Inorg. Chem. **1983**, *22*, 2573–2577 **2573**

Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1062

Further Study of the Phosphorus(III) Ylide $CF_3P{=}CF_2$: Its Isomeric Dimers, the Trimer, and New Diastereomers. NMR Confirmation of Structures

ANTON B. BURG

Received November 24, 1982

The previously reported formation of $(CF_3PCF_2)_2$ (and now also the trimer), by the liquid-phase action of $Zn(CH_3)_2$ on $(CF_3)_2PH$, requires base catalysis, without which the diastereomeric $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ becomes the main product of a far slower reaction. Catalysis by $(CH_3)_3N$ gives high yields of the monomer $CF_3P{=}CF_2$, now found to be stable as a gas at 100 °C or liquid at −78 °C (volatility 15 mm), but the warmed liquid polymerizes rapidly. Low-pressure flow of $(CF_3PCF_2)_2$ at 440 °C yields the monomer almost quantitatively; similarly, the trimer goes to monomer, dimer, and unidentified products, and high-vacuum pyrolysis of nonvolatile $(CF_3PCF_2)_n$ gives monomer, dimer, and trimer. Catalyzed by diborane at 100 °C, $CF_3P{=}CF_2$ goes mainly to a 4:1 mixture of $(CF_3PCF_2)_2$ isomers having CF_3 either trans or cis on the $\overline{P{-}C{-}P{-}C}$ ring; some $(CF_3PCF_2)_3$ also is formed. The ^{19}F NMR spectrum of CF_2 in the cis dimer is basically an A_2B_2 type, with unusual parameters explained by steric compression. Also for steric reasons, the trimer $(CF_3PCF_2)_3$ has one axial and two equatorial CF_3 groups, confirmed by the ^{19}F NMR spectrum.

The monomeric phosphorus(III) ylide $CF_3P{=}CF_2$ was assumed to be an intermediate in the attack upon $(CF_3)_2PH$ by ammonia,[1] in the formation of $(CF_3PCF_2)_2$ (and now also the expected trimer) from $(CF_3)_2PH$ and $Zn(CH_3)_2$ (the "Kang reaction"),[2] and in the BF_3-catalyzed decomposition of $SiH_3P(CF_3)_2$ to yield a 4:1 mixture of $(CF_3PCF_2)_2$ isomers.[3] Also apparent was its involvement in the formation of interesting new polyphosphines from $(CF_3)_2PH$ and $(CH_3)_3N$.[4] Meanwhile, it was obtained as a manageable compound by passing $(CF_3)_2PH$ over dry KOH.[5]

This monomer is formed more cleanly by the low-pressure dissociation of $(CF_3PCF_2)_2$ or $(CF_3PCF_2)_3$ in a flow system at 440 °C; purification then is easy. It proved to be stable for convenient lengths of time as a liquid at −78 °C (volatility 15 mm); or in the vapor phase with a noncatalytic wall it seems to be inert even at 100 °C. It promises new and interesting chemical variety, little of which has been explored. One new effect is its catalytic conversion (in the vapor phase at 100 °C) to the 4:1 mixture of $(CF_3PCF_2)_2$ isomers.

These isomers now are found to represent cis and trans placement of CF_3 groups on the same $\overline{P{-}C{-}P{-}C}$ ring: the less stable form is the sterically crowded cis isomer. The most immediate evidence here was the spontaneous conversion of the cis to the trans form; then a fuller study of the ^{19}F NMR spectrum left no doubt.

The earlier belief in a $\overline{P{-}P{-}C{-}C}$ ring for this isomer was based upon a ^{19}F NMR spectrum for CF_3 (Varian T60 instrument) showing a doublet of triplets of triplets, interpretable as due to FCP, FCPCF, and FCPCCF couplings; and the upfield aspect appeared to be a second-order C_2F_4 spectrum.[3] In fact, other components of the CF_2 spectrum, completing a very interesting A_2B_2 pattern, were not noticed because they were outside of the usual medium-resolution range (500 s^{-1}) of the T60 chart.

The present work includes a new study of the Kang reaction, which yields not only the original trans dimer but also traces of the cis dimer, minor amounts of the trimer $(CF_3PCF_2)_3$, probably a trace of tetramer, and surely some higher polymers dissociable by heat to CF_3PCF_2 monomer, dimer, and trimer. Also new is the observation that the Kang reaction requires a basic catalyst, without which the process is far slower, yielding very little of the CF_3PCF_2 oligomers; the major product then is the decidedly unpredicted new bis(phosphino)difluoromethane $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ (hereinafter "MePCP").

The catalyst in the original Kang reaction was the wall of the borosilicate glass container. More effective is a trace of trimethylamine, whereby the monomer can be formed in high yields, escaping to the vapor phase more rapidly than it can dimerize in the liquid reaction mixture. Then it usually will be contaminated by unused $(CF_3)_2PH$, but vapor-phase catalysis leads to a clean mixture of the dimer isomers.

