Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90007

The Reaction of Bis(trifluoromethyl)phosphine with Trimethylamine: New Bis(phosphino)methanes, Including an Unusual Triphosphine and a Related Tetraphosphine

ANTON B. BURG

Received March 27, 1981

Trimethylamine dehydrofluorinates $(CF_3)_2PH$, forming $(CH_3)_3NH_2F_2$ and presumably $CF_3P{=}CF_2$, initiating a series of further reactions yielding $P_2(CF_3)_4$, the recently described diphosphines $R(CF_3)P{-}P(CF_3)_2$ (in which R = CHF_2, CH_2F, or CH_3), the unusual new triphosphine $(CF_3)_2PCH_2P(CF_3)P(CF_3)_2$, and less volatile products. With $(CH_3)_3SiCl$ as an added reactant, leading to $(CH_3)_3NHCl$ and $(CH_3)_3SiF$, the same volatile polyphosphines are formed in better yields, and $(CH_3)_3SiP(CF_3)_2$ is observable—a probable reaction intermediate. Cleavage of the diphosphine fraction by HCl gives mostly $(CF_3)_2PH$ and $R(CF_3)PCl$ but also $(CF_3)_2PCl$ and $R(CF_3)PH$ in yields increasing in the order R = CH_3, CH_2F, CHF_2. The usually HCl-inert $P_2(CF_3)_4$ also is cleaved. The triphosphine is HCl cleaved to $(CF_3)_2PH$ and $(CF_3)_2PCH_2P(CF_3)Cl$; from this, the corresponding F and $N(CH_3)_2$ derivatives are made. The Cl derivative evidently forms P-CH_2 bond-rotational isomers at low temperatures, with NMR coalescence beginning near −10 °C. The triphosphine disproportionates to $P_2(CF_3)_4$ and $[(CF_3)_2PCH_2PCF_3]_2$, equilibrating at 44% forward reaction. Both the triphosphine and the tetraphosphine have interesting NMR spectra, challenging interpretation.

It has long been known that an amine with a CF_3-phosphine (and protons from either) can form messy nonvolatiles, but their possible volatile products have been virtually unknown. It now is found that the white solid complex $(CH_3)_3N{\cdot}H{-}P(CF_3)_2$ is stable at −78 °C, dissociates slightly at −65 °C, and melts over a range near −40 °C; meanwhile, the amine removes HF from $(CF_3)_2PH$, with results explainable by eq 1-9.

$$(CF_3)_2PH \rightarrow HF + CF_3P{=}CF_2 \quad (1)$$

$$(CF_3)_2PH + CF_3P{=}CF_2 \rightarrow CHF_2(CF_3)P{-}P(CF_3)_2 \quad (2)$$

$$CHF_2(CF_3)P{-}P(CF_3)_2 + (CF_3)_2PH \rightarrow P_2(CF_3)_4 + CHF_2(CF_3)PH \quad (3)$$

$$CHF_2(CF_3)PH \rightarrow HF + CF_3P{=}CHF \quad (4)$$

$$CF_3P{=}CHF + (CF_3)_2PH \rightarrow CH_2F(CF_3)P{-}P(CF_3)_2 \quad (5)$$

$$CH_2F(CF_3)P{-}P(CF_3)_2 + (CF_3)_2PH \rightarrow P_2(CF_3)_4 + CH_2F(CF_3)PH \quad (6)$$

$$CH_2F(CF_3)PH \rightarrow HF + CF_3P{=}CH_2 \quad (7)$$

$$CF_3P{=}CH_2 + (CF_3)_2PH \rightarrow CH_3(CF_3)P{-}P(CF_3)_2 \quad (8)$$

$$CF_3P{=}CH_2 + P_2(CF_3)_4 \rightarrow (CF_3)_2PCH_2(CF_3)P{-}P(CF_3)_2 \quad (9)$$

Here it is to be understood that the HF is removed by either $(CH_3)_3N$ or the F^- ion, for the final salt is $(CH_3)_3NH_2F_2$. The observable volatiles are $P_2(CF_3)_4$ and the products of reactions 2, 5, 8, and 9. Less volatile products probably are longer-chain polyphosphines.

Reaction 1 gains credibility from the recent detection of $CF_3P{=}CF_2$ as an unstable product of the flow contact of $(CF_3)_2PH$ with dry KOH.[1] Much earlier, it was a presumed intermediate in the NH_3-$(CF_3)_2PH$ reaction[2] and in the conversion of $(CF_3)_2PH$ by dimethylzinc to the ring dimer $(CF_3PCF_2)_2$.[3] Then reactions 4 and 7 also seem reasonable in view of the well-known principle that C-F bonds become more vulnerable when there are fewer of them on the same carbon atom.

Reactions 2, 5, and 8 imply that the P=C bond always receives $(CF_3)_2P{-}H$ with H going to C and P to P. The opposite mode of addition would lead to results not observed.

Reaction 9 would suggest similar additions of $P_2(CF_3)_4$ to $CF_3P{=}CHF$ or $CF_3P{=}CF_2$, leading to triphosphines having CHF or CF_2 connections. However, the connecting CHF and CF_2 units would have been seen in the upfield regions of the ^{19}F NMR spectra but never were detectable. It appears that the expected triphosphines either were destroyed under the reaction conditions or were not formed because reactions 2 and 5 are far faster. On the other hand, reaction 9 is faster than 8, which can be minimized by frequent removal of the products. Thus it may be that the main path to the methyldiphosphine is the reaction

$$(CF_3)_2PH + (CF_3)_2PCH_2(CF_3)P{-}P(CF_3)_2 \rightarrow P_2(CF_3)_4 + CH_3(CF_3)P{-}P(CF_3)_2 \quad (10)$$

which seems reasonable in view of the susceptibility of the PCH_2P chain to cleavage by proton sources. A direct test did not confirm this reaction, but it still could occur during the original main reaction, wherein catalysts and activated species are far more effective than ground-state molecules.

More generally, it should be emphasized that steps 1-9 are oversimplified. Surely we cannot assume that H and F are removed simultaneously in steps 1, 4, and 7. The detailed mechanisms may involve "hot molecules" or free radicals not here mentioned. Three-body processes are probable, for the overall reaction does not go well in the vapor phase, even at 25 °C.

A different procedure for the $(CF_3)_2PH$-$(CH_3)_3N$ reaction uses $(CH_3)_3SiCl$, whereby HF comes out as $(CH_3)_3SiF$ and $(CH_3)_3NHCl$. The same polyphosphines are formed, with higher yields of the new diphosphines and less of the longer-chain products. This method arose from attempts to make $(CH_3)_3SiP(CF_3)_2$ more directly than by the literature methods,[4,5] but equimolar $(CH_3)_3SiCl$, $(CF_3)_2PH$, and $(CH_3)_3N$ gave only slight yields of it, and then only when the mixture was kept at low temperatures. With excess $(CH_3)_3SiCl$, however, encouraging yields of $(CH_3)_3SiP(CF_3)_2$ can be obtained, at temperatures too low for significant production of the new polyphosphines.

It seems probable that this silylphosphine can act as an intermediate for making the new polyphosphines: in the

(1) H. Estiagh-Hosseini, H. W. Kroto, J. F. Nixon, and O. Ohashi, *J. Organomet. Chem.*, **181**, C1 (1979).
(2) H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *J. Chem. Soc.*, 6878 (1965).
(3) D.-K. Kang and A. B. Burg, *J. Chem. Soc., Chem. Commun.*, 763 (1972).
(4) J. Grobe, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.*, **23**, 1609 (1968).
(5) L. Maya and A. B. Burg, *Inorg. Chem.*, **14**, 698 (1975).

