observed by NMR spectroscopy (Table I).

The unsymmetric tripnicogen $Me_2PP(CF_3)AsMe_2$ was prepared by transferring equimolar quantities of $Me_2PP(CF_3)PMe_2$ and $Me_2AsP(CF_3)AsMe_2$ in benzene-d_6 solution into an NMR tube. Scrambling to yield the product was immediate, as monitored by NMR spectroscopy (Table I).

(Dimethylphosphino)(trifluoromethyl)phosphine, $Me_2PP(CF_3)H$, was prepared by the neutral water hydrolysis of $Me_2PP(CF_3)PMe_2$. A 1:1 mole ratio of $Me_2PP(CF_3)PMe_2$ and H_2O was condensed into a glass ampule fitted with a Teflon stopcock. This mixture was allowed to warm to room temperature at which time a white precipitate, $Me_2P(O)OH$, started to form. After about 1 h at room temperature, the volatile products were returned to the vacuum line and fractioned through traps held at −15, −78, and −196 °C. (Dimethylphosphino)(trifluoromethyl)phosphine was retained in the −78 °C trap and was characterized by vapor pressure, IR spectroscopy, and ^1H, ^{19}F, and ^{31}P NMR spectroscopy (Table II). A gas-phase molecular weight determination yielded a value of 156 (calculated 162). The IR spectrum gave the following peaks (cm^{-1}): 2990 (m), 2950 (m), 2296 (m), 1435 (m), 1305 (m), 1170 (vs), 1130 (vs), 1050 (s), 1020 (s), 950 (m), 835 (m), and 735 (m). The product, which is stable for weeks at ambient temperature, is a clear liquid, which is soluble in organic solvents and has a vapor pressure of 19 Torr at 25 °C. An excess of water causes further hydrolysis to occur. The hydrolysis reaction was also performed in benzene-d_6 solvent in a sealed NMR tube. The reaction was complete by the time a spectrum was obtained. The chiral diphosphine $Me_2PP(CF_3)H$ will slowly react with the byproduct Me_2PH[10] (identified by ^1H and ^{31}P NMR spectroscopy). Dimethylphosphinic acid, $Me_2P(O)OH$, was the only nonvolatile product formed from hydrolysis of either $Me_2PP(CF_3)PMe_2$ or $Me_2PP(CF_3)H$. This compound was identified by ^{31}P NMR spectroscopy[25] and mass spectral evidence. The mass spectrum showed the following major peaks (mass (*m/e*), intensity): $(CH_3)_2P(O)H^+$ (94, 100%), $CH_3P(O)OH^+$ (79, 100%), POO^+ (63, 40%), CH_3PO^+ (62, 41%), PO^+ (47, 99%).

(Dimethylarsino)(trifluoromethyl)phosphine, $Me_2AsP(CF_3)H$, was prepared by the neutral water hydrolysis of bis(dimethylarsino)(trifluoromethyl)phosphine, $Me_2AsP(CF_3)AsMe_2$. Typically, a 1:1 mole ratio (stoichiometry is very critical) of $Me_2AsP(CF_3)AsMe_2$ and H_2O was condensed into a glass ampule at −196 °C. The ampule was sealed and allowed to warm slowly to room temperature. After a few minutes at room temperature, a white precipitate of cacodylic acid, $Me_2As(O)OH$, began to appear. After approximately 2 h, precipitation was complete, and the ampule was reopened to the vacuum line and the volatile products transferred for analysis. Fractionation yielded Me_2AsH (−196 °C trap), $Me_2AsP(CF_3)H$ (−84 °C trap), and unreacted $Me_2AsP(CF_3)AsMe_2$ (−15 °C trap). Fractionation in a grease-stopcock high-vacuum line, in contrast to one with Teflon stopcocks, always leads to some decomposition. The $Me_2AsP(CF_3)H$ has a vapor pressure of 13.4 Torr at 22 °C and a gas-phase molecular weight of 212 (calculated 206). The IR spectrum has the following absorbtions (cm^{-1}): 2980 (m), 2910 (m), 2305 (m), 2070 (w), 1415 (m), 1255 (w), 1160–1180 (vs), 1060 (sh), 890 (m), 830 (s), 730 (m), and 665 (m). The compound was characterized by ^1H, ^{31}P, and ^{19}F NMR (Table II). It is less thermodynamically stable than the congeneric diphosphine $Me_2PP(CF_3)H$, disproportionating considerably after 1 day at ambient temperature. A cleaner and more rapid reaction can be effected in benzene solvent. The cacodylic acid $Me_2As(O)OH$ produced as a byproduct in this reaction was isolated and identified by melting point, mass spectrum, and ^1H NMR measurements, as compared to an authentic sample.

The chiral dipnicogens $Et_2PP(CF_3)H$, $Bu_2PP(CF_3)H$, and $Me_2PP(C_2F_5)H$ were synthesized by hydrolysis with neutral water of the tripnicogens $Et_2PP(CF_3)PEt_2$, $Bu_2PP(CF_3)PBu_2$, $Me_2PP(C_2F_5)PMe_2$, respectively. The hydrolysis times increased with steric bulk. These chiral dipnicogens were not isolated because of low volatility, but rather were characterized by NMR (Table II).

Hydrolysis of the dipnicogens $Me_2PP(CF_3)H$, $Me_2AsP(CF_3)H$, $Et_2PP(CF_3)H$, $Bu_2PP(CF_3)H$, and $Me_2PP(C_2F_5)H$ was performed by the addition of an equimolar quantity of water to a benzene solution of the dipnictide. The products R_2PH (or R_2AsH), R_fPH_2, and $R_2P(O)OH$ (or $R_2As(O)OH$) were identified by either NMR spectral parameters or by isolation. The hydrolysis times were all longer than the hydrolysis times of the parent tripnictide.

Acknowledgment. The support of the Robert A. Welch Foundation is gratefully acknowledged. We also thank Professor A. W. Cordes for attempts to obtain ESR spectra, Dr. J. P. Albrand for helpful discussions concerning interpretation of NMR data, and M. E. Grice for computer expertise.

Registry No. $Me_2PP(CF_3)PMe_2$, 19307-60-9; $(CF_3P)_4$, 393-02-2; Me_4P_2, 3676-91-3; $(C_2F_5P)_3$, 29634-17-1; Et_4P_2, 3040-63-9; Bu_4P_2, 13904-54-6; Me_4As_2, 471-35-2; $(MeP)_5$, 1073-98-9; $Et_2PP(CF_3)PEt_2$, 117583-82-1; $Bu_2PP(CF_3)PBu_2$, 117606-54-9; $Me_2PP(C_2F_5)PMe_2$, 117606-55-0; $Me_2AsP(CF_3)AsMe_2$, 24595-87-7; $Me_2PP(CF_3)PEt_2$, 117606-56-1; $(CF_3)_2PPMeP(CF_3)_2$, 2195-42-8; $Me_2PP(CF_3)AsMe_2$, 24595-95-7; $Me_2PP(CF_3)H$, 117583-73-0; $Me_2P(O)OH$, 3283-12-3; $Me_2AsP(CF_3)H$, 117583-81-0; $Et_2PP(CF_3)H$, 117583-76-3; $Bu_2PP(CF_3)H$, 117606-57-2; $Me_2PP(C_2F_5)H$, 117606-58-3; $(CF_3)_2PP(CF_3)_2$, 2714-60-5; $(CF_3)_5$, 745-23-3; $(C_2F_5P)_4$, 35449-91-3.

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[25] Crofts, P. C. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds., Wiley-Interscience: New York, 1973; Vol. VI, Chapter 14.

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Reactions of Secondary Phosphines with a Phosphorus–Phosphorus Bond and Related Reactions

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The reaction of a secondary alkyl- or arylphosphine or -arsine with the cyclic polyphosphine $(CF_3P)_{4,5}$ produces chiral dipnicogens[1] of the type $R_2EP(CF_3)H$ (E = P or As). Thus, for example, $(CF_3P)_{4,5}$ plus either Me_2PH or Me_2AsH yields $Me_2PP(CF_3)H$ or $Me_2AsP(CF_3)H$, respectively. In addition, a number of other products are produced in a complex equilibrium mixture. In the reaction of Me_2PH with $(CF_3P)_{4,5}$, other products identified at equilibrium in addition to $Me_2PP(CF_3)H$ are CF_3PH_2, Me_2PPMe_2, $CF_3(H)PP(H)CF_3$, $Me_2PP(CF_3)PMe_2$, $Me_2PP(CF_3)P(CF_3)H$, and $Me_2PP(CF_3)P(CF_3)PMe_2$. The origin of the complex equilibrium has been studied by examining the reaction of pairs of reactants and/or products, and a reaction mechanism has been proposed. Other secondary phosphines used as a reactant with $(CF_3P)_{4,5}$ were Ph_2PH and $Ph(Me)PH$. In an analogous reaction $(CF_3)_2PH$ reacts with the alkyl-substituted cyclic polyphosphine $(MeP)_5$ to produce $(CF_3)_2PP(Me)H$.