Experimental Methods

Recent papers on related subjects have described some of the high-vacuum methods employed in the present work.[4] The usual container for the Kang reaction was a thick-walled Pyrex bulb, leading through a long, narrow neck and a Teflon-plugged O-ring valve to the vacuum line. Methane pressures up to 8 atm could be sustained, with small leakage toward the automatic Sprengel pump which collected the methane for measurement.[6] For high-temperature flow processes, the glass coil (7–8 mm tubing, 1-m length with six turns) was immersed in molten Woods metal, contained in an electrically heated steel test tube ("bull plug") of 60 mm i.d. The temperature was read on a mercury-in-glass thermometer, the 10-degree inaccuracy of which was not significant. The pressure always was minimal.

For purification of very small samples (e.g., 0.05 mmol) it was convenient to employ a 2.4 mm (i.d.) vertical tube (with a small bulb at the bottom end), leading through a Stock valve to the vacuum line. Reflux at 0 or −78 °C could be maintained by ice or dry ice in a surrounding cylindrical container. For intermediate temperatures, the column could be wrapped in a paper towel doused with a cooled liquid such as dichloromethane at −78 °C; then when the mercury in the adjacent Stock valve showed a slight pressure, the vapor could be drawn off by lowering the mercury below the U-bend of the valve. The paper wrapping held the reflux temperature down until the brief fractionation was complete. For compounds having strong mutual solubility, this technique proved to be far better than the more traditional fractional condensation through U-tubes.

For ultimate purification of *trans*-$(CF_3PCF_2)_2$, and for an increase in the concentration of *cis*-$(CF_3PCF_2)_2$, fractional crystallization was effective. The special device was a vertical 7 mm (i.d.) Pyrex tube

---

(1) Goldwhite, H.; Haszeldine, R. N.; Rowsell, D. G. *J. Chem. Soc.* **1965**, 6875. Burg, A. B. *Inorg. Chem.* **1981**, *20*, 2739.

(2) Kang, D.-K.; Burg, A. B. *J. Chem. Soc., Chem. Commun.* **1972**, 763.

(3) Maya, L.; Burg, A. B. *Inorg. Chem.* **1975**, *14*, 698.

(4) Burg, A. B. *Inorg. Chem.* **1981**, *20*, 3731.

(5) Eshtiagh-Hosseini, H.; Kroto, H. W.; Nixon, J. F.; Ohashi, O. *J. Organomet. Chem.* **1979**, *181*, C1.

(6) Bartocha, B.; Graham, W. A. G.; Stone, F. G. A. *J. Inorg. Nucl. Chem.* **1958**, *6*, 121. This pump (originally suggested in principle by the present author, but designed and brought to practice by F. G. A. Stone and R. I. Wagner) has been modified to include two parallel fall tubes, a side entrance for delivery to the gasometer, provision for larger calibrated volumes, and protection against blowover of mercury from the upper reservoir.

0020-1669/83/1322-2573$01.50/0

with a valve consisting of a 3-mm steel ball resting on a conically ground constriction near the lower (rounded off) end. The sample could be condensed as a solid above the valve and half-melted by a warming acetone bath. Then the ball was displaced, either by a magnet or by manual vibration, allowing the liquid to flow to the bottom. With the ball valve closed, the higher melting fraction now could be distilled away to another part of the vacuum line. With further separations and mixing of similar fractions, pure *trans*-$(CF_3PCF_2)_2$ could be obtained (mp −36 °C) and the cis isomer concentrated to 50% (incipient melting −55 °C). Such cis-enriched samples would contain any impurities from the original mixture—such as $P_2(CF_3)_4$—but these would not interfere seriously with the study of the cis isomer by means of its NMR spectra on the XL100 or higher frequency instruments. The pure trans and cis-rich samples all had the same volatility: 15 mm at 0 °C. Higher volatility would be due to the $P_2(CF_3)_4$ impurity, and unremoved trimer would account for lower volatility.

As before, the NMR chemical shifts (δ) are reported upfield from Cl_3CF or H_3PO_4 or downfield from Me_4Si. J values in s^{-1} ("Hz") are given in the form ${}_nJ_{XYZW}$ to represent the multiplicity n for coupling of the observed nucleus X through a chain to W. All samples were "neat" in sealed capillary tubes, centered in 5 mm o.d. standard NMR tubes containing a deuterated liquid (usually acetone-d_6) for maintaining the offset lock. For spectra requiring higher frequency instruments than the Varian XL100-FT, the XL200-FT was operated by Dr. V. V. Krishnamurthy of our Hydrocarbon Institute, or use was made of the Bruker WM500-FT instrument at the Southern California Regional NMR Facility (Caltech).

The ^{19}F NMR spectra for the CF_2 groups include complex types (AB, A_2B_2, or beyond) with branches composed of multiplets due to further coupling. For these, the actual spectra usually are too complex for presentation as printed figures, but the given data can be used to construct the patterns as vertical-line ("stick") diagrams, theoretical interpretation of which may be feasible. When δ values are reported to high precision, the purpose is to compare related spectra on the same chart rather than presume any absolute values.

