$Me_2AsAsMe_2$ (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.

Acknowledgment. The support of the Robert A. Welch Foundation is gratefully acknowledged.

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.

Contribution from the Department of Chemistry and Biochemistry,
Texas Tech University, Lubbock, Texas 79409-1061

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

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

Received August 21, 1987

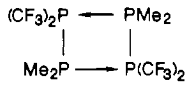
Tetrakis(trifluoromethyl)diphosphine, $(CF_3)_2PP(CF_3)_2$, reacts quantitatively with Me_2PPMe_2 via a four-centered intermediate to produce the unsymmetric diphosphine $(CF_3)_2PPMe_2$. There is no tendency for $(CF_3)_2PPMe_2$ to disproportionate to the reactant symmetric phosphines because of the 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,

---

[†] Present address: MS E501, Los Alamos National Laboratory, Los Alamos, NM 87545.

(1) Harris, R. K.; Nowal, E. M.; Fild, M. *J. Chem. Soc., Dalton Trans.* **1979**, 826.
(2) Ale, A. M.; Harris, R. K. *J. Chem. Soc., Dalton Trans.* **1983**, 583.
(3) McFarlane, H. C. E.; McFarland, W. *J. Chem. Soc., Chem. Commun.* **1972**,1189.
(4) Burg, A. B. *Inorg. Chem.* **1981**, *20*, 3731.
(5) Grant, L. R.; Burg, A. B. *J. Am. Chem. Soc.* **1962**, *84*, 1834.
(6) Avens, L. R.; Wolcott, R. A.; Cribbs, L. V.; Mills, J. L. *Inorg. Chem.*, first of two preceeding papers in this issue.
(7) Avens, L. R.; Cribbs, L. V.; Mills, J. L. *Inorg. Chem.*, preceeding paper in this issue.

0020-1669/89/1328-0211$01.50/0

Table I. NMR Parameters for Dipnicogens

compd	$\delta(^{19}F[^1H])$[a,c]	$\delta(^{31}P[^1H])$[b,c] $P(R_f)$	$\delta(^{31}P[^1H])$[b,c] PR	coupling const, Hz
$(CF_3)_2PPMe_2$	−47.9, d of d	+12.3, d of s	−55.2, d of s	$^1J_{PP} = 254$, $^2J_{PF} = 65$, $^3J_{PF} = 7.5$ $^2J_{PH} = 14$, $^3J_{PH} = 5.2$
$(CF_3)_2PAsMe_2$	−46.7, d	+10.5, s		$^2J_{PH} = 60$, $^3J_{PH} = 11$
$(CF_3)_2PNMe_2$	−60.0, d	−46.3, s		$^2J_{PF} = 86$
$(CF_3)_2PAs(CF_3)_2$	−42.9, d of s (CF_3As) −45.6, d of s (CF_3P)	−2.5, m[d]		$^2J_{PF} = 64$, $^3J_{PF} = 12$, $^5J_{FF} = 3.4$
$(CF'_3)_2PP(CF_3)H$	−50.8, d of d of s[e] −44.6, d of d of m[f]	−10.5, m $(CF_3)_2P$	−87.8, m $P(CF_3)H$	$^1J_{PP} = 185$, $^1J_{PH} = 215$, $^3J_{HF} = 11$ $^2J_{PH} = 2.8$, $^2J_{PF} = 58$, $^2J_{PF'} = 72$ $^3J_{PF'} = 20$, $^3J_{PF'} = 10$
$(CF_3)_2PAsMe_2$	−60.6, d	+47.2, s		$^2J_{PF} = 84.9$
$(CF_3)_2PPPh_2$	−47.8, d of d	+6.2, d of s $(CF_3)_2P$	−29.3, d of s PPh_2	$^1J_{PP} = 190$, $^2J_{PF} = 64$, $^3J_{PF} = 9.0$
$(CF_3)_2PP(Me)Ph$	−46.9, d of d of q[g] −48.2, d of d of q[g]			$^2J_{PF} = 61$, $^3J_{PF} = 6$, $^3J_{PF} = 11$ $^4J_{FF} = 8.0$, $^2J_{PH} = 10.6$ $^3J_{PH} = 6.8$
$[(CF_3)_2PP(Ph)]_2(CH_2)_3$	−47.8, t of m[h]	+9.8, d of s	−39.5, d	$^1J_{PP} = 221$, $^2J_{PF} = 63$
$(CF_3)_2PP(Cl)NMe_2$	−46.1, d of d of q[g] −48.8, d of d of q[g]	−3.0, d of s	+130, d	$^1J_{PP} = 185$, $^3J_{PF} = 14.2, 11.8$ $^2J_{PF} = 57.5$, $^4J_{FF} = 7.7$
$(CF_3)_2PP(Cl)Ph$		+64.9, d of s	+11.4, d of s	$^1J_{PP} = 187$, $^2J_{PF} = 58$, $^3J_{PF} = 11$ $^3J_{PH} = 9.3$
$(CF_3)_2PP(Me)H$	−50.6, d of d of q[g] −52.1, d of d of q[g]	+2.8, d of s	−120.7, d of s	$^1J_{PP} = 230$, $^1J_{PH} = 204$, $^2J_{PF} = 68$ $^3J_{PF} = 10$, $^2J_{PF} = 69$, $^3J_{PF} = 3.0$ $^4J_{FF} = 14$

