ination of the unstable species:

$$5S_2NH_3 \rightleftarrows S_6^{2-} + S_4N^- + 3NH_4^+ + NH_3 \quad (15)$$

or

$$9S_2NH_3 \rightleftarrows 2S_6^{2-} + 2S_3N^- + 6NH_4^+ + NH_3 \quad (15')$$

These equilibria are complex but may be reached through a small number of simple steps. This model for the solubilization process takes into account the nonobservation of S_7N^-. It should be noted that the formation of S_4N^- from S_2N^- considered as intermediate species has already been suggested by Chivers et al.[17] The present model takes into account our observation that S_3N^- is the precursor species of S_4N^-. Consequently, it has been assumed that S_2N^- is the precursor species of S_3N^-.

Conclusion

The experimental results reported in the present paper give a new insight into the process of formation of chemical species in the solutions of sulfur in liquid ammonia and lead unambiguously to the description of the equilibrium state. A model is proposed for the reaction mechanism between c-S_8 and liquid ammonia, which also explains the formation process of sulfur-nitrogen species such as S_4N^- and S_3N^- in liquid ammonia. It must be noted that the heptasulfur imido anion S_7N^- is not involved in this mechanism. Two points are somewhat speculative: S_2NH_3 is the zerovalent sulfur species at equilibrium, but this species has already been suggested by other investigators; our analysis of the disproportionation constant supports this point. The other speculative point is that S_2N^- could be the precursor species of S_3N^-.

It is shown that the disproportionation of sulfur in ammonia leads to an equilibrium. The quantitative determination of the amount of solubilized sulfur that remains in the zero state of oxidation (S_{am}) is given.

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Some Perfluoroalkyl-Substituted Tripnicogens and Their Hydrolysis To Yield Chiral Dipnicogens[1]

Larry R. Avens,[†] Richard A. Wolcott, Leonard V. Cribbs, and Jerry L. Mills*

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The insertion of a perfluoroalkylphosphinidene moiety R_f from perfluoroalkylcyclopolyphosphines $(R_fP)_n$ into the pnicogen-pnicogen bond of tetraalkyldipnicogens appears to be general. Thus a CF_3P unit from $(CF_3P)_{4,5}$ reacts either with R_2PPR_2 (where R = Me, Et, Bu) or with $Me_2AsAsMe_2$ to form the tripnicogen compounds $R_2PP(CF_3)PR_2$ and $Me_2AsP(CF_3)AsMe_2$, respectively. Similarly $(C_2F_5P)_{3,4}$ reacts with Me_2PPMe_2 to form $Me_2PP(C_2F_5)PMe_2$. Any two symmetric tripnicogens, such as $Me_2PP(CF_3)PMe_2$ and $Et_2PP(CF_3)PEt_2$, undergo a scrambling reaction to form an equilibrium mixture containing the asymmetric tripnicogen. The tripnicogens undergo neutral water hydrolysis surprisingly easily to form chiral dipnicogens. For example, $Me_2PP(CF_3)PMe_2$ hydrolyzes immediately at ambient temperature with an equimolar quantity of water to yield the new chiral secondary phosphine $Me_2PP(CF_3)H$ plus $Me_2P(O)OH$ and Me_2PH. Similarly, hydrolysis of the appropriate tripnicogen yields the chiral dipnicogen secondary phosphines $Me_2PP(C_2F_5)H$, $Et_2PP(CF_3)H$, $Bu_2PP(CF_3)H$, and $Me_2AsP(CF_3)H$. A second equivalent of water hydrolyzes the dipnicogens to the primary perfluoroalkylphosphine. Possible reaction mechanisms are discussed together with NMR data.

Introduction

The RP moiety in a cyclopolyphosphine $(RP)_n$ is isoelectronic with sulfur. Burg synthesized the phosphinidene complex $Me_3P \rightarrow P(CF_3)$ from the reaction of Me_3P with $(CF_3P)_{4,5}$, analogous to the formation of $Me_3P{=}S$.[2] Cowley and Dierdorf observed that the reaction of Me_2PPMe_2 with $(CF_3P)_{4,5}$ yields neither the mono- nor the diphosphinidene complex, but rather the insertion product $Me_2PP(CF_3)PMe_2$.[3] We observed that the phosphorus-phosphorus bond in the triphosphine $Me_2PP(CF_3)PMe_2$ is surprisingly easily hydrolyzed by neutral water at ambient temperature to quantitatively yield the new chiral diphosphine $Me_2PP(CF_3)H$.[4] Because of the potentially interesting chemistry of this type of chiral diphosphine relative to addition to alkenes, alkynes, or metal-metal bonds, we have examined the generality of the insertion reaction of perfluoroalkylphosphinidenes and the subsequent hydrolysis to the tripnicogens to yield chiral dipnicogens. These chiral disphosphines may also be of interest because of the catalytic properties of chiral phosphines in asymmetric syntheses. Perfluoroalkyl-substituted polyphosphines are of current general interest.[5]

Results

Insertion of Perfluoroalkylphosphinidene into the Pnicogen-Pnicogen Bond of Diphosphines and Diarsines. As reported by Cowley and Dierdorf, the reaction of equimolar amounts[6] of tetramethyldiphosphine Me_2PPMe_2 with $(CF_3P)_{4,5}$ quantitatively

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(6) Equimolar quantities of $(R_fP)_n$ means equimolar quantities of R_fP units.