New Studies of the Kang Reaction

Original Process. The reaction of $(CF_3)_2PH$ with slightly less than equimolar $Zn(CH_3)_2$ was repeated many times, with yields of $(CF_3PCF_2)_2$ varying from 5 to 52%. The trimer was reasonably expected as a byproduct and now was observed as a new compound. At the onset of the reaction, as indicated by a slight precipitate, the bulb was cooled to −196 °C and rewarmed (usually to 0 or 25 °C) thereby consigning the methane to the upper part of the tube and confining the $(CF_3)_2PH$ to the liquid phase.

The best such experiment employed 4.091 mmol of $(CF_3)_2PH$ and 3.569 mmol of $Zn(CH_3)_2$. It progressed only 10% during 5 days at 0 °C, but during 16 h at 25 °C it consumed 97.7% of the $(CF_3)_2PH$ and 55% of the $Zn(CH_3)_2$; much of the recovered $Zn(CH_3)_2$ came by heating the residue in vacuo, first at 100 °C and finally to 250 °C. This process yielded also 0.187 mmol of $CF_3P{=}CF_2$ (5.4%), along with some dimer and trimer. The final yield of dimer was 0.909 mmol (52%) and of trimer, 0.130 mmol (11%, but of uncertain purity). There was also 0.061 mmol (3.5% yield) of MePCP; products with still smaller yields were not identified.

Recognition of Basic-Wall Catalysis. A far slower process, giving low yields of the dimer and methane and higher yields of MePCP, occurred when the same reaction tube was used again for similar experiments, with or without cleaning by acids. It appeared that the formation of the dimer (with some monomer and trimer) depended upon catalysis by the wall, attributed to the basic effect of borosilicate oxygen. Then this effect diminished as the $(CF_3PCF_2)_n$ polymer film covered the active points; and washing with nitric acid or dilute HF also destroyed the catalyst. The catalytic effect could be restored by washing with dilute KOH, rinsing well, and baking out in vacuo.

The requirement of a basic catalyst seems obvious in retrospect: the direct removal of HF from $(CF_3)_2PH$ by $Zn(CH_3)_2$ would fail because the covalently bonded CH_3 group would not easily take a proton from the strong P–H bond. But a generally weaker, hydrogen-bonding base would dehydrofluorinate $(CF_3)_2PH$ to $CF_3P{=}CF_2$; then the proton-active (base)·HF would attack $Zn(CH_3)_2$ to make CH_4 and CH_3ZnF, restoring the base for further action.[7] The base also would oligomerize $CH_3P{=}CF_2$, most effectively during a fairly slow overall process.

Table I. Amine-Catalyzed Kang Reaction

time interval, min	added amt of $(CH_3)_3N$, mmol	increment of CH_4, mmol	total amt of CH_4, mmol
0	0.022		
60		0.923	0.923
60		0.411	1.334
105	0.022	0.714	2.048
110		0.411	2.459
80		0.263	2.722
55	*a*	0.910	3.632
60		0.384	4.016
65	*b*	0.054	4.070
50		0.004	4.074
90	0.022	1.463	5.537
90	0.013^b	0.348	5.885
120	*c*	0.370	6.255

[a] At this point, the volatile components had been removed, with heating in vacuo to 100 °C. The dimer and less volatile products were taken away, and the more volatile components, including recovered amine and $Zn(CH_3)_2$, were brought to a clean reaction tube. [b] The conditions were as in footnote *a*, but the residue had been heated in vacuo to 250 °C, fully converting CH_3ZnF to ZnF_2 and $Zn(CH_3)_2$ and forming small yields of monomer, dimer, and trimer from the polymer. [c] The conditions were as in footnote *b*, with an estimate that a 3.087-mmol fraction passing a U-trap at −90 °C (volatility 11 mm at −78.5 °C) included 2.1 mmol of $CF_3P{=}CF_2$, with unused $(CF_3)_2PH$.

Trimethylamine Catalysis. For such a mechanism, $(CH_3)_3N$ seemed promising: it is known to be effective for removal of HF from $(CF_3)_2PH$,[4] and $(CH_3)_3NH^+$ surely would attack $Zn(CH_3)_2$. Also, the present work shows that it catalyzes dimerization of $CF_3P{=}CF_2$ in the liquid phase.

Indeed, a trace of $(CH_3)_3N$ caused $CF_3P{=}CF_2$ to be produced more rapidly than it could dimerize. For example, 5.331 mmol of $(CF_3)_2PH$, 3.975 mmol of $Zn(CH_3)_2$, and 0.027 mmol of $(CH_3)_3N$, during 160 min in the 17-mL reaction tube at 0 °C, gave only 0.04 mmol of dimer. The main effluent was 4.00 mmol of a fraction estimated as equimolar $(CF_3)_2PH$ and $CF_3P{=}CF_2$ (60% yield). Further reaction was slow because the catalyst was trapped in the nonvolatile solid. High-vacuum pyrolysis of this solid gave 0.12 mmol (3.6%) of additional monomer and brought the yield of dimer to 0.18 mmol (11%). An impure trimer fraction amounted to 0.10 mmol (9%).