[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, s = septet, and m = multiplet. [d] Decoupling fluorine yields a sharp singlet. [e] Shift for $(CF_3)_2P$ fluorines, where CF_3 groups, although anisochronous, have very similar shifts. See text. [f] Shift for $H(CF_3)P$ fluorines. [g] Anisochronous CF_3 groups. See text. [h] Approximate appearance of spectrum.

then the electron-withdrawing effects of the aromatic group might be expected to render the pendant phosphorus atom relatively acidic, resulting in a unsymmetric diphosphine that was stable in disproportionation. Indeed, $Ph_2P\text{-}PMe_2$ is a stable species in CH_2Cl_2 solvent.[1]

This paper reports the exchange (or scrambling) reactions of $(CF_3)_2PP(CF_3)_2$ with a variety of compounds containing pnicogen–pnicogen, phosphorus–hydrogen, and phosphorus–chlorine bonds.

Results and Discussion

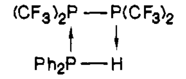
Consideration of the reverse reaction to eq 1 suggests a very simple preparation for unsymmetric diphosphines where the electronegativity of the pendant R groups are sufficiently different. We find, for example, that

$$Me_2PPMe_2 + (CF_3)_2PP(CF_3)_2 \rightarrow 2(CF_3)_2PPMe_2 \quad (3)$$

is benzene solvent is rapid and quantitative. The reaction will occur without solvent, but leads to a considerable amount of a red-orange oil. The analogous reaction of $(CF_3)_2PP(CF_3)_2$ with either $Me_2AsAsMe_2$ or Me_2NPMe_2 quantitatively yields $(CF_3)_2PAsMe_2$ and $(CF_3)_2PNMe_2$, respectively. NMR data are given in Table I. The dipnicogens $(CF_3)_2PPMe_2$,[5] $(CF_3)_2PAsMe_2$,[8,9] and $(CF_3)_2PNMe_2$[10] have all been made previously, but by less direct methods. As expected, the reaction of $(CF_3)_2PP(CF_3)_2$ with $(CF_3)_2AsAs(CF_3)_2$, yields an equilibrium mixture of reactants plus $(CF_3)_2PAs(CF_3)_2$, in an approximately statistical distribution, since there is little acid–base driving force for the reaction.

In an exchange reaction between $(CF_3)_2PP(CF_3)_2$ and a dipnicogen containing a P–H bond, two reaction schemes are possible, one involving P–H bond cleavage and the other, as above, involving pnicogen–pnicogen bond cleavage. Thus, the reaction of $(CF_3)_2PP(CF_3)_2$ with either $Me_2PP(CF_3)H$ or $Me_2AsP(CF_3)H$ yields the expected dipnicogens $(CF_3)_2PPMe_2$ and $(CF_3)_2PAsMe_2$, respectively, in addition to $(CF_3)_2PP(CF_3)H$, $(CF_3P)_{4,5}$, and $(CF_3)_2PH$. The chiral diphosphine, as has been noted previously,[11] cannot be isolated because of disproportionation into $(CF_3P)_{4,5}$ and $(CF_3)_2PH$. However, the compound has a distinctive and unequivocal ^{31}P and ^{19}F NMR spectrum (Table I). The compound $(CF_3)_2PH$ could also be formed directly from the reactants if P–H bond cleavage were the initial step. Since all products are seen upon immediate observation by NMR spectroscopy, a distinction between the reactions mechanisms is not possible.