0020-1669/81/1320-3734$01.25/0

presence of $(CF_3)_2PH$ and $(CH_3)_3N$ it could dissociate to $(CH_3)_3SiF$ and $CF_3P{=}CF_2$, for further reaction according to equations 2 and 3; then further intermediates could be $(CH_3)_3SiP(CF_3)CHF_2$ etc. In fact, $(CH_3)_3SiP(CF_3)_2$ with $(CF_3)_2PH$ alone at −78 °C does form the new polyphosphines, in quite significant yields, but at 25 °C the products are only $(CH_3)_3SiF$, $P_2(CF_3)_4$, and nonvolatiles. Accordingly, it is suggested that the best yields of volatile polyphosphines come only when the intermediate silylphosphines are consumed as fast as they are formed at low temperatures. At minimal steady-state concentrations, they might be less prone to reactions leading to nonvolatiles.

The $R(CF_3)P{-}P(CF_3)_2$ diphosphines could not be isolated from the main-product mixture, but they have been made by more direct methods;[6] then their ^{19}F NMR spectra made it possible to recognize them without separation. Confirmation, with rough estimates of the individual yields, came from the HCl cleavage of the P–P bond; just as for the earlier $(CH_3)_2P{-}P(CF_3)_2$,[7] the reaction

$$R(CF_3)P{-}P(CF_3)_2 + HCl \rightarrow (CF_3)_2PH + R(CF_3)PCl \quad (11)$$

is virtually quantitative for R = CH_3 or $(CF_3)_2PCH_2$, but when R is more electronegative, some $R(CF_3)PH$ and $(CF_3)_2PCl$ will form: for R = CHF_2, 35%, and for R = CH_2F, about 10%, as shown by NMR analyses based upon the ^{19}F spectra of the monophosphine products.[8] However, these results could be complicated by the presence of hybrid diphosphines not yet recognized, namely $CH_3(CF_3)P{-}P(CF_3)CHF_2$, $CH_3(CF_3)P{-}P(CF_3)CH_2F$, and $CH_2F(CF_3)P{-}P(CF_3)CHF_2$. A special effect concerns $P_2(CF_3)_4$: when pure, it resists HCl at 300 °C,[7] but in the present diphosphine mixture, HCl cleaves it to $(CF_3)_2PH$ and $(CF_3)_2PCl$ at 65 °C; its P–P bond evidently exchanges with the others.

This kind of P–P bond exchange, namely

$$2R(CF_3)P{-}P(CF_3)_2 \rightleftarrows P_2(CF_3)_4 + (RCF_3P)_2 \quad (12)$$

was described in an earlier paper,[6] but it was not easily observable by NMR spectroscopy of the present main-product mixture. However, the triphosphine was easily isolated, and then its P–P bond exchange became obvious, forming the far less volatile $[(CF_3)_2PCH_2PCF_3]_2$, and $P_2(CF_3)_4$. Then after recognition of the same reaction for the $R(CF_3)P{-}P(CF_3)_2$ diphosphines,[6] parts of the characteristic ^{19}F NMR spectra of all three $(RCF_3P)_2$ compounds could be recognized in the crude diphosphine mixtures. Thus the abstract of the paper on this subject at a recent international meeting[9] requires correction: when that abstract was written, only $CH_2F(CF_3)P{-}P(CF_3)_2$ and the triphosphine had been observed to undergo reaction 12.

The main HCl-cleavage product of the triphosphine is $(CF_3)_2PCH_2P(CF_3)Cl$, from which many other bis(phosphino)methanes might be made by replacing Cl—in the present work, only by F or $N(CH_3)_2$. Of the four PCH_2P compounds here reported, only the Cl derivative shows the temperature-sensitive NMR spectra that would indicate interconversion of conformational isomers at rates measurable on the NMR time scale; for the others, such isomerism is less obvious.

Such bis(phosphino)methanes, applied to metal carbonyls, might be expected to make new bicyclooctane structures.[10] Also, the P–P bond in either the triphosphine or the tetraphosphine might well add into C=C or C≡C bonds to make PC—CP, PC=CP, or even $P_2C{-}CP_2$ connections, in interesting new polyfunctional ligands. In sum, the present paper and its immediate predecessors[6,8] can serve only as a brief introduction to a potentially large chemistry of delicate contrasts among analogous compounds.

Experimental Methods

All volatile compounds were managed by the classical Stock high-vacuum methods, modified or improved to meet special needs or to employ more modern equipment. Small mixtures were resolved by repeated high-vacuum fractional condensations in a series of U-tubes connected by mercury float valves designed to serve also as accurate short-range manometers. For larger samples it was better to use high-vacuum reflux columns. An effective microcolumn was constructed from a thin-wall NMR tube (5 mm wide), for samples as small as 0.2 mmol. For the removal of $P_2(CF_3)_4$ or anything more volatile, the reflux was maintained by finely powdered dry ice (without any contact liquid); then the poor thermal contact and the low thermal capacity of the wall aided the establishment of the thermal gradient required for good separation. A high reflux ratio could be maintained by careful adjustment of a stopcock leading to the vacuum line. With such a column, an intermediate mixed fraction might be as small as 0.02 mmol, separable further by fractional condensation.

Chemical methods also were used. For example, $(CF_3)_2PH$ could be freed from the usual impurity $(CF_3)_3P$ by forming the complex $(CH_3)_3N{\cdot}HP(CF_3)_2$ at −78 °C and recovering it by action of HCl; also phosphines such as $CHF_2(CF_3)PH$ could be distilled away from the complex. Another example was the isolation of four monophosphines from the mixture formed by the action of HI and Hg on the crude diphosphine mixture.[6,11] After removal of $CH_2F(CF_3)PH$ and $(CF_3)_2PH$ (the least and most volatile products) by distillation methods, $CH_3(CF_3)PH$ was removed from the almost equally volatile $CHF_2(CF_3)PH$ by formation of the considerably less volatile complex $CH_3(CF_3)PH{\cdot}BH_3$.[12]

Equilibrium vapor pressures ("volatility") could be measured either by a manometer attached to a U-tube in the fractional-condensation line (with volume calibration) or by the use of an immersible bulb–manometer system.[13]

Detachable weighing bulbs and reaction tubes (with standard-taper glass joints) usually were closed off by O-ring valves, always with the plunger directed toward the interior. For the main phosphine–amine reaction, the container usually was a 20-mL bulb with a long, narrow neck leading through the O-ring valve to the vacuum line; thus the vapor volume was kept small.

When heat was required for reaction, the container was a sealed-off Pyrex tube or bulb, to be opened by a modified ground joint like that described by Stock,[14] except that the side arm is much closer to the bearing, for better leverage and less danger of breakage in the wrong place.

The main tool for identifying the reaction products and estimating impurities was the Varian XL-100-FT instrument, used for neat samples as small as 0.02 mmol, in vertical capillary tubes narrow enough for sample depths usually not less than 20 mm. The chemical shifts (δ) were measured in ppm upfield from Cl_3CF or H_3PO_4 but downfield from Me_4Si for protons. In the present paper, coupling multiplicity is indicated by a lower left subscript on J; thus $_3J_{FCH}$ means F observed as a triplet. Since the units ppm and Hz (s^{-1}) represent the standard language of NMR spectra, these symbols usually will be omitted.