Another such experiment, employing 6.803 mmol of $(CF_3)_2PH$ and 6.224 mmol of $Zn(CH_3)_2$, was conducted in the 17-mL tube as described in Table I. The monomer remained with the reactants, and methane production was used to monitor progress. The amine was added as needed to maintain a good reaction rate.

The yield of dimer directly from this process was 0.565 mmol (18% relative to methane production), of which one-fifth was the cis isomer. A 0.015-mmol yield of $P_2(CF_3)_4$ could be ascribed to the previously described reaction of $(CF_3)_2PH$ with

---

(7) Another aspect of the mechanism could involve direct base–$Zn(CH_3)_2$ bonding, whereby activation for methidic action would be facilitated. The unstable white solid $[(CH_3)_3N]_2Zn(CH_3)_2$ was observed in a single experiment by the author at The University of Chicago in the year 1938. Its dissociation pressures (7 mm at −20 °C and 56 mm at 0 °C) would suggest $\log P = 13.181 - 3133/T$. Analogous R_2NH compounds have been reported by: Thiele, K. H.; Bendull, M. *Z. Anorg. Allg. Chem.* **1970**, *379*, 199.

$(CH_3)_3N$.[4] The dimer from vacuum pyrolysis of the nonvolatiles amounted to 0.853 mmol (27.4%), of which only 0.051 mmol was the cis isomer. Saved out from these pyrolyses was 0.848 mmol (13.6%) of monomer. The direct yield of the trimer $(CF_3PCF_2)_3$ was 0.051 mmol (2.5%) and from the pyrolysis, 0.089 mmol (4.3%)—altogether representing about one-seventh as much monomer as the total yield of dimer. MePCP was sought but could not have exceeded 0.003 mmol, in contrast to fairly good yields from the uncatalyzed Kang reaction.

In sum, this experiment gave a yield of $CF_3P{=}CF_2$ and its volatile oligomers representing 66% of the consumed $(CF_3)_2PH$. The chief loss would be represented by the dark residues of vacuum pyrolysis of the high polymer. Indeed, in another such experiment, a 75% yield of the monomer was obtained by frequently removing it, before polymerization could become important. Then the yield of other $(CF_3PCF_2)_n$ volatiles was 10%.

The Monomer $CF_3P{=}CF_2$

Sources. As obtained directly from the catalyzed Kang reaction, the monomer is mixed with residual $(CF_3)_2PH$ (volatility 6.2 mm at −78.5 °C), which is not easily eliminated. The most certain route to pure $CF_3P{=}CF_2$ then is catalytic dimerization (see below) and restoration by flow dissociation of the dimer at 440 °C. In general, pyrolysis of $(CF_3PCF_2)_n$ leads to very clean samples of the monomer. For this purpose, the cleanest high polymer comes from the liquid-phase polymerization of the separated monomer fraction. Then heating in vacuo to 250 °C gives roughly equal yields of monomer and dimer, with less trimer. The pure monomer is isolated by passage through a high-vacuum U-tube at −100 °C.

The amine-catalyzed polymer, heated slowly in vacuo to 250 °C, may form a black solid and relatively little monomer, dimer, or trimer. A far cleaner polymer is formed by warming the liquid monomer to 25 °C under pressure, or traces of a transparent film may form when the monomer is condensed with mercury vapor in the vacuum line. Such clean polymers can be vacuum pyrolyzed quantitatively to monomer, dimer, and trimer.

Also very clean is the flow pyrolysis of pure $(CF_3PCF_2)_2$ at 440 °C. Conversion to monomer occurs at a rate of 10% per pass, and the yield is at least 90%. The loss is correlated with the formation of a remarkably inert black film in the coil. The similar pyrolysis of the trimer is more wasteful: after 60% conversion in one experiment, the yield of monomer was only 34% and of dimer, 10%. Numerous unidentified (but NMR observable) volatiles amounted to 10%, relative to the consumed trimer. The conversion of trimer to dimer and monomer would be expected to be less efficient under such conditions, for the opened trimer chain would be prone to a wider variety of other processes.

Characterization. The vapor-phase molecular weight of $CF_3P{=}CF_2$ was determined as 151 (calculated 150). Its infrared spectrum showed the following frequencies (cm^{-1}), with relative intensities in parentheses: 1363 (64) and 1248 (33) for CF_2 stretching, 1148 (80) and 1132 (86) for CF_3 stretching, 737–742 (2.3) for $P{=}CF_2$ stretching and CF_3 δ_s, 541 (0.5) for CF_3 δ_a, and 458 (0.6) for $P{-}CF_3$ stretching. Peaks at 992 (1.9), 875 (0.4), and 600 (0.2) cm^{-1} are not assigned.