Phosphorus–hydrogen bond breaking is the only mode of reaction when a secondary phosphine reacts with $(CF_3)_2PP(CF_3)_2$. It has been previously been shown[11] that Me_2PH reacts with $(CF_3)_2PP(CF_3)_2$ to form $(CF_3)_2PPMe_2$ and $(CF_3)_2PH$. An analogous reaction using Ph_2PH, rather than Me_2PH, quantitatively produces $(CF_3)_2PPPh_2$ and $(CF_3)_2PH$. NMR data for $(CF_3)_2PPPh_2$ is given in Table I. The proposed mechanism involves, as in eq 2, a four-centered intermediate.



$$\begin{array}{ccc}(CF_3)_2P & — & P(CF_3)_2 \\ \uparrow & & \downarrow \\ Ph_2P & — & H\end{array} \quad (4)$$

In an entirely similar reaction, the reaction of $(CF_3)_2PP(CF_3)_2$ with $Ph(Me)PH$ proceeds quantitatively to produce $(CF_3)_2PP(Me)Ph$ and $(CF_3)_2PH$. Because the $P(Me)Ph$ phosphorus atom in $(CF_3)_2PP(Me)Ph$ is a chiral center, there are two diastereomers; additionally the CF_3 groups are anisochronous, making interpretation of the NMR data (Table I) somewhat complex (vide infra).

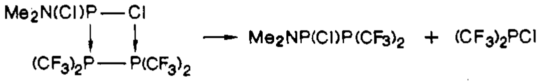
A potentially very interesting multidentate ligand can be synthesized by using an analogous reaction of $(CF_3)_2PP(CF_3)_2$ with bis(1,3-phenylphosphino)propane $H(Ph)P(CH_2)_3P(Ph)H$ to produce $(CF_3)_2P(Ph)P(CH_2)_3P(Ph)P(CF_3)_2$ and $(CF_3)_2PH$. The compound was not isolated, but the NMR data (Table I), as well as the reaction mass balance and compound volatility, are consistent with the assigned structure.

In an attempt to prepare the previously unknown diphosphine $(CF_3)_2PPCl_2$, Me_2NPCl_2 was mixed with $(CF_3)_2PP(CF_3)_2$. The new diphosphine, along with $Me_2NP(CF_3)_2$, would be produced if P–N bond exchange occurred. The analogous difluoro derivative $(CF_3)_2PPF_2$ is a known compound[12] that is reasonably stable. The desired product $(CF_3)_2PPCl_2$ was not observed by either ^{31}P or ^{19}F NMR spectroscopy, but $Me_2NP(CF_3)_2$, the other expected product, was observed. Thus, the reaction may proceed as expected, but with the product $(CF_3)_2PPCl_2$ disproportionation to

---

(8) Cavell, R. G.; Dobbie, R. C. *J. Chem. Soc. A* **1968**, 1406.
(9) Cullen, W. R.; *Can. J. Chem.* **1963**, *41*, 322.
(10) Kober, F. *Chem.-Ztg.* **1976**, *100*, 197. Harris, G. S. *J. Chem. Soc.* **1958**, 512.
(11) Burg, A. B.; Joshi, K. K. *J. Am. Chem. Soc.* **1964**, *86*, 353.
(12) Schiller, H. W.; Rudolph, R. W. *Inorg. Chem.* **1971**, *10*, 2500.

yield $(CF_3)_2PCl$ and $(PCl)_n$ polymer. Both products were observed as the reaction proceeds, $(CF_3)_2PCl$ spectroscopically and $(PCl)_n$ as an observed yellow solid. An alternate or competing reaction scheme could involve the P–Cl bond, however.



$$\begin{array}{l}\mathrm{Me_2N(Cl)P-Cl}\\ \quad\ \ | \qquad\quad | \\ \mathrm{(CF_3)_2P-P(CF_3)_2}\end{array} \longrightarrow \mathrm{Me_2NP(Cl)P(CF_3)_2} + \mathrm{(CF_3)_2PCl} \qquad (5)$$

