CHEMISTRY OF THE TRIFLUOROMETHYL GROUP

PART IV. DIPHENYLTRIFLUOROMETHYLPHOSPHINE AND COMPLEX FORMATION BY PHENYLTRIFLUOROMETHYLPHOSPHINES[1]

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ABSTRACT

Three methods of preparing diphenyltrifluoromethylphosphine are described. The hydrolysis of the phosphine to diphenylphosphinic acid and fluoroform, and the formation of dibromo- and diiodo-phosphoranes from the phosphine are reported. The adducts $(C_6H_5)_3P.BF_3$ and $(C_6H_5)_2CF_3P.BF_3$ are described and the latter is found to be the less stable. With platinum (II) chloride, the complexes *trans*-$[(C_6H_5)_2PCF_3]_2PtCl_2$ and *trans*-$[C_6H_5P(CF_3)_2]_2PtCl_2$ are formed. The properties of the BF_3 adducts and $PtCl_2$ complexes are interpreted in terms of the electronegativity and size of the trifluoromethyl group.

INTRODUCTION

In the previous paper (1) of this series, the preparation and physical and chemical properties of phenylbistrifluoromethylphosphine were described. We now report the preparation of diphenyltrifluoromethylphosphine, and also the results of experiments designed to determine the abilities of both these phosphines to participate in complex formation.

DISCUSSION AND RESULTS

Three methods have been found successful in preparing diphenyltrifluoromethylphosphine. Since phenylbistrifluoromethylphosphine can be obtained by the addition of trifluoroiodomethane to the P—P bonds of tetraphenylcyclotetraphosphine, one obvious route to diphenyltrifluoromethylphosphine lay in the reaction of tetraphenyldiphosphine with trifluoroiodomethane:

$$(C_6H_5)_2P\text{—}P(C_6H_5)_2 + CF_3I \rightarrow (C_6H_5)_2PCF_3 + (C_6H_5)_2PI.$$

This and other reported additions (2, 3) to compounds of the type $R_2P\text{—}PR_2$ involve cleavage of the weak P—P bond. Its bond energy is only 50 kcal mole^{-1} (4), much less than that of the P—C bond (62 kcal mole^{-1}), so that the P—P bond will be the potential point of attack by a reactive species.

Tetraphenyldiphosphine is prepared by the reaction of diphenylphosphine and diphenylchlorophosphine (5, 6), preferably in a high-boiling solvent such as xylene. When tetraphenyldiphosphine is heated with excess trifluoroiodomethane at 185°, or when the two reactants are exposed to ultraviolet radiation, a mixture of diphenyltrifluoromethylphosphine and diphenyliodophosphine is produced, from which the former can be extracted with petroleum ether. Since the reaction will occur either thermally or on ultraviolet irradiation, a free-radical mechanism involving the attack of CF_3 radicals on the P—P bond seems probable.

The alternative methods of preparation require the reaction of either diphenylchlorophosphine or triphenylphosphine with trifluoroiodomethane at 185–200°. Although in both cases the yields are not high (approx. 20%), these methods are advantageous in

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that the reactants are readily available and the preparation of the diphosphine is not required. A number of secondary products are obtained in each case so that the overall reactions can be represented as

$$(C_6H_5)_3P + CF_3I \rightarrow (C_6H_5)_2PCF_3 + (C_6H_5)_2PI + C_6H_5CF_3$$

$$(C_6H_5)_2PCl + CF_3I \rightarrow (C_6H_5)_2PCF_3 + (C_6H_5)_2PI + (C_6H_5)CF_3PCl + C_6H_5CF_3 + CF_3Cl.$$

The nature of the products strongly suggests that these reactions involve a radical mechanism, presumably the attack of CF_3 radicals on the P—C_6H_5 or P—Cl bonds.

Diphenyltrifluoromethylphosphine is a colorless, viscous liquid which boils at 255–257°. This is 28° lower than the boiling point of the methyl analogue, $(CH_3)_2PCF_3$, and 24° lower than that of the secondary phosphine, $(C_6H_5)_2PH$. Such low boiling points are common for the perfluoroalkyl derivatives of the group V elements and reflect the reduced molecular polarity and hence the weaker intermolecular interactions.

Diphenyltrifluoromethylphosphine is stable in air and is not decomposed easily on heating. After being heated to 300° for 24 hours, 85% of the phosphine is recovered. The phosphine is unaffected by water or by hydrochloric acid up to 150°. Only slight hydrolysis occurs with aqueous sodium hydroxide at 100°, in marked contrast to phenylbistrifluoromethylphosphine which is quantitatively hydrolyzed under these conditions. Diphenyltrifluoromethylphosphine can be hydrolyzed with alcoholic potassium hydroxide, although the reaction is only 78% complete after 96 hours at 80°. The hydrolysis products are fluoroform and diphenylphosphinic acid, $(C_6H_5)_2P(O)OH$.