Catalytic Polymerization. The $CF_3P{=}CF_2$ unit may attach a base at P or use its π-bonding electrons to seize a Lewis acid—in either case forming a complex with enhanced ability to hold another $CF_3P{=}CF_2$ unit, thus initiating chain polymerization. However, this effect may fail in the vapor phase: for lack of a way to remove the energy of complex formation, only elastic collisions may occur. Indeed, when samples of $CF_3P{=}CF_2$ with traces of HCl, BF_3, or $(CH_3)_3N$ were flash evaporated at 100 °C, they failed to react during many hours at that temperature. But when the same mixtures were cooled quickly to −196 °C and warmed slowly to −78 °C, the liquid monomer changed rapidly to transparent films in which the catalysts were trapped, presumably as end groups. Traces of $CF_3P{=}CF_2$ remained in the vapor phase, as expected.

This rapid low-temperature catalytic polymerization is the reason that $CF_3P{=}CF_2$ from the Kang reaction cannot be purified by formation of the complex $(CF_3)_2PH{\cdot}N(CH_3)_3$:[4] the far faster reaction is polymerization.

Dimerization Catalysis by Diborane. The effective catalyst for the vapor-phase dimerization of $CF_3P{=}CF_2$ proved to be B_2H_6. There had been some success when $CF_3P{=}CF_2$ was kept at 100 °C for 1 h or longer in a new, vacuum-baked Pyrex bulb; but the catalytic wall soon lost effect: when it became film-coated or "poisoned", it still could be renewed by dilute KOH washing (with rinsing and vacuum bake out) but again soon became ineffective. In the same inactive 50-mL bulb, however, 0.821 mmol of $CF_3P{=}CF_2$ with 0.04 mmol of diborane, during 30 min at 100 °C, was all consumed to give 0.321 mmol (78% yield) of dimer, 0.021 mmol (7.7%) of trimer, and a slight nonvolatile film. The dimer proved to be 80% trans and 20% cis, as usual when it is formed in the vapor phase.

This vapor-phase catalysis by diborane—in contrast to the failure of other Lewis acids—seems to require a special explanation. The first step of the process could be a collision whereby $CF_3P{=}CF_2$ forms a complex with one BH_3 group from B_2H_6, displacing the other. The complex would not be rapidly dissociated because the BH_3 displacement would take away some of the complex-bonding energy and because the free BH_3 would have a very low probability of finding its way back to the complex for reversal of its formation; far more probably, the free BH_3 would encounter another $CF_3P{=}CF_2$ unit. Meanwhile, each molecule of the complex would have a high probability of encounter with another $CF_3P{=}CF_2$ unit; then ring closure would occur easily, with displacement of BH_3 to carry away some of the ring-bonding energy.

Isomeric Dimers

Isomer Ratios and Stability. The restudy of the Kang reaction showed that the fresh dimer fraction may contain as much as 5% of the cis isomer, not evident in the records of the original work—probably because the samples had aged enough for full conversion to the trans isomer. This conversion was observed first when an enriched sample changed from 45 to 30% cis during 10 days at 25 °C. During some hours at 100 °C, another sample fell to 1% cis, but at 200 °C the equilibrium was near 3% cis. The dimer surviving dissociation in the flow process at 440 °C proved to be 7% cis. Thus the molar enthalpy (ΔH) of the cis isomer may exceed that of the trans by about 3 kcal, subject to uncertainty of equilibration.

The Cis Dimer: Structure and NMR Spectra. A soldered-wire model (with CPC angles near 95% and normal bond and van der Waals radii) shows that *cis*-$(CF_3PCF_2)_2$ must have a bent-rhombic ring with strong contact between the CF_3 groups and axial F atoms in the CF_2 groups. The equatorial F atoms can have no such contacts. Thus the "geminal" F atoms in each CF_2 group must be very different: the simplest expectation would be an A_2B_2 ^{19}F NMR spectrum with $_2J_{FCP}$ and $_7J_{FCPCF}$ having first-order effects because of resonance frequencies far from CF_2 fluorine. In fact, the A_2B_2 calculation gives the observed intensity ratios of outer to inner branches: 0.69 on the Varian T60 instrument, 0.80 on the XL100-FT, 0.89 on the XL200-FT, and 0.95 on the Bruker WM500-FT.

Figure 1 shows the main positions for the downfield (equatorial F) branch, and Table II summarizes all empirical data. The major deviation from AB simplicity is splitting into

Table II. NMR Spectral Data (^{19}F) for CF_2 in the Cis Dimer

	A1	A2	A3	B1	B2	B3
freq[a]	2579.09 (o) 2286.00 (i)	2564.95 (o) 2302.76 (i)	2562.33 (o) 2300.14 (i)	−2286.00 (i) −2579.09 (o)	−2302.82 (i) −2565.00 (o)	−2300.02 (i) −2562.20 (o)
δ(cor)[b]	81.7751	82.1380	82.1089	108.1158	107.7529	107.7819
$_2J_{FCF}$,[c] s^{-1}	293.10	262.20	262.20	293.08	262.17	262.17
$_3J_{FCP}$, s^{-1}	191.90	191.91	191.89	18.5	18.5	18.5
$_7J_{FCPCF}$, s^{-1}	3.48	3.48	3.48	12.4	12.4	12.4
$_2J$(fine), s^{-1}	0.89	0.45	2.2	0.89	0.44	2.3

[a] From the XL200 spectrum, with exciting frequency 188.16 × 10^6 s^{-1}. Each frequency here represents the center of an outer or inner branch consisting of a triplet of septets of doublets–relative to the center of the entire spectrum at $\delta = 94.9454$. [b] Corrected by use of the usual A_2B_2 mathematics. [c] Apparent observed values, subject to correction by the equatorial-to-far axial FCPCF coupling (cf. Figure 1). True value: 277.65 s^{-1} for all aspects.