The new tripnicogen $Me_2NP(Cl)P(CF_3)_2$ is indeed formed and has a very interesting ^{19}F NMR spectrum (Table I); since the $Me_2N\mathit{P}Cl$ phosphorus atom is a chiral center, the CF_3 groups, as well as the Me groups, as anisochronous (vide infra). The reactivity of a P–Cl bond with $(CF_3)_2PP(CF_3)_2$ was further studied by its reaction with $PhPCl_2$. The reaction occurs slowly under ambient conditions to form an equilibrium mixture of reactants and the expected $(CF_3)_2PP(Cl)Ph$ species together with $(CF_3)_2PCl$. Reaction of the methyl substituent $MePCl_2$ with $(CF_3)_2PP(CF_3)_2$ proved to be a more complex. No reaction occurred after 12 days at ambient temperature, so UV photolysis was used to aid the reaction. NMR analysis indicated high yields of $(CF_3)_2PCl$ and the tripnicogen $(CF_3)_2PP(Me)P(CF_3)_2$, together with only a trace quantity of the expected $(CF_3)_2PP(Cl)Me$. The tripnicogen $(CF_3)_2PP(Me)P(CF_3)_2$ could arise either from disproportionation of $(CF_3)_2PP(Cl)Me$ (also regenerating $MePCl_2$, which was observed) or from reaction of the remaining P–Cl bond in $(CF_3)_2PP(Cl)Me$ with $(CF_3)_2PP(CF_3)_2$. The photolysis of a mixture of $MePCl_2$ and $(CF_3)_2PP(CF_3)_2$ is a more rapid and direct synthesis of $(CF_3)_2PP(Me)P(CF_3)_2$ than previous methods.[6,11] The difference in the reactivity and product distribution of the methyl- versus phenyldichlorophosphine reaction with $(CF_3)_2PP(CF_3)_2$ is poorly understood but presumably must result from a subtle combination of steric and electronic effects.

NMR Data. As can be seen in Table I, the multinuclear NMR data for the compounds $(CF_3)_2PPMe_2$, $(CF_3)_2PAsMe_2$, $(CF_3)_2PNMe_2$, and $(CF_3)_2PAs(CF_3)_2$, while informative as an aid in structural elucidation, are ordinary in both aspects of chemical shifts and coupling constants. However, as noted earlier, the compound $(CF_3)_2PP(CF_3)H$ deserves some comments relative to interpretation of NMR data.

In addition to the $^{31}P[^1H]$ NMR data in Table I, the $^{31}P[^{19}F]$ NMR spectrum of $(CF_3)_2PP(CF_3)H$ consists of doublet of doublets centered at −87.8 ppm due to the $\mathit{P}(CF_3)H$ phosphorus coupled to an adjacent proton and to a nonequivalent phosphorus, and a second doublet or doublets centered at −10.5 ppm. Chemical shifts and coupling constants were verified by computer simulation of the slightly second-order spectrum. Analysis of the ^{19}F NMR spectra was more difficult for several reasons. First, the two CF_3 groups bonded to the $(CF_3)_2\mathit{P}$ phosphorus are anisochronous[13] because the adjacent $\mathit{P}(CF_3)H$ phosphorus is chiral. The ^{19}F chemical shift difference between these two anisochronous groups is only about 0.5 ppm; only the average is listed in Table I. Because of the similarities in chemical shifts, the degree of fluorine to fluorine coupling, and thus the extreme number of overlapping peaks, it was not possible to extract all the coupling constants.

For the diphosphine $(CF_3)_2PPPh_2$, in addition to the $^{31}P[^1H]$ and $^{19}F[^1H]$ NMR data in Table I, the $^{31}P[^{19}F]$ NMR spectrum gives is a doublet at +6.2 ppm for the $(CF_3)_2\mathit{P}$ phosphorus and a doublet of multiplets at −29.3 ppm for the $\mathit{P}Ph_2$ phosphorus atom with a spacing of about 18 Hz due to phenyl proton coupling. The ^1H NMR spectrum is a broad, poorly resolved multiplet +7.1 ppm.

The chiral diphosphine $(CF_3)_2PP(Me)Ph$ again has anisochronous CF_3 groups, due to the neighboring chiral phosphorus atom, resulting in two ^{19}F NMR resonances, centered at −46.9 and −48.2 ppm with two different $^3J_{FP}$ couplings and a $^4J_{FF}$ coupling, as indicated in Table I. Proton NMR observation indicated a poorly resolved multiplet at +7.1 ppm (Ph) and a doublet of doublets at +1.3 ppm (Me).

