amine showed the maxima listed in the final column of the table; no analysis of this spectrum has been reported. Bands considered comparable, *i.e.* arising from the presence of coördinated triethylamine, are listed in the same horizontal row of the table. The asymmetric and symmetric B–F stretching vibrations have been assigned[10] respectively to maxima at 1150 and 911 cm.$^{-1}$ [for $BF_3 \cdot (CH_3)_3N$] and 1165 and 893 cm.$^{-1}$ [for $BF_3 \cdot C_5H_5N$]. However, the pyridine complex also was examined by Luther, Mootz and Radwitz[12] who assigned absorption at 900 and 695 cm.$^{-1}$ to these B–F vibrations. The triethylamine–boron trifluoride spectrum has bands at 1150, 925 and 665 cm.$^{-1}$ which are absent in the spectra of the other complexes and are apparently associated with the BF_3 group. These probably result from the two stretching vibrations and a deformation mode. Corresponding absorptions for the boron trichloride analog appear at 703, 725 and 765 cm.$^{-1}$. The spectrum of the isothiocyanate compound showed the expected bands at 2090 and 975 cm.$^{-1}$ associated with the isothiocyanate stretching vibrations.

The spectrum of the isothiocyanate compound in the 1100 cm.$^{-1}$ region is similar to that found with the pyridine adduct. While the boron trifluoride and trichloride–triethylamine compounds each show a strong, sharp maximum at 1100 cm.$^{-1}$, the isothiocyanate adduct gives two strong bands at 1076 and 1110 cm.$^{-1}$, with evidence of fine structure. This similarity with the pyridine complex would indicate that these maxima also are associated with B–N vibrations. Triethylamine has a strong absorption band at 1075 cm.$^{-1}$, but in the trichloride and trifluoride compounds this appears in a similar position (1077 and 1075 cm.$^{-1}$, respectively) with greatly reduced intensity. It is unlikely then that the strong absorption at this position in the isothiocyanate adduct is due entirely to this band of triethylamine. However, the spectra of boron trihalide–trimethylamine compounds in chloroform solution have been reported,[10] with a band at 1249 cm.$^{-1}$ being assigned to the B–N stretch in the boron trifluoride compound.

Nitrile Adducts.—The nitrile addition compounds show the asymmetric isothiocyanate stretching frequency as a strong doublet at 2130 and 2060 cm.$^{-1}$ for acetonitrile and 2140 and 2050 cm.$^{-1}$ for benzonitrile. Weaker absorption at 2350 and 2305 cm.$^{-1}$, respectively, can be assigned to the C≡N stretching vibration of the coördinated nitrile group. As is the case with the boron halide–nitrile addition compounds,[13,14] this absorption occurs at higher frequencies than in the free nitrile.

---

[12] H. Luther, D. Mootz and F. Radwitz, *J. prakt. Chem.*, [4], **5**, 242 (1958).

[13] H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).

[14] W. Gerrard, M. F. Lappert, H. Pyszora and J. W. Wallis, *J. Chem. Soc.*, 2182 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIFORNIA]

The Hybrid Diphosphine $(CH_3)_2PP(CF_3)_2$[1,2]

BY LOUIS R. GRANT, JR., AND ANTON B. BURG

RECEIVED NOVEMBER 21, 1961

The new diphosphine $(CH_3)_2PP(CF_3)_2$ (m.p. −79°; b.p. est. 120°) was made from $(CH_3)_2PH$ and $(CF_3)_2PCl$ at −78°, with or without $(CH_3)_3N$ to remove HCl. Its ultraviolet spectrum is more like that of $P_2(CH_3)_4$ than $P_2(CF_3)_4$. It is far less stable than either of these, apparently because the respective P atoms offer electron donor and acceptor action, as shown by its 1:1 adducts with BH_3 and with $(CH_3)_3N$. Its protolytic cleavage gives high yields of $(CF_3)_2PH$ with the anion going to the $(CH_3)_2P$ group, in accord with thermochemical expectations. Methyl iodide causes it to disproportionate, forming mostly $P_2(CF_3)_4$ and apparently $(CH_3)_2PP(CH_3)_3{}^+I^-$.