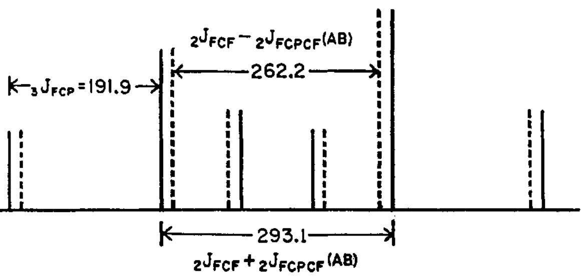

Figure 1. Skeleton downfield (A) branch of the A_2B_2 NMR spectrum of CF_2 in *cis*-$(CF_3PCF_2)_2$, with $_7J_{FCPCF}$ and smaller splittings omitted. The solid lines show the A1 positions; the dotted lines, the partially superposed A2 and A3 parts. The upfield (B) branch is difficult to portray because $_3J_{FCP}$ there is unusually small, leading to mixing with $_7J_{FCPCF}$.

three interlaced spectra for each branch, with intensity relation A1 = A2 + A3 and B1 = B2 + B3; and possibly A2 > A3, B2 > B3. Then the A_2B_2 calculation gives $_2J_{FCPCF} = 15.45$ for equatorial to far-axial coupling; the effect of this J is shown in Figure 1. The same equations give the value 2.62 for $_2J_{eq}$–$_2J_{ax}$ (equatorial vs. axial cross-ring coupling). Such coupling should relate to the "$_2J$(fine)" values given in Table II. The exact origin of these is beyond the simple A_2B_2 equations; the attention of professional NMR theorists is invited.

The shape of each component of the B spectrum is governed by an almost exact 3:2 ratio of $_3J_{FCP}$ to $_7J_{FCPCF}$. Ideal mixing would give a 17-component pattern, with the following relative intensities: 1:6:2:10:12:16:20:16:30:16:20:16:12:10:2:6:1. The actual B1, B2, and B3 interlaced spectra fit this closely enough to give the $_3J$ and $_7J$ values (Table II) within about 0.2 s^{-1}, confirmed by the spectra of other nuclei.

The CF_3 spectrum of the cis dimer is like the original T60 pattern,[3] except that we now see a low-lying corrugated catenary of more than 40 weak peaks symmetrically placed between the two main branches, with main spacings 3–4 s^{-1} and fine J near 0.5, all suggesting some degree of complexity. The main coupling constants ($_2J_{FCP} = 93.8$, $_3J_{FCPCF} = 12.3$ axial and 3.48 equatorial; cf. Table II) agree with those for the other nuclei. The spectrum center is 1.84 ppm downfield of the trans dimer.

The extreme difference between axial and equatorial F in regard to FCP coupling is to be understood as a steric effect: both CF_3 groups push axial F away from its normal bond angles, sharply decreasing the s-orbital contribution to such coupling. Then equatorial FCP bonding must gain s-orbital components, accounting for an unusually large $_3J_{FCP}$. Meanwhile, the large $_7J_{FCPCF}$ (12.4) in the B (axial) branch would include a through-space component, while CF_3 bond distortion would account for a lower than normal $_7J_{FCPCF}$ (3.48) for equatorial F.

Phosphorus NMR Spectra. The ^{31}P spectra of the cis and trans dimers could be separated only by use of the WM500 instrument. The cis isomer is centered at $\delta = -85.55$, with $_3J_{PCF} = 191.2$, $_4J_{PCF} = 93.8$, and $_3J_{PCF} = 18.2$, consistent with equatorial F, CF_3, and axial F, respectively. However, symmetrical to this clear and simple spectrum is a myriad of minor peaks requiring a very difficult mathematical analysis.

