icantly *longer* for unsaturated esters. The available data do suggest that there are significant changes in multiple-bond character in the various cyclic esters, but these changes appear to be electronic in origin and do not seem to be induced by ring strain.

Acknowledgment. We are grateful to Professor E. T. Kaiser for supplying the compound and some helpful commentary, and are also pleased to acknowledge valuable discussions with Drs. Francis Johnson and Steven W. Tobey.

The Reaction of $(CF_3P)_4$ with Some Compounds with Nonmetal–Nonmetal Bonds

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Abstract: The cyclotetraphosphine $(CF_3P)_4$ reacts with $(CH_3)_4As_2$ and $(CH_3)_2S_2$ to insert a CF_3P group into the As–As or S–S bond. A variety of products was formed by the action of $(CF_3P)_4$ on $(CH_3)_2NP(CH_3)_2$ with the major component being the phosphinidene complex $(CH_3)_2N(CH_3)_2P \rightarrow PCF_3$. Tetramethylhydrazine behaves like $(CH_3)_3N$ in that it catalyzes the interconversion of $(CF_3P)_4$ and $(CF_3P)_5$. However, no N–N bond cleavage was detected. No reaction takes place between $(CF_3P)_4$ and $(CH_3)_6Si_2$ up to 138°. The temperature dependence of the pmr spectrum of the diarsinophosphine, $[(CH_3)_2As]_2PCF_3$, has been studied. The spectral changes are ascribed to a bimolecular exchange reaction.

The present work was undertaken as part of a general program of investigation of the carbenoid behavior of phosphinidene (RP) groups. This particular paper is concerned with attempts to insert the CF_3P moiety into various nonmetal–nonmetal bonds.[2] Prior to our work, Schmidt and Osterroht[3] reported the insertion of a C_6H_5P group into a sulfur–sulfur bond.

Experimental Section

All volatile materials were handled in high-vacuum manifolds with U-traps interconnected by mercury float valves or Apiezon-greased stopcocks. Materials of low volatility were handled under a dry nitrogen atmosphere or in a helium-filled drybox.

Materials. The compounds $(CF_3P)_4$,[4] $(CH_3)_4As_2$,[5] B_2H_6,[6] $(CH_3)_2NP(CH_3)_2$,[7] $[(CH_3)_2P]_2PCF_3$,[2] and $[(CH_3)_2N]_2PCF_3$[8] were made and purified according to literature methods. Tetramethylhydrazine was kindly donated by Dr. W. E. Thun of the Naval Weapons Center, China Lake, Calif. Hydrogen chloride, $(CH_3)_6Si_2$, and $(CH_3)_2S_2$ were procured commercially and used without subsequent purification. The solvents C_6H_6 and C_6D_{12} were distilled prior to use.

The Reaction of $(CF_3P)_4$ with $(CH_3)_4As_2$. A mixture of 0.536 g (2.553 mmoles) of $(CH_3)_4As_2$ and 2.696 g (0.624 mmole) of $(CF_3P)_4$ was sealed in an evacuated ampoule at −196° and allowed to warm slowly to ambient temperature. The initial yellow color of the solution faded after a few minutes. After standing overnight at ambient temperature the ampoule was opened and the traces of volatiles were pumped off to leave an essentially quantitative yield of clear, colorless bis(dimethylarsino)trifluoromethylphosphine (I). *Anal.* Calcd for $C_5H_{12}As_2F_3P$: C, 19.37; H, 3.90. Found: C, 19.26; H, 4.06. The vapor tension of I is 0.5 mm at 24°. The ^1H and ^{19}F nmr data for I are presented in Table I. The ir spectrum of I (liquid film) consisted of peaks (cm^{-1}) at 2979, 2910, and 2805 in the C–H stretching region, 1420 and 1258 in the CH_3 deformation region, and 1167, 1122, and 1093 in the C–F stretching region. The CH_3 rock and wag occurred at 895 and 842, the CF_3 symmetrical deformation at 732, the As–C stretch at 576, the CF_3 asymmetric deformation at 563, and the P–C stretch at 435. The vapor-phase uv spectrum of I displays maxima at 2194 and 2484 Å.