It is of considerable interest that trifluoromethyl-metallic and -metalloidal derivatives are much more susceptible to hydrolytic attack than the analogous alkyl and aryl compounds. Exceptions among the phosphorus–trifluoromethyl compounds are trifluoromethylphosphonic acid (7) and compounds which also contain a phenyl group, e.g. diphenyltrifluoromethylphosphine. These show much greater resistance to hydrolysis, as do the comparable arsenic derivatives (8), this presumably being a consequence of electron delocalization involving the aromatic systems.

In general, however, the ready removal of the trifluoromethyl group on hydrolysis, usually to give fluoroform, can be understood in terms of its high electronegativity, and high electron-withdrawing effect, as shown by the value of the Taft polar substituent constant σ^*.

Group	σ^*	Electronegativity
CH_3	0.00 (9)	2.34 (11)
H	0.49 (9)	2.10 (11)
C_6H_5	0.60 (9)	2.70 (12)
OCH_3	1.46 (9)	2.92 (12)
Br	2.80 (9)	2.94 (12)
CCl_3	2.65 (10)	2.76 (11)
Cl	2.94 (9)	3.19 (12)
CF_3	2.81 (10)	3.3 (13)
F	3.08 (9)	3.93 (12)

These values indicate the high polarity of the M—CF_3 bond compared with M—CH_3 or M—C_6H_5, and suggest that the M—CF_3 bond will therefore be a very likely point of hydrolytic attack.

Bromine and iodine react readily with diphenyltrifluoromethylphosphine to form diphenyltrifluoromethyl-dibromophosphorane and -diiodophosphorane respectively. These are stable oils which are unaffected by air or water and are stable to 200°. However, they are hydrolyzed quantitatively by aqueous sodium hydroxide to fluoroform, diphenylphosphinic acid, and sodium halide:

$$(C_6H_5)_2CF_3PX_2 + 2NaOH \rightarrow (C_6H_5)_2P(O)OH + CF_3H + 2NaX.$$

The fact that diphenyltrifluoromethyldiiodophosphorane can be prepared, whereas phenylbistrifluoromethyldiiodophosphorane could not be isolated (1), is interesting and must be due, at least in part, to the large steric effect of the CF_3 group. Thus, replacement of one CF_3 group in phenylbistrifluoromethylphosphine by a less bulky phenyl group gives a phosphine which is sterically capable of forming a diiodophosphorane. Similarly, triphenylphosphine in which steric effects are further reduced, also forms a stable diiodophosphorane (14). In its physical and chemical properties, therefore, diphenyltrifluoromethylphosphine is closely related to triphenylphosphine.

In an earlier paper (15), the ability of methyltrifluoromethylphosphines to take part in complex formation was examined, and one purpose of the present investigation has been the study of the corresponding properties of the phenyltrifluoromethylphosphines. Three types of reactions have been examined, namely the tendency of each phosphine to form (*a*) a phosphonium iodide with an alkyl iodide, (*b*) an addition compound with boron trifluoride, and (*c*) a planar complex with platinum (II) chloride.

As might be expected neither phenylbistrifluoromethylphosphine nor diphenyltrifluoromethylphosphine forms a phosphonium iodide with trifluoroiodomethane, nor is phenylbistrifluoromethylphosphine sufficiently basic to react with iodomethane. However, the more basic character of diphenyltrifluoromethylphosphine is shown by its reaction with iodomethane to form diphenylmethyltrifluoromethyl phosphonium iodide, $[(C_6H_5)_2CF_3CH_3P]I$. This yellow crystalline solid melts at 123–125° and is stable in dry air but it is very readily hydrolyzed by cold water to produce fluoroform, hydriodic acid, and methyldiphenylphosphine oxide:

$$(C_6H_5)_2CF_3CH_3PI + H_2O \rightarrow (C_6H_5)_2CH_3PO + CF_3H + HI.$$

Such ease of hydrolysis is consistent with other studies (16) of the decomposition of phosphonium hydroxides, which show that the most electron-withdrawing organic radical is always the one eliminated, the three less electron-withdrawing groups forming the phosphine oxide.