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Table I. NMR Parameters for Tripnicogens

		$\delta(^{31}P[^{1}H])$[b,c]		
compd	$\delta(^{19}F[^{1}H])$[a,c]	$P(R_f)$	PR_2	coupling const, Hz
$Me_2PP(CF_3)PMe_2$[d]	-41.6, d of t	-8.7, d of t	-57.7, d of m[f,g]	$^1J_{PP}$ = 242, $^2J_{PF}$ = 42 $^3J_{PF}$ = 7[i]
$Et_2PP(CF_3)PEt_2$[e]	-40.9, d of d of d[f,h]	ca. -30.0, m	ca. -30.0, m	
$Bu_2PP(CF_3)PBu_2$[d]	-42.9, d of d of d[f,h]	-25.2, d of q[f]	-42.3, d of d of q[f]	$^1J_{PP}$ = 293, $^2J_{PF}$ = 43, $^3J_{PF}$ = 4
$Me_2AsP(CF_3)AsMe_2$	-40.5, d	-11.7, q		$^2J_{PF}$ = 34.0[i]
$Me_2PP(C_2F_5)PMe_2$[e]	-102.5 (CF_2), d of d of q[f] -82.8 (CF_3), d of t of q[f]	-11.9, d of d of m[f]	-56.9, d of m[f]	$^1J_{PP}$ = 280, $^3J_{PF}$ = 41, $^3J_{FF}$ = 12 $^4J_{PF}$ = 3
$Me_2PP(CF_3)PEt_2$[e]	-42.1, d of m	-19.4, d of q	-32.8 ($P'Et_2$), d of q -62.2 (PMe_2), d of q	$^1J_{P'P}$ = 222, $^2J_{PF}$ = 41 $^1J_{PP}$ = 210, $^3J_{PF}$ = 7, $^3J_{P'F}$ = 7
$Me_2PP(CF_3)PAs_2$	-41.2, d of d	-10.8, d of q	-60.5, d of q	$^1J_{PP}$ = 252, $^2J_{PF}$ = 38, $^3J_{PF}$ = 7
$(CF_3)_2PPMeP(CF_3)_2$	-47.7, d of m	-68.6 (PMe), t of m[f]	+4.0 (PR_f), d of m[f]	$^1J_{PP}$ = 260, $^2J_{PH}$ = 8

[a] Chemical shift relative to external $CFCl_3$. Negative values indicate upfield chemical shift. [b] Chemical shift relative to external 85% H_3PO_4. Negative values indicate upfield chemical shifts. [c] d = doublet, t = triplet, q = quartet, m = multiplet. [d] Chemical shifts and coupling constants accurate for second-order specta solved by computer simulation. [e] Chemical shifts and coupling constants approximate. Second-order spectra not completely solved. [f] Approximate appearance of resonance. [g] Figure 1. [h] Figure 2. [i] This work; compare to ref 3a.

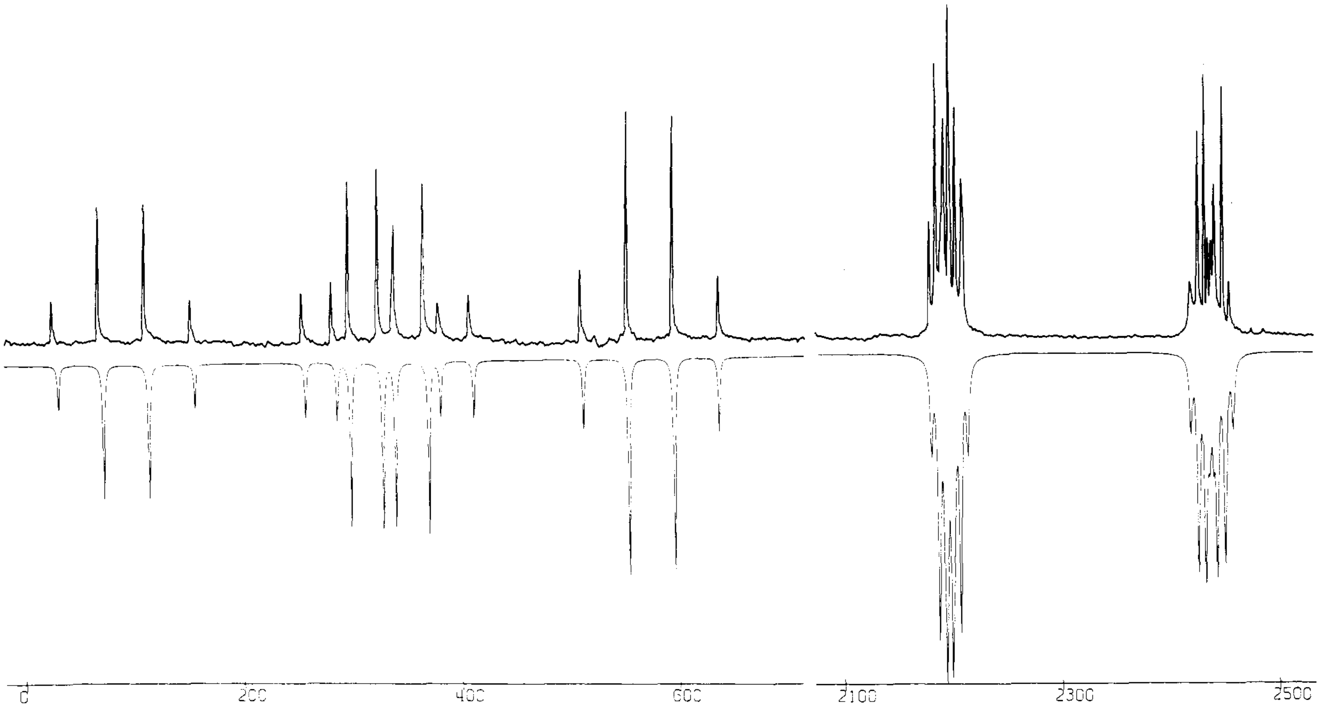

Figure 1. $^{31}P[^{1}H]$ spectrum of $Me_2PP(CF_3)PMe_2$: experimental spectrum above; computer-simulated spectrum below. Shifts are given in Hz upfield from 85% H_3PO_4. See Table I for data.