The Reaction of $[(CH_3)_2As]_2PCF_3$ (I) with HCl. The reaction $2HCl + [(CH_3)_2As]_2PCF_3 \rightarrow CF_3PH_2 + 2(CH_3)_2AsCl$ occurred essentially quantitatively, thus further confirming the formula of I. In this experiment 0.1585 g (0.511 mmole) of I consumed 1.023 mmoles (from 1.050) of HCl upon slow warming from −196° to form 0.937 mmole of $(CH_3)_2AsCl$ (91.6% yield) and 0.506 mmole of CF_3PH_2 (99.0% yield). The $(CH_3)_2AsCl$ was identified by comparison of its ir and pmr spectra with those of a known sample of this compound. Identification of CF_3PH_2 was made on the basis of its vapor tension[4] of 45 mm at −78.5° and a pmr spectrum. The latter (neat liquid) consists of a pair of quartets centered at τ 6.48 with $J_{PH} = 199.99$ Hz and $J_{FCPH} = 11.90$ Hz.

The Reaction of $[(CH_3)_2As]_2PCF_3$ (I) with B_2H_6. A mixture of 0.1633 g (0.527 mmole) of I and 0.863 mmole of B_2H_6 was allowed to warm slowly from −196° in a sealed ampoule. Removal of the excess B_2H_6 (0.270 mmole) left the viscous colorless liquid bisborane adduct $[(CH_3)_2As]_2PCF_3 \cdot 2BH_3$ (II). *Anal.* Calcd for II: C, 17.79; H, 5.37. Found: C, 17.92; H, 5.57. The ^{11}B nmr spectrum of II (TMS solution) displayed a broad singlet at +20.6 ppm relative to external $B(OCH_3)_3$.

The Reaction of $(CF_3P)_4$ with $(CH_3)_2S_2$. A mixture of 0.1790 g (0.448 mmole) of $(CF_3P)_4$ and 0.3285 g (3.487 mmoles) of $(CH_3)_2S_2$ was allowed to warm slowly from −196° in an evacuated, sealed nmr tube containing a capillary of CCl_3F. After standing approximately 12 hr at ambient temperature the ^{19}F nmr spectrum was recorded. This indicated that approximately 20% conversion of $(CF_3P)_4$ to $(CF_3P)_5$ had occurred and that a small amount of $(CH_3S)_2PCF_3$ (III) had been formed. The CF_3P insertion reaction was completed by heating the tube at 143° for 1 hr. Fractionation of the volatiles with U-traps held at −25 and −196° resulted in the condensation of 0.1667 g (0.859 mmole) of III in the −25° trap. A further 0.1462 g (0.753 mmole) of III was isolated by using a −35° trap. The total amount of III (1.612 mmoles) represented a 90.1% yield. Identification of III was made on the basis of the conformity of its vapor tension and ir spectral data with the literature values.[9] The nmr data for III are presented in Table I.

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[1] National Science Foundation Undergraduate Participant, Summer, 1968; Welch Undergraduate Research Participant, Long Session, 1967–1968.

[2] For a preliminary report of this work, see A. H. Cowley, *J. Am. Chem. Soc.*, **89**, 5990 (1967).

[3] U. Schmidt and C. Osterroht, *Angew. Chem. Intern. Ed. Engl.*, **4**, 437 (1965); U. Schmidt, *et al.*, *Chem. Ber.*, **101**, 1381 (1968). For a review of related work on phosphinidene chemistry, see O. M. Nefedov and M. N. Manakow, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1021 (1966).

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

[5] V. Auger, *Compt. Rend.*, **142**, 1153 (1906).

[6] I. Shapiro, *et al.*, *J. Am. Chem. Soc.*, **74**, 901 (1952).

[7] A. B. Burg and P. J. Slota, *ibid.*, **80**, 1107 (1958).

[8] J. F. Nixon and R. G. Cavell, *J. Chem. Soc.*, 5983 (1964).

[9] A. B. Burg and K. Gosling, *J. Am. Chem. Soc.*, **87**, 2113 (1965).