The trans dimer also shows a complex ^{31}P spectrum, the major pattern of which seems simple: $\delta = -89.5$; $_3J_{PCF} = 215.2$ (cf. 218.9 for the main separation in the second-order CF_2 spectrum) and $_4J_{PCF} = 89.2$ (cf. 89.5 for the CF_3 spectrum). But real simplicity here would require 1:4:6:4:1 quintet coupling for $P(CF_2)_2$, instead of the precisely observable 1:2:1 triplet. Possibly the rhombic P_2C_2 ring here has a typical cyclobutane twist, forcing two F atoms into moderate contact with CF_3. Then one kind of $P(CF)_2$ coupling could be simple and the other very complex. The complexity of the original trans ^{19}F spectrum is confirmed: each minor peak or shoulder is real.[2]

The Trimer: A Triphosphacyclohexane

Sources and Characterization. The ring trimer $(CF_3PCF_2)_3$ was expected as an inevitable byproduct of any process yielding the dimers. Indeed, the best yields came from the liquid-phase Kang reaction, wherein the third CF_3PCF_2 unit was easily available. The high-vacuum pyrolysis of the nonvolatiles, or the vapor-phase dimerization of CF_3PCF_2, gave the purest samples but the lowest yields. The final purification was done by means of the micro-size reflux column at 0 °C; less volatile material (possibly including a tetramer) could not come through.

The molecular weight of the best sample (as judged by the ^{19}F NMR spectrum) was observed at 450 ± 2, just as calculated; other samples ranged from 436 to 460. Its volatility (1.70 mm at 24.5 °C, 3.12 mm at 33.7 °C, and 5.80 mm at 43.7 °C) suggests the equation $\log P = 7.2823 + 1.75 \log T - 0.0055T - 2900/T$ (bp 165 °C, Trouton constant 22.6 eu).

The high-vacuum thermal dissociation of the trimer has been mentioned in relation to the monomer. The 44% yield of monomer plus dimer (from 60% consumed) is still high enough to lend further support to the formula $(CF_3PCF_2)_3$.

Structure and NMR Spectra. It is reasonable to assume that this trimer is a chair-form 1,3,5-triphosphacyclohexane, with all CPC angles near 95°, FCF near 108°, and PCP near 111°. Then the soldered-wire model shows clearly that no two CF_3 groups can be axial, nor can all three CF_3 groups be equatorial without conflict with the CF_2 groups. Relief comes by placing one CF_3 group in an axial position; then one equatorial CF_3 can push F in one CF_2 group toward the vacant equatorial position, easing pressure on the other CF_2 group. Thus the equatorial CF_3 groups may be chemically but not magnetically equivalent, and their ^{19}F NMR spectrum must be second order. Indeed, Figure 2 shows a second-order shape, persisting over a wide range of temperatures and instrument frequencies, but not interpretable.

The axial CF_3 here shows an unusually high $_3J_{FCPCP}$, presumably including a through-space component due to com-

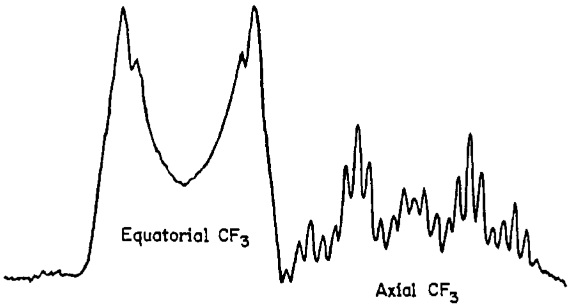

Figure 2. ^{19}F NMR spectrum of CF_3 in $(CF_3PCF_2)_3$, on the XL100 instrument. The XL200 and WM500 instruments show the axial and equatorial patterns farther apart, but with no improvement in resolution. For equatorial CF_3, $\delta = 45.00$ and the distance between maxima is 86 s^{-1}. For axial CF_3, $\delta = 46.64$, ${}_2J_{FCP} = 76$ s^{-1}, ${}_3J_{FCPCF} = 31.1$ s^{-1}, and ${}_5J_{FCPCF} = 7.70$ s^{-1}.

pression of F against phosphorus lone-pair electrons having mostly 3s character.

The unique CF_2 group (between the equatorial CF_3 groups) shows an AB spectrum as expected, with remarkably different branches. Upfield ($\delta = 102.0$) there is a clean doublet of triplets: ${}_2J_{FCF} = 305.3$; ${}_3J_{FCP} = 101$. Downfield ($\delta = 86.0$; ${}_2J_{FCP}$ confirmed as 304.9) there is only a doublet of broad peaks (half-height width 75 s^{-1}), presumably containing triplets for ${}_3J_{FCP} < 35$. In the WM500 spectrum, $I_o/I_i = 0.92$, as observed.

The other CF_2 groups show a similar axial–equatorial difference—upfield, $\delta = 88.38$ (${}_2J_{FCF} = 364$; ${}_3J_{FCP} = 139$, with minor complexity); downfield, $\delta = 83.70$ (${}_2J_{FCF} = 360$; secondary ${}_2J = 200$)—again with peaks broad enough (half-height width 60) to cover a small ${}_3J_{FCP}$. The I_o/I_i ratios (XL200, 0.40; WM500, 0.78) are the same as in the upfield branch. The secondary ${}_2J$ is far larger than would be expected for FCPCF coupling between CF_2 groups. The ultimate theoretical analysis here may not be feasible without details covered by the broad peaks.

The ^{31}P spectrum of the trimer could not be resolved: a very broad mound (half-height width 140), with $\delta = -6.2$ (downfield from H_3PO_4).