produces the triphosphine $Me_2PP(CF_3)PMe_2$. NMR data are tabulated in Table I. The ^{31}P data have not been previously reported. While the ^{19}F and ^{1}H spectra are consistent with a first-order interpretation, the $^{31}P[^{1}H]$ spectrum is distinctly second order, as expected for an AB_2X_3 spin system where $[(\delta(A) - \delta(B)]/J_{AB} = 0.12$. The second-order effects result in the phosphorus spectrum appearing as in Figure 1, rather than as a doublet of quartets (Me_2P phosphorus) and a triplet of quartets (CF_3P phosphorus), as would be the case for a completely first-order spectrum. Little spectral change occurs from -40 to +200 °C, except for some broadening of resonances and slight decomposition.

In an analogous fashion, reaction of equimolar quantities[6] of $(CF_3P)_{4,5}$ with either Et_2PPEt_2 or Bu_2PPBu_2 produces $Et_2PP(CF_3)PEt_2$ and $Bu_2PP(CF_3)PBu_2$, respectively. Both compounds exhibit $^{31}P[^{1}H]$ spectral patterns of an AB_2 portion of an AB_2X_3 spin system that are more second order than in $Me_2PP(CF_3)PMe_2$ (Table I). For $Et_2PP(CF_3)PEt_2$, the chemical shift of the two types of phosphorus atoms are so similar that the exact spectral parameters are not easily attainable without simultaneously decoupling both proton and fluorine atoms. The second-order effects are also manifest in the ^{19}F NMR spectrum (X_3 portion), where the appearance is more that of two sets of doublets of doublets for $Bu_2PP(CF_3)PBu_2$, rather than a first order doublet of triplets (Figure 2) as expected from the phosphorus spectrum; the fluorine spectrum of $Et_2PP(CF_3)PEt_2$ is even more complex.

The perfluoroethylcyclopolyphosphine $(C_2F_5P)_{3,4}$ also serves as a perfluoroalkylphosphinidene source.[7] The reaction of $(C_2F_5P)_{3,4}$ with Me_2PPMe_2 produces $Me_2PPC_2F_5PMe_2$ essentially quantitatively. Chemical shifts, coupling constants, and spectral multiplicity for ^{31}P proton-decoupled and ^{19}F proton-decoupled spectra are consistent with an $AB_2M_2X_3$ spin system (Table I) and the proposed structures.

As previously reported,[3a] $(CF_3P)_{4,5}$ also reacts with $Me_2AsAsMe_2$ to produce the tripnictide compound $Me_2AsP(CF_3)AsMe_2$. Spectral data are presented in Table I.

An alkylcyclopolyphosphine can provide a source for an alkylphosphinidene. Tetrakis(trifluoromethyl)diphosphine $(CF_3)_2PP(CF_3)_2$ reacts slowly with pentamethylcyclopentaphosphine $(MeP)_5$ to yield the tripnictide $(CF_3)_2PPMeP(CF_3)_2$. The compound $(CF_3)P_2PMeP(CF_3)_2$ has been made by a different method,[8] but no NMR data were reported (Table I). The $^{31}P[^{19}F]$ spectrum again is an AB_2X_3 spin system, but is only slightly second order, while the $^{19}F[^{1}H]$ spectrum is quite second order consisting of only

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Table II. NMR Parameters for Dipnicogens

compd	$\delta(^{19}F[^1H])^{a,c}$	$\delta(^{31}P[^1H])^{b,c}$ $P(R_f)H$	$\delta(^{31}P[^1H])^{b,c}$ PR_2	coupling const, Hz
$Me_2PP(CF_3)H^{d,e}$	−43.7, d of d	−57.1, d of q	−68.5, d of q	$^1J_{PP}$ = 198, $^2J_{PH}$ = 11, $^2J_{PF}$ = 45 $^1J_{PH}$ = 200, $^3J_{PF}$ = 11, $^3J_{PF}$ = 12
$Me_2PP(C_2F_5)H^f$	−83.6 (CF_3), m −101.4 (CF_2), m	−70.8, d of m	−56.5, d of d of m	$^1J_{PH}$ ≅ 180, $^1J_{PP}$ ≅ 180, $^2J_{PF}$ ≅ 55, $^3J_{PF}$ ≅25, $^3J_{FF}$ ≅ 3.0
$Et_2PP(CF_3)H^d$	−43.6, d of d	−65.5, d of q	−35.5, d of q	$^1J_{PP}$ = 210, $^1J_{PH}$ = 209, $^2J_{PF}$ = 46, $^3J_{PF}$ = 10, $^3J_{FH}$ = 11
$Bu_2PP(CF_3)H^d$	−43.3, d of d	−62.6, d of q	−44.3, d of q	$^1J_{PP}$ = 209, $^1J_{PH}$ = 201, $^2J_{PF}$ = 46, $^2J_{PH}$ = 11, $^3J_{PF}$ = 11
$Me_2AsP(CF_3)H$	−42.0, d	−58.6, q		$^1J_{PH}$ = 194, $^2J_{PF}$ = 40, $^3J_{FH}$ = 12

[a] Chemical shift relative to external $CFCl_3$. Negative values indicate upfield chemical shift. [b] Chemical shift relative to external 85% H_3PO_4. Negative values indicate upfield chemical shifts. [c] d = doublet, t = triplet, q = quartet, m = multiplet. [d] Spectra slightly second order. Appearance approximates first order. [e] Proton chemical shift data: CH_3's = δ 1.38, m; P–H = δ 3.8,, d of d of q. [f] Since [^{1}H] NMR spectra are for an ABM_2X_3 spin system, the coupling constants, chemical shifts, and description of spectral appearance are approximate.