The widely different chemical behavior of the diphosphines $P_2(CH_3)_4$[3] and $P_2(CF_3)_4$[4] makes it difficult to predict the properties of the intermediate diphosphines having P-CH_3 and P-CF_3 bonds in the same molecule. Accordingly we have made and explored the chemical character of one such intermediate type, namely, 1,1-dimethyl-2,2-bis-(trifluoromethyl)-diphosphine; and in fact it is found that some of its properties are quite different from the mean between the extremes represented by $P_2(CH_3)_4$ and $P_2(CF_3)_4$. For example, it can be made from $(CH_3)_2PH$ and $(CF_3)_2PCl$ without using an additional base to remove the HCl—whereas $(CF_3)_2PH$ fails to react with $(CF_3)_2PCl$. Also, the $(CH_3)_2P$ group has good base action, whereby it can bond to such an electron acceptor as a BH_3 group; and the $P(CF_3)_2$ group has a tendency toward electron-acceptor bonding, accounting for the formation of a $(CH_3)_3N$ adduct. Then also $(CH_3)_2PP(CF_3)_2$ molecules can attack their own kind in the donor–acceptor manner, causing a far lower thermal stability than observed

---

[1] The name "diphosphine" (instead of "biphosphine") for a substitution derivative of P_2H_4 conforms to the most recent IUPAC report on inorganic nomenclature. To avoid confusion, the class of double phosphines having P-(chain)-P connections can be distinguished by the term "bis-phosphines," related to individual names such as 1,2-bis-(dimethylphosphino)-ethane; *cf.* ref. 3.

[2] This research is described in fuller detail in Chapter II of the Ph.D. dissertation by Louis R. Grant, Jr., University of Southern California Libraries, 1961. It was initiated under Office of Naval Research Contract Nonr-228(13) but was supported primarily by the United States Air Force under a subcontract of Prime Contract AF 33(616)-5435, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[3] A. B. Burg, *J. Am. Chem. Soc.*, **83**, 2226 (1961), and other papers there cited.

[4] F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

for $P_2(CH_3)_4$ or for $P_2(CF_3)_4$. More detailed discussions of the properties of this new diphosphine accompany the following presentation of experimental results.

These studies were accomplished by means of a high-vacuum manifold, using Stock-type mercury float-valves where feasible. Most reactions occurred in sealed Pyrex tubes, which could be opened to the vacuum system by a ground-joint type of tube opener.

Synthesis and Proof of Formula.—The phosphinolysis reaction $2(CH_3)_2PH + (CF_3)_2PCl \rightarrow (CH_3)_2PP(CF_3)_2 + (CH_3)_2PH_2Cl$ proved to be fairly straightforward but gave good yields only when the heat of reaction was effectively dispersed. Thus 0.417 mmole of $(CF_3)_2PCl$ and 0.893 mmole of $(CH_3)_2PH$, warmed at a moderate rate to 25°, vigorously formed non-volatile solids and 0.360 mmole of $(CF_3)_2PH$ (86% conversion), but none of the desired diphosphine; but when a mixture of 3.77 and 1.80 mmoles of the respective phosphines was warmed from −78 to −10° during 15 hr., the yield of $(CF_3)_2PH$ was only 27%, and there was a 66% yield of $(CH_3)_2PP(CF_3)_2$— some of which was released from the non-volatile solid by the action of dimethylamine. Still better results were obtained from the reaction in ether at −78°, as next described.