Table I. Nmr Parameters for CF_3P Insertion and Scrambling Reaction Products

Compound	^{19}F chemical shift[a]	^1H chemical shift (τ)	Coupling constants, Hz
$[(CH_3)_2P]_2PCF_3$[b]	Doublet of triplets, 42.2	Complex multiplet	$J_{PCF} = 42.1$; $J_{PPCF} = 7.1$
$[(CH_3)_2As]_2PCF_3$[c]	Doublet, 41.0	Two doublets of quartets 8.70, 8.79	$J_{PCF} = 33.9$; $J_{PAsCH} = 9.67$; $J_{PAsCH}' = 8.16$; $J_{FCPAsCH} = 0.84$; $J_{FCPAsCH}' = 0.74$
$(CH_3S)_2PCF_3$[b]	Doublet, 60.4	Doublet of quartets	$J_{PCF} = 68.29$; $J_{PSCH} = 11.38$; $J_{FCPSCH} = 0.74$
$(CH_3)_2PP(CF_3)N(CH_3)_2$	Doublet of doublets, 55.9	*d*	$J_{PCF} = 53.0$; $J_{PPCF} = 11.3$
$(CH_3)_2PP(CF_3)As(CH_3)_2$	Doublet of doublets, 41.8	*d*	$J_{PCF} = 37.7$; $J_{PPCF} = 7.3$

[a] In ppm upfield relative to external CCl_3F. [b] Neat sample. [c] C_6D_{12} or TMS solution. [d] ^1H spectra not well resolved in reaction mixture.

Table II. Nmr Spectral Data for $(CF_3P)_4$–$(CH_3)_2NP(CH_3)_2$ Reaction Mixture

		^{19}F Spectrum			
Chemical shift[a]	Multiplet structure	Coupling constants, Hz	Assignment	%	Ref
37.2	Doublet of doublets	23.4, 35.8	$(CH_3)_2N{-}\underset{\underset{PCF_3}{\downarrow}}{P}(CH_3)_2$	83.6	
42.4	Doublet of triplets	6.8, 41.0	$(CH_3)_2P{-}\underset{\underset{CF_3}{\vert}}{P}{-}P(CH_3)_2$	8.0	*b*
55.7	Doublet of doublets	49.8, 11.6	$(CH_3)_2N{-}\underset{\underset{CF_3}{\vert}}{P}{-}P(CH_3)_2$	1.8	
61.5	Doublet	84.8	$[(CH_3)_2N]_2PCF_3$	4.4	*c*
69.8	Doublet	84.8	$(CH_3)_2\underset{\underset{PCF_3}{\downarrow}}{N}{-}P(CH_3)_2$ (?)	2.2	

		^1H Spectrum			
$\tau CH_3(P)$	Multiplet structure and coupling constants, Hz	$\tau CH_3(N)$	Multiplet structure and coupling constants, Hz	Assignment	Ref
9.01	Doublet 5.55	7.53	Doublet, 9.77	$(CH_3)_2NP(CH_3)_2$	*d*
8.29	Doublet of doublets 5.10, 11.82	7.39	Doublet, 11.95	$(CH_3)_2N{-}\underset{\underset{PCF_3}{\downarrow}}{P}(CH_3)_2$	
8.85	Complex multiplet			$[(CH_3)_2P]_2PCF_3$	*b*
		7.25	Doublet, 9.30	$[(CH_3)_2N]_2PCF_3$	*c*

[a] ^{19}F chemical shifts in ppm relative to external CCl_3F. [b] Reference 2. [c] Reference 8. [d] A. H. Cowley and R. P. Pinnell, *J. Am. Chem. Soc.*, **87**, 4454 (1965).

The Attempted Reaction of $(CF_3P)_4$ with $(CH_3)_6Si_2$. The ^{19}F and ^1H nmr spectra of a mixture of 0.825 g (0.406 mmole) of $(CF_3P)_4$ and 0.3133 g (2.141 mmoles) of $(CH_3)_6Si_2$ indicate that no reaction takes place on prolonged standing or heating to 138°. No conversion of $(CF_3P)_4$ to $(CF_3P)_5$ was detectable.

The Reaction of $(CF_3P)_4$ with $(CH_3)_2NP(CH_3)_2$. A mixture of 0.1084 g (0.271 mmole) of $(CF_3P)_4$ and 0.2185 g (2.081 mmoles) of $(CH_3)_2NP(CH_3)_2$ was sealed in a 5-mm nmr tube *in vacuo* at −196°. Upon slow warming to ambient temperature the sample developed a permanent yellow-orange color. The observed ^{19}F and ^1H resonances are shown in Table II along with the relative yields. The assignments are discussed in the Results and Discussion section.