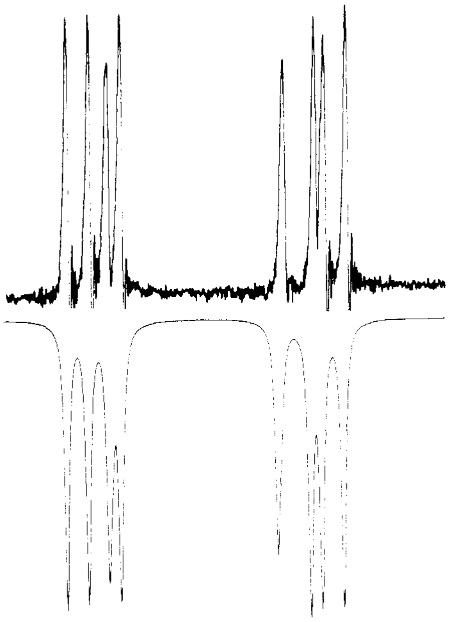

Figure 2. $^{19}F[^1H]$ spectrum of $Bu_2PP(CF_3)PBu_2$: experimental spectrum above; computer-simulated spectrum below. See Table I for data.

two broad featureless resonances. No reaction is observed between $(MeP)_5$ and Me_2PPMe_2.

If Me_2PPMe_2, Et_2PPEt_2, and $(CF_3P)_{4,5}$ are mixed in a 1:1:2 mole ratio, respectively, then three compounds are produced: $Me_2PP(CF_3)PMe_2$, $Et_2PP(CF_3)PEt_2$, and $Me_2PP(CF_3)PEt_2$. The mixed triphosphine, as expected, exhibits very complex $ABCX_3$ $^{31}P[^1H]$ and $^{19}F[^1H]$ NMR spectra, which overlap with the spectra of the two symmetric triphosphines. Trends in chemical shifts and general spectral appearance support the proposed structure, as does a scrambling experiment. Thus, if equimolar quantities of $Et_2PP(CF_3)PEt_2$ and $Me_2PP(CF_3)PMe_2$ are mixed in benzene solvent, within a few minutes at ambient temperature the mixed triphosphine $Me_2PP(CF_3)PEt_2$ is produced, yielding spectra essentially identical with those mentioned above. Similarly, if $Me_2PP(CF_3)PMe_2$ and $Me_2AsP(CF_3)AsMe_2$ are mixed in benzene solvent, the metathesized tripnictide $Me_2PP(CF_3)AsMe_2$ is formed rapidly.

In a cursory experiment[9] equimolar quantities of $Me_2PP(CF_3)PMe_2$ were mixed with $(CF_3)_2PPMeP(CF_3)_2$. The diphosphine $Me_2PP(CF_3)_2$ is formed, together with a compound tentatively identified as the tetraphosphine $Me_2PP(CF_3)PMeP(CF_3)_2$ (see Discussion).

In most of the reactions above, the stoichiometry is important. For example, an excess of the perfluoroalkylcyclopolyphosphine $(R_fP)_n$, the phosphinidene source, leads to additional compounds, as observed by ^{31}P and ^{19}F NMR spectroscopy.[10] These compounds presumably arise from the tripnictide reaction with $(R_fP)_n$ to form higher linear polyphosphines. In general, reactivity and reaction rates of the tripnicogens can be approximately correlated with steric bulk. Thus, the reaction of $Bu_2PP(CF_3)PBu_2$ with an excess $(CF_3P)_{4,5}$ occurs very slowly, while reaction of $Me_2PP(CF_3)PMe_2$ with $(CF_3P)_{4,5}$ occurs rapidly and to an appreciable extent in benzene solvent. The solvents must also be scrupulously dry or hydrolysis will occur very rapidly. The progress of the reactions is highly dependent on whether or not a solvent is used.

While some of the above insertion reactions can be carried out neat, others yield polymers without solvent. Thus, as originally reported by Cowley,[3] $(CF_3P)_{4,5}$ reacts cleanly with either Me_2PPMe_2 or $Me_2AsAsMe_2$ without solvent. However, we observe that most of our reactions involving other diphosphines rapidly produce a black, viscous polymer if the reactions are performed neat. The rate of reaction of the dipnicogens with $(R_fP)_n$ phosphinidene source to produce the tripnicogens are roughly related to steric bulk. The reaction of $(CF_3P)_{4,5}$ with Me_2PPMe_2 is complete within several minutes at room temperature, while reaction with Bu_2PPBu_2 requires about a day to reach completion. Arsenic compounds react more slowly than analogous phosphorus compounds, as do perfluoroethyl derivatives relative to perfluoromethyl compounds. During reaction, the solutions are yellow, possibly indicating free radicals. Numerous attempts to find ESR signals, either at ambient or liquid-nitrogen temperature, were unsuccessful, however.