A 3.5 ml. diethyl ether solution containing 3.250 mmoles of $(CH_3)_2PH$ and 1.625 mmoles of $(CF_3)_2PCl$ was formed by stirring at −78° and allowed to stand for 15 hr. at that temperature. The precipitated $(CH_3)_2PH_2Cl$ was filtered off at a low temperature and sublimed away in the high-vacuum system; weight 149.3 mg., or 1.516 mmoles (93% of calcd.). The filtrate was subjected to high-vacuum fractional condensation, with the −65° trap holding 1.406 mmole (87% yield) of $(CH_3)_2PP(CF_3)_2$.

The next experiment employed 3.698 mmoles of $(CH_3)_2PH$ and 3.540 mmoles of $(CF_3)_2PCl$, with 3.728 mmoles of $(CH_3)_3N$ to remove the HCl— all in 10 ml. of ether at −78°. The yield of $(CH_3)_2PP(CF_3)_2$ was 3.281 mmoles, representing 93% of the $(CF_3)_2PCl$.

These nearly quantitative syntheses, taken with the mol. wt. value 230.2 (calcd., 230.1) left no serious doubt of the molecular formula $(CH_3)_2PP(CF_3)_2$, which was further confirmed by the quantitative aspects of the cleavage reactions, yet to be described.

Physical Properties.—A highly purified sample of the new diphosphine $(CH_3)_2PP(CF_3)_2$ melted in the range −79.2 to −79.1°. Its vapor tensions, examples of which are given with an equation in Table I, indicate the normal b.p. as 115° and the Trouton constant as 23.8 cal./deg. mole; but this high value would imply a curvature of the log P *vs.* $1/T$ graph above the observed range, such as to bring the true b.p. closer to 120°.

TABLE I

VAPOR TENSIONS OF $(CH_3)_2PP(CF_3)_2$

($\log P_{\text{mm.}} = 8.0938 - 2022/T$)

Temp. (°C.)	0.00	12.9	24.5	35.9	45.1	51.1	58.7
$P_{\text{mm.}}$ (obsd.)	4.94	10.7	19.9	35.6	55.1	72.2	100.2
$P_{\text{mm.}}$ (calcd.)	4.92	10.6	20.0	35.6	55.0	72.1	100.2

Ultraviolet Spectra.—The delocalization of lone-pair electrons across P–P bonds has been well demonstrated by the intense ultraviolet absorption spectra of various polyphosphines such as $(CF_3P)_4$ and $(CF_3P)_5$.[5] This effect, not shown by monophosphines unless there is an effective π-dative ligand on phosphorus, is attributed to the π-acceptor bonding power of the P_{3d} orbitals of phosphorus. Thus it is interesting to compare the three diphosphines whose ultraviolet spectra are shown in Table II. The data for $P_2(CF_3)_4$ are cited from the literature.[6] The other results were recorded by the Cary Model 14 double beam spectrophotometer, with the samples in a quartz-glass cell with a ground-joint adaptor for connection to the high-vacuum system. The molar extinction coefficients were calculated by the usual definition $\epsilon = \frac{D \times T \times 22.4 \times 760}{L \times 273 \times P}$, wherein D is the measured optical density, T the absolute temperature, P the pressure in mm. of Hg and L the path length in cm. The data for $P_2(CH_3)_4$ were obtained by W. Mahler.

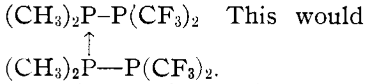
TABLE II

ULTRAVIOLET SPECTRA OF THREE DIPHOSPHINES

Compound:	$(CF_3)_2PP(CF_3)_2$	$(CH_3)_2PP(CF_3)_2$	$(CH_3)_2PP(CH_3)_2$
λ_{max}, Å.	2160 (ϵ = 7800)	2330 (ϵ = 4520)	2420 (ϵ = 4000)
λ_{min}, Å.	1960 (ϵ = 1500)	2120 (ϵ = 1850)	2320 (ϵ = 2900)

It is interesting that replacement of CF_3 by CH_3 moves the spectrum toward higher wave lengths, corresponding to a closer spacing of energy levels for less electronegative phosphorus. The corresponding decrease of intensity of the maxima would agree with the expectation of less delocalization of the phosphorus lone-pair electrons and higher base strength. In this relation it is noteworthy that $(CH_3)_2PP(CF_3)_2$ is much closer to $(CH_3)_2PP(CH_3)_2$ than to $(CF_3)_2PP(CF_3)_2$.

