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New (Trifluoromethyl)diphosphines Having Methyl, Fluoromethyl, or Difluoromethyl Groups. NMR Evidence of Conformational Isomerism

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The new chiral diphosphines $R(CF_3)P{-}P(CF_3)_2$ ($R = CH_3$, CH_2F, or CHF_2) have been made from the appropriate phosphines and chlorophosphines by use of $(CH_3)_3N$ to remove HCl. The P–P bond-exchange disproportionation equilibrates near 48% for $R = CHF_2$, 31% for $R = CH_2F$, and 6% for $R = CH_3$; thus $CH_3(CF_3)P{-}P(CF_3)_2$ seems to have an especially stable structure. Its ^{19}F NMR spectrum (including two probable $CF_3{-}P$ through-space couplings) suggests a gauche form with CH_3 held in the geminal-CF_3 notch by H···F attraction. This effect would be far less for $R = CH_2F$ and absent for $R = CHF_2$. For these, spectral blurring can be attributed to isomer mixtures. The new $(RCF_3P)_2$ diphosphines have interesting second-order NMR spectra, not yet fully interpretable. The new iodophosphine $CH_2F(CF_3)PI$ also is reported.

New chiral diphosphines can be made by reactions such as

$$R(CF_3)PH + (CF_3)_2PCl + (CH_3)_3N \rightarrow (CH_3)_3NHCl + R(CF_3)P{-}P(CF_3)_2 \quad (1)$$

(where $R = CH_3$, CH_2F, or CHF_2), or the obverse process using $R(CF_3)PCl$ and $(CF_3)_2PH$. Molecular models of these diphosphines (with the expected bond angles and distances) indicate high energy barriers against rotation about the P–P bond, so that for each diphosphine the trans and two gauche isomers would be interconverted only very slowly relative to the NMR time scale; and indeed the NMR spectra seem to indicate mutual interference by isomers having similar stability.

Reactions of the type

$$2R(CF_3)P{-}P(CF_3)_2 \rightleftarrows P_2(CF_3)_4 + (RCF_3P)_2 \quad (2)$$

occur easily, and the equilibrium constants have a qualitative relation to the relative stability of the isomers.

All such diphosphines are candidates for addition to alkenes or alkynes, to make new bifunctional ligands (chiral but not always chelate) for fine tuning of the electronic states of transition-element complexes.

Experimental Methods

All volatile compounds were managed by the classical Stock-type high-vacuum methods, modified or improved for special purposes or for the employment of more modern equipment. Separations were performed by microsize high-vacuum reflux columns or by fractional condensation through a series of U-tubes. These U-tubes were connected through mercury float valves designed to serve also as accurate short-range manometers.

Infrared spectra (Beckman IR-20A instrument) are reported in cm^{-1} with relative intensities in parentheses after each frequency.

The NMR spectra were recorded by the Varian XL-100-FT instrument, for neat samples as small as 0.02 mmol, in which any impurities still could be determined. The chemical shifts are reported in ppm: for protons, downfield from Me_4Si; for fluorine, upfield from Cl_3CF; for phosphorus, upfield from H_3PO_4. For the coupling constants J, the multiplicity is indicated by left-hand subscripts. Since the units ppm and Hz (s^{-1}) are universally understood, these units usually will be omitted.

The Methyldiphosphine. Pure $CH_3(CF_3)P{-}P(CF_3)_2$ was made from 0.692 mmol each of $CH_3(CF_3)PCl$,[1] $(CF_3)_2PH$, and $(CH_3)_3N$, in a vertical tube warming to −78 °C. Occlusion of the reactants was overcome by heating the solid residue after distilling the volatiles to a fresh reaction tube, repeatedly until no more solid was formed on warming to 25 °C: recoverable yield 0.558 mmol (81%); volatility 10.5 mm at 0 °C. The NMR spectra showed traces of the disproportionation products $P_2(CF_3)_4$ and $(CH_3CF_3P)_2$. Unlike $(CH_3)_2P{-}P(CF_3)_2$[2] and $(CH_3CF_3P)_2$,[1] the monomethyldiphosphine failed to form a demonstrable BH_3 complex.