By examining the stability of phosphine – boron trifluoride adducts, information is obtained concerning the strength of the dative σ-bond between phosphorus and boron. Such studies for the phenyltrifluoromethylphosphines give results which parallel those obtained for the methyltrifluoromethylphosphines (15). Triphenylphosphine-boron trifluoride is a stable white solid of low volatility with a melting point of 128–130°. The boron trifluoride adduct of diphenyltrifluoromethylphosphine is an oil whose saturation pressure is greater than that of its triphenylphosphine analogue. Boron trifluoride adducts of phenylbistrifluoromethylphosphine and tristrifluoromethylphosphine could not be formed. In confirmation of our previous results (8), it is therefore clear that the introduction of one CF_3 group causes a very substantial reduction in the basicity of a phosphine, and the introduction of two such groups makes the phosphine such a weak base that a BF_3 adduct is not formed.

In complexes of phosphines with transition metal halides, such as platinum (II) chloride, the metal–phosphorus bonds contain both σ and π components. The way in which each of these components is influenced by the type of group attached to phosphorus is reasonably well understood and was briefly outlined earlier (15). Bis(triphenylphosphine) dichloroplatinum (II) has been prepared by Jensen (17) as the cis isomer, but preparations of the corresponding complexes of diphenyltrifluoromethylphosphine and phenylbistrifluoromethylphosphine give only the trans isomers. This is shown by their zero dipole moments. Some caution must be used in interpreting these results in terms of the relative stabilities of cis and trans isomers, since the proportions of the two isomers obtained in such cases often varies somewhat according to the preparative method used. Although detailed studies of the cis–trans equilibria would be necessary to reach a conclusion regarding the stabilities of the two isomers, it is of interest that both the phenyltrifluoromethylphosphines seem to give chiefly the trans isomer. As in the methyltrifluoromethylphosphines, therefore, stepwise replacement of methyl by trifluoromethyl imposes steric restrictions on the phosphine which have the effect of stabilizing the trans isomer with respect to the cis. However, in the phenyl series, the introduction of only one CF_3 group seems to have a much greater effect, since methylbistrifluoromethylphosphine gives a very stable cis complex (15). The situation is parallel to that for tri-*n*-butylarsine and phenyldi-*n*-butylarsine, of which the former gives only the trans complex, but for the latter the cis–trans equilibrium is shifted in favor of the cis isomer (18).

Both bis(phenylbistrifluoromethylphosphine) dichloroplatinum (II) and bis(diphenyltrifluoromethylphosphine) dichloroplatinum (II) react with bromine and iodine to form the compounds $[C_6H_5P(CF_3)_2]_2PtCl_2X_2$ and $[(C_6H_5)_2PCF_3]_2PtCl_2X_2$, where $X = Br$ or I. These are stable solids which are presumably Pt (IV) complexes of the type $[R_2R'P]_2PtX_2Cl_2$, although further investigation is required to establish such a formulation.

The above studies on complex formation emphasize the effect of the highly electronegative trifluoromethyl group in reducing the donor properties of phosphines, and they also reveal the importance of steric factors in the chemistry of the trifluoromethyl group.

EXPERIMENTAL

The general techniques used in the preparation, manipulation, and determination of physical and chemical properties of these compounds have been described previously (1).

Diphenylchlorophosphine was prepared by the method of Steube, LeSuer, and Norman (19). After aluminum chloride (222 g) had been added to a mixture of phosphorus pentasulphide (208 g) and benzene (224 g), the mixture was refluxed for 5 hours and after being cooled was poured onto crushed ice. The resultant dark green solution of diphenylphosphinodithiioc acid was diluted with an equal volume of benzene and chlorinated at 0° by a stream of chlorine. Diphenyltrichlorophosphorane crystallized out and, after separation, was heated with red phosphorus (15.5 g) to 180°. After the more volatile products had been removed, the residual mixture was vacuum distilled to give diphenylchlorophosphine (64 g, 63% yield), which boiled at 178° at 20 mm.

Diphenylphosphine was obtained by the reaction of diphenylchlorophosphine with lithium metal in ether solution, followed by hydrolysis (6).

Tetraphenyldiphosphine was prepared by refluxing an ethereal solution of diphenylchlorophosphine (11 g) and diphenylphosphine (9 g). The precipitated white solid was washed with ether and dried.

Preparation of Diphenyltrifluoromethylphosphine

(*a*) Tetraphenyldiphosphine (1.2 g) and excess trifluoroiodomethane (12.2 g) were heated in a sealed Pyrex tube at 185° for 12 hours. Removal of the volatile products, which were excess trifluoroiodomethane and a trace of fluoroform, left an involatile liquid (0.4 g). Analysis of a sample purified by vapor phase chromatography showed it to be diphenyltrifluoromethylphosphine. (Found: C, 60.86%; H, 4.25%; F, 22.69%; P, 11.79%. Calc. for $C_{13}H_{10}F_3P$: C, 61.41%; H, 3.94%; F, 22.45%; P, 12.21%.)

