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

By R. S. NYHOLM.

The compounds $PtBr_2,3AsR_3$ and $PdBr_2,3AsR_3$ (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., $[Pd(AsR_3)_3Br]^+Br^-$.

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 NiBr₃,2PEt₃. When preparing the compound PtBr₂,2AsMePh₂ 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 PtBr₂,3AsMePh₂. Further investigation showed that this orange compound could be obtained readily by heating the bisarsine compound (PtBr₂,2AsMePh₂) 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.

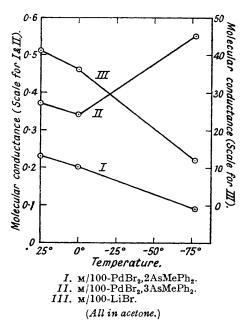
The corresponding palladium compound was prepared in a similar manner, starting with the orange compound PdBr₂,2AsMePh₂ and using a greater excess of arsine. Conditions were found to be more critical than in the case of the platinum compound, for the trisarsine complex dissociated very readily. It forms 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 $MBr_2,3AsMePh_2$ (M=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 $(MBr_2,3AsMePh_2)_2$; (c) as a salt of the type $[M(AsR_3)_3Br]^+Br^-$; (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.

A solution of the palladium trisarsine complex in acetone has a very light orange colour at 25° , and is only very slightly darker than a solution of the bisarsine compound at the same concentration (M/100). When a solution of the bisarsine complex is cooled there is no perceptible change in colour but the trisarsine solution gradually deepens in colour as the temperature is reduced below -25° , and at about -78° the colour is deep red. As the trisarsine complex in the solid state is black with a red streak, it is reasonable to assume that recombination of the bisarsine complex and arsine to form the complex isolated in the solid state has taken place.

This colour change is also observed if one cools similarly a mixture of free arsine and the bisarsine compound or a benzene solution of these two substances; the dark reddish-black mixture which is observed at low temperatures becomes orange again on warming to room temperatures. The great ease with which temperature caused dissociation, together with other properties mentioned above, led to the possibility of a weak covalent bond between the arsine and the metal. Conductivity measurements, however, show that at low temperatures an electrolyte is being formed. In the figure are shown the molecular conductivities of M/100-solutions of the bisarsine and the trisarsine complex in acetone at various temperatures, m/100-lithium bromide having been measured for comparison. Although for both lithium bromide and the bisarsine complex there is the expected decrease in conductivity as the temperature falls over the 100° range, yet the trisarsine complex shows a remarkable rise in conductivity below 0°. This increase in conductivity parallels the deepening in colour which occurs at the same temperature. No significance is attached to the actual conductance of PdBr₂,2AsMePh₂, and PdBr2,3AsMePh2 at 25°, it being due, no



doubt, to traces of impurity or partial solvolysis; at -78° , however, it is clear that the amount of salt formation is more than sufficient to balance the natural decrease due to the fall in temperature. The amount of salt formation at -78° is still relatively small as judged by comparison with lithium bromide at the same temperature. One may conveniently represent the changes which take place when the trisarsine compound dissolves as follows:

One originally confusing observation was the fact that it was found possible to dissolve in benzene a higher molar concentration of the platinum trisarsine complex than of the bisarsine complex alone; this appeared especially unusual since all measurements showed that the trisarsine complex immediately dissociated into the bisarsine complex and arsine. However, the presence of arsine may enhance the solubility to some extent, but of greater importance is the probable formation of the *trans*-bisarsine complex initially on dissociation. This is much more soluble than the *cis*-form but the latter is gradually produced on standing. The yellow bisarsine compound used in the preparation is only slightly soluble in benzene at room temperatures and is hence undoubtedly the *cis*-isomer.

These compounds appear to be the first known examples of salts of the triammine type formed by tertiary arsines or phosphines with bivalent platinum or palladium. These ligands, unlike ammonia, have a great tendency to form non-ionic complexes but some salt-like compounds have been obtained; Jensen (Z. anorg. Chem., 1936, 229, 225) described salts of the type [Pt(PR₃)₄]Cl₂ and [Pt(PR₃)₄][PtCl₄] which passed over into the monomeric covalent complexes PtCl₂,2PR₃ on heating in organic solvents but no evidence of a trisarsine or trisphosphine complex was obtained. Morgan and Yearsley (J., 1925, 127, 184) have described complexes of

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. Phenyldimethylarsine 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 10n-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 ½ 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. C₂₈H₂₆Br₂As₂Pd 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 After drying in a vacuum desiccator the compound was obtained as black crystals with singlify soluble. After drying in a vacuum desictator 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. C₃₉H₃₃Br₂As₃Pd 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 C₂₆H₂₆Br₂As₂Pt: 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. 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% soltm., 567, 1·45% soltm., 587; in ethylene dibromide (cryoscopic), 1·21% solm., 548; in acetone (ebullioscopic), 1·81% solm., 541; 3·70% solm., 560; in benzene * (cryoscopic), 1·60% solm., 485; 1·84% solm. 478. C₃₉H₃₉Br₂As₃Pt 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 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 $\chi_{295^{\circ}\kappa} = -0.46 \times 10^{-6}$.

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 The celt constant (0.0308 cm. 7) was determined at 25 with M/100-potassium chroride. 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 $2\cdot 1 \times 10^{-7}$, $1\cdot 75 \times 10^{-7}$, and $7\cdot 3 \times 10^{-8}$ mho/cm.³ at 25°, 0°, and -78°, respectively. The PdBr₂,2AsMePh₂ and PdBr₂,3AsMePh₂ 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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