Fractionation of the volatiles with U-traps held at −20, −40, −50, and −196° resulted in the recovery of 0.1119 g (1.066 mmoles) of $(CH_3)_2NP(CH_3)_2$ in the −50° trap and the isolation of 7.8 mg (0.041 mmole) of $[(CH_3)_2N]_2PCF_2$ in the −40° trap. Identification of both the aminophosphines was made on the basis of their ir spectral and vapor tension data.[7,8] The −20° trap contained an inseparable mixture of $(CF_3P)_4$, $(CF_3P)_5$, and $[(CH_3)_2P]_2PCF_3$. These species were identified by their characteristic ^{19}F nmr spectra.[2,10]

The Reaction of $[(CH_3)_2P]_2PCF_3$ with $[(CH_3)_2N]_2PCF_3$. A mixture of 1.285 mmoles of $[(CH_3)_2P]_2PCF_3$ and 1.298 mmoles of $[(CH_3)_2N]_2PCF_3$ was sealed in a 5-mm nmr tube which contained a sealed capillary of CCl_3F. No new ^{19}F nmr peaks were detected after the tube had stood 48 hr at room temperature. Similarly, no reaction was detectable after the sample had been heated for 1.5 hr at 98°. New ^{19}F nmr peaks, which are attributable to $(CH_3)_2PP(CF_3)N(CH_3)_2$ (VI) (Table I), were recorded after the sample had been heated for 2 hr at 132°. Attempts to separate the diphosphinoamine from the starting materials were unsuccessful due to the closeness in volatilities of VI and the starting materials.

The Reaction of $[(CH_3)_2P]_2PCF_3$ with $[(CH_3)_2As]_2PCF_3$. A mixture of 0.663 mmole of $[(CH_3)_2P]_2PCF_3$ and 0.735 mmole of $[(CH_3)_2As]_2PCF_3$ was treated in a similar manner to that described in the preceding experiment. Heating the mixture to 130° for 3.8 hr was necessary to cause the appearance of ^{19}F nmr peaks due to $(CH_3)_2PP(CF_3)As(CH_3)_2$ (VII) (Table I). Similarly, it was not possible to separate VII from the reaction mixture by vacuum fractionation.

The Reaction of $(CF_3P)_4$ with $(CH_3)_4N_2$. A mixture of 0.1136 g (0.284 mmole) of $(CF_3P)_4$ and 0.2740 g (3.108 moles) of $(CH_3)_4N_2$ was condensed in a 5-mm nmr tube which contained a capillary of CCl_3F. The tube was sealed *in vacuo* at −196° and the ^{19}F nmr spectrum run at −90°. The spectrum consisted of peaks attributable to $(CF_3P)_4$[10] and $(CF_3P)_5$.[10] Integration of the signals indicated that the CF_3P groups were approximately evenly distributed among the tetramer and pentamer. Immediately after the nmr experiments the reaction mixture was a uniformly yellow color. After standing a few hours at ambient temperature the reaction mixture darkened and separated into two layers, the lower of which was dark brown.

Ir Spectra. Most of the infrared spectra were measured on a Perkin-Elmer Model 337 grating spectrophotometer. Beckman

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(10) E. J. Wells, H. P. K. Lee, and L. K. Peterson, *Chem. Commun.*, 894 (1967).

IR-7 and IR-11 instruments were employed when more accurate data were desirable.

Uv Spectra. The uv spectra were measured on a Cary Model 14 spectrophotometer.

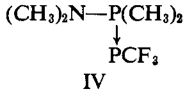
Nmr Spectra. All the pmr spectra were recorded on a Varian A-60 spectrometer. Most of these spectra were also recorded on a Varian HA-100 spectrometer. The variable-temperature studies of $[(CH_3)_2As]_2PCF_3$ were conducted on the Varian HA-100 instrument. The probe temperatures, which are believed to be accurate to ±1°, were calibrated using the peak separation of methanol. Line widths and frequencies were read directly off the chart paper. The ^{19}F spectra were measured on a Varian HA-100 spectrometer operating at a frequency of 94.1 MHz. The ^{19}F chemical shifts are in parts per million upfield from external CCl_3F.