Synthesis of Chiral Dipnicogens from Hydrolysis of Tripnicogens. If equimolar amounts of $Me_2PP(CF_3)PMe_2$ and water are allowed to react, the chiral diphosphine $Me_2PP(CF_3)H$, $Me_2P(O)OH$, and Me_2PH are formed quantitatively. The chiral diphosphine is a clear liquid that is soluble in organic solvents, has a vapor pressure of 19 Torr at 25 °C, and exhibits $^{31}P[^1H]$ and $^{19}F[^1H]$ NMR spectra consistent with an ABX_3 spin system (Table II). The diphosphine $Me_2PP(CF_3)H$ can be additionally characterized by its gas-phase molecular weight, the P–H stretching frequency at 2295 cm^{-1} in the IR spectrum, and the complex ^1H NMR spectrum showing P–H coupling of approximately 200 Hz of relative intensity of 1 compared to the six methyl protons. The pure diphosphine is stable for weeks at room temperature, showing almost no evidence of disproportionation. The other hydrolysis product, $Me_2P(O)H$, disproportionates (as monitored by ^1H and ^{31}P NMR spectroscopy) to form $Me_2P(O)OH$ and Me_2PH, the rate being dependent on solvent and whether the volatile Me_2PH is removed.[11] The stoichiometry for the reaction is important. Too much water results in further hydrolysis of the diphosphine.

The triphosphines $Et_2PP(CF_3)PEt_2$, $Bu_2PP(CF_3)PBu_2$, and $Me_2PP(C_2F_5)PMe_2$ all are hydrolyzed by equimolar amounts of water to form the chiral diphosphines $Et_2PP(CF_3)H$, $Bu_2PP(CF_3)H$, and $Me_2PP(C_2F_5)H$, respectively. The rate of hydrolysis is dependent on the steric bulk of the triphosphine, as well as whether or not the hydrolysis is carried out in solution or by simply

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(9) Unpublished results.

(10) See: Avens, L. R.; Gribbs, L.; Mills, J. L. *Inorg. Chem.*, following paper in this issue.

(11) Trenkle, A.; Vahrenkamp, H. *Z. Naturforsch.* **1979**, *34B*, 642.

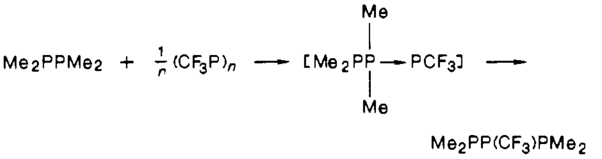
adding water to neat triphosphine. Addition of water to the neat triphosphine forms two layers, slowing the reaction rate. The chiral diphosphines $\mathrm{Et_2PP(CF_3)H}$, $\mathrm{Bu_2PP(CF_3)H}$, and $\mathrm{Me_2PP(C_2F_5)H}$ are characterized by NMR spectral parameters (Table II).

The diarsinophosphine $\mathrm{Me_2AsP(CF_3)AsMe_2}$ also undergoes facile hydrolysis by neutral water to yield the chiral arsinophosphine $\mathrm{Me_2AsP(CF_3)H}$, as well as $\mathrm{Me_2AsH}$ and $\mathrm{Me_2As(O)OH}$. The chiral arsinophosphine is characterized by its gas-phase molecular weight (vapor pressure 13.4 Torr at 22 °C) and by the P–H stretching frequency in the IR region at 2305 $\mathrm{cm^{-1}}$. The NMR data (Table II) are consistent with the assigned structure. The methyl protons are anisochronous because of the chiral phosphorus atom. Thus the $^1\mathrm{H}[^{19}\mathrm{F}]$ spectrum in the methyl region consists of two doublets, one doublet (from phosphorus coupling) for each set of methyl protons. The anisochronicity is confirmed by observing ^{1}H NMR spectra at both 60 and 100 MHz and is also apparent in the ^{31}P NMR spectrum. The methyl groups on any one arsenic atom in $\mathrm{Me_2AsP(CF_3)AsMe_2}$ are similarly anisochronous.[3a] (Obviously, several other compounds such as $\mathrm{Me_2PP(CF_3)H}$ contain diastereotopic groups. Only in the compounds with the simplest spin systems is it possible to directly observe anisochronicity.) The arsinophosphine $\mathrm{Me_2AsP(CF_3)H}$ is considerably less thermodynamically stable than is the congeneric diphosphine $\mathrm{Me_2PP(CF_3)H}$. In 1 day at ambient temperature the neat arsinophosphine undergoes significant decomposition, the extent of decomposition being dependent on initial compound purity and exposure to apparent catalysts such as stopcock grease.

Hydrolysis of Chiral Dipnicogens. The diphosphine $\mathrm{Me_2PP(CF_3)H}$ is quantitatively hydrolyzed over several minutes at room temperature by neutral water to form $\mathrm{CF_3PH_2}$, $\mathrm{Me_2PH}$, and $\mathrm{Me_2P(O)OH}$ in a ratio of 2:1:1. (An excess of water seems to prolong the disproportionation of $\mathrm{Me_2P(O)H}$ to $\mathrm{Me_2PH}$ and $\mathrm{Me_2P(O)OH}$.) The hydrolysis occurs more slowly than the hydrolysis of the parent triphosphine. Hydrolysis of the other chiral diphosphines and the chiral arsinophosphine proceeds in an analogous manner.