Introduction

In the previous paper[2] we reported the general reaction of a dipnicogen,[1] such as Me_2PPMe_2 or $Me_2AsAsMe_2$, with an equimolar quantity of perfluoroalkylphosphinidine units R_fP from a perfluoroalkylcyclopolyphosphine, such as $(CF_3P)_{4,5}$, to yield quantitatively a tripnicogen where the R_fP species has undergone insertion into the original pnicogen–pnicogen bond.

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(1) Pnicogens refer to main group V compounds. Therefore, for example, a dipnicogen simply refers to a compound containing two main group V elements such as a diphosphine, a diarsine, or a arsinophosphine. Suchow, L. *Inorg. Chem.* **1978,** *17,* 2041.

(2) Avens, L. R.; Wolcott, R. A.; Cribbs, L.; Mills, J. L. *Inorg. Chem.* preceding paper in this issue.

$$R_2EER_2 + (1/n)(R_fP)_n \rightarrow R_2EP(R_f)ER_2 \quad E = P \text{ or } As \qquad (1)$$

The tripnicogens are easily hydrolyzed by 1 equiv of water to yield chiral dipnicogens of the type $R_2EP(R_f)H$. Addition of a second equivalent of water to the chiral dipnicogen $R^2EP(R_f)H$ quantitatively produces the primary phosphine R_fPH_2.

The product distribution of these reactions is highly dependent on stoichiometry; if other than equimolar quantities of reactants are used, a number of products with competing equilibria result. In this paper, we report the results of our study of some of these complex equilibria and related chemistry.

Results and Discussion

Chiral phosphines are very useful reagents in asymmetric organic syntheses. Due to the potential usefulness of chiral dipnicogens of the type $R_2EP(R_f)H$, where E = P or As and R_f = perfluoroalkyl, which can be generated by the hydrolysis of tripnicogens, we decided to examine alternate synthetic pathways. Another goal was to study the chemistry of the chiral dipnicogens, particularly relative to the reactivity of the P–H bond versus either the P–P or P–As bond. A possible route to compounds of the type $R_2EP(R_f)H$ is

$$R_2EH + (R_fP)_n \rightarrow R_2PP(R_f)H \qquad (2)$$

The desired product would result from the "insertion" of the R_fP moiety into the P–H bond of the secondary pnicogen. Albrand used a similar reaction to prepare Ph(H)PP(H)Ph.[3]

$$PhPH_2 + (PhP)_6 \rightarrow Ph(H)PP(H)Ph \qquad (3)$$

Interestingly, the reaction proposed in eq 2 was performed by Cowley in 1967 as a synthesis for the tripnicogen $Me_2PP(CF_3)PMe_2$.[4] However, an excess of Me_2PH was used, which obscured much of the chemistry that we have studied. We find that if Me_2PH is used in either equimolar, or less, quantities relative to CF_3P units, then the chiral diphosphine, $Me_2PP(CH_3)H$, is quickly produced at room temperature. As time passes, additional compounds are formed that are clearly products of the further reaction of the diphosphine with other species in solution. The overall reaction can be represented by

$$\begin{aligned} Me_2PH + (CF_3P)_{4,5} \xrightarrow[\text{1 week}]{\text{23 °C, } C_6D_6} {} & CF_3PH_2 + Me_2PPMe_2 + \\ & CF_3(H)PP(H)CF_3 + Me_2PP(CF_3)H + \\ & Me_2PP(CF_3)P(CF_3)H + Me_2PP(CF_3)P(CF_3)PMe_2 + \\ & Me_2PP(CF_3)PMe_2 \qquad (4) \end{aligned}$$

The origin of the products, together with their characterization, is discussed below. The number of products and the complexity of their NMR spectra make analysis difficult. This complexity is graphically demonstrated by the calculated $^{31}P[^{19}F]$ second-order NMR pattern exhibited by the relatively simple compound $CF_3(H)PP(H)CF_3$ (Figure 1), which exists in a *d,l* pair and meso isomers.[5] In this figure, the AA′ portion of the AA′XX′ spin system is shown for each isomer as compared to the observed spectrum.

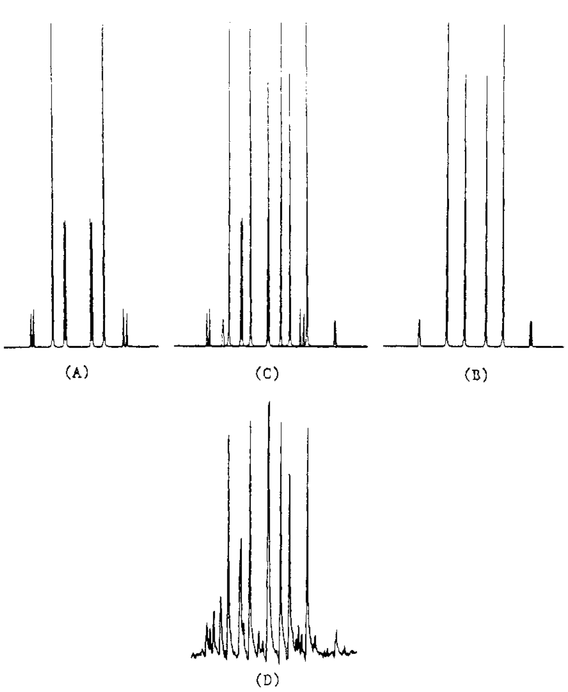
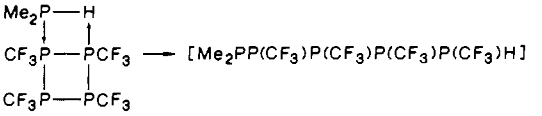
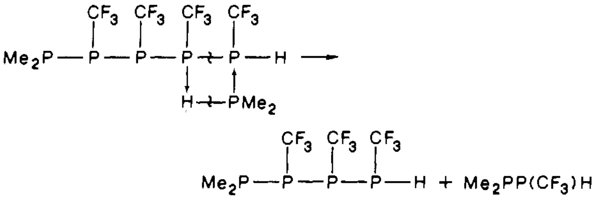


Figure 1. $^{31}P[^{19}F]$ NMR spectra of $CF_3(H)PP(H)CF_3$: (A) computer-simulated spectrum of isomer a; (B) computer-simulated spectrum of isomer b; (C) computer-simulated spectrum combining spectra A and B; (D) observed spectrum of $CF_3(H)PP(H)CF_3$. NMR parameters for isomer a: $\delta(^{19}F[^1H] = -45.9$ (doublet); $\delta(^{31}P) = -90.3$ (multiplet); $^2J_{PF} = 54.0$, $^3J_{PF} = 17.0$, $^1J_{PP} = 135$, $^1J_{PH} = 205.6$, $^2J_{PH} = 3.2$, $^3J_{HH} = 9.2$ Hz. NMR parameters for isomer b: $\delta(^{19}F[^1H]) = -46.3$ (doublet); $\delta(^{31}P) = -92.0$ (multiplet); $^2J_{PF} = 55.5$, $^3J_{PF} = 7.3$, $^1J_{PP} = -184$, $^1J_{PH} = 213.9$, $^2J_{PH} = 15.5$, $^3J_{HH} = 3.0$ Hz. Data were taken from ref 5.

The first clearly identified product formed (as monitored by NMR spectroscopy; see Table I in ref. 2) in the reaction represented by eq 4 was $Me_2PP(CF_3)H$. The proposed mechanism involves a four-centered intermediate, as proposed for a similar system by Cavell and Dobbie.[7]

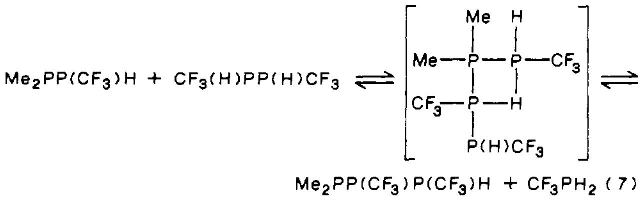

(5)

Rapid reaction of the intermediate with additional Me_2PH yields the observed chiral diphosphine $Me_2PP(CF_3)H$.