The Compound MePCP

The new compound $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ ("MePCP") was obtained in 25% yield from the reaction of 2.46 mmol of $(CF_3)_2PH$ with 2.34 mmol of $Zn(CH_3)_2$ (both about 92% consumed) during 11 h at 50 °C in a 22-mL reaction tube that had been washed with dilute aqueous HF and vacuum baked. The yield of $(CF_3PCF_2)_2$ was only 8% and of the trimer, somewhat less. The purest sample of MePCP from this process contained 12% trimer; with correction for this, the vapor-phase molecular weight was 318 (calculated 316). The volatility is 1.5 mm at 0 °C and 8.4 mm at 26.6 °C; the estimated boiling point is 140 °C if the Trouton constant is 21.6 eu.

The ^1H NMR spectrum clearly showed a 3:4 ratio of the diastereomers, respectively at $\delta = 6.4844$ (${}_3J_{HCF} = 50.7$; ${}_2J_{HCP} = 6.70$) and $\delta = 6.4503$ (${}_3J_{FCP} = 50.7$; ${}_2J_{HCP} = 7.00$). The CH_3 spectrum ($\delta = 1.31$; ${}_2J_{HCP} = 5.1$) showed no resolution of the diastereomers.

The ^{19}F NMR spectrum showed the component groups just in the regions expected on the basis of earlier experience with the same groups. The doublet of multiplets at $\delta = 49.7$ (${}_2J_{FCP} = 71$) belongs to CF_3 in the CF_3PCHF_2 group, and $\delta = 55.9$ (${}_2J_{FCP} = 72$) is correct for the CH_3PCF_3 group. In the connecting PCF_2P group, F appears at $\delta = 101$, as an AB spectrum in which the A and B parts have superposed inner branches, even in the WM500 spectrum; ${}_2J_{FCF}$ might be near 60. The CHF_2 group shows well-separated A and B branches, only the latter of which is easily sorted out into the diastereomeric components: δ range 115.7–119.9.

For still further confirmation of the formula, an authentic synthesis of MePCP was performed, beginning with a methoxide-catalyzed methanolysis of $(CF_3PCF_2)_2$ to MeOPCP, convertible to ClPCP and so by action of $Zn(CH_3)_2$ to MePCP. The product has the same NMR spectra as the MePCP here described. A fuller description of MePCP and the other PCP compounds mentioned here, with a fuller analysis of their NMR spectra and the further consequences of dimer methanolysis, is planned for future publication.

Acknowledgment. Gratitude is due to the operators of the XL200-FT and WM500-FT NMR spectrometers and to Dr. K. L. Servis for critical and constructive suggestions concerning NMR spectra.

Registry No. $(CF_3)_2PH$, 460-96-8; $Zn(CH_3)_2$, 544-97-8; $CF_3P{=}CF_2$, 72344-34-4; $(CH_3)_3N$, 75-50-3; *cis*-$(CF_3PCF_2)_2$, 86350-48-3; *trans*-$(CF_3PCF_2)_2$, 86350-49-4; $(CF_3PCF_2)_3$, 86350-50-7; $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ (isomer 1), 86350-51-8; $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ (isomer 2), 86350-52-9; diborane, 19287-45-7.

Contribution from the Department of Chemistry,
University of California, Riverside, California 92521

Synthesis and Characterization of Tetramethylammonium Superoxide

DONALD T. SAWYER,* THOMAS S. CALDERWOOD, KENNETH YAMAGUCHI, and CHARLES T. ANGELIS

Received December 2, 1982

The experimental conditions for the synthesis (and isolation) of tetramethylammonium superoxide $[(Me_4N)O_2]$ from KO_2 and $(Me_4N)OH\cdot 5H_2O$ in liquid ammonia have been optimized. The isolated solid salt has an assay of greater than 99.5% purity but a magnetic susceptibility that indicates only 10–20% of the molecules are paramagnetic and monomeric. In dry acetonitrile a 4 mM solution of $(Me_4N)O_2$ initially is 25% monomeric; after 2.5 days it has increased to 90% monomeric at the expense of the dimer, $[(Me_4N)_2O_2]_2$. Dissociation of the dimer is accelerated by trace levels of water (5–10 mM). The absorption spectrum of the monomer in dry acetonitrile has a single band that is characteristic of O_2^- (λ_{max} 257 nm (ϵ 10.1/mM^{-1} cm^{-1})). The diamagnetic dimer, $[(Me_4N)O_2]_2$, has a single absorption band at 289 nm (ϵ 11.6 mM^{-1} cm^{-1}) (dimer), and there is an isosbestic point at 278 nm (ϵ 5.0 mM^{-1} cm^{-1}) (monomer). The monomeric species has been characterized in the solid phase and in aprotic solvents by ESR, infrared, and Raman spectroscopy and by electrochemistry.

Since the observations that superoxide (O_2^-) is a respiratory intermediate[1] and an effective nucleophile in aprotic media,[2,3] there has been growing interest in the chemistry of O_2^-. At present, the most effective methods for the in situ generation