Results and Discussion

(a) CF_3P Insertion Reactions. Proton and ^{19}F nmr spectroscopy was used to ascertain whether CF_3P insertion reactions had occurred. The nmr parameters of the insertion products are presented in Table I. The reaction of $(CF_3P)_4$ with $(CH_3)_4As_2$ proceeds to virtual completion at room temperature to yield the diarsinophosphine, $[(CH_3)_2As]_2PCF_3$ (I). This compound and Dobbie and Cavell's arsinophosphines,[11] $R_2AsPR'_2$, represent the first examples of compounds with P(III)–As(III) bonds. The chemistry of I has been investigated briefly. The P–As bonds are cleaved quantitatively by HCl to yield CF_3PH_2 and $(CH_3)_2AsCl$. The capture of the proton by the presumably less basic phosphorus atom is not unexpected in view of the findings of Grant and Burg[12] on the hydrochlorination of $(CH_3)_2PP(CF_3)_2$. A bis-borane adduct $[(CH_3)_2As]_2PCF_3 \cdot 2BH_3$ (II) is formed when I is exposed to excess B_2H_6. The observation of a singlet in the ^{11}B nmr spectrum of II and the fact that the P–C stretching frequency does not shift upon coordination of I suggest that the BH_3 units are bonded to arsenic. However, it is not possible to exclude a borane-exchange process of the type postulated[13] for $P_2F_4 \cdot BH_3$.

In order to produce useful yields of $(CH_3S)_2PCF_3$ (III), it was necessary to heat the $(CF_3P)_4$–$(CH_3)_2S_2$ reaction to 135°. Burg and Gosling[9] have previously reported the preparation of III by methanethiolysis of CF_3PI_2. No reaction between $(CF_3P)_4$ and $(CH_3)_6Si_2$ was detectable even when the reaction mixtures were heated. This result suggests that lone-pair electrons are necessary for the apparently nucleophilic attack of the $(CF_3P)_4$ ring.

The ambient-temperature reaction of $(CH_3)_2NP(CH_3)_2$ with $(CF_3P)_4$ gives rise to five products, the nmr parameters and yields of which are presented in Table II. The major component of the reaction mixture is identified as the phosphinidene complex IV for two reasons: (i) the coupling constants J_{PCF} and J_{PPCF} and the ^{19}F chemical shift are very similar to those of the phosphinidene complex $(CH_3)_3PPCF_3$;[14] and (ii) J_{PCH} is larger (in magnitude)[15] for IV than for the parent aminophosphine. The presence of $[(CH_3)_2N]_2PCF_3$ and $[(CH_3)_2P]PCF_3$ is also well established because the nmr spectra of these compounds have been published previously.[2,8] The identity of $(CH_3)_2PP(CF_3)N(CH_3)_2$ (VI) was confirmed by a scrambling experiment (*vide infra*). The assignment of the highest field ^{19}F resonance to the nitrogen-bonded phosphinidene complex V must be regarded as speculative.



$$\begin{array}{c}(CH_3)_2N{-}P(CH_3)_2\\ \downarrow\\ PCF_3\end{array}$$

IV

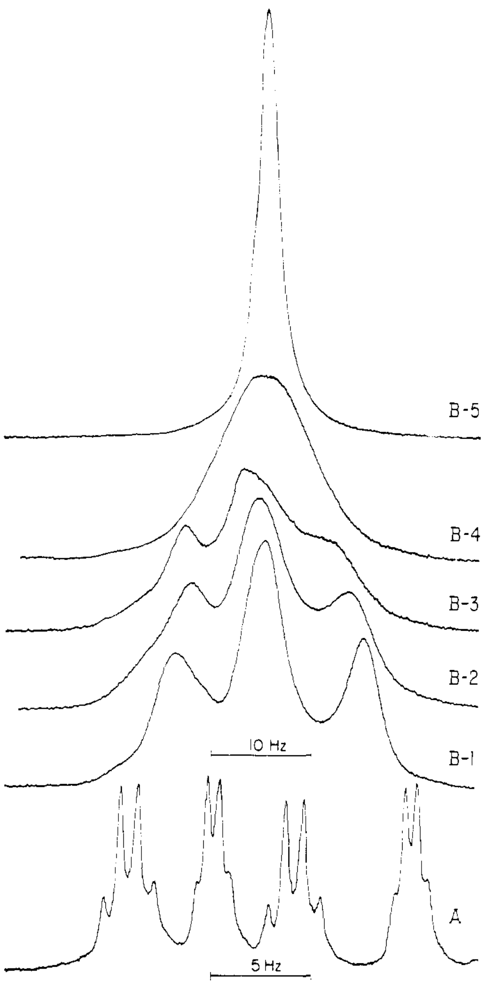
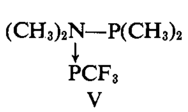


Figure 1. Solution pmr spectra of $[(CH_3)_2As]_2PCF_3$: (A) 60-MHz spectrum in C_6D_{12} under nonexchanging conditions; (B) 100-MHz spectrum in C_6H_6 at various temperatures: (B-1) 40°; (B-2) 55°; (B-3) 60°; (B-4) 70°; and (B-5) 95°. The B traces result from the collapse of overlapping doublets.