The Main Phosphine–Amine Reaction

The Binary Process. Reactions 1–9 begin even at −78 °C if the ratio of $(CF_3)_2PH$ to $(CH_3)_3N$ is near 3:1, offering a liquid phase for the solid 1:1 complex. More practical rates develop when this complex begins to melt (near −40 °C), but temperatures in the range −20 to 0 °C give good results more rapidly. The yields of nonvolatiles and $CH_3(CF_3)P{-}P(CF_3)_2$

(6) A. B. Burg, *Inorg. Chem.*, companion paper in this issue.
(7) L. R. Grant, Jr., and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 1834 (1962).
(8) A. B. Burg, *Inorg. Chem.*, **20**, 2739 (1981).
(9) A. B. Burg, Abstracts, 2nd Chemical Congress of the North American Continent, San Francisco, CA, Aug 1980, No. FLUO 12.
(10) A. B. Burg and R. A. Sinclair, *J. Am. Chem. Soc.*, **88**, 5354 (1966); *Inorg. Chem.*, 7, 2160 (1968).
(11) R. G. Cavell and R. C. Dobbie, *J. Chem. Soc. A*, 1380 (1967).
(12) A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Am. Chem. Soc.*, **88**, 34 (1966).
(13) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 785 (1937); newer models of this device are more compact.
(14) A. Stock, *Chem. Ber.*, **51**, 985 (1918).

Table I. The Phosphine–Amine Reaction[a]

	expt no.				
	1	2	3	4	5
$(CF_3)_2PH$ in	8.30	4.63	8.766	7.517	4.836
out	0	1.19	0.236	0.129	0.032
used	8.30	3.44	8.53	7.388	4.804
$(CH_3)_3N$ in	9.73	2.05	4.510	2.257	1.856
out	7.37	0.78	1.653	0.114	0.451
used	2.36	1.27	2.857	2.143	1.405
$P_2(CF_3)_4$	0.79	0.41	?	1.034	0.917
	(19%)	(24%)		(28%)	(38%)
$RP_2(CF_3)_3$	0.19	0.70	?	0.68	0.37
	(5%)	(41%)		(18%)	(15%)
triphosphine	0.7	0.154	0.384	0.07?	0.207
	(25%)	(13%)	(13%)	(3%)	(13%)
less volatile	0.11	0.006	?	?	?
	(4%)	(0.05%)			

[a] All quantities in the tables are in mmol. The percent yields are based upon phosphorus consumed and found. In experiment 3 the diphosphines were not separated; the total was 2.51 mmol (59%). Missing phosphorus is ascribed to nonvolatiles.

Table II. The Phosphine–Amine–Trichlorosilane Process

	expt. no.			
	1	2	3	4
$(CF_3)_2PH$ in	9.436	8.21	7.14	12.55
out	0	0	0.56	0
used	9.436	8.21	6.58	12.55
$(CH_3)_3N$ in	5.89	6.20	4.30	8.29
out	0.16	1.60	0	0.33
used	5.73	4.60	4.30	7.96
$(CH_3)_3SiCl$ in	5.93	4.93	4.31	8.30
out	0.23	0.33	0.19	0.55
used	5.70	4.60	4.12	7.75
$(CH_3)_3SiF$	5.66	4.60	4.11	7.7
$(CH_3)_3NHCl$		4.75[a]		
$P_2(CF_3)_4$	2.18	1.88	1.11	2.40
	(46%)	(46%)	(34%)	(38%)
$RP_2(CF_3)_3$	0.87[b]	0.70[c]	1.25[d]	1.88[e]
	(18%)	(17%)	(38%)	(30%)
$(CF_3)_2PCH_2P_2(CF_3)_3$	0.93	0.87	0.61	1.26
	(30%)	(28%)	(28%)	(30%)
less volatile	0.019			
	(0.6%)			

[a] Including a trace of air-reactive nonvolatiles. [b] Roughly estimated as 50% $CH_3(CF_3)P–P(CF_3)_2$. [c] CH_2F and CHF_2 diphosphines in ratio roughly 3:1. [d] R = CHF_2, 0.70; R = CH_2F, 0.37; R = CH_3, 0.18 (by comparison of the ^1H NMR spectral intensities). [e] R = CHF_2, 0.99; R = CH_2F, 0.67; R = CH_3, 0.22 (estimated from the monophosphines obtained by HI–Hg cleavage).

are minimized and the other new diphosphines maximized, if the process is conducted in a series of short steps, each time with removal of the products by fractional condensation at –65 °C.

The reaction balances for five relatively well-monitored experiments are shown in Table I. Experiment 1 ran once for 2 h at –20 °C, giving the highest yield of the triphosphine and less volatile products. Experiment 2 ran for three 5-min periods at –20 °C, giving higher yields of the new diphosphines. Experiment 3 had five steps, again favoring the diphosphines. The six brief steps of experiment 4 were in the range –40 to –20 °C. Experiment 5 went in two 15-min steps at –20 °C. Each experiment ended with addition of HCl for determination of the excess amine; then the remaining $(CF_3)_2PH$ and the excess HCl were easily separated for measurement. In the cleanest experiments the stoichiometry clearly shows that $(CH_3)_3NH_2F_2$ is the main nonvolatile product, confirmed by weighing the aqueous extract.

Even the most volatile of the diphosphines, $P_2(CF_3)_4$, could not be completely recovered in better than 90% purity (19 mm at 0 °C vs. 22 mm if pure), and accurate estimation of the other diphosphines (average 10 mm at 0 °C) was even more difficult. From many multistep experiments, however, it was clear that frequent removal of the products favors $CHF_2(CF_3)P–P(CF_3)_2$, while $CH_2F(CF_3)P–P(CF_3)_2$ may suffer from rapid conversion to the triphosphine, and $CH_3(CF_3)P–P(CF_3)_2$ (very clearly visible in the ^{19}F NMR spectrum) is minimized.

In no experiment was it possible to find the least trace of $(CF_3PCF_2)_2$, which came in good yields when dimethylzinc was used for dehydrofluorination of $(CF_3)_2PH$,[3] nor was there ever any HCF_3, which reactions analogous to basic hydrolysis might have been expected to produce.[15]

The fraction listed as "less volatile" in Table I is about one-fourth as volatile as the triphosphine but decidedly more volatile than the tetraphosphine derived from P–P bond exchange by the triphosphine. It might be like the triphosphine except for some replacement of CF_3 by CH_2F or CHF_2, causing lower volatility. Its CF_3 NMR spectrum showed only broad, unresolved bands. Cleavage by methanol or HCl might yield simpler products, leading to elucidation, but larger samples would be needed.

The Process with Trimethylchlorosilane. The presence of $(CH_3)_3SiCl$ during the $(CF_3)_2PH$–$(CH_3)_3N$ reaction may actually simplify the process, for the fluoride ion is removed as $(CH_3)_3SiF$ and so cannot act as a secondary agent for capturing HF. The action can proceed at lower temperatures, leading to higher yields of volatile products, especially the new diphosphines. Table II gives the millimolar reaction balances for four relatively well-monitored experiments on this process. After preliminary experiments had indicated the stoichiometry, the proportions were planned so as to avoid a great excess of any reactant.

Experiments 1 and 2 began with 18-h storage of the three-component mixture at –78 °C, with about 15% progress of reaction. After many hours at –60 to –70 °C, with frequent removal of the products, each process was completed by more drastic warming: 16 h at 0 °C for experiment 1 and 5 min at 40 °C for experiment 2. Experiment 3 began with a 3-h run at –66 to –52 °C and then 2 h at –45 °C and 1 h at –31 °C. However, most of the action occurred during brief runs at 0 °C (1, 1, 5, 10, 15, and 20 min), ending with 90 min at 25 °C. Experiment 4 was done similarly, except for longer and fewer steps. Comparison of all results again leaves no doubt that frequent removal of the products increases the yield of the diphosphine fraction and minimizes products less volatile than the triphosphine.