Thermal Decomposition.—The diphosphine $(CH_3)_2PP(CF_3)_2$ decomposes observably at 110°, forming chiefly a non-volatile oil, with traces of unidentified vapors having phosphine character. Thus it is far less stable than either $P_2(CH_3)_4$ or $P_2(CF_3)_4$, both of which withstand heating up to 300°.[3,5] The most credible reason for the low stability of this hybrid diphosphine is the tendency to form an intermolecular P–P dative bond, thus



$$\begin{array}{l}(CH_3)_2P\text{–}P(CF_3)_2 \\ \qquad\quad\uparrow \\ (CH_3)_2P\text{—}P(CF_3)_2.\end{array}$$

This would be the first step toward removing a CF_3 group from the acceptor phosphorus atom, making polymerization a probable result.

A typical decomposition occurred during a 7-day heating of 223.3 mg. (0.971 mmole) of $(CH_3)_2PP(CF_3)_2$ in a sealed tube at 110°. The remaining diphosphine amounted to 28.1 mg. (0.122 mmole), meaning that 87.4% had decomposed. The 45 mg. mixture of more volatile components was not fully resolved, but the less volatile half (vapor tension 43 mm. at 0°) had an average mol. wt. of 144 and the more volatile half, 159. The non-volatile brown oil, estimated as 152 mg., was exposed to neutral water for 20 hr. at 100°, yielding

---

(5) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

(6) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

as the only volatile product 42.3 mg. of HCF_3, representing 40% of the CF_3 groups in the decomposed diphosphine. Another sample of the oil, obtained from another decomposition experiment, was treated with trimethylamine in the hope that it would displace any weaker base forming a dative bond in the oil. However, the only result was a solution of the oil in the amine. Ammonia was irreversibly absorbed, forming no volatile product.

Cleavage Reactions.—The P–P bond cleavage of a diphosphine by an acidic reagent evidently depends upon base action by at least one of the phosphorus atoms, for $(CH_3)_2PP(CF_3)_2$, like $(CH_3)_2PP(CH_3)_2$, is attacked rapidly by HCl or water, whereas $(CF_3)_2PP(CF_3)_2$ is inert toward BF_3 or HCl up to 300°, fails to combine with either CH_3I or B_2H_6, and is only poorly reactive toward water—although far more reactive toward alcohols and stronger bases.[7] The protic-acid cleavage of $(CH_3)_2PP(CF_3)_2$ is interesting because it produces $(CF_3)_2PH$ quantitatively, even though the capture of the proton by the more basic P atom would suggest $(CH_3)_2PP(CF_3)_2 + HX \rightarrow (CH_3)_2PH + (CF_3)_2PX$ as the initial cleavage step. If this does occur, it must be followed by a fast exchange: $(CH_3)_2PH + (CF_3)_2PX \rightarrow (CH_3)_2PX + (CF_3)_2PH$, driven by an increase of bond energy from the virtually non-polar $H—P(CH_3)_2$ and $(CF_3)_2P—X$ to the far more polar $H—P(CF_3)_2$ and $(CH_3)_2P—X$ linkages. One example seems to be the fast reaction $(CH_3)_2PH + (CF_3)_2POH \rightarrow (CF_3)_2PH + (CH_3)_2POH$, although the disproportionation of the resulting $(CH_3)_2POH$[8] might alone explain its quantitative completion. A bond-energy increase also would explain the $(CF_3)_2PI$–PH_3 reaction to make $(CF_3)_2PH$.[9]