$$\begin{array}{c}(CH_3)_2N{-}P(CH_3)_2\\ \downarrow\\ PCF_3\end{array}$$

V

The reaction which ensues when mixtures of $(CF_3P)_4$ and $(CH_3)_4N_2$ are allowed to warm to ambient temperature resembles the reaction of $(CF_3P)_4$ with $(CH_3)_3N$[14] in two respects: (i) $(CH_3)_4N_2$ interconverts $(CF_3P)_4$ and $(CF_3P)_5$; and (ii) the reaction mixture develops a darker lower layer upon standing. No CF_3P insertion product was detected; hence the reaction does not appear to proceed beyond the phosphinidene complex stage.

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(11) R. C. Dobbie and R. G. Cavell, *J. Chem. Soc.*, 1406 (1968).

(12) L. R. Grant and A. B. Burg, *J. Am. Chem. Soc.*, 84, 1834 (1962).

(13) K. W. Morse and R. W. Parry, *ibid.*, 89, 172 (1967).

(14) A. B. Burg and W. Mahler, *ibid.*, 83, 2388 (1961).

(15) Actually J_{PCH} decreases when a phosphine is quaternized or enters into adduct formation due to a sign change in this coupling constant. See S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *ibid.*, 88, 2689 (1966); (b) A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Commun.*, 89 (1966); (c) G. Mavel in "Progress in N.M.R. Spectroscopy," Vol. 1, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, New York, N. Y., 1966, p 251; (d) W. McFarlane, *Chem. Commun.*, 58 (1967); (e) E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, 7, 165 (1968).

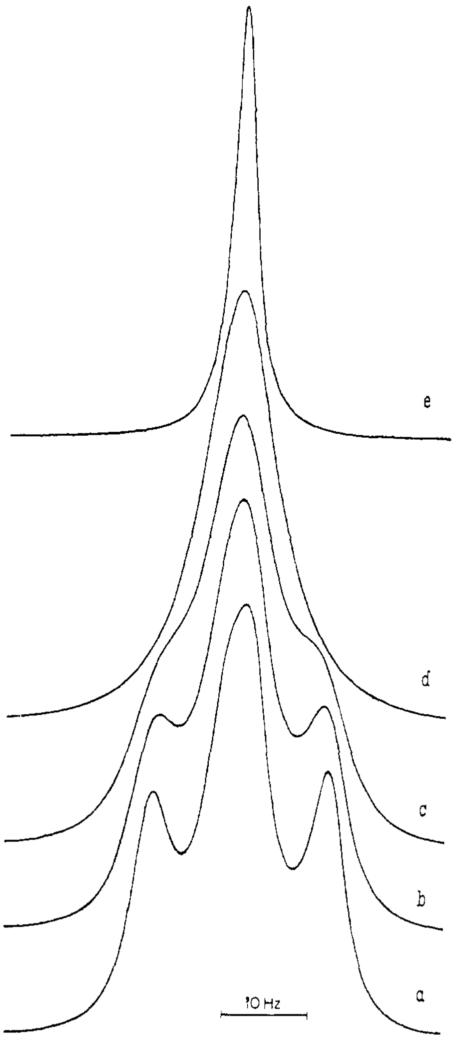
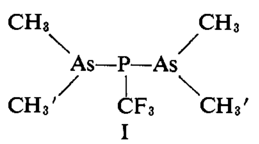


Figure 2. Calculated spectra of $[(CH_3)_2As]_2PCF_3$ in C_6H_6 solution for various inverse mean lifetimes ($1/\tau$, sec^{-1}): (a) 70.0; (b) 100.0; (c) 150.0; (d) 450.0; and (e) 4500.

(b) Scrambling Reactions. No new peaks were discernible in the ^{19}F nmr spectra when equimolar mixtures of $[(CH_3)_2N]_2PCF_3$ and $[(CH_3)_2P]_2PCF_3$, or $[(CH_3)_2As]_2PCF_3$ and $[(CH_3)_2P]_2PCF_3$, were allowed to stand at ambient temperature for prolonged periods. In both cases it was found necessary to heat the samples to ~130° to observe new ^{19}F resonances. The nmr data (Table I) are those expected for the scrambled products $(CH_3)_2PP(CF_3)N(CH_3)_2$ (VI) and $(CH_3)_2PP(CF_3)As(CH_3)$ (VII). Isolation of VI and VII proved impossible due to the close similarity of their vapor tensions to those of the starting materials. Future efforts will be directed toward cleaner syntheses of these new materials.

