Correspondence

On the Probable Nonexistence of Tetramethylplatinum

Sir:

The preparation of tetramethylplatinum was first reported by Gilman and Lichtenwalter[1,2] in 1938, and the crystal structure was reported by Rundle and Sturdivant.[3] Cowan, *et al.*,[4] have shown that the structure determined[3] was actually that of trimethylplatinum hydroxide. Spiro,[5] *et al.*, have recently reported the refined structure of trimethylplatinum hydroxide. The report[1,2] of the preparation appears to be in error,[4] and thus only trimethylplatinum hydroxide was prepared. The original method of preparation, as reported, involved the reaction of trimethylplatinum(IV) iodide with methylsodium under cover of hexane and nitrogen. Afterward, the reaction mixture was solvolyzed with pentyl alcohol, and the product was extracted with and crystallized from petroleum ether (bp 60–68°). This method was tried repeatedly by us and several others[4,6–9] without success. The only product that we found was trimethylplatinum hydroxide or its mixture with a trimethylplatinum alkoxide, depending on which alcohol was used for the solvolysis. The presence of the trimethylplatinum alkoxide was indicated by comparing X-ray powder patterns of these products with those of trimethylplatinum alkoxide samples prepared directly from $(CH_3)_3PtI$ and ethoxide or methoxide ions. Infrared spectra also supported this conclusion. Since the product was reported to be soluble in the hydrocarbon covering liquid for the reaction, attempts were made to recover the product by siphoning out the covering liquid. In each case, unreacted starting material was recovered from the supernatant liquid. The rest of the liquid along with the reactive intermediates was treated with methanol, and a mixture of trimethylplatinum hydroxide with trimethylplatinum methoxide was obtained.

The analytical data that had been given with the original preparation may have been unreliable: the authors reported[1,2] that the samples tended to detonate. The hydroxide–alkoxide mixture we prepared also detonated upon heating. It was reported[1,3] that the product reacted with hydrochloric acid to produce trimethylplatinum chloride. Trimethylplatinum hydroxide reacts with hydrochloric acid to give trimethylplatinum chloride.

We were unsuccessful in obtaining a sample of the original material,[1–3] with which we hoped to check both the X-ray data and the infrared spectrum. This could easily have resolved the problem, since the ir spectrum of trimethylplatinum hydroxide has been characterized.[10,11] A print of a powder X-ray diffraction pattern of the original material was provided by J. H. Sturdivant, and both relative intensities and spacings of the diffraction rings were the same as those we obtained for trimethylplatinum hydroxide and thus we agree with the recent findings of Cowan, *et al.*[4]

Kettle[6] has pointed out that an electronically deficient compound with methyl donor groups should be violently reactive, as in the case with dimethylberyllium polymers and trimethylaluminum dimers. By contrast we found the "tetramethylplatinum" to be relatively unreactive.

Recently Donnay, *et al.*,[12] have shown that the hexamethyldiplatinum synthesis[1,2] is not valid. We have also attempted to duplicate the preparation of hexamethyldiplatinum—also without success. The method requires the reaction of trimethylplatinum iodide with metallic potassium under cover of hydrocarbon liquid and nitrogen. The only solid product we recovered was platinum black.

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[9] L. P. Quinn and N. A. Daugherty, while in this laboratory, also attempted to reproduce the synthesis of tetramethylplatinum.

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