Table I. NMR Parameters for $CH_3(CF_3)P{-}P(CF_3)_2$

Protons: $\delta = 1.42$; $J_{HCP} = J_{HCPP} = 6$ ("triplet")

Fluorine

δ	45.9 *gem*	50.1 *gem*	55.4 lone
${}_{2}J_{FCP}$	71.0	70.1	65.0
${}_{2}J_{FCPP}$	4.01	17.3	20.7
${}_{4}J_{FCPCF}$	8.05	8.08	
${}_{4}J_{FCPPCF}$	2.48	2.49	
${}_{7}J_{FCPPCF}$			2.51

Phosphorus

δ	2.70 *gem*	25.63 lone
${}_{7}J_{PCF}$	70.5	
${}_{4}J_{PCF}$		65.1
${}_{4}J_{PPCF}$	20.8	17.25, 4.0
${}_{4}J_{PCH}$		6.5
${}_{4}J_{PPCH}$	6.0	
${}_{2}J_{PP}$	224.5	225.4

Table II. NMR Parameters for $CH_2F(CF_3)P{-}P(CF_3)_2$

Proton[a]

$\delta_A = 5.055$; ${}_{2}J_{HCF} = 47.5$; ${}_{2}J_{HCP} = 11.3$
$\delta_B = 5.015$; ${}_{2}J_{HCF} = 47.7$; ${}_{2}J_{HCP} = 10.8$

Fluorine

	CF_3-A	CF_3-B	lone CF_3	CH_2F[b]
δ	46.5	49	50	226
${}_{2}J_{FCP}$	67	67	64	81
${}_{2}J_{FCPP}$	9?		18	
${}_{4}J_{FCPCF}$	8.0			2.1
${}_{4}J_{FCPPCF}$	2.0			6?

[a] No outer clusters nor finer J's were observed. [b] ${}_{3}J_{FCH}$ = 47.7.

In Table I, "*gem*" refers to the $(CF_3)_2P$ group and "lone" to the $CH_3(CF_3)P$ group. The ^1H spectrum looks like a simple triplet because ${}_{2}J_{HCP}$ and ${}_{2}J_{HCPP}$ are nearly the same, as confirmed by the ^{31}P spectrum. No H···F coupling is visible.

The geminal CF_3 groups show a marginal AB pattern, with the intensity ratio of outer to inner clusters $I_0/I_i = 0.96$. For ^{31}P, the AB calculation gives the intensity ratio as 0.61; the observed ratio is 5:8. Confirmatory J values are observed.

The (Fluoromethyl)diphosphine. The compound $CH_2F(CF_3)P{-}P(CF_3)_2$ was made from equimolar $CH_2F(CF_3)PH$,[3] $(CF_3)_2PCl$, and $(CH_3)_3N$ in a number of experiments, but even though the reaction occurred in the range −110 to −78 °C, catalysis of reaction 2 reduced the yields below 50%, and the byproducts were not easily eliminated. The best sample had a volatility of 6.5 mm at 0 °C and 27.0 mm at 24.6 °C; then by assuming normal curvature and Trouton constant (21.2 eu), it is possible to extrapolate to bp = 111 °C by means of the equation $\log P = 6.9037 + 1.75 \log T - 0.005T - 2734/T$. The ^{19}F NMR spectrum never was quite free of the patterns for $P_2(CF_3)_4$ and $(CH_2FCF_3P)_2$.

The NMR data (Table II) include some uncertain J values, especially for the ^{19}F spectra, wherein sharp peaks appeared as spikes surmounting mound shapes, and the sorting out was confused by some

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(1) A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Am. Chem. Soc.*, **88**, 31 (1966).
(2) L. R. Grant, Jr., and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 1834 (1962).
(3) A. B. Burg, *Inorg. Chem.*, **20**, 2739 (1981).