(6)

It is clear that a large number of reactions are possible among the numerous products in this system. To study some of these reactions and to aid in product identification, several reactions among the pairs of the molecules present in the reaction mixture, particularly those involving $Me_2PP(CF_3)H$, were undertaken. These reactions are discussed below.

Reaction between $Me_2PP(CF_3)H$ and $CF_3(H)PP(H)CF_3$. The reaction of $Me_2PP(CF_3)H$ with $CF_3(H)PP(H)CF_3$ produces CF_3PH_2 and the new triphosphine $Me_2PP(CF_3)P(CF_3)H$ (see Experimental Section, vide infra). The proposed mechanism is


(7)

The reaction reaches equilibrium in several days at room temperature. It is instructive to note that no nonvolatile polymeric tars or noncondensable gases are created by this reaction or in any reactions reported in this section. The $^{31}P[^1H]$ and $^{31}P[^1F]$ NMR spectra of this reaction mixture are shown in Figure 2. While the triphosphine has not been unambiguously characterized,

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(3) Albrand, J. P.; Gaignaire, D. *J. Am. Chem. Soc.* **1972**, *94*, 8630.

(4) Cowley, A. H. *J. Am. Chem. Soc.* **1967**, *89*, 5990.

(5) Albrand, J. P.; Robert, J. B.; Goldwhite, H. *Tetrahedron Lett.* **1976**, 949.

(6) NMR data, both ^{31}P and ^{19}F, for the dipnicogens $Me_2PP(CF_3)H$, $Et_2PP(CF_3)H$, $Me_2AsP(CF_3)H$, and the tripnicogens $Me_2P\text{-}P(CF_3)PMe_2$, $Et_2PP(CF_3)PEt_2$, $Me_2AsP(CF_3)AsMe_2$ are tabulated in the previous paper, ref 2.

(7) Cavell, R. G.; Dobbie, R. C. *J. Chem. Soc. A* **1968**, 1406.

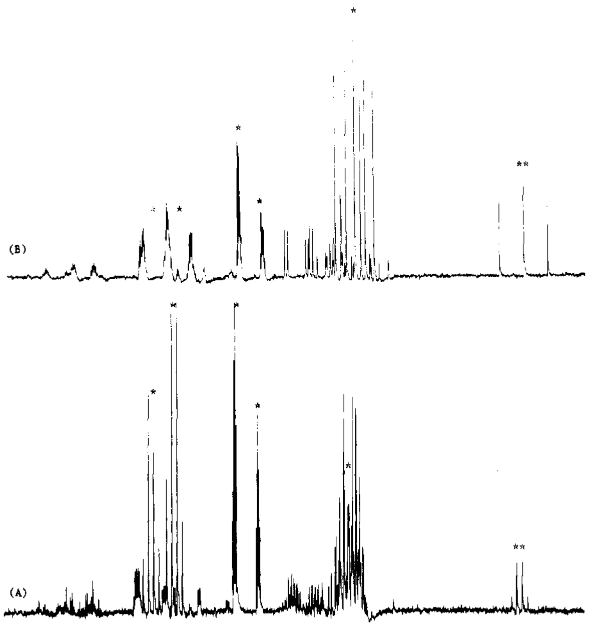
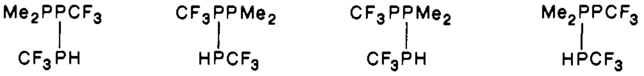


Figure 2. (A) $^{31}P[^1H]$ and (B) $^{31}P[^{19}F]$ NMR spectra of $Me_2PP(CF_3)H$ + $CF_3(H)PP(H)CF_3$ reaction mixture at equilibrium. Chemical shifts are in ppm upfield from 85% H_3PO_4. A single asterisk denotes $Me_2PP(CF_3)H$ resonances (see ref 2) + $CF_3(H)PP(H)CF_3$ (see Figure 1). A double asterisk denotes CF_3PH_2 resonances. All other resonances are due to $Me_2PP(CF_3)P(CF_3)H$.

material balance, volatility, and multinuclear NMR spectra support the assigned structure, as evidenced by the following reaction.

Reaction between Me_2PPMe_2 and $CF_3(H)PP(H)CF_3$. Further evidence for the triphosphine $Me_2PP(CF_3)P(CF_3)H$ arises from the reaction of Me_2PPMe_2 with $CF_3(H)PP(H)CF_3$. Figure 3 shows the progress of this reaction as monitored by ^{19}F NMR spectroscopy. The first product seen is $Me_2PP(CF_3)P(CF_3)H$, followed after a short time by both $Me_2PP(CF_3)H$ and $Me_2PP(CF_3)PMe_2$ in equal amounts. Finally, CF_3PH_2 is produced, which probably arises from reaction 7, since both reactants are present.

The foregoing reactions strongly support the structural assignment for the triphosphine $Me_2PP(CF_3)P(CF_3)H$. For this compound, there are four stereoisomers, two *d,l* pairs, *threo* and *erythro*:



$$\begin{array}{c}\mathrm{Me_2PPCF_3}\\ |\\ \mathrm{CF_3PH}\end{array}\qquad\begin{array}{c}\mathrm{CF_3PPMe_2}\\ |\\ \mathrm{HPCF_3}\end{array}\qquad\begin{array}{c}\mathrm{CF_3PPMe_2}\\ |\\ \mathrm{CF_3PH}\end{array}\qquad\begin{array}{c}\mathrm{Me_2PPCF_3}\\ |\\ \mathrm{HPCF_3}\end{array}$$

Since the solvent is achiral, only the two diastereomers can potentially be observed in the NMR spectra. However, the problem of two isomers, the possibility of second-order character in the spectra, and the large number of spins prohibit definitive interpretation of the ^{31}P and ^{19}F NMR spectra. Nevertheless, chemical shift trends and multiplicity support the structural assignment of $Me_2PP(CF_3)P(CF_3)H$, as follows.

The ^{31}P NMR spectrum shows, in the downfield region where the central CF_3P phosphorus atom should be expected, an approximate triplet of multiplets ($\delta = -31.8$) arising from coupling to the two terminal phosphorus atoms. This is similar both in chemical shift and in appearance to that of the $P(CF_3)$ group in $Me_2PP(CF_3)PMe_2$.[2] The $P(CF_3)H$ phosphorus appears as a doublet of multiplets slightly downfield of the phosphorus resonance in $CF_3(H)PP(CF_3)H$ ($\delta = -80.4$), as would be expected from coupling to the neighboring phosphorus, while the Me_2P phosphorus atom is seen as an approximate doublet of doublets ($\delta = -55.5$) between the chemical shift extremes of the other two phosphorus atoms in the molecule. The $^{19}F[^1H]$ NMR spectrum of the $P(CF_3)H$ fluorine appears as the expected doublet of doublets of multiplets; while proton coupled, the resonances become a doublet of triplets of multiplets. The spectral appearance is a doublet of triplets of multiplets due to the similarity in magnitude of $^3J_{PPCF}$ and $^3J_{HPCF}$. The central CF_3P fluorine appears as a doublet of doublets of doublets of multiplets ($\delta = -46.5$) as expected from coupling to two nonequivalent phosphorus atoms, a proton, and fluorine atoms. The spectral argument is for an approximately first-order system in gross appearances only.

