) The solution was again heated to boiling and about 30 ml. of alcohol were removed by boiling, and on cooling slowly, dark brownish-red, almost black crystals were obtained. Formation of these crystals was hastened if the cold solution was carefully seeded with a crystal of the pure compound. The complex was filtered off after the solution had been kept for 24 hours and washed several times with cold alcohol, in which it is slightly soluble. After drying in a vacuum desiccator the compound was obtained as black crystals with a reddish streak [Found: C, 47.2; H, 3.95; Pd, 11.0%; *M* (cryoscopic), in bromoform (0.494%), 452; in ethylene dibromide (0.833%), 477. $C_{39}H_{39}Br_2As_3Pd$ requires C, 47.4; H, 4.0; Pd, 10.9%; *M*, 1003]. It dissolved readily in most organic solvents except light petroleum and was quite insoluble in water. On heating the compound melts at 109°, the colour changing instantly from black to orange.

Bisdiphenylmethylarsinedibromoplatinum(II).—This compound, m. p. 201°, prepared as in Part I (preceding paper), was recrystallised twice before use from acetone (Found: C, 37.5; H, 3.1; Pt, 23.1. Calc. for $C_{26}H_{26}Br_2As_2Pt$: C, 37.0; H, 3.1; Pt, 23.1%).

Trisdiphenylmethylarsinemonobromoplatinum(II) Monobromide.—The foregoing compound (4.0 g.) was heated under reflux with diphenylmethylarsine (5 g.) dissolved in alcohol (200 ml.) for about 15 minutes. Practically all the bisarsine complex had then dissolved, the solution becoming orange. The solution was filtered hot, and on cooling, orange crystals of the *trisarsine* compound were deposited. These were filtered off and washed many times with alcohol; yield, 407 g. [Found: C, 43.0; H, 3.5; Br, 14.8; Pt, 17.9%; *M*, in bromoform (cryoscopic), 0.875% soltn., 567, 1.45% soltn., 587; in ethylene dibromide (cryoscopic), 1.21% soln., 548; in acetone (ebullioscopic), 1.81% soln., 541; 3.70% soln., 560; in benzene* (cryoscopic), 1.60% soln., 485; 1.84% soln., 478. $C_{39}H_{39}Br_2As_3Pt$ requires C, 43.0; H, 3.6; Br, 14.7; Pt, 17.9%; *M*, 1087]. The compound melts sharply at 151° if heated fairly rapidly, the colour changing on fusion from orange to yellow. When cooled, the orange colour returns but the m. p. is then 2—3° lower, indicating that dissociation products are present. The compound is quite insoluble in water, practically insoluble in cold alcohol, but moderately soluble in acetone. An acetone solution slowly deposits yellow crystals of the bisarsine compound unless excess of arsine is added. On shaking, the compound dissolves fairly readily in benzene, chloroform, bromoform, and ethylene dibromide, but it is quite insoluble in light petroleum. Although an acetone solution reacts immediately with silver nitrate solution, this is not taken as significant, for the bisarsine complex also reacts immediately with silver nitrate.

Magnetic susceptibility. This was measured in powder form and the compound was found to be diamagnetic with a specific susceptibility $\chi_{295^\circ K.} = -0.46 \times 10^{-6}$.

Electrical conductivity. These measurements were carried out in a pipette-type cell of volume about 15 ml. The cell constant (0.0508 cm.⁻¹) was determined at 25° with *m*/100-potassium chloride. It was not re-determined at lower temperatures because only comparative values of conductivity were required. The acetone used was A.R., which was distilled over potassium permanganate, dried [$Mg(ClO_4)_2$], and fractionated. The specific conductivity (κ) was 2.1×10^{-7} , 1.75×10^{-7} , and 7.3×10^{-8} mho/cm.³ at 25°, 0°, and -78°, respectively. The $PdBr_2 \cdot 2AsMePh_2$ and $PdBr_2 \cdot 3AsMePh_2$ were recrystallised twice before use and dried in a vacuum desiccator. The *m*/100-solutions were made up at 25°. After measurement of the conductivity of a solution at 25°, the cell was placed in a bath of distilled water and ice, and the conductivity measured at 0°. The cell was then placed in a long Dewar flask containing alcohol and solid carbon dioxide, the flask being stoppered to prevent the entry of moisture. Throughout all measurements the temperature was checked with a toluene thermometer which remained constant to within 1° of -78°.

* The results in benzene are unreliable because the bisarsine compound crystallised out after about two determinations of the freezing point; the solution is supersaturated and this probably explains the larger depression.

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