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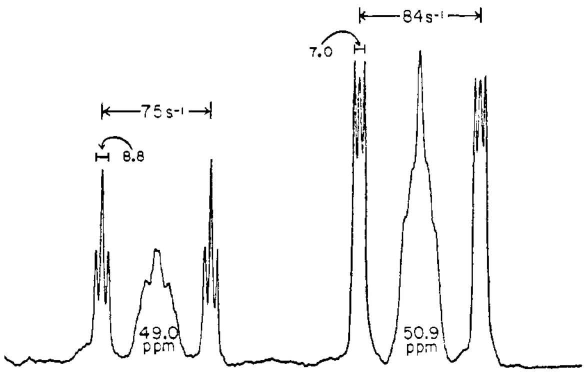

Figure 1. Second-order ^{19}F NMR spectra for the meso and optically active isomers of (CH$_2$FCF$_3$P)$_2$ in the CF$_3$ region. The triple boundary peaks most probably are doublets of doublets. Neither pattern is changed by decoupling protons.

irregularities. The presence of a minor isomer would explain such spectra.

The AB calculation for the geminal CF$_3$ groups would give I_o/I_i as 0.94, not confirmable by such a blurred spectrum. At lower temperatures (−10, −30, and −60 °C) the spectra were not significantly different—only somewhat more blurred.

The (Difluoromethyl)diphosphine. A relatively successful synthesis employing 0.322 mmol each of CHF$_2$(CF$_3$)PH,[3] (CF$_3$)$_2$PCl, and (CH$_3$)$_3$N gave 0.268 mmol (83%) of nearly pure CHF$_2$(CF$_3$)P-P(CF$_3$)$_2$. Elimination of the byproducts P$_2$(CF$_3$)$_4$ and (CHF$_2$CF$_3$P)$_2$ (altogether about 6%) was not quite successful. The volatility data (10 mm at 0 °C and 43 mm at 26.2 °C), taken with the assumption of normal curvature, would indicate bp = 100 °C.

The ^{1}H NMR spectrum of this diphosphine shows $\delta = 6.42$ ($_3J_{HCF} = 50.2$, $_2J_{HCP} = 17.5$, and $_3J_{HCPP} = 3.2$). The ^{19}F spectrum for the geminal CF$_3$ groups appears as four completely blurred clusters: $\delta_A = 46.2$, $\delta_B = 48.1$, and $_2J_{FCP} = 71$ for both. The lone CF$_3$ group is partly superposed on the CF$_3$–B part, roughly at $\delta = 51$ ($_2J_{FCP} = 60$). Irregular spikes surmounting the clusters are not assignable.

The CHF$_2$ group shows four clusters centered at $\delta = 112$, with $_2J_{FCP} = 117$ and $_2J_{FCH} = 52$, selected by proton decoupling. The outer clusters of a possible AB pattern are not to be seen; doubtless J_{FCF} is far larger than $\Delta\delta_{FF}$. Well-resolved spikes can be seen, but their spacings (1–4 s^{-1}) are irregular and unique for each cluster. Multiple superpositions reduce the number of observable frequencies to 130 (expected number, 320). Cooling to −40 °C did not appreciably change any of these spectra.

P–P Bond Exchange Reactions and Products. The new hybrid diphosphines were stored in sealed NMR tubes at 25 °C, over time periods long enough to assure equilibria according to eq 2. Then the ^{19}F NMR spectra were used to determine the relative intensities of the three components of each mixture (with not too much difficulty due to overlapping or superposition), leading to equilibrium constants of the type $K = xy/z^2$.

For CH$_3$(CF$_3$)P–P(CF$_3$)$_2$ the forward reaction gave $K = 0.0011$ (after 15 months at 25 °C); the reverse process (57% complete in 45 min; equilibrated after 24 or 72 h) gave $K = 0.0009$. The average value, 0.0010, corresponds to 6% disproportionation in the manner of eq 2. This determination depended upon the previously reported ^{19}F NMR spectra of P$_2$(CF$_3$)$_4$ and (CH$_3$CF$_3$P)$_2$;[4] for the latter, the chemical shifts are δ 54.77 and 56.24; for P$_2$(CF$_3$)$_4$, δ is 47. The accuracy of the K values was limited by the low intensities of these products, and for P$_2$(CF$_3$)$_4$, some covering by the spectrum of the main diphosphine caused difficulty.

