(4) R. Rogowski and K. Cohn, *Inorg. Chem.*, 7, 2193 (1968).
(5) W. B. Fox, D. E. Young, R. Foester, and K. Cohn, *Inorg. Nucl. Chem. Lett.*, 7, 861 (1971).
(6) A. H. Cowley and R. H. Neilson, to be submitted for publication.
(7) J. E. Griffiths, R. P. Carter, and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964).

Correspondence

Improved Isolation Procedure for the Preparation of Iodo(trimethyl)platinum(IV)

AIC50149D

Sir:

The standard method for the preparation of iodo(trimethyl)platinum(IV) has been that of Clegg and Hall[1] which typically uses 10 g of potassium hexachloroplatinate and twice the stoichiometric quantity of methyl Grignard reagent. Our repeated attempts to reproduce this synthesis on a smaller scale with less than 10 g of potassium hexachloroplatinate have led to little or no product.

Decomposition of the excess Grignard reagent with cold 10% HCl solution invariably has given orange and black insoluble products which are the dimethylplatinum diiodide complex and platinum iodides,[2] respectively. Repeated extraction of the orange-black mixture with benzene at reflux gives less than 2% of iodo(trimethyl)platinum(IV) iodide. The present method ensures the removal of the magnesium salts by filtration of the reaction mixture prior to decomposition of excess Grignard reagent. Then the clear filtrate is decomposed with acetone instead of 10% HCl. The *tert*-butyl alcoholate which is formed from interaction with acetone and excess Grignard reagent serves to complex magnesium iodides. These are then dissolved in a normal fashion with dilute HCl and the product is isolated from the benzene layer.

Since other workers[3] have apparently experienced similar difficulties, the following procedure is submitted. Adherence to this work-up gives consistently 80–82% of a pure product.

Experimental Work. Potassium chloroplatinate, K_2PtCl_6,[4] is dried overnight at 110° under reduced pressure (about 0.2 Torr). Diethyl ether and benzene, both Mallinckrodt AR grade, are dried by distillation under argon immediately prior to use from lithium aluminum hydride and sodium diethylaluminum dihydride, respectively. Methyl iodide, Mallinckrodt AR grade, was distilled from anhydrous $CaSO_4$ under nitrogen and stored under nitrogen until used.

The Grignard reagent, CH_3MgI, is prepared by dropping 5.0 ml (11.4 g, 80 mmol) of methyl iodide in 20 ml dry ether onto 1.10 g (45.2 mmol) of flame-dried magnesium turnings under nitrogen. The alkyl halide solution is added at a rate to maintain a steady reflux; the addition requires about 20 min. The resulting black suspension is then stirred until the last pieces of magnesium are dissolved and filtered through a sintered-glass disk (medium porosity) directly into a dropping funnel mounted atop a flask which contains 2.00 g (4.12 mmol) of finely powdered K_2PtCl_6.[5]

The Grignard reagent is then added dropwise over a 10-min period to an ice-cooled suspension of K_2PtCl_6 in 10 ml of ether and 40 ml of benzene. The reaction mixture is allowed to warm gradually to room temperature after the addition and is left to stir under nitrogen. Within 4 hr the mixture fades from yellow to white.

After stirring the mixture overnight, the white salts are allowed to settle. The supernatant is then filtered through a medium sintered-glass disk under nitrogen. The clear, nearly colorless filtrate (not orange as previously described[1]) is cooled to 0° and 5 ml of ice-cold acetone is slowly added dropwise to the stirring filtrate. As the acetone is added a vigorous reaction takes place, which turns the mixture yellow and then orange. A two-phase mixture results with a yellow layer at the top and an orange layer below.

After opening the flask to the air, 25 ml of ice-cold water is added to the stirring mixture, which coagulates the bottom layer into a light yellow solid and produces an orange supernatant. This mixture is acidified with 30 ml of 10% HCl which dissolves the solid and gives an orange-yellow organic layer over a pinkish orange aqueous layer with a small amount of orange solid at the interphase. The orange solid is filtered and the layers are separated. The aqueous layer is extracted with 3 30-ml aliquots of benzene. After extraction the aqueous layer is the color of claret. The extracts are combined with the organic layer and dried by filtration through a cone of anhydrous $CaSO_4$. The clear, yellow-orange solution is then rotary evaporated to dryness and the resulting yellow solid is dissolved in 30 ml of $CHCl_3$. This solution is evaporated to about 15 ml on the hot plate, 15 ml of acetone is added, and the mixture is cooled in ice. The yellow crystals formed are collected with suction and air-dried. The yield is 1.21–1.22 g (80–81%), mp 195° dec; ir and NMR data are identical with those reported in the literature.[6]

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Registry No. Iodo(trimethyl)platinum(IV), 14364-93-3; K_2PtCl_6, 16921-30-5; CH_3MgI, 917-64-6.

References and Notes

(1) D. E. Clegg and J. R. Hall, *Inorg. Synth.*, **10**, 71 (1967).
(2) J. R. Hall and G. A. Swile, *Aust. J. Chem.*, **24**, 423 (1971).
(3) K. H. von Dahlen and J. Lorberth, *J. Organomet. Chem.*, **65**, 267 (1974).
(4) Potassium hexachloroplatinate was obtained from Engelhard Minerals Corp. and J. Bishop and Co.
(5) The filtered Grignard reagent is colorless.
(6) J. M. Homan, J. M. Kawamoto, and G. L. Morgan, *Inorg. Chem.*, **9**, 2533 (1970).

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Tin–Halogen Stretching Frequencies and the Hard and Soft Acid–Base Theory

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Sir:

Since the proposal of the HSAB theory,[1] at least two papers have shown that, in the application toward certain areas, the HSAB fails.[2,3] In a recent report by Ohkaku and Nakamoto[4] it was pointed out that the Sn–X stretching frequency is sensitive to the nature of the donor ligands in compounds of formula SnX_4L_2 or $SnX_4L\text{-}L$. The observation was made that the Sn–X bond becomes stronger as the Sn–L bond becomes weaker. On that basis, the order of metal–ligand force constant