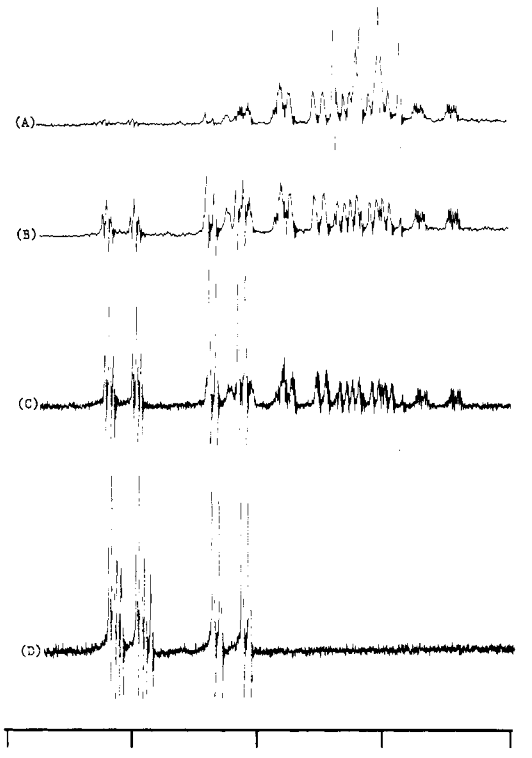
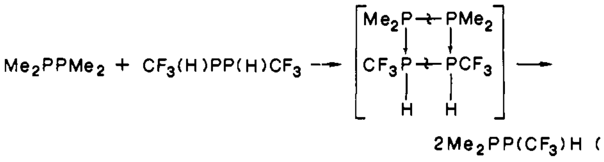
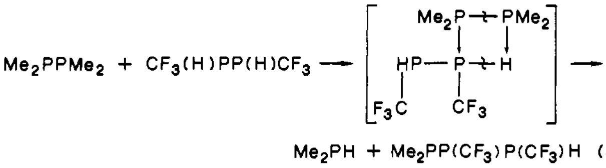


Figure 3. $^{19}F[^1H]$ NMR spectra of the Me_2PPMe_2 + $CF_3(H)PP(H)CF_3$ reaction mixture: (a) after 0.5 h; (b) after 5 h; (c) after 18 h; and (d) after 2 weeks. Chemical shifts are in ppm upfield from $CFCl_3$. The doublet of doublets at −43.7 ppm arises from $Me_2PP(H)CF_3$., while the doublet of triplets at −41.6 ppm is from $Me_2PP(CF_3)PMe_2$. The doublet at −41.7 ppm is due to CF_3PH_2 (spectrum D). The doublet of doublets near −45.5 ppm (spectrum A) results from $F_3C(H)PP(H)CF_3$. All other resonances (most clearly apparent in spectrum A) are attributed to $Me_2PP(CF_3)P(CF_3)H$.

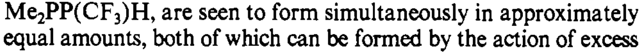
Since the first products in the reaction of Me_2PPMe_2 with $CF_3(H)PP(H)CF_3$ are $Me_2PP(CF_3)P(CF_3)H$ and Me_2PH, and not the chiral diphosphine $Me_2PP(CF_3)H$, then the mechanism for the reaction initially involves not PP bond fission as in eq 8a, but rather P–H bond fission as in eq 8b. As the reaction proceeds towards equilibrium, two more products, $Me_2PP(CF_3)$-PMe_2 and $Me_2PP(CF_3)H$, are seen to form simultaneously in approximately equal amounts, both of which can be formed by the action of excess Me_2PPMe_2 on $Me_2PP(CF_3)P(CF_3)H$, as shown in eq 9. The



$$\mathrm{Me_2PPMe_2 + CF_3(H)PP(H)CF_3} \longrightarrow \left[\begin{array}{ccc}\mathrm{Me_2P} & \nleftrightarrow & \mathrm{PMe_2}\\ \downarrow & & \downarrow\\ \mathrm{CF_3P} & \nleftrightarrow & \mathrm{PCF_3}\\ | & & |\\ \mathrm{H} & & \mathrm{H}\end{array}\right] \longrightarrow \mathrm{2Me_2PP(CF_3)H} \qquad (8a)$$



$$\mathrm{Me_2PPMe_2 + CF_3(H)PP(H)CF_3} \longrightarrow \left[\begin{array}{ccc} & \mathrm{Me_2P} \nleftrightarrow & \mathrm{PMe_2}\\ & \downarrow & \downarrow\\ \mathrm{HP} & — & \mathrm{P} \nleftrightarrow \mathrm{H}\\ | & & |\\ \mathrm{F_3C} & & \mathrm{CF_3}\end{array}\right] \longrightarrow \mathrm{Me_2PH + Me_2PP(CF_3)P(CF_3)H} \qquad (8b)$$



$$\begin{array}{ccc}\mathrm{Me_2P} — \mathrm{(CF_3)P} & — & \mathrm{P(CF_3)H}\\ \uparrow\quad\ \uparrow & & \\ \mathrm{Me_2P} — \mathrm{PMe_2} & & \end{array} \longrightarrow \mathrm{Me_2PP(CF_3)H + Me_2PP(CF_3)PMe_2} \qquad (9)$$

compound $Me_2PP(CF_3)H$ could also be formed by the slow re-

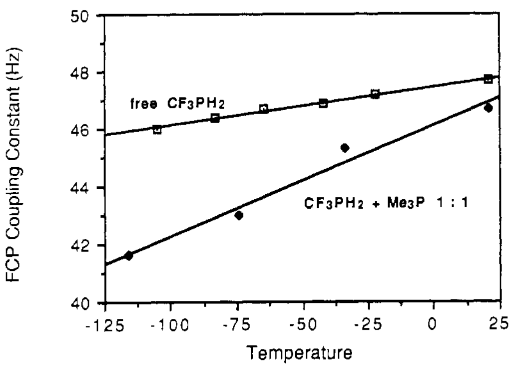
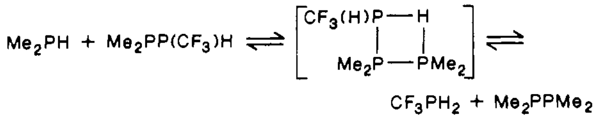


Figure 4. $^2J_{FCP}$ as a function of temperature for free CF_3PH_2 and a 1:1 mixture of CF_3PH_2–Me_3P in methylcyclohexane.

action (eq 8a) (relative to the rate of eq 8b). If eq 9 proceeds as indicated, then eq 8a would be expected to occur at approximately the same rate. The last product formed, bringing this reaction to equilibrium, is CF_3PH_2. We assume that the reaction in eq 7 is the source for CF_3PH_2, since both reactants are present in solution. The high concentration of Me_2PPMe_2 in this reaction mixture forces the equilibrium away from $Me_2PP(CF_3)P(CF_3)H$ via reaction 9. Thus only $Me_2PP(CF_3)H$, CF_3PH_2, and $Me_2PP(CF_3)PMe_2$ are seen in equilibrium (Figure 3D).

Reaction between Me_2PH and $Me_2PP(CF_3)H$ and between CF_3PH_2 and Me_2PPMe_2. Next, consider the reaction between Me_2PH and $Me_2PP(CF_3)H$. Both of these species are present when Me_2PH reacts with $(CF_3P)_4$ (eq 4). When mixed in benzene they do react to produce Me_2PPMe_2 and CF_3PH_2. To confirm that this is indeed an equilibrium process, a separate experiment was executed. Thus Me_2PPMe_2 and CF_3PH_2 were mixed in benzene, and after several hours $Me_2PP(CF_3)H$ and Me_2PH were observed. The equilibrium lies largely to the right (~80%).



$$\mathrm{Me_2PH + Me_2PP(CF_3)H} \rightleftharpoons \left[\begin{array}{ccc} \mathrm{CF_3(H)P} & — & \mathrm{H} \\ | & & | \\ \mathrm{Me_2P} & — & \mathrm{PMe_2} \end{array}\right] \rightleftharpoons \mathrm{CF_3PH_2 + Me_2PPMe_2} \quad (10)$$

The formation of CF_3PH_2 seems to be a thermodynamic driving force in many of the equilibria in this study.

It is interesting that CF_3PH_2 must act as an acid as well as a base in this process. This interaction was examined more closely. Figure 4 shows the result of an experiment where the FCP coupling constant $^2J_{FCP}$ was measured as a function of temperature both for free CF_3PH_2 and for a 1:1 mixture of CF_3PH_2 and Me_3P. The equilibrium interaction between Me_3P and CF_3PH_2 is clearly indicated by the change in the coupling constant with temperature. The acidic nature of CF_3PH_2 has also been shown in a much different manner, i.e., by passing gaseous CF_3PH_2 over solid KOH to yield the two novel species $FC{\equiv}P$ and $F_2C{=}PH$ via HF elimination.[8]

Action of Heat on Diphosphines. Isolated diphosphines of the type $R_2PP(CF_3)H$ are stable for months at room temperature.[2] However, heating the diphosphines causes disproportionation.

$$2R_2PP(CF_3)H \rightarrow R_2PP(CF_3)PR_2 + CF_3PH_2 \quad (11)$$

When R = Me, a temperature of 60 °C for 24 h was sufficient to effect reaction. Further heating produced small amounts of Me_2PH and $(CF_3P)_{4,5}$, presumably from a hydrogen atom shift in $Me_2PP(CF_3)H$. When R = Et, 100 °C was necessary to give a good conversion rate to the tripnicogen and CF_3PH_2 (eq 11). The $^{19}F[^1H]$ NMR spectra is shown in Figure 5. Extended heating at 100 °C did not produce Et_2PH or $(CF_3P)_{4,5}$. It can be assumed that steric crowding in the transition state causes both the higher reaction temperature necessary for disproportionation of $Et_2PP(CF_3)H$ relative to the methyl analogue and the lack of further reaction of the ethyl derivative tripnicogen.