The diphosphine (CH$_2$FCF$_3$P)$_2$ showed relatively low volatility (1.1 mm at 0 °C and 5.8 mm at 24.9 °C; for the Trouton constant 21.6 eu, the bp would be 148 °C), making it easy to isolate from the equilibrium mixture. Its identity was confirmed by a direct synthesis from equimolar CH$_2$F(CF$_3$)PH, CH$_2$F(CF$_3$)PCl, and (CH$_3$)$_3$N. Its infrared spectrum (Beckman IR-20A; vapor phase) shows the expected features: 2927 (0.55), 2885 (0.32), 1429 (1.8), 1380 (1.2), 1302 (3.8), 1280 (1.2), 1230 (1.6), 1143 (79), 1128 (67), 1020 (11), 908 (1.0),

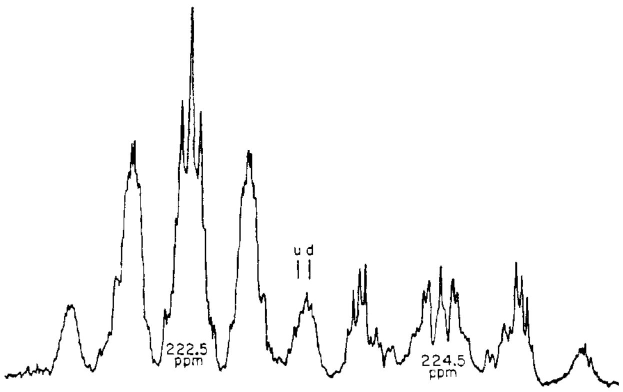

Figure 2. ^{19}F NMR spectra of the CH$_2$F groups in the meso and optically active isomers of (CH$_2$FCF$_3$P)$_2$. In the overlapping clusters at the middle, u marks the position of a member of the upfield pattern, and d marks the downfield pattern. For the latter, the cluster spacing is like a normal quintet with $_5J = 45$ s^{-1}. In the upfield pattern, the distance between the outermost maxima is 215 s^{-1}. With ^{1}H decoupled, each pattern loses its small outermost clusters, with little change in the others.

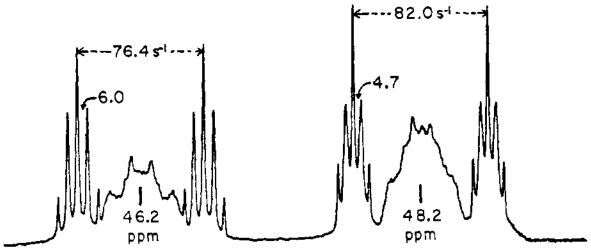

Figure 3. ^{19}F NMR spectrum of (CHF$_2$CF$_3$P)$_2$ in the CF$_3$ region. The intensity ratio of the diastereomers is 4:5. The end clusters cannot be normal quintets (or septets); as in Figure 1, each must represent a combination of J values.

855 (2.4), 740 (1.2), 590 (0.4), 535–565 (0.6), 420 (1.2), and 370–390 (1.0). Its ^{1}H NMR spectrum shows a main doublet of triplets at $\delta = 6.2$, with $_2J_{HCF} = 48.8$; the triplets are interpreted as composites of doublets with $_2J_{HCP} = {}_3J_{HCPP} = 6.5$, just as for CH$_3$(CF$_3$)P–P(CF$_3$)$_2$. A weaker spectrum for the other diastereomer is slightly upfield and mostly occluded, but $_2J_{HCF} = 50.1$ is recognizable. The ^{19}F spectra are shown by Figures 1 and 2; the former was used to determine the disproportionation constant of CH$_2$F(CF$_3$)P–P(CF$_3$)$_2$ as 0.050 (31% forward) after 14 weeks at 25 °C.