The same product was obtained when tetraphenyldiphosphine (10 g) and trifluoroiodomethane (10 g) were exposed to ultraviolet radiation for 7 days.

(*b*) Triphenylphosphine (2.5 g) was heated with excess trifluoroiodomethane (14.0 g) at 185° for 4 hours. Fractionation of the volatile products gave trifluoroiodomethane (10.6 g), fluoroform (0.46 g), and trifluoromethylbenzene (0.04 g). Vacuum distillation of the involatile residue gave diphenyltrifluoromethylphosphine (0.2 g), which was identified by its infrared spectrum. There remained a residue of diphenyliodophosphine. No reaction occurred between triphenylphosphine and trifluoroiodomethane at 110°, while heating at 214° gave only a resinous material which could not be identified.

(*c*) Diphenylchlorophosphine (5.6 g) and trifluoroiodomethane (17.0 g) were heated at 205° for 12 hours. The reactants were miscible and after being heated gave a reddish brown solution. The volatile products consisted of trace amounts of hexafluoroethane and fluoroform, unreacted trifluoroiodomethane (8.8 g), trifluorochloromethane (1.24 g), and trifluoromethylbenzene (0.04 g). The ethereal extract of the involatile materials was found to contain more trifluoromethylbenzene, phenyltrifluoromethylchlorophosphine, and diphenyltrifluoromethylphosphine. These were separated by distillation.

Diphenyltrifluoromethylphosphine is a colorless, oily liquid which boils at 255–257°. Its vapor pressure equation is $\log P_{\mathrm{mm}} = 7.781-(2598/T)$, whence the latent heat of vaporization is 11,850 kcal mole^{-1}, and Trouton's constant is 22.9. Diphenyltrifluoromethylphosphine is stable in air, and prolonged heating at 300° causes only 15% decomposition.

Hydrolysis Reactions

(*a*) Water: The phosphine (0.22 g) was sealed in a Pyrex tube with water (1.2 g) and heated at 120° for 48 hours. The compounds were immiscible and the phosphine was recovered quantitatively.

(*b*) Hydrochloric acid: Diphenyltrifluoromethylphosphine (0.34 g) was recovered unchanged after being heated with concentrated hydrochloric acid (2.4 g) at 150°.

(*c*) Aqueous sodium hydroxide: Diphenyltrifluoromethylphosphine (0.24 g) was unaffected by heating to 100° for 24 hours with 5 ml of 20% sodium hydroxide solution.

(*d*) Alcoholic potassium hydroxide: The phosphine (0.21 g) was heated to 70° with 5 ml of 20% alcoholic potassium hydroxide solution for 96 hours. The volatile product was fluoroform (0.046 g), corresponding to 78% hydrolysis of the phosphine. From the residual solution, diphenylphosphinic acid was recovered. This was identified by its infrared spectrum and its melting point of 193° (20).

Reactions with Halogens

(*a*) Iodine (0.18 g) reacted with diphenyltrifluoromethylphosphine (0.18 g) in carbon tetrachloride at 25°. After the mixture had stood for an hour, a brown oil separated, which was identified as diphenyltrifluoromethyldiiodophosphorane. (Found: I, 49.32%. Calc. for $C_{13}H_{10}F_3I_2F$: I, 50.0%.) When the phosphorane (0.123 g) was heated to 80° with aqueous sodium hydroxide solution, fluoroform (0.016 g) was evolved, representing 91.7% hydrolysis. The phosphorane was unaffected by water and only slight decomposition occurred after heating of the solution to 200° for 24 hours.

(*b*) Bromine (0.105 g) and diphenyltrifluoromethylphosphine (0.166 g) were reacted in carbon tetrachloride solution. The resulting orange oil was identified as diphenyltrifluoromethyldibromophosphorane. (Found: Br, 38.07%. Calc. for $C_{13}H_{10}F_3Br_2P$: Br, 38.64%.) Diphenyltrifluoromethyldibromophosphorane (0.272 g) was treated with aqueous sodium hydroxide solution at 80° to give fluoroform (0.044 g), representing 96.1% hydrolysis. Acidification of the remaining solution gave diphenylphosphinic acid, m.p. 194°.

