stirred another 20 hr at room temperature. The mixture was poured in the air onto silica gel and the solvent was removed by rotary evaporation. The solids were chromatographed on a 5 × 40 cm column of silica gel. Elution with hexane–CH_2Cl_2 (9:1 v/v) resulted in a red band which was recrystallized from hexane to give 0.23 g of II (mp 201°) (17% yield). The red band was closely followed by the yellow band of I of which 0.6 g was recovered. Anal. Calcd for $C_{13}H_{21}B_{10}Co$: C, 45.34; H, 6.15; B, 31.39; Co, 17.11. Found: C, 45.24; H, 6.15; B, 31.00; Co, 16.69. Infrared spectrum, cm^{-1} (intensity): 2505 (s), 1590 (w), 1010 (m), 990 (m), 980 (m), 915 (w), 880 (w), 845 (s), 755 (s), 700 (s).

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Registry No. I, 11056-78-3; II, 55492-95-0; $C_6H_5BCl_2$, 873-51-8.

References and Notes

(1) G. E. Herberich, G. Greiss and H. F. Heil, *Angew. Chem., Int. Ed. Engl.*, **9**, 805 (1970).
(2) G. E. Herberich, G. Greiss, H. F. Heil, and J. Miller, *Chem. Commun.*, 1328 (1971).
(3) M. F. Hawthorne and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 4392 (1965).
(4) M. F. Hawthorne and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 896 (1965).
(5) C. J. Jones and M. F. Hawthorne, *Inorg. Chem.*, **12**, 608 (1973).

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Reaction of Boron Trichloride with Phosphorus Pentafluoride. A Convenient Synthesis of PF_4Cl

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The potential of chlorotetrafluorophosphorane as a synthetic intermediate is illustrated by its reaction with ammonia which results in the formation of the parent aminotetrafluorophosphorane, H_2NPF_4.[1] The dynamic stereochemistry of PF_4Cl has also attracted recent attention.[2] However, more extensive studies of the chemistry of this interesting molecule have been hampered by the difficulties which are associated with the previously published preparations.

Carter and Holmes[3] first described the synthesis of PF_4Cl using a two-step procedure

$$PF_3 + Cl_2 \rightarrow PF_3Cl_2 \xrightarrow[-50°]{SbF_3} PF_4Cl$$

This method affords rather low yields (~20%) and requires the preliminary isolation of PF_3Cl_2. In a different approach Rogowski and Cohn[4] reported the synthesis of PF_4Cl by the HCl cleavage of the N–P bond of Me_2NPF_4

$$Me_2NPF_4 + 2HCl \rightarrow Me_2NH_2Cl + PF_4Cl$$

However, subsequent unpublished results by the same workers have indicated that the reaction is difficult to reproduce.[5]

More recently Fox and coworkers[5] have reported the preparation of PF_4Cl in good yield (~50%) via the oxidative addition of ClF to PF_3

$$PF_3 + ClF \rightarrow PF_4Cl$$

One disadvantage of this method is that it requires the use of the expensive reagent chlorine monofluoride. Furthermore, in numerous attempts to repeat this reaction, several workers in this laboratory have found it to be uncontrollably violent even at −196°. Typical yields of PF_4Cl have been in the range 0–10%.

As part of a study of the chemistry of silylaminophosphines an interesting halogen-exchange reaction between BCl_3 and $(Me_3Si)_2NPF_2$ was discovered[6]

$$3(Me_3Si)_2NPF_2 + 2BCl_3 \rightarrow 3(Me_3Si)_2NPCl_2 + 2BF_3$$

In turn this prompted the investigation of the reaction of boron trichloride with phosphorus pentafluoride as a possible synthetic route to PF_4Cl.

It was found that the reaction

$$3PF_5 + BCl_3 \rightarrow 3PF_4Cl + BF_3$$

proceeds slowly in the gas phase at ambient temperature. Chlorotetrafluorophosphorane is obtained in reproducible yields of 45–52%, if a rather low (~250 Torr) total pressure of PF_5 and BCl_3 is employed together with a reaction time of about 36 hr. Higher pressures or longer reaction times lead to the formation of large amounts of by-products (e.g., PF_3Cl_2) and greatly reduced yields of the tetrafluorophosphorane.

This relatively facile reaction employing mild conditions and readily available starting materials therefore seems to be the method of choice for the preparation of chlorotetrafluorophosphorane, which may prove to be a useful precursor to several novel tetrafluorophosphorane systems.

Experimental Section

All manipulations were carried out in a standard Pyrex glass vacuum system. As with most fluorophosphorane chemistry, thoroughly dried apparatus is imperative. Phosphorus pentafluoride and BCl_3 were procured from Matheson Gas and distilled through traps held at −140° (retained at −196°) and −78° (retained at −117°), respectively, prior to use.

In a typical experiment a 2-l. glass reaction bulb equipped with a glass–Teflon stopcock was evacuated and flame-dried. Boron trichloride (5.0 mmol) and PF_5 (20.0 mmol) were condensed together in the reaction vessel at −196° and then allowed to warm to room temperature. After 36 hr traces of an unidentified white solid were observed in the reaction bulb. The gaseous products were then bled slowly into the vacuum system (preliminary work had shown that condensation of the mixture at this point caused the formation of more solids and lower yields of PF_4Cl) passing directly through traps held at −117, −140, and −196°. The −117° trap retained PF_3Cl_2 (2.3 mmol) which was identified by its infrared spectrum.[7] The −196° fraction (14.1 mmol) consisted of a mixture of BF_3 and PF_5. Chlorotetrafluorophosphorane (7.7 mmol, 51% yield) was retained at −140°. The infrared spectrum was identical with that reported in the literature.[3] The product of this single distillation may contain small amounts (~5%) of PF_5 and SiF_4. Further purification of PF_4Cl is complicated by its disproportionation into PF_5 and PF_3Cl_2 which occurs readily in the liquid phase, particularly in glass systems.

In separate experiments the progress of the reaction was followed by infrared spectroscopy. Reaction periods of less than 24 hr result in incomplete conversion of BCl_3 and low yields of PF_4Cl. Beyond 36 hr PF_3Cl_2 is formed in increasing amounts.

Other experiments have shown that rather slight deviations from the above procedure can result in lower yields of PF_4Cl. For example, when 9.0 mmol of PF_5 and 3.0 mmol of BCl_3 were allowed to react in a 500-ml vessel (~450 Torr total pressure) for 12 hr copious amounts of white solids were formed and the only volatile products were PF_5 and BF_3.

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Registry No. BCl_3, 10294-34-5; PF_5, 7647-19-0; PF_4Cl, 13637-88-2.

References and Notes

(1) A. H. Cowley and J. R. Schweiger, *J. Chem. Soc., Chem. Commun.*, 560 (1972).
(2) M. Eisenhut, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutch, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 5385 (1974).
(3) R. P. Carter and R. R. Holmes, *Inorg. Chem.*, **4**, 738 (1965).

(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-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