Discussion

As shown by Cowley and Dierdorf, the reaction of tetramethyldiphosphine with either $\mathrm{(CF_3P)_4}$ or $\mathrm{(CF_3P)_5}$ forms the triphosphine $\mathrm{Me_2PP(CF_3)PMe_2}$.[3] This reaction might proceed through the initial formation of a phosphinidene adduct:



$$\mathrm{Me_2PPMe_2} + \frac{1}{n}(\mathrm{CF_3P})_n \longrightarrow [\mathrm{Me_2P}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{P}}}\rightarrow\mathrm{PCF_3}] \longrightarrow \mathrm{Me_2PP(CF_3)PMe_2} \qquad (1)$$

followed by rapid rearrangement to the triphosphine. The phosphinidene adduct is similar to the well-known $\mathrm{Me_3P{\rightarrow}PCF_3}$.[2] We find that the *apparent* insertion of a (perfluoroalkyl)phosphinidene into a dipnictide bond of tetraalkyldipnictides is general: thus

$$\mathrm{R_2PPR_2} + (1/n)(\mathrm{CF_3P})_n \rightarrow \mathrm{R_2PP(CF_3)PR_2}$$

$$\mathrm{R = Me,\ Et,\ Bu}$$

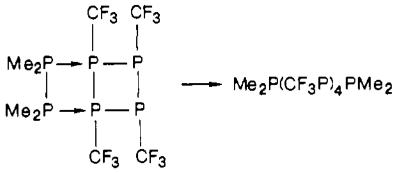
$$\mathrm{Me_2PPMe_2} + (1/n)(\mathrm{C_2F_5P})_n \rightarrow \mathrm{Me_2PP(C_2F_5)PMe_2}$$

$$\mathrm{Me_2AsAsMe_2} + (1/n)(\mathrm{CF_3P})_n \rightarrow \mathrm{Me_2AsP(CF_3)AsMe_2}$$

The pure tripnictides are indefinitely stable when dissolved in benzene.

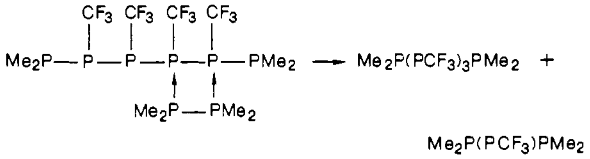
The reaction sequence proposed in eq 1 should yield free radicals resulting from the opened ring of the cyclopolyphosphine. Indeed, the solutions are colored during the reaction. We are unable to observe an ESR signal, however. Attempts to observe the proposed phosphinidene intermediate by monitoring the ^{31}P and ^{19}F NMR spectra during reaction at low temperature show no new resonances. In other related work, we observe that (perfluoroalkyl)phosphinidene phosphorus atoms in trialkylphosphine–phosphinidene complexes exhibit resonances at high field in ^{31}P NMR experiments (approximately −100 ppm).[12] Therefore any phosphinidene complex, as proposed in eq 1, must be very short-lived or nonexistent. The solution color might arise from conjugation of transient linear phosphorus chains (vide infra).

An alternate mechanism that explains (1) the observed tripnicogen product, (2) the stability of the tripnicogen, (3) the absence of an ESR signal during reaction, and (4) the results of scrambling experiments between tripnicogens (vide infra) is as follows. The initial step in the reaction sequence involves a four-centered intermediate formed by the nucleophilic attack by both phosphorus atoms in $\mathrm{Me_2PPMe_2}$ on the perfluoroalkylcyclopolyphosphine. For the specific example of the cyclotetraphosphine, the reaction is



(2)

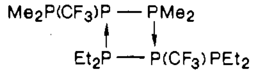
The linear six-phosphorus chain is subsequently attacked at the (perfluoroalkyl)phosphorus site by $\mathrm{Me_2PPMe_2}$:



(3)

Continued attack on the five-phosphorus chain will lead only to $\mathrm{Me_2P(PCF_3)PMe_2}$ (as long as the stoichiometry is one $\mathrm{PCF_3}$ unit per $\mathrm{Me_2PPMe_2}$ molecule), due to the basicity of $\mathrm{Me_2}P$ phosphorus atoms and the relative acidity of the $\mathrm{CF_3}P$ phosphorus atoms. Attack of $\mathrm{Me_2P(PCF_3)PMe_2}$ upon itself is nonproductive.

This type of mechanism is also consistent with a number of scrambling experiments. If two diphosphines ($\mathrm{Me_2PPMe_2}$ and $\mathrm{Et_2PPEt_2}$) are mixed with $\mathrm{(CF_3P)_{4,5}}$, the two symmetric triphosphines $\mathrm{Me_2P(PCF_3)PMe_2}$ and $\mathrm{Et_2P(PCF_3)PEt_2}$ are formed. Also formed is the mixed unsymmetric triphosphine $\mathrm{Me_2P(PCF_3)PEt_2}$, the presence of which can be explained by the reaction of the intermediate $\mathrm{Me_2P(PCF_3)_{\mathit{n}}PMe_2}$ with $\mathrm{Et_2PPEt_2}$, as in eq 3. In a separate experiment, we find that equimolar amounts of $\mathrm{Me_2P(PCF_3)PMe_2}$ and $\mathrm{Et_2P(PCF_3)PEt_2}$ mixed in benzene solvent at ambient temperature also immediately yield the asymmetric triphosphine $\mathrm{Me_2P(PCF_3)PEt_2}$, again probably via a four-centered intermediate, as originally proposed by Cowley[3a] and also supported by Krannich[13] in his studies of alkyldiarsine exchange reactions.



