562. *The Nature of the Co-ordinate Link. Part III.* Improved Preparation of Tertiary Phosphine, Arsine, and Stibine Complex Compounds with Platinous Chloride.*

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Jensen's method for the preparation of the isomeric $(R_3M)_2PtCl_2$ (M = P, As, or Sb) yields a mixture of isomers. Often one isomer is present only in very small quantity. A method is devised for converting the crude product, almost quantitatively, into either isomer, except in the two limiting cases, (1) when spontaneous isomerisation is rapid and only the less soluble *cis*-isomer can be isolated, and (2) when the equilibrium between the two isomers is so far on the *trans*-side that only the *trans*-isomer can be isolated.

The complex compounds formed by tertiary phosphines, arsines, and stibines with platinous chloride are readily prepared by shaking a suspension of the organic ligand in aqueous potassium chloroplatinite (Jensen, *Z. anorg. Chem.*, 1936, **229**, 237). The products from the tertiary alkyl phosphines and arsines are usually mixtures of *cis*- and *trans*-$(R_3M)_2PtCl_2$ (M = P or As). The stibines have invariably given only *cis*-$(R_3Sb)_2PtCl_2$. The isomers are easily separated by extraction of the *trans*-isomer with ether or light petroleum (b. p. 40—60°), leaving the *cis*-isomer as a completely insoluble residue. The only serious difficulty occurs if the required isomer is formed in very small quantity, which is frequently the case. Thus Jensen was unable to obtain any *cis*-bis(tri-*n*-propylarsine)dichloroplatinum, and in numerous preparations of bis(tri-*n*-propylphosphine)dichloroplatinum we rarely obtained more than 10% of the *trans*-isomer, but on one occasion obtained 20%. The preparation by the reaction of the phosphine on the bridged complex, $(Pr_3P)_2Pt_2Cl_4$, has also given very variable ratios with as much as 85% of the *trans*-isomer (Chatt, *J.*, 1950, 2306).

A study of the equilibrium *cis*- $\rightleftharpoons$ *trans*-$(Pr_3M)_2PtCl_2$ (where M = P, As, or Sb) has led us to devise means of producing almost entirely the required isomer, except in the stibine series where only the *cis*-isomer can be obtained crystalline. Our observations apply particularly to the tri-*n*-propyl series but are of wider validity if we make allowance for the reduced solubility and shift of the above equilibrium to the left in lower homologues, to the right when the chlorine is replaced by more covalently bound acid radicals, *e.g.*, bromine, iodine, or nitrito, and to the left by less covalently bound radicals, *e.g.*, nitrate. A limitation of our method is imposed by spontaneous isomerisation of some isomers. This occurs particularly when the platinum atom is combined with atoms from the higher series of the Periodic Table, *e.g.*, iodine, tellurium, or antimony. Thus we were unable to obtain from solution the very soluble *trans*-$(Pr_3Sb)_2PtCl_2$ although the less soluble *cis*-isomer is well known.

The conversion of the crude product from Jensen's preparation into the required isomer depends on the following observations: (1) The equilibrium between stable isomers in solution can be labilised by the addition of a trace of the free ligand. Thus approx. 0·002 g. of tri-*n*-propylphosphine added to 50 c.c. of a benzene solution of 1 g. of either isomeric $(Pr_3P)_2PtCl_2$ causes equilibrium to be established in 15 minutes at 25°. (2) The catalysed lability can be frozen and the spontaneous isomerisation can be arrested, sometimes completely for a short time as in the arsenic series, by addition of a trace of the corresponding bridged complex (Chatt, *J.*, 1951, 652) sufficient to remove all the free ligand, *e.g.*, $2Pr_3P + (Pr_3P)_2Pt_2Cl_4 = 2(Pr_3P)_2PtCl_2$. (3) The equilibrium lies well to the side of the *trans*-isomer, *e.g.*, there is 97% of *trans*-$(Pr_3P)_2PtCl_2$, 99·8% of the arsine, and 80% of the stibine analogue in the equilibrium mixture with the corresponding *cis*-isomers in benzene solution at 25°. (4) The *cis*- are considerably less soluble in all solvents than the *trans*-isomers, and particularly they are almost insoluble in ether and light petroleum which dissolve the *trans*-isomers readily. (5) The effect of spontaneous isomerisation can be greatly reduced by rapid recrystallisations and immediate drying of the crystalline product at 0·01 mm.

When the *trans*-isomer is required, the mixed isomers, as prepared (Jensen, *loc. cit.*), are dissolved in benzene, the equilibrium established by addition of a trace of the free ligand, then frozen by addition of bridged complex. The *trans*-isomer, together with its small equilibrium concentration of *cis*-isomer, is obtained by evaporation of the solution and can then be extracted entirely from the *cis*-isomer by light petroleum or another suitable solvent.

* Part II, *J.*, 1951, 652.

The *cis*-isomer is obtained by evaporating the labilised equilibrium solution, preferably in light petroleum; the less soluble *cis*-isomer, in spite of its low concentration relative to the *trans*-isomer, separates, and as evaporation proceeds all the *trans*- is converted into the *cis*-isomer from which the catalyst may be washed with light petroleum.