(c) The ^1H Nmr Spectrum of $[(CH_3)_2As]_2PCF_3$. Under nonexchanging conditions the pmr spectrum of I consists of two doublets of quartets of equal intensity


I

$(CH_3)(CH_3')As{-}P(CF_3){-}As(CH_3)(CH_3')$

(see Figure 1A and Table I). By running the ^1H spectra of I at 60 and 100 MHz, we have established that the CH_3 and CH_3' groups are anisochronous.[16] This nonequivalence arises because the phosphorus atom is only an asymmetric center with respect to a particular $(CH_3)_2As$ moiety and not with respect to the molecule as a whole. This means that it takes phosphorus or arsenic atom inversion *plus* rotation around the P–As bonds to achieve equivalence of the CH_3 and CH_3' groups. This is a somewhat similar stereochemical situation to that reported by McFarlane[17] for $(i\text{-}C_3H_7)_2PC_6H_5$.

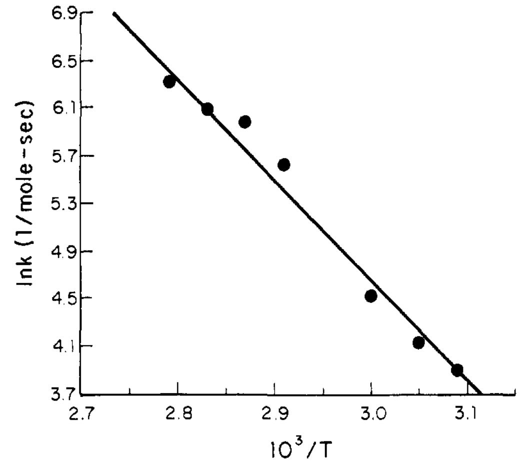
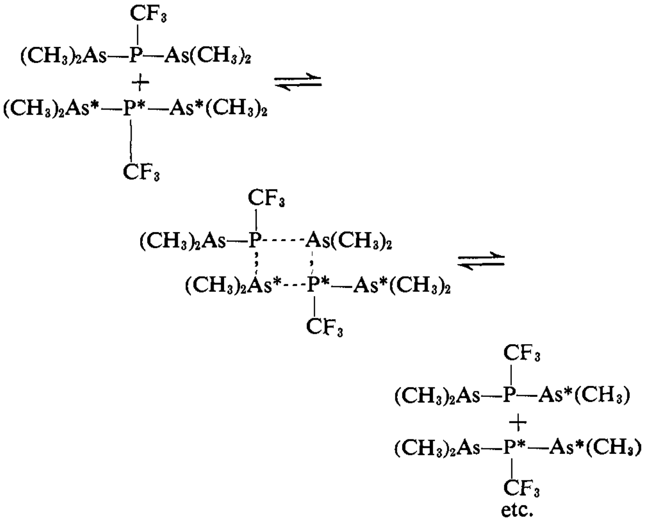


Figure 3. Arrhenius plot for $[(CH_3)_2As]_2PCF_3$ in C_6H_6 solution. The rate constants, k, were calculated from the values of $1/\tau$ and M_0 (2.79 moles/l.).

It was anticipated that at higher temperatures (>150°)[18] the pmr spectrum of I would collapse to a doublet. However, as indicated in Figure 1, the ^1H spectrum of I (C_6H_6 solution) collapses to a singlet above 65°. These spectral changes are reversible. We attribute the loss of phosphorus coupling to an intermolecular exchange reaction which is probably of the four-center type, *viz.*



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[16] The terms "chemical shift nonequivalence" and "magnetic nonequivalence" are not desirable because the latter has been taken to mean the former as well as "magnetic nonequivalence in the spin coupling sense." Accordingly, we prefer the terms "anisochronous" and "spin-coupling nonequivalence," see K. Mislow and M. Raban, *Topics Stereochem.*, **1**, 23 (1967).

[17] W. McFarlane, *Chem. Commun.*, 229 (1968).

[18] Temperatures of this order of magnitude are necessary to cause pyramidal inversion in diphosphines and diarsines; see J. B. Lambert, G. F. Jackson, and D. C. Mueller, *J. Am. Chem. Soc.*, 90, 6401 (1968).