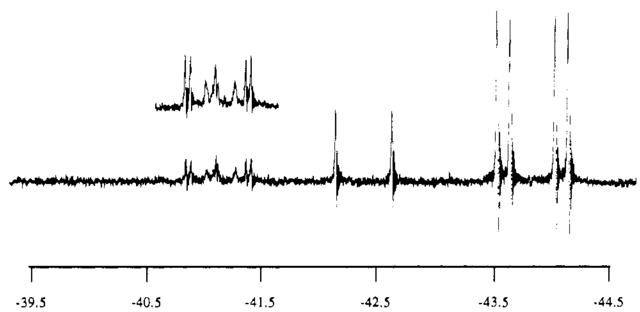


Figure 5. ^{19}F NMR spectrum of $Et_2PP(CF_3)H$ at equilibrium after heating. Chemical shifts are in ppm upfield from $CFCl_3$. Low-field peaks are the second-order pattern of $Et_2PP(CF_3)PEt_2$. The doublet at –42.2 ppm is CF_3PH_2, while the doublet of doublets upfield is from $Et_2PP(CF_3)H$ (see ref 2).

Reaction of $(CF_3P)_{4,5}$ with $Me_2PP(CF_3)H$ and with $Me_2PP(CF_3)PMe_2$. Since the triphosphine $Me_2PP(CF_3)P(CF_3)H$ can be considered as the product of CF_3P "insertion" into $Me_2PP(CF_3)H$ (eq 7), an attempt was made to produce $Me_2PP(CF_3)P(CF_3)H$ by reaction of $Me_2PP(CF_3)H$ with $(CF_3P)_{4,5}$. Reaction gave the triphosphine in addition to other products. The success of this insertion reaction suggested a route to the tetraphosphine $Me_2PP(CF_3)P(CF_3)PMe_2$. The reaction apparently occurs as written:

$$Me_2PP(CF_3)PMe_2 + (CF_3P)_{4,5} \rightarrow Me_2PP(CF_3)P(CF_3)PMe_2 \quad (12)$$

As expected, the tetraphosphine exhibits very complex NMR spectra (see Experimental Section), the general features of which are consistent with the structure, as is the compound volatility.

Reaction between Ph(Me)PH and $(CF_3P)_{4,5}$. To demonstrate the generality of the reaction between secondary phosphines and $(CF_3P)_{4,5}$, the reaction between Ph(Me)PH and the perfluoroalkylcyclopolyphosphine was studied. For several reasons an extremely complex system arises. These include the second-order character of the NMR spectra, the large number of isomers present, and the inability to separate the product mixture into its components due to low volatility.

In this reaction the first products seen are the expected Ph(Me)PP(CF_3)H, which exists as two diastereometers, and $CF_3(H)PP(H)CF_3$ (Figure 1).

Each *d,l* pair of Ph(Me)PP(CF_3)H exhibits the X portion of an ABX spin system in the ^{19}F proton-coupled and proton-decoupled NMR spectrum as shown in Figure 6. As is observed in general, the two diastereoisomers are indistinguishable. As time passes, two additional compounds are formed; by analogy with the ^{19}F NMR spectrum of the Me_2PH system, the tripnicogens Ph(Me)PP(CF_3)P(CF_3)H and Ph(Me)PP(CF_3)P(Me)Ph were identified. These two triphosphines should exhibit numerous distinct NMR observable isomers. Just as the triphosphine $Me_2PP(CF_3)PMe_2$ gives a doublet of triplets pattern in the ^{19}F NMR spectrum, in the reaction mixture of Ph(Me)PH with $(CF_3P)_{4,5}$, a doublet of triplets occurs with a similar chemical shift and similar coupling constants and is assigned to the compound Ph(Me)PP(CF_3)P(Me)Ph. The other triphosphine Ph(Me)PP(CF_3)P(CF_3)H exhibits a complex ^{19}F NMR spectrum very similar to its dimethyl analogue. The ^{31}P NMR spectrum also shows resonances at the expected chemical shifts (by analogy) for both isomers of Ph(Me)PP(Me)Ph, to further complicate an already complex spectrum.

Figure 7 shows a series of reactions consistent with both the observed products and with previous mechanistic arguments.

The reaction of Ph_2PH with excess $(CF_3P)_{4,5}$ was also briefly studied. The results were in accord with the above Ph(Me)PH + $(CF_3P)_{4,5}$ reaction. Thus the first observed products were

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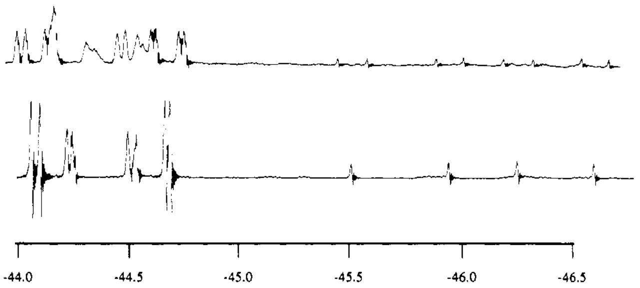

Figure 6. ^{19}F NMR spectrum of $Ph(Me)PH + (CF_3P)_{4,5}$ after 1 h at 23 °C. Chemical shifts are in ppm upfield from $CFCl_3$. Low-field peaks are from the two isomers of $Ph(Me)PP(CF_3)H$, while the high-field peaks are due to $CF_3(H)PP(H)CF_3$ (see Figure 1). The lower spectrum is proton decoupled, and the upper spectrum is proton coupled. NMR data for isomer a: $\delta(^{19}F) = -44.1$ (doublet of doublets); $^2J_{PF} = 54$, $^2J_{PF} = 4.1$ (lower field doublet separation), 2.6 Hz (upfield doublet separation). NMR data for isomer b: $\delta(^{19}F) = -44.0$ (doublet of doublets); $^2J_{PF} = 27$, $^2J_{PF} = 2.6$ (lower field doublet separation), 4.1 Hz (upfield doublet separation). Chemical shifts and coupling constants are approximate; the second-order spectrum was not solved.

$Ph_2PP(CF_3)H$ (see Experimental Section) and $CF_3(H)PP(H)CF_3$. At equilibrium the additional compounds CF_3PH_2 and $Ph_2P–PPh_2$ were clearly identifiable. Spectral evidence also indicated higher oligomers, as in the above reaction between Ph(Me)PH and $(CF_3P)_{4,5}$.

Reaction between $(CF_3P)_{4,5}$ and Me_2AsH. Having demonstrated the generality of the reaction of the P–H bond in secondary diphosphines with the phosphorus–phosphorus bond, we extended our study to secondary arsines. The reaction of $(CF_3P)_{4,5}$ with a stoichiometric amount of Me_2AsH yielded products analogous to the reaction of $(CF_3P)_{4,5}$ with Me_2PH (eq 4).

$$Me_2AsH + (CF_3P)_{4,5} \rightarrow CF_3PH_2 + Me_2AsAsMe_2 + CF_3(H)PP(H)CF_3 + Me_2AsP(CF_3)H + Me_2AsP(CF_3)AsMe_2 \quad (13)$$

Immediately when Me_2AsH was mixed with $(CF_3P)_{4,5}$ in C_6D_6, a yellow color developed and ^{31}P and ^{19}F NMR resonances indicated the presence of high catenates (vide supra), as expected from a reaction scheme analogous to that proposed for eq 4, where the products can be formed from a four-centered intermediate involving either four pnicogen atoms (and thus an apparent CF_3P "insertion" into a pnicogen–pnicogen bond), or three pnicogen atoms and a hydrogen atom (and thus CF_3P "insertion" into a pnicogen–hydrogen bond). The first clearly observed product in eq 14 was $Me_2AsP(CF_3)H^{2,6}$, exactly analogous to eq 4. After

$$Me_2AsH + Me_2AsP(CF_3)H \rightleftharpoons CF_3PH_2 + Me_2AsAsMe_2 \quad (14)$$

several hours at ambient temperature, CF_3PH_2 and $Me_2AsAsMe_2$ were observed spectroscopically, which would be expected from the reaction of Me_2AsH with $Me_2AsP(CF_3)H$, analogous to eq 10. To demonstrate that the system containing CF_3PH_2, $Me_2AsAsMe_2$, $Me_2AsP(CF_3)H$, and Me_2AsH is an equilibrium system, equimolar amounts of CF_3PH_2 and $Me_2AsAsMe_2$ were mixed in C_6D_6 in an NMR tube. After several days at 70 °C, an equilibrium was achieved, lying largely to the right, analogous to the all-phosphorus system (eq 10).