The most accurate aspect of Table II is the equimolar consumption of $(CH_3)_3SiCl$ and $(CH_3)_3N$, with an equimolar yield of $(CH_3)_3SiF$; the process consumes twice as much trimethylamine as the binary reaction. The consumption of $(CF_3)_2PH$ is somewhat below expectations based upon eq 1–9. The estimates of the yields of the individual $R(CF_3)P–P(CF_3)_2$ compounds are not highly reliable because they are based upon cleavage reactions leading to monophosphines, which are not easily isolated. The individual yields of $CHF_2(CF_3)P–P(CF_3)_2$ and $CH_2F(CF_3)P–P(CF_3)_2$ will not be controllable until many more experiments have shown the effects of all variables upon the results.

The Silylphosphine Aspect. The first indication of the direct formation of $(CH_3)_3SiP(CF_3)_2$ from $(CH_3)_3SiCl$, $(CF_3)_2PH$, and $(CH_3)_3N$ came in an experiment in which the equimolar mixture of these reactants failed to react much in the vapor phase at 0 °C but reacted far more extensively in the liquid phase at –78 °C. The ^{19}F NMR spectrum now included a small component having the parameters of $(CH_3)_3SiP(CF_3)_2$.[4]

(15) F. W. Bennett, R. N. Haszeldine, and H. J. Emeléus, *J. Chem. Soc.*, 3598 (1954).

Reactions at 25 °C gave none of it, but it always was formed when the temperature was low enough, with best yields when $(CH_3)_3SiCl$ was in large excess. From a 10:2:1 ratio of $(CH_3)_3SiCl$:$(CF_3)_2PH$:$(CH_3)_3N$ reacting in three steps at −40 °C, with repeated product removal, $(CH_3)_3SiP(CF_3)_2$ was obtained in a yield representing 15% of the $(CF_3)_2PH$. The development of an optimum procedure might make this the preferred way to make this silylphosphine.

The failure of higher temperature procedures suggested that the silylphosphine was consumed to make the observed polyphosphines; possibly the reaction

$$(CH_3)_3SiP(CF_3)_2 \rightarrow (CH_3)_3SiF + CF_3P{=}CF_2$$

would be followed by reactions 2 and 3, etc. The first test of this idea using a 3:1 $(CF_3)_2PH$:$(CH_3)_3SiP(CF_3)_2$ ratio at 25 °C did indeed produce $(CH_3)_3SiF$ but no volatile polyphosphines except $P_2(CF_3)_4$; much nonvolatile white solid was formed. However, after 23 h at −78 to −65 °C, the equimolar mixture of the same reactants had given a 100% yield of $(CH_3)_3SiF$, and the ^{19}F NMR analysis of the other volatiles showed 27% $(CF_3)_2PH$, 44% $P_2(CF_3)_4$, and 29% $R(CF_3)P$–$P(CF_3)_2$, including the triphosphine.

Pure $(CH_3)_3SiP(CF_3)_2$ seems stable at 25 °C, but the crude product slowly forms nonvolatiles. The decomposition is not like the BF_3-induced process,[5] for no $(CF_3PCF_2)_2$ is observed.

The Triphosphine and Its Consequences

The triphosphine $(CF_3)_2PCH_2P(CF_3)P(CF_3)_2$ could be surely identified only by postulating the presence of a P–P bond; then indeed a nearly quantitative cleavage by HCl to identifiable products made it possible to write a molecular structure consistent with the blurred and interlaced NMR spectra, molecular weights complicated by reaction 12, and an infrared spectrum having only confirmatory significance.

HCl Cleavage. The cleavage of the triphosphine in the manner of eq 11 may be complicated by minor impurities and the P–P bond exchange (eq 12). The best experiment employed a 0.451-mmol sample of the triphosphine with 0.494 mmol of HCl. The process was 30% complete after 23 h at 25 °C, 80% after 16 h at 40–50 °C, and 100% after 6 h at 60 °C. The main products were 0.404 mmol of $(CF_3)_2PH$ (infrared-pure) and 0.415 mmol of $(CF_3)_2PCH_2P(CF_3)Cl$; the HCl consumed was 0.420 mmol. These numbers all were at least 90% as predicted by eq 11. The yield of $P_2(CF_3)_4$ was 0.045 mmol, suggesting 10% occurrence of reaction 12; then the accompanying tetraphosphine would restore half of the lost yield of the chloro derivative. In sum, then, sure identification of the chloro derivative would identify the triphosphine.

The Chlorobis(phosphino)methane. The major cleavage product of the triphosphine was easily purified, with volatility 3.7 mm at 0 °C and 16.57 mm at 24.6 °C; for normal curvature and Trouton constant (21.2 eu), the equation $\log P = 6.3611 + 1.75 \log T - 0.0052T - 2359/T$ (bp 122 °C) is suggested. At higher temperatures in the immersible tensimeter, the weighed sample was vaporized, giving the molecular weight as 320.8 at 38 °C or 318.5 at 47 °C, as calculated for the formula $(CF_3)_2PCH_2P(CF_3)Cl$.

The infrared spectrum (Beckman IR-20A; frequencies in cm^{-1}, with relative intensities in parentheses) showed the CH_2 group as clean peaks at 2972 (0.5), 2918 (0.2), 1390 (1.1), and 1297 (1.2). The CF_3 groups appeared at 1202 (58), 1174 (97), 1167 (93), 1141 (77), 1113 (46), 1085 sh (7), 758 (1.5), 738 (2.2), and 548 (2.2), with P–CF_3 stretching at 433 (3.6) and possibly 460 (2.7). The P–Cl stretching was obvious at 518 (4). Less assignable were 1027 sh (0.5), 903 (0.7), 827 (1.8), 715 (2.3), 686 (1.4), and 352 (2.8).

NMR Spectra and Rotational Isomerism. The NMR spectra of $(CF_3)_2PCH_2P(CF_3)Cl$ are very complex, with temperature effects suggesting rotational isomerism. Simplest is the very clean ^{19}F spectrum of the lone CF_3 group at δ 68.3, with $_2J_{FCP}$ = 77.4 and $_2J_{FCPCP}$ = 10.4 at 30 °C, or 76.1 and 8.8 at −50 °C. An accurate wire model (with the expected bond distances and angles, including 100° at each P atom) shows that this CF_3 group could fit snugly into the CH_2 notch, with stabilization by $H^+\cdots F^-$ attraction. Other attitudes of the CF_3PCl group, or even free rotation about the C–P bond, would cause severe collisions with the $P(CF_3)_2$ group. Either of the geminal CF_3 groups could fit into the CH_2 notch, but one of the resulting isomers would have a grazing collision of the outside CF_3 with Cl, making it less stable. Much less stable would be the isomer with both CF_3 groups outside of the CH_2 notch; this would have no H···F attraction, and some destabilizing collision with Cl.