Two additional chiral diphosphines having anisochronous CF_3 groups are $(CF_3)_2PP(Cl)NMe_2$ and $(CF_3)_2PP(Cl)Ph$. In the compound $(CF_3)_2PP(Cl)NMe_2$, $^2J_{PF}$ is indistinguishable for both anisochronous groups, but $^3J_{PF}$ differs. In $(CF_3)_2PP(Cl)Ph$, the $^{31}P[^{19}F]$ NMR spectrum (in addition to the data in Table I), further supports the structural characterization, yielding a doublet at +64.9 ppm for the $(CF_3)_2\mathit{P}$ phosphorus atom and a doublet of triplets at +11.4 ppm for the $\mathit{P}(Cl)Ph$ phosphorus atom, the triplet arising from coupling to the two ortho protons on the phenyl group.

The diphosphine $(CF_3)_2PP(Me)H$ was first prepared by Burg,[11] but NMR data were not reported. Since the compound is closely related to those reported here, NMR parameters for $(CF_3)_2PP(Me)H$ are reported. Using benzene-d_6, we have observed the ^{31}P, ^{19}F, and ^1H NMR spectra. Considering first the ^{31}P spectrum, the $(CF_3)_2\mathit{P}$ phosphorus resonance is at +2.8 ppm and that for the $\mathit{P}(Me)H$ is at −120.7 ppm, which separates the resonances sufficiently for a first-order interpretation. Even though first order, the ^{31}P coupled spectrum is somewhat complicated by the presence of three spin-active species and the overlap of multiplets. The perfluoroalkyl-substituted phosphorus is split into a doublet of septets of doublets of quartets by the adjacent phosphorus, six fluorines, a proton, and methyl group protons, respectively. With $^1J_{PP}$ = 230 Hz, the two septets overlap considerably, making analysis difficult. Separated by an additional bond from the fluorines, the alkyl-substituted phosphorus gives a portion of the spectrum that appears as a doublet of doublets of multiplets, as expected. Decoupling the protons greatly simplifies the spectrum to yield a downfield of septets and an upfield doublet of septets. The ^1H NMR spectrum appears as a multiplet centered at +1.8 ppm for the methyl group and a doublet of multiplets centered at +4.1 ppm for the phosphorus-bonded proton. Since the CF_3 groups are anisochronous, the observed ^{19}F NMR spectrum appears very much like four multiplets; however, closer inspection reveals the spectrum to consist of two doublets of doublets of quartets. Coupling of each set of nonequivalent fluorine atoms to the two nonequivalent phosphorus atoms and the other CF_3 group, respectively, yields the observed spectrum. The slight difference in appearance of the multiplet representing each CF_3 group results from different values for $^2J_{PF}$ and $^3J_{PF}$ for the nonequivalent CF_3 groups. Thus, $^2J_{PF}$ for $CF_3 \neq {}^2J_{PF}$ for CF'_3, and the same is true for $^3J_{PF}$. Fluorine chemical shifts for the two CF_3 groups are −50.6 and −52.1 ppm, a difference of 1.5 ppm.

Experimental Section

The standard experimental methods and instrumentation have been previously described.[6,7] The following chemicals were synthesized and/or characterized by literature procedures: Me_2PPMe_2,[14] $Me_2AsAsMe_2$,[15] $(CF_3)_2PP(CF_3)_2$,[8,16] $(CF_3)_2AsAs(CF_3)_2$,[8,17] $(CF_3)_2PP(CF_3)H$,[11] $Me_2PP(CF_3)H$,[11] $Me_2AsP(CF_3)H$,[6] $(CF_3)_2PH$,[18] $(CF_3P)_{4,5}$,[19] Me_2NPCl_2,[20] $MePH_2$,[21] and $(CF_3)_2PI$.[19] Obtained commercially and used without further purification were Ph(Me)PH (Strem), Ph_2PH (Strem), Ph(H)P$(CH_2)_3$-P(H)Ph (Strem), $MePCl_2$ (Strem), and $PhPCl_2$ (Aldrich).