Reaction between $(CF_3)_2PH$ and $(MeP)_5$. All of the above reactions are dependent on the relative acidity of CF_3-substituted phosphorus atoms. The CF_3-substituted phosphorus atoms are derived from the $(CF_3P)_{4,5}$ ring. To extend the analogy and to examine the generality of secondary phosphines or arsines reacting with cyclic polyphosphine rings to produce chiral dipnicogens, we examined one system where the electronegative CF_3 group originated on the secondary phosphine rather than on the cyclic polyphosphine. The reaction of equimolar quantities of $(CF_3)PH$ and $(MeP)_5$ in benzene does indeed produce the chiral dipnocogen $(CF_3)_2PP(Me)H$. The reaction is much slower than that in eq 4, and although the reaction is quite clean, the equilibrium lies far in favor of the reactants. Burg has previously synthesized $(CF_3)_2PP(Me)H$ from the reaction of $(CF_3)_2PCl$ with $MePH_2$, but no NMR data were reported.[9] The anisochronicity of the two CF_3 groups results in a very complex ^{19}F NMR spectrum (see Experimental Section).

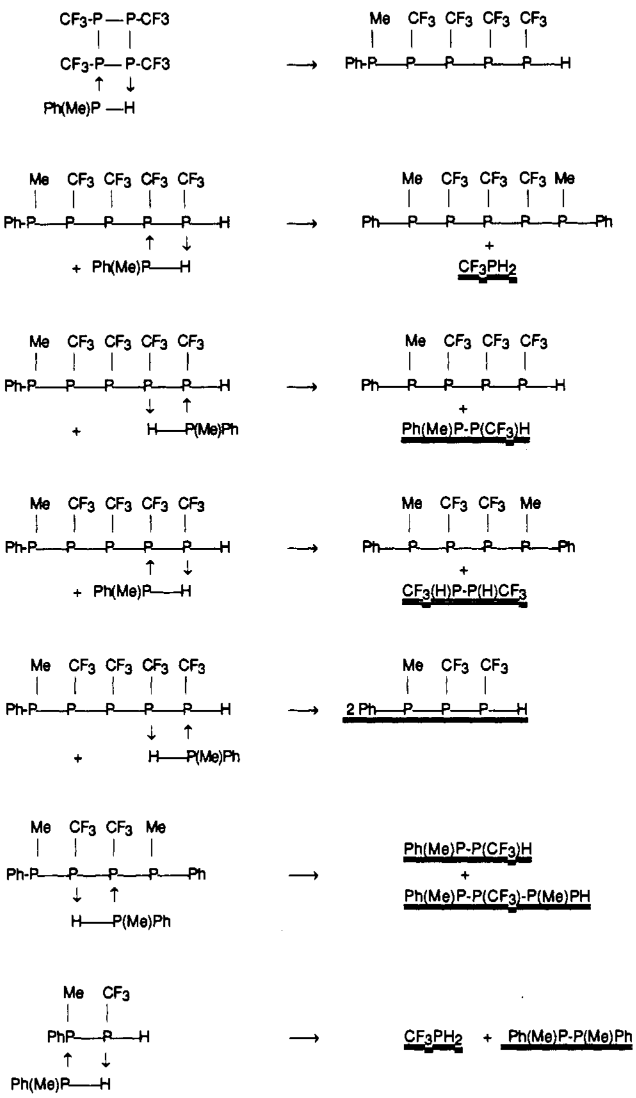

Figure 7. Mechanistic scheme for the reaction of $(CF_3P)_4$ with Ph(Me)PH. The underlined products were observed spectroscopically.

Experimental Section

General experimental and instrumental methods have been described previously.[2] The following compounds were prepared and/or characterized according to literature procedures: Me_2PH,[10] Me_2AsH,[11] $(CF_3)_2PH$,[12] CF_3PH_2,[4] Ph_2PH,[13] Me_3P,[14] Me_2PPMe_2,[15] $Me_2AsAsMe_2$,[16] Ph_2PPPh_2,[17] $Me_2PP(CF_3)H$,[2] $Et_2PP(CF_3)H$,[2] $Me_2AsP(CF_3)H$,[2] CF_3-

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$(H)PP(H)CF_3$,[18] $(CF_3P)_{4,5}$,[19] $(MeP)_5$,[20] $Me_2PP(CF_3)PMe_2$,[2] $Et_2PP(CF_3)PEt_2$,[2] and $Me_2AsP(CF_3)AsMe_2$.[2] The compound Ph(Me)PH was obtained commercially (Strem) and used without further purification.

Reaction of Me_2PH with $(CF_3P)_{4,5}$. To a thin-walled NMR tube containing ca. 0.15 mL of benzene-d_6 were added $(CF_3P)_{4,5}$ (1.71 mmol, 0.181 g) and Me_2PH (1.55 mmol, 0.096 g). Upon warming to room temperature, the solution developed a slight yellow color, which persisted for about 1 h. Initially many unidentified resonances centered at −60 ppm were found in the $^{31}P[^1H]$ NMR spectrum. After about 1 h, a considerable amount of $Me_2PP(CF_3)H$ was observed spectroscopically. The reaction proceeded to equilibrium after several days at 23 °C. The following compounds were observed in solution via ^{31}P and ^{19}F NMR spectral analysis: $(CF_3P)_{4,5}$, CF_3PH_2, $Me_2PP(CF_3)H$, $CF_3(H)PP(H)CF_3$, $Me_2PP(CF_3)PMe_2$, and two new compounds, which were identified as $Me_2PP(CF_3)P(CF_3)PMe_2$ and $Me_2PP(CF_3)P(CF_3)H$. Both of the latter compounds exhibit complex second-order ^{31}P and ^{19}F NMR patterns.[21] Neither of these compounds could be isolated by using vacuum-line techniques due to the similar volatility of these products and $(CF_3P)_{4,5}$. Structural assignments were arrived at by analysis of NMR spectra and by numerous experiments, which are described below. Fractional distillation of the products on the vacuum line afforded the following separation: −196 °C trap contents, benzene-d_6 CF_3PH_2, $Me_2PP(CF_3)H$, $CF_3(H)PP(H)CF_3$; −63 °C trap contents, benzene-d_6 $Me_2PP(CF_3)H$, $Me_2PP(CF_3)P(CF_3)H$; −37 °C trap contents, $(CF_3P)_{4,5}$, $Me_2PP(CF_3)P(CF_3)H$, $Me_2PP(CF_3)P(CF_3)PMe_2$.

Reaction of $Me_2PP(CF_3)H$ with $CF_3(H)PP(H)CF_3$. The contents of the −196 °C trap from the previous reaction was distilled through a −126 °C trap to remove CF_3PH_2, leaving a solution of the reactants in benzene-d_6. While the quantity of each reactant could not be determined exactly, the concentrations were judged essentially equal via NMR spectroscopy. After the reaction was allowed to proceed in an NMR tube for 1 week at 23 °C, the products of the reaction were observed to be CF_3PH_2 and $Me_2PP(CF_3)P(CF_3)H$. After 2 weeks, no change was seen in the spectra. Thus, the reaction attained equilibrium in less than 1 week.

Reaction of $CF_3(H)PP(H)CF_3$ with Me_2PPMe_2. To an NMR tube containing ca. 0.15 mL of benzene-d_6 were added $CF_3(H)PP(H)CF_3$ (0.13 mmol, 0.026 g) and an excess of Me_2PPMe_2 (0.56 mmol, 0.068 g). The NMR tube was sealed and allowed to warm to room temperature, at which point no obvious reaction occurred. Immediate ^{19}F NMR spectral analysis showed that the reaction proceeded at a rate appropriate for observation at room temperature. The first product observed was the triphosphine $Me_2PP(CF_3)P(CF_3)H$. The second product, $Me_2PP(CF_3)PMe_2$, was formed concurrently with the third product $Me_2PP(CF_3)H$. After several days only CF_3PH_2, $Me_2PP(CF_3)H$, and $Me_2PP(CF_3)PMe_2$ were seen in the ^{19}F NMR spectrum. ^{31}P NMR spectral analysis revealed the presence of both Me_2PPMe_2 and Me_2PH.