The cleavage of 0.335 mmole of $(CH_3)_2PP(CF_3)_2$ by HCl (0.713 mmole) occurred easily at room temperature, producing 0.329 mmole (98% yield) of $(CF_3)_2PH$, which was identified by its infrared spectrum and mol. wt. (obsd., 171.5; calcd., 170.0). After repeated fractional condensations, only 0.213 mmole of HCl was recovered. Thus the remaining volatile material would correspond to 0.17 mmole of HCl and 0.33 mmole of $(CH_3)_2PCl$. The difficulty of separating these components has been noticed before: they seem to combine at low temperatures to form an unstable hydrochloride.[10] The present mixture had the same properties as previously observed for HCl–$(CH_3)_2PCl$ mixtures, including a tendency to react slightly with mercury.

For the hydrolytic cleavage, 66.2 mg. (0.288 mmole) of $(CH_3)_2PP(CF_3)_2$ and 0.4 ml. of water were left together at 25° for 5 hr., producing 0.228 mmole (79% yield) of $(CF_3)_2PH$. The yield of HCF_3 was 0.039 mmole, bringing the CF_3-account to 93%. The isolation of the $(CH_3)_2PH$ from the excess water was attempted by exposure to anhydrous calcium sulfate, which absorbed so much of this phosphine that only 0.027 mmole of it could be demonstrated. This amount, representing 18% of the $(CH_3)_2PH$ expected from the sequence $(CH_3)_2PP(CF_3)_2 + H_2O \rightarrow (CF_3)_2PH + (CH_3)_2POH$; $2\,(CH_3)_2POH \rightarrow (CH_3)_2PH + (CH_3)_2POOH$, is in accord with earlier experience with the hydrolysis of $(CH_3)_2NP(CH_3)_2$.[10]

The Reaction with Methyl Iodide.—Many types of aliphatic phosphine derivatives including $(CH_3)_2NP(CH_3)_2$[10] and $P_2(CH_3)_4$,[3] rapidly form 1:1 adducts with methyl iodide. A similar adduct formation doubtless represents the first step of the reaction between $(CH_3)_2PP(CF_3)_2$ and CH_3I. In this case, however, it is possible to argue the following sequence of further reactions.

$$(CH_3)_2PP(CF_3)_2 + CH_3I \longrightarrow (CH_3)_3\overset{+}{P}P(CF_3)_2\ I^- \quad (1)$$

$$(CH_3)_3\overset{+}{P}P(CF_3)_2\ I^- \rightleftarrows (CH_3)_3P + (CF_3)_2PI \quad (2)$$

$$(CH_3)_2PP(CF_3)_2 + (CH_3)_3P \longrightarrow (CH_3)_3\overset{+}{P}P(CH_3)_2P(CF_3)_2^- \quad (3)$$

$$(CF_3)_2PI + P(CF_3)_2^- \longrightarrow (CF_3)_2PP(CF_3)_2 + I^- \quad (4)$$

$$(CH_3)_3\overset{+}{P}P(CF_3)_2 + I^- \longrightarrow (CH_3)_3P^+P(CH_3)_2\ I^- \quad (5)$$

Of these, (1) is based upon the assumption that the more basic P atom will receive the CH_3^+ group. Then (2) is an equilibrium, the forward progress of which is favored by the removal of $(CH_3)_3P$ according to (3). This step is a reasonable action by the strong base $(CH_3)_3P$ to displace the weakly basic anion $P(CF_3)_2^-$, which is yet strong enough to displace the still weaker base I^- according to (4). Finally, (5) represents the formation of an adduct which is known to be stable.[3] These equations do not necessarily represent the exact mechanism of the whole process; but they do provide a basis for qualitative consideration of the driving forces leading to the observed results. The occurrence of some other processes is indicated by the minor byproducts; for example the formation of some $(CF_3)_3P$ shows that CF_3 groups could move from one phosphorus atom to another.