Reaction with Trifluoroiodomethane

Diphenyltrifluoromethylphosphine (0.22 g) was quantitatively recovered after being heated with trifluoroiodomethane (0.86 g) at 100° for 24 hours.

Reaction with Iodomethane

Diphenyltrifluoromethylphosphine (0.234 g) was heated with iodomethane (0.269 g) to 100° for 12 hours. An orange oil separated from which the excess iodomethane was removed to give a yellow powder, identified as methyldiphenyltrifluoromethyl phosphonium iodide, m.p. 123–126°. (Found: C, 42.4%; H, 3.3%; F, 14.2%; P, 7.6%. Calc. for $C_{14}H_{13}F_3PI$: C, 42.6%; H, 3.3%; F, 14.3%; P, 7.9%.) Reaction of the phosphonium iodide (0.127 g) with water (3.5 g) gave fluoroform (0.022 g, 99.1%) and left an acidic solution. Evaporation of this solution and extraction of the residue with benzene gave a white solid identified as methyldiphenylphosphine oxide, m.p. 111–112°.

Reactions with Boron Trifluoride

(*a*) The passage of boron trifluoride through a petroleum ether solution of triphenylphosphine (0.368 g) precipitated a white solid which analyzed for triphenylphosphine-boron trifluoride. (Found: C, 65.5%; H, 5.02%. Calc. for $C_{18}H_{15}PBF_3$: C, 64.6%; H, 4.7%.) The adduct melted at 128–130°; it was stable in dry air but was decomposed rapidly by moisture and was insoluble in non-polar solvents. The saturation pressure is given by the equation $\log P_{\mathrm{mm}} = 3.840-(972/T)$ in the range 80–170°, whence the heat of sublimation is 4.43 kcal mole^{-1}.

(*b*) Diphenyltrifluoromethylphosphine (0.254 g) was mixed with boron trifluoride (0.136 g). No reaction occurred at room temperature but when the mixture was cooled to −78°, an oil formed from which excess boron trifluoride (0.063 g) was removed by pumping. This loss of BF_3 corresponds to the formation of a 1:1 compound. The adduct, which is an oil, has the same properties towards air, moisture, and non-polar solvents as the triphenylphosphine adduct. The saturation pressure in the range 40–110° C is given by the expression $\log P_{\mathrm{mm}} = 6.609-(1753/T)$, whence the heat of vaporization is 8.04 kcal mole^{-1}.

No reaction occurred between boron trifluoride and phenylbis(trifluoromethyl)phosphine either at 25° or at −78°.

Reactions with Platinum (II) Chloride

(*a*) Diphenyltrifluoromethylphosphine (0.254 g) in acetone was added to an aqueous solution of potassium chloroplatinite (0.21 g), and the mixture was heated for 30 minutes. Removal of the acetone gave a resinous mass which, after purification with animal charcoal and water, gave a pale yellow solid, bis(diphenyltrifluoromethylphosphine) dichloroplatinum (II). (Found: CF_3, 16.9%. Calc. for $C_{26}H_{20}F_6P_2PtCl_2$: CF_3, 17.8%.) Treatment with ether gave a small portion melting at 230°, while the bulk of the product was soluble in ether, and melted at 63–65°.

Reaction of the complex with a carbon tetrachloride solution of bromine or iodine gave a yellow and brown precipitate respectively. With bromine the product was bis(diphenyltrifluoromethylphosphine) dichlorodibromoplatinum (II). (Found: CF_3, 14.5%. Calc. for $C_{26}H_{20}F_6P_2PtCl_2Br_2$: CF_3, 14.7%.)

(*b*) Phenylbis(trifluoromethyl)phosphine (0.793 g) was heated with platinum (II) chloride (0.308 g) to 100° for 7 days. The product was recrystallized from acetone and was bis(phenylbistrifluoromethylphosphine) dichloroplatinum (II), m.p. 134–136°. (Found: C, 25.6%; H, 1.36%; F, 29.44%. Calc. for $C_{16}H_{10}F_{12}P_2PtCl_2$: C, 25.4%; H, 1.37%; F, 30.16%.) The same product was obtained by adding the phosphine to an aqueous solution of potassium chloroplatinite, although in this case, the product also contained a small amount of material which melted above 300°.

Treatment of the complex with a carbon tetrachloride solution of either bromine or iodine, as in (*a*) above, gave the dibromo or diiodo derivative. These were characterized by weight gain and by alkaline hydrolysis.

Dipole moments were measured as described previously (8); the platinum (II) complexes of both phenylbis(trifluoromethyl)phosphine and diphenyltrifluoromethylphosphine were found to have zero dipole moments.

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