Reaction of Me_2PH with $Me_2PP(CF_3)H$. To an NMR tube containing ca. 0.15 mL of benzene-d_6 were added Me_2PH (0.59 mmol, 0.036 g) and $Me_2PP(CF_3)H$ (0.23 mmol, 0.037 g). The tube was flame-sealed and allowed to warm to room temperature, at which point no obvious reaction occurred. Daily ^{31}P NMR analysis showed the formation of Me_2PPMe_2 and CF_3PH_2 at the expense of the reactants. Equilibrium was established after ca. 7 days at 23 °C.

Reaction of CF_3PH_2 with Me_2PPMe_2. To an NMR tube containing ca. 0.15 mL of benzene-d_6 were added CF_3PH_2 (1.1 mmol, 0.11 g) and Me_2PPMe_2 (0.18 mmol, 0.011 g). The tube was flame-sealed and allowed to warm to room temperature, at which point no obvious reaction occurred. Immediate ^{31}P NMR spectral analysis confirmed the presence of Me_2PH. After several hours at 23 °C, $Me_2PP(CF_3)H$ was observed. After 2 weeks, the reaction was found to be at equilibrium.

Action of Heat on $Me_2PP(CF_3)H$. To an NMR tube containing ca. 0.15 mL of benzene-d_6 was added $Me_2PP(CF_3)H$ (0.25 mmol, 0.039 g). After 24 h at 60 °C about half of the starting material had been consumed to give CF_3PH_2 and $Me_2PP(CF_3)PMe_2$. After 48 h at 60 °C, the following compounds were observed spectroscopically: CF_3PH_2, Me_2PH, $Me_2PP(CF_3)H$, $(CF_3P)_{4,5}$, and $Me_2PP(CF_3)PMe_2$. NMR analysis after 80 h at 60 °C showed no change in product distribution, and the system was assumed to be at equilibrium after 40 h of heating.

Action of Heat on $Et_2PP(CF_3)H$. A spectroscopically pure sample of $Et_2PP(CF_3)H$ obtained from the tripnicogen,[2] which contained benzene-d_6, was sealed in the NMR tube. It was necessary to heat this diphosphine to 100 °C for 24 h to reach equilibrium, where the products were again CF_3PH_2 and the tripnicogen $Et_2PP(CF_3)PEt_2$. Further heating caused no change.

Reaction of $Me_2PP(CF_3)H$ with $(CF_3P)_{4,5}$. To an NMR tube containing ca. 0.15 mL of benzene-d_6 were added $(CF_3P)_{4,5}$ (0.50 mmol, 0.050 g) and $Me_2PP(CF_3)H$ (0.44 mmol, 0.071 g). The tube was sealed, and when it was warmed to room temperature, the resulting solution yellowed for a few moments and then lost its color. After 24 h at 23 °C, NMR analysis showed that CF_3PH_2, $Me_2PP(CF_3)H$, $Me_2PP(CF_3)PMe_2$, and $Me_2PP(CF_3)P(CF_3)H$ were present. After 4 days at 23 °C, no change was seen in the spectrum.

Reaction of $Me_2PP(CF_3)PMe_2$ with $(CF_3P)_{4,5}$. To an NMR tube containing ca. 0.15 mL of benzene-d_6 and $Me_2PP(CF_3)PMe_2$ (0.62 mmol, 0.14 g) was added, on the vacuum line, $(CF_3P)_{4,5}$ (0.63 mmol, 0.063 g). The tube was flame-sealed and allowed to warm to room temperature. Near 0 °C, the solution yellowed and remained yellow for about 10 min and then turned colorless. ^{31}P and ^{19}F NMR analysis showed the following compounds in the solution: $(CF_3P)_{4,5}$, $Me_2PP(CF_3)PMe_2$, and $Me_2PP(CF_3)P(CF_3)PMe_2$. Spectra acquired several days later showed no change in product distribution, and the system was assumed to be at equilibrium.

Reaction of Ph(Me)PH with $(CF_3P)_{4,5}$. In the glovebox, Ph(Me)PH (0.54 mmol, 0.066 g) was syringed into an NMR tube, which was placed on the vacuum line. Solvent and $(CF_3P)_{4,5}$ (0.5 mmol, 0.050 g) were distilled into the tube, which was then flame-sealed. As the tube warmed to room temperature, a slight yellow color developed, which persisted for about 24 h. Immediate ^{19}F NMR spectral analysis showed that the first two products were $CF_3(H)PP(H)CF_3$ and $Ph(Me)PP(CF_3)H$. Slowly, the additional compounds $Ph(Me)PP(CF_3)P(CF_3)H$,[21] $Ph(Me)PP(CF_3)P(Me)Ph$,[21] and CF_3PH_2 formed. ^{31}P NMR analysis showed that some Ph(Me)PH was still present, and two resonances occurred at the expected chemical shift (by interpolation between Ph_2PPPh_2 and Me_2PPMe_2) for the two isomers of Ph(Me)PP(Me)Ph.[21] NMR data for the diphosphine $Ph(Me)PP(CF_3)H$ is given in Figure 6.

Reaction of Ph_2PH with $(CF_3P)_{4,5}$. In a glovebox, Ph_2PH (0.63 mmol, 0.12 g) was syringed into an NMR tube and then attached to the vacuum line and degassed. Next, ca. 0.2 mL of benzene-d_6 and $(CF_3P)_{4,5}$ (1.46 mmol, 0.146 g) were vacuum transferred into the tube. As the solution reached room temperature, the characteristic yellow tint of analogous reactions was not observed; ^{31}P NMR indicated only reactants in the solution. Within a few days, ^{31}P and ^{19}F NMR revealed the reaction progressing, although at a rate considerably slower than that observed for secondary alkylphosphines with $(CF_3P)_{4,5}$. The first products observed spectroscopically were $Ph_2PP(CF_3)H$ and $CF_3(H)PP(H)CF_3$. After several days of heating at 50 °C, spectroscopy revealed the reaction had reached equilibrium and the additional compounds CF_3PH_2 and Ph_2PPPh_2 were identified. NMR data for the new compound $Ph_2PP(CF_3)H$: $\delta(^{31}P(P\text{-}H)) = -54.5$; $\delta(^{31}P(PPh_2)) = -31.8$; $\delta(^{19}F) = -44.6$; $^2J_{PP} = 168.0$, $^2J_{PF} = 44.2$, $^3J_{PF} = 14.0$, $^1J_{PH} = 207.2$. NMR spectra are slightly second order, so chemical shifts and coupling constants are approximate.

Reaction of Me_2AsH with $(CF_3P)_{4,5}$. On a Teflon-stopcock high-vacuum line, $(CF_3P)_{4,5}$ (1.68 mmol, 0.16 g) was transferred into an NMR tube followed by the addition of an equimolar quantity of Me_2AsH (1.1 mmol, 0.18 g). The two reactants, either with or without benzene-d_6 solvent, were warmed to room temperature, and after about 10 min, the solution developed a slight yellow color indicative of reaction. The progress of the reaction was followed by observation of ^{31}P and ^{19}F NMR spectra, and the following compounds were detected in solution: CF_3PH_2, $Me_2AsAsMe_2$, $CF_3(H)PP(H)CF_3$, $Me_2AsP(CF_3)H$, and $Me_2AsP(CF_3)AsMe_2$. After several hours were allowed for the reaction equilibrium, the mixture was separated into the following components by fractional distillation on the vacuum line: −196 °C trap contents, CF_3PH_2; −84 °C trap contents, $Me_2AsP(CF_3)H$; −45 °C trap contents, $Me_2AsAsMe_2$; −15 °C trap contents, $Me_2AsP(CF_3)AsMe_2$. The lower thermal stability and apparent decomposition by stopcock grease made isolation of $Me_2AsP(CF_3)H$ much more difficult than the congeneric phosphorus compound $Me_2PP(CF_3)H$. Significant decomposition of the arsinophosphine $Me_2AsP(CF_3)H$ over several hours at room temperature led to the appearance of peaks corresponding to CF_3PH_2 and $Me_2AsP(CF_3)AsMe_2$ in the ^{31}P and ^{19}F NMR spectra.

Reaction of $Me_2AsAsMe_2$ with CF_3PH_2. To an NMR tube containing ca. 0.2 mL of benzene-d_6 were added CF_3PH_2 (1.6 mmol, 0.16 g) and

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[21] Reporting of chemical shifts, coupling constants, and peak multiplicities for compounds with very complex spin systems and several NMR observable isomers is impractical, particularly when several compounds are present in the reaction mixture. The gross spectral appearance and position are predicatable by analogy with simpler compounds such as those reported in this paper and ref 2.