Reaction of Me_2PPMe_2 with $(CF_3)_2PP(CF_3)_2$. To an NMR tube on the vacuum line were added approximately 0.10 mL of benzene-d_6, Me_2PPMe_2 (0.19 mmol, 0.023 g), and $(CF_3)_2PP(CF_3)_2$ ((0.19 mmol, 0.064 g). The tube was flame-sealed and allowed to warm to room temperature, at which point no outward sign of reaction was observed. Immediate ^{31}P NMR analysis showed qualitative conversion to the diphosphine Me_2P-$P(CF_3)_2$.

Reaction of $Me_2AsAsMe_2$, Me_2NPMe_2, or $(CF_3)_2AsAs(CF_3)_2$ with $(CF_3)_2PP(CF_3)_2$. In a similar manner to the above reaction, equimolar amounts of $Me_2AsAsMe_2$, Me_2NPMe_2, or $(CF_3)_2AsAs(CF_3)_2$, were added to $(CF_3)_2PP(CF_3)_2$ in benzene-d_6. Immediate ^{31}P NMR analysis

---

(13) Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307.

(14) Niebergall, H.; Langenfeld, B. *Chem. Ber.* **1962**, *95*, 64.

(15) Waser, J.; Schomaker, V. *J. Am. Chem. Soc.* **1945**, *67*, 2014. Rheingold, A. L.; Choudhury, P. *J. Organomet. Chem.* **1977**, *128*, 155.

(16) Bennett, F. W.; Emeleus, H. J.; Haszeldine, R. N. *J. Chem. Soc.* **1953**, 1565.

(17) Emeleus, H. J.; Haszeldine, R. N.; Walachewski, E. G. *J. Chem. Soc.* **1953**, 1552.

(18) Cavell, R. G.; Dobbie, R. C. *J. Chem. Soc. A* **1967**, 1308.

(19) Burg, A. B.; Mahler, W. *J. Am. Chem. Soc.* **1961**, *83*, 2388. Cowley, A. H.; Dierdorf, D. S. *J. Am. Chem. Soc.* **1969**, *91*, 6609.

(20) Burg, A. B. *J. Am. Chem. Soc.* **1958**, *80*, 1107.

(21) Mahler, W.; Burg, A. B. *J. Am. Chem Soc.* **1958**, *80*, 6161. Cowley, A. H. *J. Am. Chem. Soc.* **1967**, *89*, 5990.

showed quantitative conversion to the arsinophosphine $Me_2AsP(CF_3)_2$, in the first reaction, and to $Me_2NP(CF_3)_2$ and $Me_2PP(CF_3)_2$ in the second reaction. The third reaction yielded an approximately statistical equilibrium mixture of reactants plus $(CF_3)_2AsP(CF_3)_2$.

Reaction of $Me_2PP(CF_3)H$ with $(CF_3)_2PP(CF_3)_2$. To an NMR tube on the vacuum line was added approximately 0.15 mL of benzene-*d*$_6$, $Me_2PP(CF_3)H$ (0.11 mmol, 0.018 g) and $(CF_3)_2PP(CF_3)_2$ (0.13 mmol, 0.044 g). The tube was sealed and removed from the vacuum line. When the tube was warmed to room temperature, no visible signs of reaction were observed. Analysis by ^{31}P NMR showed not only that the reaction was relatively slow but also that more than one process was occurring. Initially $Me_2PP(CF_3)_2$ and $(CF_3)_2PP(CF_3)H$ were formed, but the latter diphosphine slowly disproportionated to yield $(CF_3)_2PH$ and $(CF_3P)_{4,5}$.

Reaction of $Me_2AsP(CF_3)H$ with $(CF_3)_2PP(CF_3)_2$. As the solution warmed to room temperature, there were no obvious signs of reaction, but spectroscopic analysis indicated an immediate and quantitative reaction had occurred to form $Me_2AsP(CF_3)_2$ and $(CF_3)_2PP(CF_3)H$. As in the reaction described immediately above, the diphosphine $(CF_3)_2PP(CF_3)H$ is unstable relative to disproportionation, with spectra observed over time reflecting an increase in the concentrations of $(CF_3)_2PH$ and $(CF_3P)_{4,5}$ at the expense of $(CF_3)_2PP(CF_3)H$. In an attempt to isolate the diphosphine $(CF_3)_2PP(CF_3)H$, the reaction was repeated and vacuum fractionated to yield the following: −45 °C trap contents, $(CF_3P)_{4,5}$; −64 °C trap contents, $Me_2As–P(CF_3)_2$; −84 °C trap contents, $Me_2AsP(CF_3)_2$; −196 °C trap contents, $(CF_3)_2P–P(CF_3)H$ and $(CF_3)_2PH$. The isolated yield of $(CF_3)_2PP(CF_3)H$ was quite low, further attempts at purification and isolation were ineffective.