Difficulty is experienced when there is so little *cis*-compound in the equilibrium that the *trans*-compound separates on evaporation of the labilised equilibrium mixture, and also when the tendency to spontaneous isomerisation is so great that isomerisation cannot be arrested sufficiently by addition of the bridged compound. The preparation of the tri-*n*-propyl series of complexes supplies examples of all possible combinations of circumstances, except those when only the *trans*-isomer can be isolated. In such an event, the *cis*-isomer may be obtained indirectly provided that spontaneous isomerisation can be prevented, as Jensen (*loc. cit.*, p. 239) obtained *cis*-$(Pr_3P)_2PtI_2$ by the reactions: *cis*-$(Pr_3P)_2PtCl_2 + Ag_2SO_4 \longrightarrow$ *cis*-$(Pr_3P)_2Pt(SO_4) + 2KI \longrightarrow$ *cis*-$(Pr_3P)_2PtI_2$.

Experimental.

The light petroleum used in these preparations had b.p. 40—60°. All the *cis*-isomers described here are completely insoluble in light petroleum. The complete solubility of a sample of *trans*-isomer provided a quick and reliable test that it contained no *cis*-isomer.

cis-*Bis*(*tri*-n-*propylphosphine*)*dichloroplatinum*.—Crude $(Pr_3P)_2PtCl_2$ (3·6 g.) obtained by reaction of tri-*n*-propylphosphine with aqueous potassium chloroplatinite (Jensen, *loc. cit.*) was suspended in warm light petroleum (30 c.c.). About 0·005 g. of tri-*n*-propylphosphine in 1 c.c. of light petroleum was added and equilibrium established within a few minutes. The solution was then evaporated to dryness at 15—20 mm. and entirely *cis*-material separated (3·6 g.). This was washed with light petroleum, then twice recrystallised from ethanol (yield, 2·0 g. plus 0·8 g. from the mother-liquors). It had m. p. 150·5—152° (Jensen gives m. p. 149—150°).

trans-*Bis*(*tri*-n-*propylphosphine*)*dichloroplatinum*.—Crude $(Pr_3P)_2PtCl_2$ (1·5 g.) was dissolved in benzene (20 c.c.), and tri-*n*-propylphosphine (about 0·002 g.) added. After 30 minutes dichlorobis(tri-*n*-propylphosphine)-$\mu\mu'$-dichlorodiplatinum (0·006 g.) was added. The solution was evaporated at 15—20 mm. and the dry residue extracted with light petroleum, leaving a small white residue of the *cis*-isomer. The yellow extract was evaporated to dryness and the residue twice recrystallised from ethanol, yielding pure *trans*-isomer (0·7 g., plus 0·45 g. from the mother-liquors), m. p. 85—86° (Jensen gives m. p. 82—82·5°).

cis-*Bis*(*tri*-n-*propylarsine*)*dichloroplatinum*.—The direct reaction of tri-*n*-propylarsine with aqueous potassium chloroplatinite (as in Jensen's preparation) gave us only the *trans*-isomer. Crude $(Pr_3As)_2PtCl_2$ (4·6 g.) in warm light petroleum (20 c.c.) was isomerised by tri-*n*-propylarsine (0·006 g.). The solution was evaporated to dryness at 15—20 mm. and the solid residue treated with light petroleum (*ca.* 20 c.c.) and re-evaporated. This treatment was repeated until the residue consisted entirely of the crude *cis*-material. This was washed with light petroleum several times to remove any trace of catalyst and recrystallised twice from methanol, yielding pure cis-*isomer* (2·2 g., plus 1·7 g. from the mother-liquors), m. p. 131—132·5° (Found: C, 32·15; H, 6·2. $C_{18}H_{42}Cl_2As_2Pt$ requires C, 32·1; H, 6·3%).

trans-*Bis*(*tri*-n-*propylarsine*)*dichloroplatinum*.—This is most readily obtained by recrystallisation of crude $(Pr_3As)_2PtCl_2$ from methanol but can be obtained from the *cis*-isomer. The *cis*-isomer (4·5 g.) in warm benzene (25 c.c.) was isomerised with tri-*n*-propylarsine (0·003 g.) (15 minutes). Dichloro(tri-*n*-propylarsine)-$\mu\mu'$-dichlorodiplatinum (0·008 g.) was added and the solution evaporated to dryness. The residue, consisting almost entirely of the *trans*-compound, was recrystallised several times from methanol (until completely free from the *cis*-isomer). Pure *trans*-isomer (4·0 g.) was obtained, having m. p. 52—53° (Jensen gives m. p. 51—52°).

The above arsine complexes, to be sufficiently pure not to isomerise slowly but spontaneously in benzene solution, must be dried immediately under *ca.* 0·01 mm. pressure.

cis-*Bis*(*tri*-n-*propylstibine*)*dichloroplatinum*.—This was prepared by direct reaction between tri-*n*-propylstibine and aqueous potassium chloroplatinite. Recrystallised several times from ethanol it had m. p. 79—80° (Jensen gives m. p. 80—81°). The product, even after careful drying at 0·01 mm., isomerised slowly in pure benzene, equilibrium being reached in about 2 days. Drying in a vacuum-desiccator in the normal manner gave a product which isomerised much more quickly, equilibrium being reached in 1½—2 hours.

Attempted Preparation of trans-*Bis*(*tri*-n-*propylstibine*)*dichloroplatinum*.—Addition of dichlorobis(tri-*n*-propylstibine)-$\mu\mu'$-dichlorodiplatinum (*ca.* 0·008 g.) to an equilibrium mixture of $(Pr_3Sb)_2PtCl_2$ (1·5 g.) in benzene which contained about 80% of *trans*-isomer, followed by evaporation of the solution at 15—20 mm., gave a dark-red oil which did not crystallise but isomerised rapidly to the solid canary-yellow *cis*-compound.

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