(4)

The ease of this exchange at ambient temperature is surprising in light of Cowley's scrambling reaction of $\mathrm{Me_2PP(CF_3)PMe_2}$ with either $\mathrm{Me_2NP(CF_3)NMe_2}$ or $\mathrm{Me_2AsP(CF_3)AsMe_2}$ in the absence of solvent, which required a temperature of 130 °C before reaction ensued.[3a] Modifying Cowley's experiment by using benzene solvent and mixing of $\mathrm{Me_2PP(CF_3)PMe_2}$ with $\mathrm{Me_2AsP(CF_3)AsMe_2}$ at ambient temperature immediately yields the mixed unsymmetric tripnicogen $\mathrm{Me_2AsP(CF_3)PMe_2}$. Thus both the rate of these polypnicogen reactions and the product stability are solvent dependent. Diphosphine exchange reactions are known to be greatly solvent dependent.[14] Four-centered intermediates also have been used to explain dipnicogen exchange reactions.[13,15] Such a

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(12) Unpublished results. Also see: Cowley, A. H.; Cushner, M. C. *Inorg. Chem.* **1980**, *19*, 515.

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mechanism is also consistent with the relative rates of reaction; that is, the larger the R groups on the diphosphines or diarsines and the larger the R_f group on $(R_fP)_n$, the slower is the rate of formation of the tripnicogens.

A four-centered intermediate with basic phosphorus atoms attacking acidic phosphorus atoms is also consistent with the reaction of $(CF_3)_2PP(CF_3)_2$ with $(MeP)_5$ to form $(CF_3)_2PPMeP(CF_3)_2$, as it is with the scrambling reaction between $(CF_3)_2PPMeP(CF_3)_2$ and $Me_2PP(CF_3)PMe_2$ to form $Me_2PP(CF_3)_2$ and $(CF_3)_2PPMeP(CF_3)PMe_2$.

Finally, perhaps the strongest evidence arguing in favor of a four-centered intermediate, as in eq 2, and against phosphinidene formation, as in eq 1, is the lack of reaction of the asymmetric diphosphine $(CF_3)_2PPMe_2$ with $(CF_3P)_{4,5}$. If phosphinidene formation were the operative mechanism, then the alkyl-substituted phosphorus atom of $(CF_3)_2PPMe_2$ should be sufficiently basic to produce $(CF_3)_2PPMe_2{\rightarrow}PCF_3$, which would be expected to rearrange to yield $(CF_3)_2PP(CF_3)PMe_2$. However, if nucleophilic attack by both phosphorus atoms of the diphosphine on the ring is required, as in the four-centered mechanism, then no reaction would be expected between $(CF_3)_2PPMe_2$ and $(CF_3P)_{4,5}$, since the perfluoroalkyl-substituted phosphorus atom is insufficiently basic. The lack of reaction between Me_2PPMe_2 and $(MeP)_5$ also strongly supports the four-centered mechanism.

The phosphorus–phosphorus bond is normally very resistant to hydrolysis by neutral water at ambient temperature.[16] However, the phosphorus–phosphorus bond in the triphosphines in this study (or the As–P bond in the case of $Me_2AsP(CF_3)AsMe_2$) undergoes facile and quantitative hydrolysis. Specifically in the case of $Me_2PP(CF_3)PMe_2$, neutral water hydrolysis occurs in a few seconds at room temperature (or somewhat longer with bulkier substituents) to yield the diphosphine $Me_2PP(CF_3)H$ and Me_2POH. The reactive intermediate Me_2POH forms $Me_2P(O)H$ and finally disproportionates to $Me_2PO(OH)$ and Me_2PH.[11]

$$R_2EP(R_f)ER_2 \rightarrow R_2EP(R_f)H + [R_2E(OH)] \qquad (5)$$

$$[R_2E(OH)] \rightarrow R_2E(O)H \qquad (6)$$

$$2R_2E(O)H \rightarrow R_2E(O)(OH) + R_2EH \qquad (7)$$

$$R = Me, Et, Bu;\ E = P;\ R_f = CF_3$$

$$R = Me;\ E = P;\ R_f = C_2F_5$$

$$R = Me;\ E = As;\ R_f = CF_3$$

Although nucleophilic attack by H_2O might be expected to be at the R_fP site, the observed products are as expected considering the hydrochlorination reaction of $Me_2PP(CF_3)_2$, where the presumably less basic phosphorus atom captures the proton to yield $HP(CF_3)_2$.[17] Similarly hydrochlorination of $Me_2PP(CF_3)PMe_2$ has been shown to yield Me_2PCl and H_2PCF_3.[3a]

Addition of a second equivalent of water to the diphosphines (or the arsinophosphine) produces quantitatively the (perfluoroalkyl)phosphine R_fPH_2.

$$R_2EP(R_f)H + H_2O \rightarrow R_fPH_2 + [R_2E(OH)] \qquad (8)$$

$$[R_2E(OH)] \rightarrow R_2E(O)H \qquad (9)$$

$$2R_2E(O)H \rightarrow R_2E(O)(OH) + R_2EH \qquad (10)$$

The hydrolysis rate of the tripnictides is much more rapid than that of the derivative dipnictides. Thus addition of 1 equiv of H_2O to, e.g., $Me_2PP(CF_3)PMe_2$, yields quantitatively $Me_2PP(CF_3)H$; CF_3PH_2 would be expected if hydrolysis rates of the tri- and dipnictides were comparable.