Reaction of $(CF_3)_2PP(CF_3)_2$ with Ph_2PH. In a dry box, Ph_2PH (0.60 mmol, 0.11 g) was syringed into an NMR tube, which was then attached to the vacuum line and degassed. An equimolar quantity of $(CF_3)_2PP(CF_3)_2$ together with approximately 0.2 mL of benzene-*d*$_6$ were condensed into the tube, and the tube was sealed. When the tube was warmed to room temperature, a biphasic solution with no obvious appearance of reaction was observed. After 2 days at room temperature, the solution was homogeneous, and observation by ^{19}F NMR revealed the presence of $(CF_3)_2PP(CF_3)_2$, $(CF_3)_2PH$, and the diphosphine $(CF_3)_2PPPh_2$. Further observation by ^{31}P and ^{19}F NMR spectroscopy indicated the reaction was essentially quantitative.

Reaction of $(CF_3)_2PP(CF_3)_2$ with Ph(Me)PH. In a reaction analogous to that directly above, equimolar quantities of $(CF_3)_2PP(CF_3)_2$ and Ph(Me)PH were mixed together in benzene-*d*$_6$. Analysis of NMR indicated essentially quantitative production of the new unsymmetric diphosphine $(CF_3)_2PP(Me)Ph$ and $(CF_3)_2PH_2$.

Reaction of $(CF_3)_2PP(CF_3)_2$ with Bis(1,3-phenylphosphino)propane, $Ph(H)P(CH_2)_3P(H)Ph$. The phosphinopropane (0.843 mmol, 02.19 g) was transferred to an NMR tube in the drybox. The NMR tube was attached to the vacuum line and about 0.15 mL of benzene-*d*$_6$ and $(CF_3)_2PP(CF_3)_2$ (2.35 mmol, 0.803 g) were vapor transferred to the tube. The tube was flame-sealed and allowed to warm to room temperature, at which point two phases separated. Reaction was complete in 2 days at ambient temperature, yielding $(CF_3)_2PH$ and the tetraphosphine $(CF_3)_2P\text{-}P(Ph)\text{-}(CH_2)_3\text{-}P(Ph)\text{-}P(CF_3)_2$.

Reaction of Me_2NPCl_2 with $(CF_3)_2PP(CF_3)_2$. To an NMR tube on the vacuum line was added approximately 0.15 mL of benzene-*d*$_6$, Me_2NPCl_2 (1.18 mmol, 0.172 g) and $(CF_3)_2PP(CF_3)_2$ (1.20 mmol, 0.406 g). The tube was flame-sealed and allowed to warm to room temperature; two clear, colorless layers separated. Over a period of several days at room temperature, the lower layer of $(CF_3)_2PP(CF_3)_2$ was consumed with concurrent yellowing and solid formation. Small amounts of $Me_2NP(CF_3)_2$ was observed in the ^{31}P NMR spectrum, but the expected compound $(CF_3)_2PPCl_2$ was not found. After 2 weeks at 23 °C, the reaction achieved equilibrium. The tube contents were fractionally distilled, and the new compound $(CF_3)_2PP(Cl)NMe_2$ was retained in a −37 °C trap together with unreacted Me_2NPCl_2. Repeated fractional distillation led to an enrichment of about equal quantities of $(CF_3)_2PP(Cl)NMe_2$ and Me_2NPCl_2. The tripnicogen $(CF_3)_2PP(Cl)NMe_2$ is stable indefinitely at 23 °C and showed no decomposition after heating at 70 °C for 2 h in solution with benzene and Me_2NPCl_2.