The onset of this reaction proved to be far slower than the formation of $(CH_3)_2NP(CH_3)_2 \cdot CH_3I$ or $P_2(CH_3)_4 \cdot CH_3I$; thus process (3) could occur long before the supply of $(CH_3)_2PP(CF_3)_2$ would be exhausted by (1) even with methyl iodide present in excess. The stoichiometry of the volatile components of two experiments is summarized by Table III, with amounts in mmoles.

TABLE III

THE $(CH_3)_2PP(CF_3)_2$–CH_3I REACTION

Reactants			Volatile products		Recov.
$(CH_3)_2$-$PP(CF_3)_2$	CH_3I	Reaction ratio	$P_2(CF_3)_4$	$P(CF_3)_3$	$(CF_3)_2P$ groups
1.361	1.736				
0.000	−0.68				
1.361	1.056	1.19	0.478	0.10	70%
1.268	1.627				
−0.210	−0.790				
1.058	0.837	1.26	0.307	0.11	58%

The first reaction mixture was held at 50° for 45 hr., after shorter times had proved inadequate for total consumption of the diphosphine. The presence of $(CF_3)_3P$ in the residual CH_3I was suggested by the infrared spectrum; hence this fraction was analyzed by basic hydrolysis to give HCF_3 and

---

[7] W. Mahler, unpublished observations in these Laboratories. For the hydrolysis at 100° see F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 3896 (1954).

[8] J. E. Griffiths and A. B. Burg, *Proc. Chem. Soc.*, 12 (1961).

[9] G. S. Harris, *J. Chem. Soc.*, 512 (1958).

[10] A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

titrable iodide. The $P_2(CF_3)_4$ (also not highly purified) was determined by reaction with chlorine to form $(CF_3)_2PCl_3$, which was reduced by mercury to the relatively well-known $(CF_3)_2PCl$ (195.3 mg.; mol. wt. 203.9 *vs.* calcd. 204.5; 288 mm. at 0°, as known). The white solid product was almost completely sublimable *in vacuo* at 200°; more generally, its properties corresponded to those of $P_2(CH_3)_4 \cdot CH_3I$.[3]

The second experiment was allowed to run for 10 days at 25°, consuming only 83% of the original diphosphine; the unused portion was determined by difference after it had been removed from the $P_2(CF_3)_4$ fraction by a half-hr. hydrolysis at 25°. This hydrolysis produced 0.193 mmole of $(CF_3)_2PH$, or 92% of that expected from the calcd. remainder of $(CH_3)_2PP(CF_3)_2$. After the hydrolysis, the purified $P_2(CF_3)_4$ was measured and weighed: mol. wt. 337.7 (calcd., 338.0); 22 mm. at 0°, as known. The excess CH_3I was converted to $(CH_3)_4N^+I^-$ and determined by titration of the iodide; then the remainder of the CH_3I fraction was nearly pure $(CF_3)_3P$ (mol. wt., 227; calcd., 238) and was determined as such.

The Trimethylamine Adduct.—It has been observed quite generally that PX_3 compounds having very electronegative X groups can form adducts with strong tertiary bases. Examples include the easily demonstrable $(CF_3)_2POP(CF_3)_2 \cdot (CH_3)_3N$ and the somewhat less stable $(CH_3)_3N \cdot PF_3$,[11] as well as the PCl_3 adducts of $(CH_3)_3N$ and $(CH_3)_3As$.[12] Also related to the subject are the monomer complexes $(CH_3)_3PPCF_3$ and $(CH_3)_3NPCF_3$ (derived from the PCF_3 tetramer or pentamer) and the probable adduct of $P_2(CF_3)_4$ with $(CH_3)_3P$.[13]

In the case of $(CH_3)_2PP(CF_3)_2$ one could argue for some internal P_{3p}–P_{3d} π bonding, working against the attachment of an external electron-donor. However, this effect cannot be very important, for we find that this diphosphine actually does form a 1:1 adduct with trimethylamine. The reaction is far slower than the formation of other base-adducts of CF_3-phosphines, and it is this slowness of adduct formation that made it feasible to use trimethylamine to remove the HCl during the synthesis of the diphosphine.