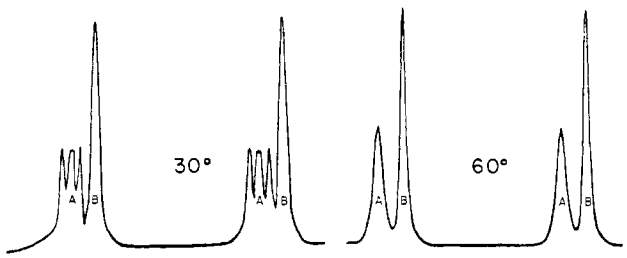

Figure 1. ^{19}F NMR spectra of the geminal CF_3 groups in $(CF_3)_2P$-$CH_2P(CF_3)Cl$. The A doublet has δ 56.35, with J_{FCP} = 76.6; the B doublet is at δ 56.45, with J_{FCP} = 77.2 s^{-1}. It is interesting that the two CF_3 groups show very different coalescence temperatures.

True to this analysis, the ^{19}F NMR spectrum at −50 °C shows two major doublets of doublets, at δ 56.524 ($_2J_{FCP}$ = 76.9 and $_2J_{FCPCP}$ = 6.0) and δ 56.320 ($_2J_{FCP}$ = 75.3 and $_2J_{FCPCP}$ = 15.4), and half as intense, at δ 56.374 ($_2J_{FCP}$ = 76.2 and $_2J_{FCPCP}$ = 12.8) and δ 56.241 ($_2J_{FCP}$ = 75.5 and $_2J_{FCPCP}$ = 15.0). Smaller peaks and shoulders are present but cannot be sorted out on account of superposition. At −30 °C, the same whole spectrum shows slightly smaller J values. At −10 °C partial coalescence gives an unintelligible spectrum. At 10 °C, the 30 °C pattern appears (Figure 1), and this blurs out at 60 °C. Some persistence of isomers at 30 °C is confirmed by the slightly different peak-to-peak widths of the A pseudotriplets: downfield, 6.6 s^{-1}; upfield, 7.7 s^{-1}. It means that slightly different $_2J_{FCP}$ values cause slightly different interlacing of FCPCP doublets.

The ^{31}P spectrum for the $(CF_3)_2P$ group at 30 °C is very well resolved, at δ 9.5, with $_2J_{PCP}$ = 118.7, $_7J_{PCF}$ = 77.2, and $_4J_{PCPCF}$ = 10.4, consistent with the ^{19}F spectrum. Further coupling is barely observable: $_3J_{PCH}$ = 0.5. The CF_3PCl group shows a partially superposed doublet of quartets of messy clusters, centered at δ −68.7, with $_2J_{PCP}$ confirmed as 118.4 and $_4J_{PCF}$ as 77.5. With fluorine decoupled, $_3J_{PCH}$ is seen as 11.1, remarkably different from the other P atom. The phosphorus AB pattern is recognizable with outer-to-inner intensity ratio calculated and observed as 0.93. Proton decoupling did not lead to satisfactory values of $_7J_{PCPCF}$; messy clusters persisted.

The ^1H spectrum again suggests isomers in unequal proportions, with interesting temperature variability. At −40 °C one sees an irregular pattern of five peaks, with average δ near 2.65. The relative frequencies (s^{-1}, with parenthetical judgements of intensity) are 0 (m), 1.18 (mw), 2.66 (mw), 12.36 (ms), and 13.21 (s). The low-frequency cluster collapses to two peaks at 30 °C, and at 70 °C one finds only a doublet at δ 2.47 with $_2J_{HCP}$ = 10.7, like $_3J_{PCH}$ from the ^{31}P spectrum of the CF_3PCl group. However, this doublet may be deceptive, for at 80 °C the lower frequency peak begins to show a spike on the low-frequency side, as though superposed peaks were beginning to separate.

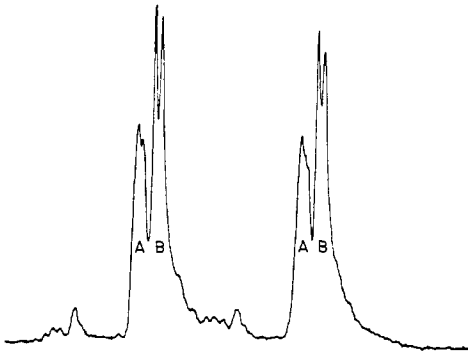

Figure 2. ^{19}F NMR spectra of the geminal CF_3 groups in $(CF_3)_2P$-$CH_2P(CF_3)F$. The somewhat similar spectrum of the Cl derivative is seen at the impurity level but does not interfere. However, an ineradicable trace of the triphosphine may be the cause of the observed discrepancy in the A spectrum.

The Fluorobis(phosphino)methane. The Cl derivative was converted to $(CF_3)_2PCH_2P(CF_3)F$ by contact with freshly sublimed SbF_3 at 25 °C. The yield never exceeded 50%; the rest apparently became nonvolatile. The fluorination could not be quite completed, and all attempts to remove the last 10% of the chloro derivative were unsuccessful; the mixture may have been azeotropic. The volatility of the mixture (11.3 mm at 0 °C and 39.4 mm at 21.7 °C) suggested $\log P = 6.385 + 1.75 \log T - 0.005T - 2248/T$ (bp 91 °C; Trouton constant 21.5 eu). After correction for the NMR-determined impurities, the molecular weight was 305 (calculated, 302).

The NMR spectra of $(CF_3)_2PCH_2P(CF_3)F$ lacked evidence for rotational isomers; the geminal CF_3 groups would not collide with the lone F atom. The ^1H spectrum was simplified by setting the decoupler for the lone F atom (with the correct assumption that all HCPCF couplings would be negligible); then a very clear AB pattern appeared for the geminal protons, with $J_{HH} = 15.0$. Corrected by the AB equations, $\delta_A = 2.471$ ($_2J_{HCP} = 4.84$ or 1.39) and $\delta_B = 2.111$ ($_2J_{HCP} = 10.3$; other J not seen). The intensity ratio of outer to inner clusters was 0.44, as calculated. Without the decoupler, $_2J_{HCPF} = 16.8$ for proton A and 21.8 for B.

The ^{19}F spectra at 30 and −60 °C showed no significant differences except in coupling constants. For the lone CF_3 group at 30 °C, $\delta = 72.8$, with $_2J_{FCP} = 82.0$, $_2J_{FCPCP} = 9.88$, and $_2J_{FCPF} = 2.70$. At −60 °C, these J values became 80.5, 7.74, and 3.25. The geminal CF_3 groups at 30 °C are shown in Figure 2. Here $\delta_A = 57.257$ ($_2J_{FCP} = 79.1$) and $\delta_B = 57.342$ ($_2J_{FCP} = 78.2$; second $_2J = 2.98$). At −60 °C, the pattern is almost the same, with the respective J values 77.0, 76.7, and 2.50. The second J for B could be to either the far P or the lone F.

The lone F atom (δ 209.7) varies more obviously with temperature. At 30 °C one sees a doublet of poorly resolved quartets with $_2J_{FP} = 963$ and $_4J = 16.4$, but at −60 °C these "quartets" have changed to look like triplets ($_2J_{FP} = 959$ and $_3J = 19.6$). In fact, each cluster is composed of several multiplets, with changing J values leading to different overall shapes. With the protons decoupled at 30 °C, it appears that $_2J_{FPCP} = 12.9$ and $_4J_{FPCF} = 2.90$, assigned by agreement with the lone-CF_3 spectrum.

The ^{31}P spectrum for the $(CF_3)_2P$ group shows δ 9.5 with $_2J_{PCP} = 108.9$, $_7J_{PCF} = 78.15$, $_2J_{PCPF} = 13.15$, $_4J_{PCPCF} = 9.86$, and $_2J_{PCH} = 1.25 \pm 0.15$; the second PCH coupling is too small to be seen, but might account for some loss of resolution. For the CF_3P group, $\delta = -155$ with $_2J_{PF} = 963$, $_2J_{PCP} = 108.6$, $_4J_{PCF} = 8.92$, and $_2J_{PCH} = 10.1$ or 4.92, as in the ^1H spectrum.