Reaction of $(CF_3)_2PP(CF_3)_2$ with $PhPCl_2$. Under N_2 flow, $PhPCl_2$ (1.72 mmol, 0.308 g) was syringed into an NMR tube and then degassed on the vacuum line. Approximately 0.2 mL of benzene-*d*$_6$ and $(CF_3)_2PP(CF_3)_2$ (3.34 mmol, 1.16 g) were then vapor transferred into the tube, and the tube was sealed. When the tube was warmed to room temperature, the resulting solution was biphasic, and analysis by ^{31}P NMR revealed no discernible reaction. Agitation of the solution over 4 days yielded a homogeneous solution. Analysis of ^{31}P and ^{19}F NMR data indicated an equilibrium was established between $PhPCl_2$, $(CF_3)_2PP(CF_3)_2$, $(CF_3)_2PCl$, and the new diphosphine $(CF_3)_2PP(Cl)Ph$. Due to similar low volatilities, $(CF_3)_2PP(Cl)Ph$ could not be isolated from Ph_2PCl.

Reaction of $(CF_3)_2PP(CF_3)_2$ with $MePCl_2$. On the vacuum line, $MePCl_2$ (0.80 mmol, 0.094 g) and $(CF_3)_2PP(CF_3)_2$ (1.60 mmol, 0.54 g) were condensed into an NMR tube and the tube was flame-sealed. Immediate observation by NMR, as well as repeated observation over 12 days, revealed no detectable reaction. The sample was then photolyzed by irradiation with a 500-W, high-pressure Hanovia UV lamp for 3 h. Spectroscopic analysis indicated the presence of $(CF_3)_2PPMeP(CF_3)_2$, $(CF_3)_2PCl$, $MePCl_2$, and a trace quantity of the expected $(CF_3)_2PP(Cl)Me$.

Preparation of $(CF_3)_2PP(Me)H$. The diphosphine was prepared[11] by condensing $MePH_2$ (21.1 mmol, 1.02 g) into an ampule with $(CF_3)_2PI$ (12.5 mmol, 3.10 g) at −196 °C. The ampule was flame-sealed and allowed to warm slowly from −78 °C to room temperature overnight. The volatile components of the ampule were then transferred onto the vacuum line and purified by passage through traps at −45, −64, and −196 °C. The diphosphine slowly passed through a trap at −45 °C and was retained at −64 °C. Identification was by vapor pressure[11] and by ^1H, ^{19}F, and ^{31}P NMR spectroscopy.

Acknowledgment. The support of the Robert A. Welch Foundation is gratefully acknowledged.

Registry No. Me_2PPMe_2, 3676-91-3; $(CF_3)_2PP(CF_3)_2$, 2714-60-5; $Me_2PP(CF_3)_2$, 666-62-6; $Me_2AsAsMe_2$, 471-35-2; Me_2NPMe_2, 683-84-1; $(CF_3)_2AsAs(CF_3)_2$, 360-56-5; $Me_2AsP(CF_3)_2$, 19863-20-8; $Me_2NP(CF_3)_2$, 432-01-9; $(CF_3)_2AsP(CF_3)_2$, 19863-18-4; $Me_2PP(CF_3)H$, 117583-73-0; $(CF_3)_2PP(CF_3)H$, 117583-83-2; $(CF_3)_2PH$, 460-96-8; $(CF_3P)_4$, 393-02-2; $(CF_3P)_5$, 745-23-3; $Me_2AsP(CF_3)H$, 117583-81-0; Ph_2PH, 829-85-6; $(CF_3)_2PPPh_2$, 117583-84-3; Ph(Me)PH, 6372-48-1; $(CF_3)_2PP(Me)Ph$, 117583-85-4; $Ph(H)P(CH_2)_3P(H)Ph$, 28240-66-6; $(CF_3)_2PP(Ph)(CH_2)_3P(Ph)P(CF_3)_2$, 117583-86-5; Me_2NPCl_2, 683-85-2; $(CF_3)_2PP(Cl)NMe_2$, 117583-87-6; $PhPCl_2$, 644-97-3; $(CF_3)_2PCl$, 650-52-2; $(CF_3)_2PP(Cl)Ph$, 117583-88-7; $MePCl_2$, 676-83-5; $(CF_3)_2PPMeP(CF_3)_2$, 2195-42-8; $(CF_3)_2PP(Cl)Me$, 117583-89-8; $MePH_2$, 593-54-4; $(CF_3)_2PI$, 359-64-8; $(CF_3)_2PP(Me)H$, 1840-12-6.