For nearly pure (CHF$_2$CF$_3$P)$_2$, the new iodophosphine CHF$_2$(CF$_3$)PI was made by contact of CHF$_2$(CF$_3$)PCl with dry, spongy NaI[1] and brought to reaction with mercury. The volatility of the product (5.2 mm at 0 °C and 22 mm at 23.6 °C) would give the bp as 112 °C, for a Trouton constant equal to 21.5 eu. Its ^{1}H NMR pattern is analyzable as $\delta = 6.548$ ($_3J_{HCF} = 50.8$, $_2J_{HCP} = 8.7$, $_3J_{HCPP} = 3.1$) for the stronger spectrum, and $\delta = 6.456$ ($_3J_{HCF} = 50.8$, $_2J_{HCP} = 9.8$, $_3J_{HCPP} = 4.6$) for the weaker. For ^{31}P, $\delta = 21.6$, with all J values uncertain. With the fluorine decoupler set for CF$_3$, five clusters appear, with average spacing 61 s^{-1}, but no two clusters have the same shape.

The ^{19}F pattern for (CHF$_2$CF$_3$P)$_2$ shows $\delta = 112$ for CHF$_2$, with $_2J_{FCH}$ recognizable as near 50, but the multicluster pattern of each diastereomer is mostly occluded by the other, so that no finer resolution seems possible. The far clearer (although not readily interpretable) patterns for the CF$_3$ group (Figure 3) were used for a relatively rough determination of the disproportionation constant of CHF$_2$(CF$_3$)P–P(CF$_3$)$_2$—with much difficulty on account of occlusion. The result, $K = 0.2$, comes from 48 ± 4% forward reaction.

Structural Discussion

Molecular models with the expected bond angles and distances (and van der Waals radii) show high P–P bond rotational barriers for these diphosphines. The gauche and trans isomers would not interconvert on the NMR time scale at feasible temperatures. Indeed, none of their ^{19}F NMR spectra change much in the range −60 to +60 °C. For each di-

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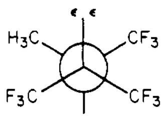
(4) D.-K. Kang, K. L. Servis, and A. B. Burg, *Org. Magn. Reson.*, 3, 101 (1971).

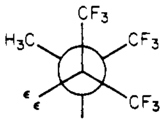
phosphine, the least energetic isomer should predominate, possibly excluding the others. Such a case would be indicated by a relatively clean and well-resolved ^{19}F NMR spectrum, whereas more nearly equal isomers would suffer mutual occlusion.

Of the three $R(CF_3)P–P(CF_3)_2$ compounds, only for R = CH_3 is the ^{19}F NMR spectrum completely resolved and interpretable, suggesting an especially stable structure. Also suggestive is the low value of the disproportionation constant, implying that the special stabilization of the unique isomer overcomes any entropy advantage of a mixture of $(RCF_3P)_2$ isomers.

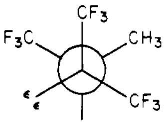
The three possible isomers (aside from their NMR-trivial mirror images) of $CH_3(CF_3)P–P(CF_3)_2$ are shown by the Newman diagrams



trans



gauche-1



gauche-2

A decision among these is indicated by the ^{19}F NMR parameters. One of the geminal CF_3 groups has $_2J_{FCPP}$ = 4.0, roughly as expected for coupling through the chain. The other has $_2J_{FCPP}$ = 17.3, high enough to suggest F···P through-space coupling. Also, the lone CF_3 group has an even higher $_2J_{FCPP}$ (20.7), again suggesting through-space coupling.[5] Then only the gauche-2 form obviously provides two and only two CF_3–P cis contacts for such coupling.

However, it could be argued that the trans form would be twisted by repulsion between the lone and cis-geminal CF_3 groups, thereby bringing each closer to its far P atom, but the trans *gem*-CF_3 would have less contact for through-space coupling. Thus the trans isomer is not eliminated by the NMR results.

The actual geometry of the trans and gauche-2 isomers (studied by means of an accurate wire model with 100° angles at each P) shows that for each CF_3 group cis to a lone pair (i.e., 60° away in the Newman projection) there would indeed be strong mutual penetration of F and P van der Waals spheres during CF_3 group torsion, justifying the idea of F···P through-space coupling. Meanwhile, the P–P bond twist due to repulsion between cis-CF_3 groups would push one CF_3 group closer to CH_3 in each structure. Then both isomers would have nearly the same interaction of one CF_3 with CH_3 (electrostatic attraction of H for F probably overcoming a slight H···F packing repulsion), but only in gauche-2 would there be further attraction between CH_3 protons and the second *gem*-CF_3 group. Then if one isomer prevails, as suggested by the very sharp NMR spectra, gauche-2 would be chosen. However, there is enough doubt to motivate other structural determinations.