The (Dimethylamino)bis(phosphino)methane. Four experiments gave better than 90% yields of $(CF_3)_2PCH_2P(CF_3)N(CH_3)_2$ from the Cl derivative with the required $2(CH_3)_2NH$, a slight excess of which caused no trouble. Its volatility (1.2 mm at 0 °C and 6.1 mm at 25 °C) is described by $\log P = 6.32 + 1.75 \log T - 0.005T - 2500/T$ (bp 149 °C; Trouton constant 21.0 eu).

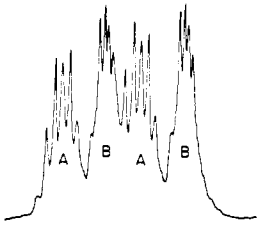

Figure 3. ^{19}F NMR spectra of the geminal CF_3 groups in $(CF_3)_2P$-$CH_2P(CF_3)N(CH_3)_2$ at −20 °C. The A pattern (δ 56.275) seems to show a doublet of doublets of triplets (to ^{14}N?) with $_2J_{FCP} = 72.2$ and $_2J_{FCPCP} = 12.0$, but for each cluster the downfield triplet has $_3J = 7.7$ vs. upfield 6.6, both unchanged at −60 or +60 °C. The B pattern (δ 56.703 with $_2J_{FCP} = 73.6$) becomes more symmetrical at 60 °C, but the finer couplings still are not clear. $\Delta\delta_{AB}$ ranges from 0.445 at −60 °C to 0.284 at 60 °C.

The ^1H NMR spectra here fail to show isomerism, but the geminal CF_3 groups hint at it, while ^{31}P remains enigmatic. The AB pattern for CH_2 is seen best at 60 °C, for a smaller $\Delta\delta_{AB}$ brings most of the A part out from under the very intense methyl-group doublet of quartets (δ 2.45; $_2J_{HCNP} = 9.25$, $_4J_{HCNPCF} = 0.83$); then by the usual calculation $\delta_A = 2.382$ ($_2J_{HCP} = 3.45$ or 0.9) and $\delta_B = 1.850$ ($_2J_{HCP} = 10.4$ or 1.12). I_o/I_i: found, 0.6; calcd, 0.58. The CH_3-group parameters lack temperature sensitivity.

The relatively simple lone-CF_3 spectrum is not much changed by heating: at 30 °C, $\delta = 65.2$ ($_2J_{FCP} = 71.1$, $_2J_{FCPCP} = 6.10$) and at 60 °C, $\delta = 65.1$ ($_2J_{FCP} = 71.9$, $_2J_{FCPCP} = 6.95$). The irregularity of the geminal CF_3 groups (Figure 3) would suggest superposed rotational isomers, but if so, the near uniformity over a 120 °C temperature range means noninterconversion.

The ^{31}P spectrum with fluorine decoupled emerges as a marginal AB pattern with $(CF_3)_2P$ at δ 4.8 and PCF_3 at δ −45.5. $I_o/I_i = 0.88$ (calculated, 0.87); $_2J_{PCP} = 134$. In the full spectrum, the two $P(CF_3)_2$ septets are interlaced, but $_7J_{PCF}$ (73.7) and $_4J_{PCPCF}$ (6.14) are clear enough and consistent with the ^{19}F spectrum. The PCH couplings are confusing: quartets appear in the second, fourth, and sixth clusters of each main septet and triplets in the third and fifth clusters, always with apparent $_4J = _3J = 1.34 \pm 0.05$; it is clear that this is the P atom that couples poorly to the CH_2 protons. For PCF_3, the doublet of quartets shows central interlacing, but $_4J_{PCF} = 72$, clearly enough. The proton-decoupled spectrum shows $_7J_{PCPCF} = 6$ as expected; some confusion here may be due to the ^{14}N quadrupole. The expected $_2J_{PCH}$ values (10.4 and 3.45) could not be sorted out from the full spectrum.

The Triphosphine Itself. The NMR spectra of these double phosphines confirm beyond doubt that the PCH_2P connection is present; all are bis(phosphino)methanes. The clean AB-type proton spectra of the CH_2 group in the F and $N(CH_3)_2$ compounds (and the possibility that such a pattern is buried in the more complicated ^1H spectrum of the Cl compound) makes it reasonable to interpret the poorly resolved ^1H spectrum of the triphosphine (looking like a 1:3:3:1 quartet) as another AB pattern, with $\delta_A = 2.567$, $\delta_B = 2.513$, $J_{HCH} = 3.25$, and $I_o/I_i = 0.32$. But the half-height width of each peak is near 3 s^{-1}, and the HCP couplings cannot be larger than that—in contrast to J_{HCP} as large as 10.3 in the F derivative. Thus the large difference between the PCF_3 and $P(CF_3)_2$ groups, in regard to HCF coupling, is not observable in this case.

The ^{19}F spectrum of the triphosphine (Figure 4) includes four unresolved downfield clusters much like those of the $R(CF_3)P$–$P(CF_3)_2$ compounds,[6] but unlike any aspect of the

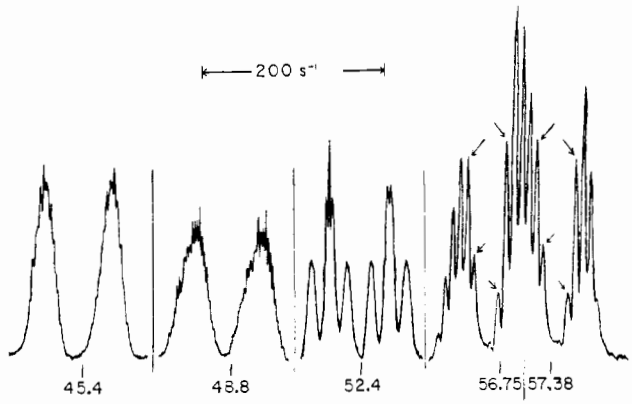

Figure 4. ^{19}F NMR spectrum of the triphosphine $(CF_3)_2PCH_2P(CF_3)P(CF_3)_2$. For the doublets at δ 45.4 and 48.8, $_2J_{FCP}$ = 71.4; at δ 52.4, $_2J_{FCP}$ = 65.2. The patterns centered at δ 56.75 and 57.38 are distinguished by slant arrows to show corresponding parts of each doublet. At δ 56.75, $_2J_{FCP}$ = 74.0 and at δ 57.38, $_2J_{FCP}$ = 75.6. The corresponding secondary splittings average as 7.8 and 8.1 s^{-1}.

PCH_2P bisphosphines; thus the assignment is to the $P–P(CF_3)_2$ part. The irregular spikes would be due to mixing of at least four coupling constants, including $_4J_{FCPCF}$ probably near 8. The asymmetry in the δ 48.8 clusters would suggest P–P bond rotational isomers, the rigidity of which would account for the virtual lack of variation in the range −40 to 70 °C. Proton decoupling also has little effect.

The doublet of pseudotriplets obviously belongs to the lone CF_3 group. These "triplets", for which "$_3J$" = 18.8, must represent a mixture of FCPP and FCPCP couplings, such that the lower-field center looks like a pseudoseptet ("J" = 3.4) and the higher-field center like a pseudosextet ("J" = 4.4). Here again, rotational isomers cannot be excluded.