$Me_2AsAsMe_2$ (0.74 mmol, 0.16 g), and the tube was flame-sealed. When the tube was warmed to room temperature, ^{31}P NMR analysis revealed CF_3PH_2 as the only phosphorus species in solution. After the tube was heated at 70 °C for 1 month, ^{31}P and ^{19}F NMR analysis revealed the presence of $Me_2AsP(CF_3)H$. After 2 more weeks, observation by ^{31}P NMR showed no further product formation and the position of equilibrium to be far toward the reactants.

Reaction of $(CF_3)_2PH$ with $(MeP)_5$. In a glovebox, an NMR tube was charged with $(MeP)_5$ (1.3 mmol, 0.61 g) and then attached to the vacuum line and degassed. Solvent (0.2 mL of benzene-d_6) and $(CF_3)_2PH$ (0.65 mmol, 0.11 g) were then transferred into the tube and flame-sealed. When the tube was warmed to room temperature, the initially biphasic solution became homogeneous, but there was no reaction as monitored by ^{31}P NMR spectroscopy. After 24 h, spectroscopic analysis revealed the formation of a small amount of $(CF_3)_2PP(Me)H$, which increased only slightly in concentration over the next several days. The sample was then heated at 60 °C for several days after which ^{31}P and ^{19}F NMR analysis indicated less than 50% conversion of the product $(CF_3)_2PP(Me)H$. NMR parameters for the compound $(CF_3)_2PP(Me)H$: $\delta(^{31}P(P\text{-}H)) = +2.5$; $\delta(^{31}P(P\text{-}CF_3)) = -120.6$; $\delta(^{19}F) = -48.9$; $^1J_{PP} = 230.5$, $^1J_{PH} = 205.1$, $^2J_{PF} = 65.5$, $^2J_{PH} = 5.9$.

Conclusions

A secondary phosphine or arsine will react quickly with $(CF_3P)_{4,5}$ to produce chiral dipnicogens to the type $R_2EP(CF_3)H$ (E = P or As). The dipnicogens are quite stable when isolated but undergo further reaction with either reactants or other products via a four-centered intermediate to produce a complex equilibrium system. The reaction to produce the chiral dipnicogens appears to be general, requiring only that one of the reactants contains relatively acidic phosphorus atoms (by having pendant CF_3 groups); thus $(CF_3)_2PH$ reacts with $(MeP)_5$ to yield $(CF_3)_2PP(Me)H$. The use of these dipnicogens as ligands is under investigation.

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Registry No. $(CF_3P)_4$, 393-02-2; Me_2PH, 676-59-5; $Me_2PP(CF_3)H$, 117583-73-0; CF_3PH_2, 420-52-0; $CF_3(H)PP(H)CF_3$, 462-57-7; $Me_2PP(CF_3)PMe_2$, 19307-60-9; $Me_2PP(CF_3)P(CF_3)PMe_2$, 117583-74-1; $Me_2PP(CF_3)P(CF_3)H$, 117583-75-2; Me_2PPMe_2, 3676-91-3; $Et_2PP(CF_3)H$, 117583-76-3; $Ph(Me)PH$, 6372-48-1; $Ph(Me)PP(CF_3)H$, 117583-77-4; $Ph(Me)PP(CF_3)P(CF_3)H$, 117583-78-5; $Ph(Me)PP(CF_3)P(Me)Ph$, 117583-79-6; $Ph(Me)PP(Me)Ph$, 3676-96-8; Ph_2PH, 829-85-6; $Ph_2PP(CF_3)H$, 117583-80-9; Ph_2PPPh_2, 1101-41-3; Me_2AsH, 593-57-7; $Me_2AsAsMe_2$, 471-35-2; $Me_2AsP(CF_3)H$, 117583-81-0; $Me_2AsP(CF_3)AsMe_2$, 24595-87-7; $(CF_3)_2PH$, 460-96-8; $(MeP)_5$, 1073-98-9; $(CF_3)_2PP(Me)H$, 1840-12-6; $Et_2PP(CF_3)PEt_2$, 117583-82-1; $(CF_3P)_5$, 745-23-3.

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Exchange Reactions of Tetrakis(trifluoromethyl)diphosphine with Pnicogen-Pnicogen, Phosphorus-Hydrogen, and Phosphorus-Chlorine Bonds

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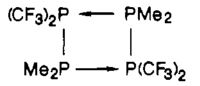
Tetrakis(trifluoromethyl)diphosphine, $(CF_3)_2PP(CF_3)_2$, reacts quantitatively with Me_2PPMe_2 via a four-centered intermediate to produce the unsymmetric diphosphine $(CF_3)_2PPMe_2$. There is no tendency for $(CF_3)_2PPMe_2$ to disproportionate to the reactant symmetric phosphines because of the stabilization provided by the large difference in relative basicities of the phosphorus atoms. In analogous exchange reactions, $(CF_3)_2PP(CF_3)_2$ mixed with $Me_2AsAsMe_2$, Me_2PNMe_2, and $(CF_3)_2AsAs(CF_3)_2$ produces the unsymmetric dipnicogens $(CF_3)_2PAsMe_2$, $(CF_3)_2PNMe_2$, and $(CF_3)_2PAs(CF_3)_2$, respectively, where the last compound is produced in an equilibrium exchange process. The reaction of the secondary diphosphine or arsinophosphine $Me_2EP(CF_3)H$, E = P or As, with $(CF_3)_2PP(CF_3)_2$ produces $Me_2EP(CF_3)_2$ in addition to $(CF_3)_2PP(CF_3)H$, which disproportionates to $(CF_3P)_{4,5}$ and $(CF_3)_2PH$. When a secondary phosphine reacts with $(CF_3)_2PP(CF_3)_2$, P–H bond exchange occurs; thus the reaction of $(CF_3)_2PP(CF_3)_2$ with Ph_2PH or $Ph(Me)PH$ yields $(CF_3)_2PPPh_2$ and $(CF_3)_2PP(Me)Ph$, respectively, in addition to $(CF_3)_2PH$. In a similar reaction with $H(Ph)P(CH_2)_3P(Ph)H$, the interesting tetraphosphine $(CF_3)_2P(Ph)P(CH_2)_3P(Ph)P(CF_3)_2$ is formed. Reaction of $(CF_3)_2PP(CF_3)_2$ with substituted phosphonous chlorides $RPCl_2$, R = Ph or NMe_2, involves P–Cl bond cleavage producing $(CF_3)_2PP(Cl)R$. However, reaction of $MePCl_2$ with $(CF_3)_2PP(CF_3)_2$ required photolysis to initiate; the products are the triphosphine $(CF_3)_2PP(Me)P(CF_3)_2$ and $(CF_3)_2PCl$.

Introduction

Unsymmetric diphosphines normally are subjected to disproportionation to form more symmetric species.[1]

$$2R_2PPR'_2 \rightarrow R_2PPR_2 + R'_2PPR'_2 \qquad (1)$$

The reverse reaction of eq 1, i.e., scrambling reactions to two symmetric diphosphines to yield unsymmetric diphosphines, is well-known,[1-4] however, these reactions rarely proceed to completion and frequently result in polymer formation instead of the desired unsymmetric diphosphine. The reactions are highly solvent dependent, and isolation of the unsymmetric diphosphine is usually not possible due to disproportionation. The exception to the above generalization is when the relative basicities of the two phosphorus atoms in a diphosphine greatly differ. For example, a diphosphine such as $(CF_3)_2PPMe_2$ has no tendency toward disproportionation.[5] Considerable evidence points toward a four-centered intermediate in diphosphine exchange reactions.[1,6,7] For a diphosphine such as $(CF_3)_2PPMe_2$, the relatively basic Me_2P phosphorus atom will always attack the relatively acidic $(CF_3)_2P$ phosphorus atom.



$$\begin{tikzcd} (CF_3)_2P \arrow[d, dash] & PMe_2 \arrow[l] \arrow[d, dash] \\ Me_2P \arrow[r] & P(CF_3)_2 \end{tikzcd} \qquad (2)$$

Such an exchange reaction is nonproductive, yielding only the initial reactants. When the relative basicities are similar, as when R and R′ are both alkyl groups, then more subtle thermodynamic effects, including solvent interactions, favor the symmetric species. If R is an alkyl group and R′ is an aryl group as in Ph_2PPMe_2,

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