This hypothesis is supported by the following observations: (i) a heated equimolar mixture of $[(CH_3)_2P]_2PCF_3$ and $[(CH_3)_2As]_2PCF_3$ developed new ^{19}F nmr peaks which are attributable to $(CH_3)_2PP(CF_3)As(CH_3)_2$ (*vide supra*); (ii) when the concentration of I in C_6H_6 was varied at 45° significant changes occurred in the inverse mean lifetimes ($1/\tau$) of the ^1H resonances of the substrate. The theoretical line shapes which are presented in Figure 2 were calculated[19] for various inverse mean lifetimes. By detailed comparisons of the intensities, frequencies, and over-all line shapes of the calculated and experimental spectra, it was possible to obtain a $1/\tau$ value corresponding to each temperature. For a bimolecular process the rate constant, k, is related to the inverse mean lifetime, $1/\tau$, by the equation[20]

$$k = \frac{1}{\tau}\left(\frac{e-1}{M_0}\right) \qquad (1)$$

where M_0 is the molar concentration. An Arrhenius plot of ln k *vs.* reciprocal temperature (Figure 3) yielded an activation energy of 16.0 kcal/mole. The entropy of activation was calculated to be −3.7 eu at 60°. We presume that the small entropy of activation is caused by strong solvation of I by benzene. This is supported by the rather marked changes in the pmr parameters of I when the solvent is changed from C_6H_6 to C_6D_{12}, $(CH_3)_6Si_2$, or $(CH_3)_4Si$. Furthermore, the coalescence temperatures were ~40° higher in the nonaromatic solvents. The effect of solvation on a number of organometallic exchange reactions has been discussed by Brown.[21]

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[19] These calculations were performed with the Saunders program. We thank Dr. D. Zetik for adapting this program for the CDC 6600 computer.

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The Ultraviolet Absorption Spectra of Derivatives of Polysilanes.[1] A Probe of (p → d)π Bonding in Organosilicon Compounds

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Abstract: The electronic absorption spectra of permethylated polysilanes, $Me(SiMe_2)_nMe$, are discussed, together with the possibility that the perturbation of the spectra by various substituents may provide an estimate of $(p \rightarrow d)_\pi$ bonding. The various possible assignments of the ground and excited states of the long-wavelength absorption band are considered in the light of ionization potential measurements, and the spectral properties of phenyl derivatives and the other group IV catenates. The ultraviolet absorption spectra of 1- and 2-substituted derivatives of heptamethyltrisilane, $Me_3SiMe_2SiMe_2SiX$ and $(Me_3Si)_2SiMeX$, where X includes hydrogen, halogen, oxygen, sulfur, and nitrogen groups, have been measured. The observed perturbations of the 216-nm absorption band of the parent trisilane are interpreted in terms of σ_{Si}–p_X and d_{Si}–p_X interactions. Some of the 2-substituted derivatives exhibit a second, low-intensity, band to the red of the 216-nm absorption. Based on the spectra of model compounds and simple energy considerations, this partially forbidden band is assigned to a charge-transfer transition from silicon to the substituent. The spectra of some di- and trisubstituted compounds are also reported. The relevance of the spectra to the question of $(p \rightarrow d)_\pi$ bonding is discussed.

Catenates of the heavier group IV elements (Si, Ge, Sn, Pb) exhibit one or more electronic transitions in the ultraviolet and visible regions of the electromagnetic spectrum.[2] Because σ electrons must be involved, and because catenates of carbon (*i.e.*, alkanes) do not absorb above 160 nm,[3] it has frequently been suggested that the low energy of these transitions is a consequence of the energetic accessibility of d orbitals in these heavier elements. If this analysis is correct and d orbitals are in fact involved in the excited state of these transitions, then electronic spectroscopy represents a latent quantitative method of studying the frequently invoked participation of d orbitals in the bonding of derivatives of the group IV elements. With this in mind, we have initiated a study of how the long-wavelength absorption of polysilanes is perturbed by the introduction of various substituents, particularly those which are commonly believed to interact with Si d orbitals. Quite apart from the question of d orbital involvement, such a study is desirable because of the increasing interest[4] in the elec-

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[2] For compilations of the published spectra, see M. Kumada and K. Tamao, *Advan. Organometal. Chem.*, **6**, 1 (1968); W. H. Atwell and H. Gilman, Proceedings of the International Symposium on the Decomposition of Organometallic Compounds to Refractory Ceramics, Metals and Metal Alloys, Dayton, Ohio, 1967.

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