Finally, the upfield $(CF_3)_2P–C$ group shows its geminal CF_3 groups so close together that their FCP doublets are crossover interlaced. The secondary splittings here would be assigned to $_4J_{FCPCF}$ and $_2J_{FCPCP}$, mixed differently for the two CF_3 groups; lesser couplings seem not to be significant. These geminal CF_3 groups are very like those shown in Figure 3, wherein $\Delta\delta_{AB}$ is just large enough to avoid central interlacing. At −40 °C, the triphosphine pattern is still much like Figure 4, except that the most upfield part now has $\Delta\delta_{AB}$ = 0.81 instead of 0.37, so that the inner clusters are almost perfectly superposed.

The ^{31}P spectrum of the triphosphine is hopelessly confused except when ^{19}F is decoupled, and even then its ABC pattern has not been closely simulated by the computer. Downfield are four major peaks having δ values (with relative intensities) −1.52 (6), 4.22 (10), 4.70 (9), and 8.22 (10). The upfield part includes a clean doublet of triplets centered at δ 25.37 ($_2J$ = 91; $_3J$ = 3.42), a relatively strong, broad, complex signal at δ 20.3, and a much weaker crooked triplet at δ 30.0.

A fresh, highly purified sample of the triphosphine showed volatility 0.7 mm at 0 °C or 3.7 mm at 25 °C, suggesting log P = 6.627 + 1.75 log T − 0.005T − 2546/T (bp 164 °C; Trouton constant 21.7 eu). When the sample was measured as a vapor and then weighed, the molecular weight result was 438, but when another sample was measured as a vapor after weighing, the result was 462 (calculated, 452). The errors are attributed to incipient disproportionation to $P_2(CF_3)_4$ and $[(CF_3)_2PCH_2PCF_3]_2$; the latter would not be completely transferred before or after weighing.

The infrared spectrum of the triphosphine vapor (given here in cm^{-1} with relative intensities in parentheses) corresponds to the expected components. The C–H stretchings at 3030–3150 (0.27) and 2920–2980 (0.35) are poorly recorded. Better are the CH_2 deformations at 1381 (1.4) and 1281 (1.6). The CF_3 aspects are normal: 1204 (60), 1189 (87), 1167 (133), 1141 (128), 1123 (99), 746 (4.3), 562 (1.0), and P–CF_3 stretching at 452 (3.8), 442 (3.7), and 428 (3.5). Less assignable peaks are at 855 (0.9), 786 (1.6), 710 (1.8), 599 (0.9), and 542 (0.9); some of these could represent P–C–P and P–P bonding.

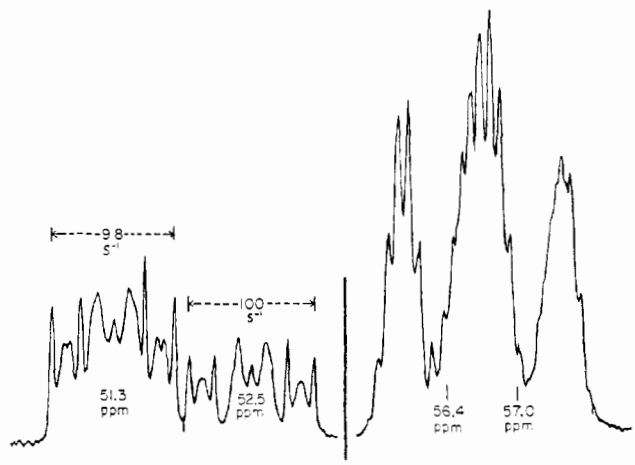

Figure 5. ^{19}F NMR spectrum of $[(CF_3)_2PCH_2PCF_3]_2$.

P–P Bond Exchange: The Tetraphosphine. Two well-purified samples of the triphosphine were stored at 25 °C, one for 6 weeks and the other for 7 months. The P–P bond exchange process was NMR detectable within 2 days. The resulting tetraphosphine and $P_2(CF_3)_4$ were isolated from the remaining triphosphine, and all three fractions were weighed. The two experiments were essentially in agreement: the equilibrium constant, of form $K = xy/z^2$, has the value 0.15, determined by the 44% forward reaction. This is comparable to the disproportionation of $CHF_2(CF_3)P–P(CF_3)_2$,[6] meaning that no component is appreciably more stable than the others.

The new tetraphosphine $[(CF_3)_2PCH_2PCF_3]_2$, purified by high-vacuum fractional condensation at 0 °C, was volatile to the extent of 0.04 mm at 0 °C, 0.24 mm at 23.1 °C, and 1.00 mm at 45.0 °C, determining the equation log P = 5.673 + 1.75 log T − 0.00377T − 2815/T (bp 227 °C; Trouton constant 21.5 eu).

The ^{19}F NMR spectrum of this tetraphosphine (Figure 5) includes the two second-order patterns expected for the lone CF_3 groups on chiral P atoms and (twice as intense) an upfield pattern for the end $P(CF_3)_2$ groups. The analogy to the upfield part of Figure 4 is obvious. The interpretation of the second-order patterns would seem to challenge the resources of modern theory, but it is interesting that one of the sharp peaks in each pattern is persistently higher than the others. The reason could be precisely coincident superpositions of peaks belonging to very similar spectra of rotational isomers.

The ^1H spectrum, a poorly resolved, narrow cluster, is interpretable as partially superposed triplets for the two diastereomers. The stronger is at δ 2.49 ($_3J$ = 5); the weaker is at δ 2.41 ($_3J$ = 4). No AB pattern is evident, and there is no second-order pattern, for lack of HCPPCH coupling.

The ^{31}P spectrum is intelligible only with fluorine decoupled. Then the two diastereomers show eight-peak patterns, interlaced but not too seriously superposed, with very small peaks toward the middle. Simulation by the 32-K computer shows for the stronger pattern δ = 2.63 and 10.46, with $_2J_{PP}$ = 200, $_2J_{PCP}$ = 137, and $_2J_{PCPP}$ = 11.5; for the weaker pattern, δ = 1.95 and 11.15 with J values 210, 137, and 12.0. The small internal peaks provide a sensitive measure of J_{PP}. For both patterns, the simulation is slightly improved by including J_{PCPPCP} = 2.0. All peaks are broad enough to include any reasonable J_{PCH}.

Acknowledgment. Dr. K. L. Servis has been very helpful in regard to the NMR aspect, with instruction and good advice

concerning computer simulation and complex spectra.

Registry No. $(CF_3)_2PH$, 460-96-8; $(CH_3)_3N$, 75-50-3; $P_2(CF_3)_4$, 2714-60-5; $CHF_2(CF_3)P\text{-}P(CF_3)_2$, 78673-09-3; $CH_2F(CF_3)P\text{-}P(CF_3)_2$, 78673-08-2; $CH_3(CF_3)P\text{-}P(CF_3)_2$, 78673-07-1; $(CF_3)_2PCH_2(CF_3)\text{-}P\text{-}P(CF_3)_2$, 78685-50-4; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3SiF$, 420-56-4; $(CH_3)_3NHCl$, 593-81-7; $CH_3(CF_3)PCl$, 4669-76-5; $CH_2F(CF_3)PCl$, 77846-29-8; $CHF_2(CF_3)PCl$, 4669-82-3; $CHF_2(CF_3)PH$, 77846-32-3; $CH_2F(CF_3)PH$, 77846-33-4; $(CF_3)_2PCl$, 650-52-2; $(CH_3)_3SiP(CF_3)_2$, 21658-00-4; $(CF_3)_2PCH_2P(CF_3)Cl$, 77846-30-1; $(CF_3)_2PCH_2P(CF_3)F$, 78673-14-0; $(CF_3)_2PCH_2P(CF_3)N(CH_3)_2$, 78673-15-1; $[(CF_3)_2PCH_2PCF_3]_2$, 78673-16-2.

