LXXIV.—*Trimethylplatinum Acetylacetone, a Volatile Platinum Compound.*

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The separation of thallous iodide from solutions of thallous acetylacetone in ethyl or methyl iodide and the preparation of ethyl ethylacetoacetate by boiling a solution of ethyl thalloacetoacetate in ethyl iodide are particular instances of double decomposition between thallous salts and halides. The reaction is a general one for the preparation of acetylacetone derivatives, *e.g.*, ferric acetylacetone is obtained in 60% yield by heating one equivalent of ferric chloride with three equivalents of thallous acetylacetone. A new application of the method is the preparation, by reaction between thallous acetylacetone and trimethylplatinic iodide (Pope and Peachey, J., 1909, **95**, 571) in dry benzene, of *trimethylplatinum acetylacetone*, $Me_3Pt\langle^{O\cdot CMe}_{O:CMe}\rangle CH$, which is now described on account of its behaviour on heating.

Experimental.

Ferric acetylacetone (2·14 g.; yield, 61%) was obtained by refluxing 1·62 g. of anhydrous ferric chloride and 9·1 g. of thallous acetylacetone in dry ether. The reaction was completed in less than ½ hour and 6·3 g. of thallous chloride (yield, 88%) were also obtained. The first two crops (1·1 g. and 0·55 g.) had m. p. 185° and 182°, respectively (Hantzsch and Desch, *Annalen*, 1902, **323**, 13, found m. p. 179°; Urbain and Debierne, *Compt. rend.*, 1899, **129**, 303, found m. p. 184°).

Trimethylplatinic iodide (7·5 g.) was prepared from chloroplatinic acid (20 g.) by Pope and Peachey's method (*loc. cit.*). Great difficulty, however, was experienced in dissolving anhydrous platinic chloride in dry ether. It was therefore dissolved in the minimum quantity of absolute alcohol; this solution, on addition of ether, separated into two layers. The presence of the alcohol necessitated the use of a large excess of the Grignard reagent.

Trimethylplatinum Acetylacetone.—Solutions of 3·7 g. of trimethylplatinic iodide and 3·03 g. of thallous acetylacetone in warm benzene free from thiophen were mixed and heated under reflux, the thallous iodide that separated was removed, the filtrate evaporated to dryness, and the residue crystallised from hexane (charcoal). Two crops (1·6 g. and 0·8 g.) of *trimethylplatinum acetylacetone* were obtained

(yield, 70%) (Found: Pt, 57·0; C, 28·5; H, 4·9. $C_8H_{16}O_2Pt$ requires Pt, 57·5; C, 28·3; H, 4·75%).

This compound separates from hot benzene, on cooling, in colourless needles, but as thick plates on slow evaporation of a cold benzene solution. It is very soluble in the usual organic solvents and is most conveniently recrystallised from light petroleum or hexane. In 3% benzene solution it is associated (Found: *M*, cryoscopic, 576. Calc.: *M*, 339·2). A solution in methyl alcohol remains transparent on mixing with cold water, but on being heated the mixture becomes cloudy.

When heated in a capillary tube, trimethylplatinum acetylacetone decomposes at about 200° without melting; but in a dry tube or flask it sublimes, a little being deposited apparently unchanged on the cooler parts of the vessel. The vapour, however, is decomposed by hot glass, on which the platinum is deposited in a coherent form; by carefully heating and shaking a small quantity in a glass vessel, it is possible to coat much of the surface with a platinum mirror. Mirrors prepared in air at the ordinary pressure do not adhere firmly, being partly stripped, but not dissolved, by boiling nitric or hydrochloric acid. If, however, the glass be heated to a dull red heat after deposition, the metal adheres more firmly. When the compound was heated in the vacuum produced by a good water-pump, in a test-tube immersed in a sulphuric acid bath, sublimation began at 160°, the compound condensing above the level of the acid. Decomposition on the hot glass below the acid took place slowly at 160° and became rapid at 190°. Subsequent heating of the evacuated tube over a flame, and finally at a red heat after the platinum had been deposited, gave the most adherent mirror yet obtained; it was not stripped by boiling with water or nitric or hydrochloric acid.

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