The Heterocyclic Bisphosphine $(CF_3PCF_2)_2$

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Summary Bis(trifluoromethyl)phosphine reacts with dimethylzinc at 0—25° to form the new four-membered ring compound $(CF_3PCF_2)_2$, apparently the first example of the P–C–P–C heterocycle.

The interesting new heterocycle $(CF_3PCF_2)_2$ is formed by the reaction of dimethylzinc with bis(trifluoromethyl)phosphine [equation (1)] in sealed tubes (2·5—6 days at 0° or 3 days at 25°), in yields of up to 32% of consumed $(CF_3)_2PH$ or 38% relative to the measured methane. The proposed intermediate $MeZnP(CF_3)_2$ would be unstable because the $P(CF_3)_2^-$ ion could act as a base to catalyse transfer of fluoride to zinc (*cf.* fluoride transfer in attempted preparations of perfluoroalkylzinc compounds[1]). The slowness of the present process confirms earlier indications that $(CF_3)_2PH$ is only weakly active as a protic acid; like $(CF_3)_3P$, it fails to form an observable complex with dimethylzinc.

$$2(CF_3)_2PH + 2ZnMe_2 \rightarrow 2CH_4 + 2MeZnF + (CF_3PCF_2)_2 \qquad (1)$$

The product $(CF_3PCF_2)_2$ was isolated by high-vacuum fractional condensation at −45° and purified with a small high-vacuum reflux column at −78°. Its equilibrium vapour pressure at 0° was 13·5 mmHg; M (vapour phase) 304; M^+ (mass spectrum) 300. It was analysed by heating with bromine in excess, in a sealed n.m.r. tube. The ^{19}F n.m.r. spectra at various stages suggested the successive formation of $CF_3P(CF_2Br)_2Br_2$, $CF_3P(CF_2Br)Br_3$, and CF_3PBr_4, meaning that bromine cleaved the P–CF_2 bonds far more rapidly than the P–CF_3 bonds. The final spectrum showed only CF_2Br_2 and CF_3Br (each measured as 2 mol. equiv.), evidence against C–C bonding. The lack of reaction with methanol precluded P–P bonding.

The ^{19}F n.m.r. spectrum (Figure) agrees with the suggested structure. The symmetry of the outer septets indicates that the four CF_2 fluorine atoms are alike, suggesting that the CF_3 groups are in *trans*-positions above and below a planar ring.

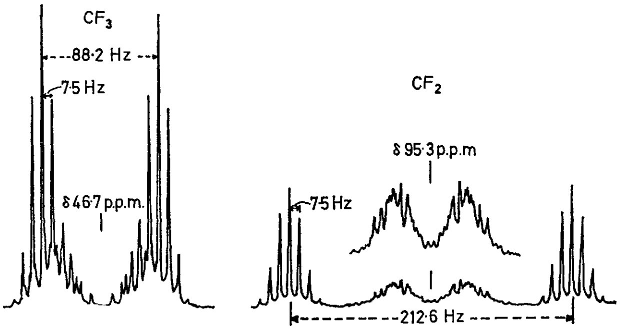

FIGURE. ^{19}F *N.m.r. spectrum of* $(CF_3PCF_2)_2$ *at* 94·1 *or* 56·4 MHz. *δ values are measured upfield from* Cl_3CF *(tube-substitution). The integrated intensity of the* CF_2 *pattern is* ⅔ *that of the* CF_3 *pattern.*

The ^{31}P n.m.r. spectrum is symmetrical, centred at δ 90·5 p.p.m. from H_3PO_4, and shows more than 40 peaks.

The i.r. spectrum (vapour phase) shows the following: ν(C–F) 1182s, 1161s, 1141vs, and 1100m cm^{-1}; $\delta(CF_3)$ 746w and 555w cm^{-1}; ν(P–C) 502w, 434w, and 371w cm^{-1}. Weak peaks at 1300, 1290, 878, and 685 cm^{-1} were not assigned. The u.v. spectrum (vapour phase) showed end-of-scale absorption at 1900 Å (ε 2284) and weak peaks at 2360 (ε 170) and 2678 (112) Å probably due to nearly forbidden transitions.

The compound $(CF_3PCF_2)_2$ displaced CO (2 mol. equiv.) from excess of $Ni(CO)_4$ suggesting that $(CF_3PCF_2)_2[Ni(CO)_3]_2$ was formed, analogous to 'NiPPNi'.[2] However, attempted distillation of the product *in vacuo* led only to liberation of CO and $Ni(CO)_4$. A *trans*-planar arrangement of the phosphorus lone-pair electrons would preclude formation of the sesquicarbonyl [*e.g.* $L_2Ni_2(CO)_3$];[3] polymerization would be more likely. However, the ligand $(CF_3PCF_2)_2$ might have suffered change, for it could not be recovered by the action of iodine.

We thank the National Science Foundation for financial support.

(*Received, 5th April* 1972; *Com.* 552.)

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