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Synthesis and Multinuclear Magnetic Resonance Studies of New Difluorophosphine Derivatives of Tetraborane(8)[1]

J. D. ODOM* and A. J. ZOZULIN[2]

Received November 11, 1980

Several new difluorophosphine complexes of tetraborane(8) have been prepared and characterized. These new adducts include $B_4H_8{\cdot}PF_2OCH_3$, $B_4H_8{\cdot}PF_2SCH_3$, $B_4H_8{\cdot}PF_2CF_3$, and $B_4H_8{\cdot}PF_2(t\text{-}C_4H_9)$. These specific molecules were prepared to gain additional insight into questions pertaining to the importance of steric and electronic effects of the X substituent in $B_4H_8{\cdot}PF_2X$ molecules on the relative populations of geometrical isomers at ambient temperature and on rotational isomers at low temperature. Multinuclear (^{11}B, ^{13}C, ^{19}F, and ^{31}P) NMR studies employing decoupling, computer line narrowing, and partially relaxed Fourier transform techniques have demonstrated that all molecules except $B_4H_8{\cdot}PF_2CF_3$ exist as two geometrical isomers. Although ^{11}B and ^{31}P NMR spectra indicate the presence of geometrical isomers, the fluorine-19 nucleus is the most sensitive indicator of the presence of these isomers. Rotational isomers were observed for some compounds in low-temperature ^{19}F NMR spectra although only in $B_4H_8PF_2CF_3$ was a limiting low-temperature spectrum obtained. Conclusions concerning relative contributions of steric and electronic factors to the population of endo and exo isomers are discussed.

Introduction

Recently, this laboratory has completed multinuclear NMR studies[1,3,4] of several difluorophosphine derivatives of tetraborane(8), $B_4H_8{\cdot}PF_2X$ (X = F, Cl, Br, I, H, and $N(CH_3)_2$). These studies, particularly low-temperature ^{19}F NMR studies, have conclusively established that all molecules except $B_4H_8{\cdot}PF_2H$ exist as geometrical isomers (endo and exo placement of the phosphine with respect to the B_4 framework as shown in Figure 1) at ambient temperature. Further, at low temperatures restricted rotation about the P–B bond in the endo geometrical isomer of these adducts gives rise to all possible combinations of rotational isomers (Figure 2).

Relative contributions of intramolecular interactions to the stabilization of the endo isomer with respect to the exo isomer are not known. There are still unanswered questions pertaining to the importance of steric and electronic effects of the X substituent of the phosphine on the relative populations of the geometrical isomers at high temperature and on the rotational isomers at low temperature. In order to gain additional insight into these factors, we have synthesized, characterized, and examined several new $B_4H_8{\cdot}PF_2X$ complexes (where X = OCH_3, SCH_3, CH_3, CF_3, and $t\text{-}C_4H_9$) by multinuclear magnetic resonance employing decoupling, computer line-narrowing, and PRFT techniques. The results of this study are reported herein.

Experimental Section

Materials. The preparation and purification of the $B_4H_8{\cdot}PF_2X$ complexes were accomplished with use of standard high-vacuum techniques in an all-glass vacuum system equipped with greaseless stopcocks.[5] The $B_4H_8{\cdot}PF_2X$ complexes were synthesized by base displacement from B_4H_8CO which was prepared directly from the pyrolysis of B_2H_6 in the presence of CO.[6] The phosphine bases were prepared as previously reported. The CH_3PF_2[7] and $(t\text{-}C_4H_9)PF_2$[8] ligands were prepared by the fluorination of CH_3PCl_2 (Alfa) and $(t\text{-}C_4H_9)PCl_2$ (Alfa), with dry NaF (Allied) in sulfolane (Parish). Methyl difluorophosphite,[9] CH_3OPF_2, was synthesized directly from PF_3(Ozark-Mahoning), CH_3OH (Baker), and C_5H_5N (Fisher). The sulfur analogue,[10] CH_3SPF_2, was prepared from PF_2Cl[11] and CH_3SH (Matheson) in the presence of trimethylamine (Matheson). (Trifluoromethyl)difluorophosphine, CF_3PF_2, was obtained from repetitive fluorinations of CF_3PI_2 with freshly sublimed SbF_3 (Ozark-Mahoning) at 100 °C.[12] Sulfolane, methanol, pyridine were dried and distilled before use. The purity of all compounds was monitored by mass spectral and ^{31}P and ^{19}F NMR spectral measurements.

The synthesis of $B_4H_8{\cdot}PF_2X$ complexes was accomplished by condensing B_4H_8CO (~2.0 mmol) and the PF_2X ligand (2.2 mol) into a small-volume reaction vessel equipped with a greaseless stopcock.

Table I. Melting Points and Vapor Pressure (P) for $B_4H_8{\cdot}PF_2X$ Complexes

compd	mp, °C	P, torr (t, °C)
$B_4H_8{\cdot}PF_2OCH_3$	−76	8 (25.8)
$B_4H_8{\cdot}PF_2SCH_3$	−112 to −110	<1 (24.8)
$B_4H_8{\cdot}PF_2CH_3$	−67 to −66	7 (24.0)
$B_4H_8PF_2CF_3$	−153 to −149	*a*
$B_4H_8{\cdot}PF_2C_4H_9$	−92 to −85	<1 (25.0)

[a] Complex was not available in sufficient quantity for vapor pressure measurement.

(1) Part 20 in the series, "Spectra and Structure of Phosphorus-Boron Compounds". For part 19 see: Odom, J. D.; Moore, T. F. *Inorg. Chem.* **1980**, *19*, 2651.
(2) Taken in part from the thesis of A. J. Zozulin, submitted to the Department of Chemistry, University of South Carolina, in partial fulfillment of the requirements for the Ph.D. degree.
(3) Odom, J. D.; Moore, T. F.; Garber, A. R. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 45.
(4) Odom, J. D.; Moore, T. F.; Dawson, W. H.; Garber, A. R.; Stampf, E. *Inorg. Chem.* **1979**, *18*, 2179.
(5) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.
(6) Onak, T.; Gross, K.; Tse, J.; Howard, J. *J. Chem. Soc., Dalton Trans.* **1973**, 2633.
(7) Seel, V. F.; Rudolph, K.; Budeng, R. *Z. Anorg. Allg. Chem.* **1965**, *341*, 196.
(8) Stelzer, O.; Schmutzler, R. *Inorg. Synth.* **1978**, *18*, 173.
(9) Centofanti, L. F.; Lines, L. *Inorg. Synth.* **1976**, *16*, 166.
(10) Foester, R.; Cohn, K. *Inorg. Chem.* **1972**, *11*, 2590.
(11) Morse, J. G.; Cohn, K.; Rudolph, R. W.; Parry, R. W. *Inorg. Synth.* **1967**, *10*, 174.
(12) Bennett, F. W.; Emeleus, H. J.; Hazeldine, R. N. *J. Chem. Soc.* **1953**, 1565.
(13) Stampf, E. J.; Garber, A. R.; Odom, J. D.; Ellis, P. D. *Inorg. Chem.* **1975**, *14*, 2446.
(14) Lowman, D. W.; Ellis, P. D.; Odom, J. D. *Inorg. Chem.* **1973**, *12*, 681.

0020-1669/81/1320-3740$01.25/0