The disproportionation of $CH_3(CF_3)P–P(CF_3)_2$ would relate to the energy states of $P_2(CF_3)_4$ and the four possible P–P bond rotational isomers of $(CH_3CF_3P)_2$. For the latter, only the structure having CH_3 trans to CH_3 and CF_3 trans to CF_3 would be stabilized by two 60° cis adjacencies of CH_3 and CF_3, with no repulsive contacts; its stabilization might be comparable to that of the gauche-2 form of $CH_3(CF_3)P–P(CF_3)_2$. Then the inhibition of disproportionation would be due to the destabilization of $P_2(CF_3)_4$ by no less than two CF_3–CF_3 repulsive adjacencies.

For $CH_2F(CF_3)P–P(CF_3)_2$ we should expect less stabilization of the gauche-2 form, and more extensive disproportionation then would result; there would be enough of the slightly less stable trans form to disturb the NMR spectra. All forms of $CHF_2(CF_3)P–P(CF_3)_2$ would be destabilized by repulsions, accounting for extensive disproportionation and mutual blurring of the NMR spectra of all three isomers.

Although favored by theory and more than one line of evidence, these ideas must be regarded as speculative until more direct structural evidence can be found.

Addendum: **A New Iodophosphine.** Equimolar addition of iodine to $(CH_2FCF_3P)_2$, obtained by the disproportionation of $CH_2F(CF_3)P–P(CF_3)_2$, gave a 96% yield of $CH_2F(CF_3)PI$. This experiment was intended to provide a satisfactory route to $CH_2F(CF_3)PX$ compounds, before the discovery of a more direct method.[3] Its volatility is near 6 mm at 0 °C. Its ^{19}F NMR spectrum shows CF_3 at $\delta = 56.5$ ($_2J_{FCP} = 61.5$, $_2J_{FCPCF} = 5.4?$) and CH_2F at $\delta = 219$ ($_2J_{FCP} = 102.5$, $_3J_{FCH} = 47.6$, $_4J_{FCPCF} = 5.60$). The ^1H spectrum shows $\delta_A = 5.45$ ($_2J_{HCF} = 47.6$, $_2J_{HCP} = 9$) and $\delta_B = 5.42$ ($_2J_{HCF} = 47.8$, $_2J_{HCP} = 15$). Dr. L. D. Field has obtained further data by means of the XL-200 instrument (in our Hydrocarbon Institute), including the ^{31}P spectrum: $\delta = 0$, with the confirmatory coupling constants $_2J_{PCF} = 102.2$, $_4J_{PCF} = 61.5$, and $_2J_{PCH} = 8.4$ or 15.6.

Acknowledgments. Drs. K. L. Servis and L. D. Field have been helpful in regard to the NMR spectra, but the author alone is responsible for the speculative structural considerations.

Registry No. $CH_3(CF_3)P$-$P(CF_3)_2$, 78673-07-1; $CH_2F(CF_3)P$-$P(CF_3)_2$, 78673-08-2; $CHF_2(CF_3)P$-$P(CF_3)_2$, 78673-09-3; $CH_2F(CF_3)PI$, 78673-10-6; $(CH_2FCF_3P)_2$, 78673-11-7; $(CHF_2CF_3P)_2$, 78673-12-8; $CHF_2(CF_3)PI$, 78673-13-9; $CH_3(CF_3)PCl$, 4669-76-5; $(CF_3)_2PH$, 460-96-8; $CH_2F(CF_3)PH$, 77846-33-4; $(CF_3)_2PCl$, 650-52-2; $CHF_2(CF_3)PH$, 77846-32-3.

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(5) For earlier examples of F–P through-space coupling cf. A. B. Burg, *Inorg. Chem.*, **17**, 593 (1978).