Experimental Section

Standard vacuum-line and inert-atmosphere techniques were used throughout the study.[18] Working vacuums were maintained at 10^{-3}–10^{-6} Torr. The argon-filled glovebox was kept free of water and oxygen by the use of a stirred sodium/potassium alloy. All solvents were scrupulously dried by using accepted literature methods. Nuclear magnetic resonance measurements were performed on a Varian Associates NMR spectrometer Model XL-100-15 operating at 100.1 MHz for ^1H, 40.5 MHz for ^{31}P, and 94.1 MHz for ^{19}F, respectively, or an EM-360 spectrometer. All NMR data are reported relative to the following external standards: ^1H, TMS; ^{31}P, 85% H_3PO_4; ^{19}F, $CFCl_3$. Positive values are downfield. Second-order NMR spectra were simulated by using NMREN, obtained from the Quantum Chemistry Exchange Program. Mass spectral data were obtained by using a Varian MAT-311 mass spectrometer operating at 20 eV, and IR spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer or on a Nicolet MS-X FT IR spectrometer. ESR spectra were recorded on a Varian E-109 spectrometer.

Chemicals. Tetraalkyldiphosphines were prepared by the desulfurization[19] of the tetraalkyldiphosphine disulfides (Alfa, Strem, or Pressure). The diphosphines Me_4P_2, Et_4P_2, and Bu_4P_2 were identified by vapor pressure and/or ^{31}P NMR spectral data.[20] The desulfurization with copper usually produces small quantities of the dialkylphosphine, which must be separated from the tetraalkyldiphosphine by vacuum distillation. Tetramethyldiarsine was produced by reduction of cacodylic acid $Me_2As(O)OH$ (Pfaultz and Bauer) with H_3PO_2[21] or by the coupling of Me_2AsH with dibenzylmercury[22] and was identified by boiling point and ^1H NMR spectra. The diphosphine $(CF_3)_2PP(CF_3)_2$[23] and the cyclopolyphosphines $(CF_3P)_{4,5}$,[24] $(C_2F_5P)_{3,4}$,[7] and $(MeP)_5$[7] were prepared and purified by literature procedures.

Reactions. Bis(dimethylphosphino)(trifluoromethyl)phosphine, $Me_2PP(CF_3)PMe_2$, was prepared by the vacuum-line reaction of $(CF_3P)_{4,5}$ with Me_4P_2. In a neat reaction 1.0 mmol equiv of Me_4P_2 was condensed into a reaction vessel equipped with a Teflon stopcock containing 1.0 mmol equiv of (CF_3P) units from $(CF_3P)_{4,5}$. The vessel was allowed to warm slowly to room temperature over a 12-h period. At that time, the volatile products were purified by trap-to-trap distillation through traps at −5, −45, and −196 °C. The product $Me_2PP(CF_3)PMe_2$ was held in the −5 °C trap, and unreacted tetramethyldiphosphine was caught in the −45 °C trap. Typical yields for this reaction were approximately 70% based on $(CF_3P)_{4,5}$. In an alternate procedure, 0.12 g (1.0 mmol) of Me_4P_2 was condensed into a medium-walled NMR tube together with 0.15 mL of benzene-d_6 and 0.10 g (1.0 mmol) of (CF_3P) units from $(CF_3P)_{4,5}$. As monitored by NMR spectroscopy, the reaction was essentially quantitative. The bis(dimethylphosphino)(trifluoromethyl)phosphine produced was identified by vapor pressure and ^1H, ^{19}F, and ^{31}P NMR spectroscopy.[3]

The tripnicogens $Et_2PP(CF_3)PEt_2$, $Bu_2PP(CF_3)PBu_2$, $Me_2PP(C_2F_5)PMe_2$, and $Me_2AsP(CF_3)AsMe_2$ were prepared in an NMR tube in an analogous fashion to the preparation of $Me_2PP(CF_3)PMe_2$. An equimolar quantity of a dipnicogen Me_4P_2, Et_4P_2, Bu_4P_2, or Me_4As_2 was transferred into an NMR tube either on the vacuum line or in the glovebox, depending on the volatility, together with benzene-d_6 and an equimolar quantity of the R_fP units from the appropriate cyclopolyphosphine $(CF_3P)_{4,5}$ or $(C_2F_5P)_{3,4}$. Then NMR tube was flame-sealed from the vacuum line. Analysis by multinuclear NMR (Table I) indicated the preparations were essentially quantitative. Reaction times increased with steric bulk, with all reactions being complete after 20 h, except for the reaction with $(C_2F_5P)_{3,4}$, which required several days. Attempts to produce the tripnicogens without solvent yielded polymers (except for $Me_2PP(CF_3)PMe_2$ and $Me_2AsP(CF_3)AsMe_2$, which can be made neat).

The tripnicogen $(CF_3)_2PPMeP(CF_3)_2$ was prepared in an NMR tube by condensing an equimolar quantity of $(CF_3)_2PP(CF_3)_2$[22] onto $(MeP)_5$[7] in benzene-d_6 on the vacuum line. As monitored by NMR (Table I), the reaction took several days to reach completion.

The unsymmetric tripnicogen $Me_2PP(CF_3)PEt_2$ was prepared in a similar fashion by allowing equimolar amounts of Me_4P_2 and Et_4P_2 to react with 2 equiv of (CF_3P) units from $(CF_3P)_{4,5}$. The unsymmetric dipnicogen was also prepared by transferring equal quantities of $Me_2PP(CF_3)PMe_2$ and $Et_2PP(CF_3)PEt_2$ in benzene-d_6 solution into an NMR tube in a glovebox. Scrambling was immediately apparent as

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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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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.

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