A 3.717 mmole sample of $(CH_3)_3N$ was condensed upon 317.0 mg. (1.378 mmoles) of $(CH_3)_2PP(CF_3)_2$. The mixture was warmed to 25° and allowed to stand for 42 hr., forming a yellow solution. Vacuum distillation from the reaction tube at 0° led to the recovery of 3.006 mmoles of the amine and 0.660 mmole of unconsumed diphosphine. Thus the remaining yellow oil had the empirical formula $(CH_3)_2PP(CF_3)_2 \cdot 0.99(CH_3)_3N$. This product was treated with HCl in excess at room temperature, forming $(CF_3)_2PH$ in a 67% yield (0.480 mmole). The less than quantitative yield suggests that the oil may have included a reaction product more complicated than the 1:1 amine adduct, but it is also possible that the action of HCl was more complex than removal of the amine and cleavage of the diphosphine.

The Borine Adduct.—It is known that $P_2(CF_3)_4$ fails to react in any way with diborane,[7] whereas $P_2(CH_3)_4$ easily forms the double adduct $P_2(CH_3)_4 \cdot 2BH_3$, convertible to the mono-BH_3 adduct $P_2(CH_3)_4 \cdot BH_3$.[3] In accord with expectations, $(CH_3)_2PP(CF_3)_2$ reacts with diborane to form a mono-BH_3 adduct. Like the earlier $P_2(CH_3)_4 \cdot BH_3$, the new $(CH_3)_2PP(CF_3)_2 \cdot BH_3$ undergoes thermal cleavage to form the appropriate monophosphine—in this case $(CF_3)_2PH$—and $[(CH_3)_2PBH_2]_3$. However, our exploratory experiment indicated that this cleavage is appreciably more difficult to complete than in the earlier case, probably because resinous material is formed more extensively and serves to isolate the individual molecules of the adduct. It is also interesting that a moderate yield of the unexpected phosphine $(CH_3)_2PH$ is produced.

The adduct was formed from 281.5 mg. (1.224 mmoles) of $(CH_3)_2PP(CF_3)_2$ and 1.254 mmoles of B_2H_6, during 17 hr. at −78 to +22°. The recovery of 0.652 mmole of B_2H_6 showed the empirical formula of the non-volatile adduct to be $(CH_3)_2PP(CF_3)_2 \cdot 0.98BH_3$. Apparently it was formed without side-reactions, for it melted in the fairly sharp range −30.2 to −29.6°.

During 22 hr. at 90° this adduct liberated 0.566 mmole of $(CF_3)_2PH$ as the only volatile product. The glassy residue gave no further volatile material during 15 hr. at 130°, but during 19 hr. at 185° it formed 0.16 mmole of $(CH_3)_2PH$ and 0.15 mmole of SiF_4—the latter indicating some slight destruction of CF_3 groups, with action by the products upon the glass container. The yield of the sublimate $[(CH_3)_2PBH_2]_3$ now was 30.3 mg., representing 0.41 mmole of $(CH_3)_2PBH_2$ units. Thus the empirical formula of the final residue was $[(CH_3)_2PP(CF_3)_2B_{1.21}H_{3.16}]_x$. This would suggest a considerable proportion of unchanged adduct, but the excess boron, taken with a H:B ratio below 3, would indicate also some of the same kind of phosphino-polyborane resin which can be obtained from $P_2(CH_3)_4$ with diborane or the higher polyboranes.[3,14]

---

[11] J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960).

[12] R. R. Holmes, *ibid.*, **82**, 5285 (1960).

[13] A. B. Burg and W. Mahler, *ibid.*, **83**, 2388 (1961).

[14] A. B. Burg, *Angew. Chem.*, **72**, 191 (1960).