Preparation and Nuclear Magnetic Resonance Parameters of Perfluoroalkyl-substituted Phosphorus(V) Hydrides

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Summary The phosphorus(V) hydrides $(CF_3)_3PH_2$ (**1**), CF_3PF_3H (**2**), and $(CF_3)_2PF_2H$ (**3**) have been prepared by the vapour phase reaction of the appropriate fluorophosphorane, $(CF_3)_nPF_{5-n}$, with Me_3SiH; the labile dihydride, $CF_3PF_2H_2$ (**4**) was detected in the (reversible) liquid phase reaction of CF_3PF_4 with Me_3SiH.

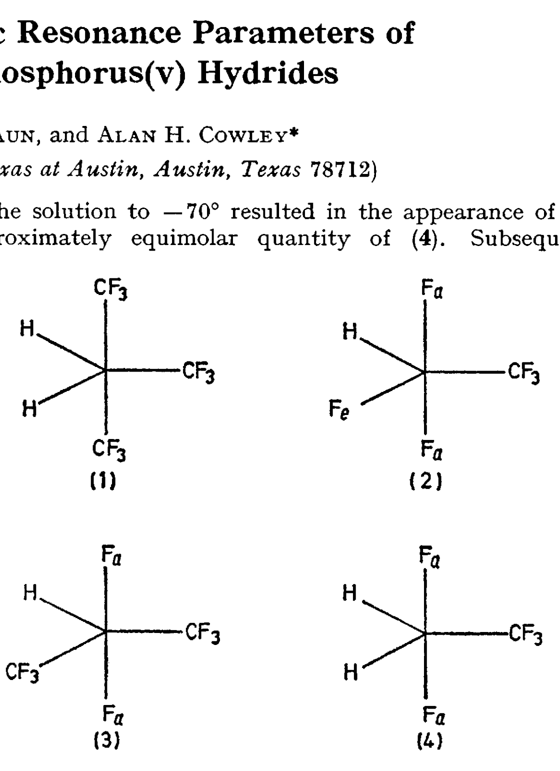
SINCE the CF_3 group is known to confer stability on a variety of structures[1] we decided to undertake the synthesis of CF_3 derivatives of the currently non-existent PH_5 molecule.[2]

In a typical reaction, equimolar quantities of $(CF_3)_3PF_2$ [3] and Me_3SiH were allowed to react for 3 min in the vapour phase at ambient temperature. Vacuum fractionation of the volatiles afforded good yields of $(CF_3)_3PH_2$ (**1**) in a −84° trap. Similarly prepared are CF_3PF_3H (**2**) (trap −126°) and $(CF_3)_2PF_2H$ (**3**) (trap −96°) by the vapour phase reactions of Me_3SiH with equimolar quantities of CF_3PF_4 [3] and $(CF_3)_2PF_3$,[3] respectively. Qualitatively the thermal stabilities lie in the order (**1**) > (**2**) > (**3**) with (**1**) being stable for several minutes at ambient temperature in the liquid phase.

No additional compounds could be isolated when the stoicheiometries of the vapour phase reactions were altered: however, it was possible to detect $CF_3PF_2H_2$ (**4**) in liquid phase ^1H n.m.r. experiments. For example, a mixture of 0·5 mmol of CF_3PF_4, 1·0 mmol of Me_3SiH, and 1·0 ml of CF_3Br in a sealed n.m.r. tube was allowed to warm slowly from −196°. After standing for 5 min at −100° the ^1H n.m.r. spectrum of (**2**) became evident. Further warming of the solution to −70° resulted in the appearance of an approximately equimolar quantity of (**4**). Subsequent cooling of the solution to −100° caused the ^1H n.m.r. spectrum of (**4**) to disappear, thus suggesting the equilibrium:

$$CF_3PF_3H + Me_3SiH \rightleftharpoons CF_3PF_2H_2 + Me_3SiF.$$

Similar observations were made in the absence of solvent. However, analogous liquid phase reactions with $(CF_3)_2PF_3$ or $(CF_3)_3PF_2$ failed to produce any new hydrides.



FIGURE

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Compounds (**1**) and (**2**) exhibit fluxional behaviour. However, below −75° and −140°, respectively, the intramolecular rearrangements become slow on the n.m.r. time scale. Assuming trigonal bipyramidal stereochemistry the low temperature ^1H and ^{19}F n.m.r. data‡ for (**2**) [$J(PF_e)$ 1008, $J(PF_a)$ 952, $J(PH)$ 955, $J(HPF_a)$ 117, $J(HPF_e)$ 35 Hz; $\delta(H)$ − 7·46, $\delta(F_a)$ 15·7, $\delta(F_e)$ 80·6], (**3**) [$J(PF_a)$ 840, $J(PH)$ 828, $J(HPF_a)$ 100 Hz; $\delta(H)$ −7·43, $\delta(F_a)$ 39·9], and (**4**) [$J(PF_a)$ 704, $J(PH)$ 792, $J(HPF_a)$ 92 Hz; $\delta(H)$ −7·14 $\delta(F_a)$ 42·9] establish the ground state geometries shown in the Figure.

Primarily this conclusion is based on previous work[4] which indicates that $J(HPF_a)$ lies in the range 100—140 Hz whilst $J(HPF_e)$ falls between 20 and 40 Hz. Confirmatory evidence is provided by the axial and equatorial ^{19}F chemical shifts.[5] The ground state geometry for (**1**) is based on the following low temperature n.m.r. observations: (a) two CF_3 resonances are detected in a 2 : 1 intensity ratio (at 61 and 36, respectively) in the ^{19}F spectrum; (b) the ^1H spectrum indicates that the hydride ligands are chemical shift equivalent [$\delta(H)$ −6·68]; (c) $J(HPCF_e)$ is essentially constant (1—2·5 Hz) for (**1**)—(**4**).

Prior to the present work the only dihydride of phosphorus(v) which had been reported was F_3PH_2.[6] The isolation of (**1**) and the detection of (**4**) demonstrate the feasibility of preparing an extensive series of di- (and possibly higher) hydrides of pentaco-ordinate phosphorus. The fluxional character of (**1**) establishes the fact that the CF_3 group can exhibit migratory behaviour. Previously it had been argued[7] that the CF_3 group is too bulky to participate in intramolecular rearrangements. The ground state ^{19}F spectrum of (**1**) is particularly useful since it yields the first n.m.r. parameters for an axially substituted CF_3 group.

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‡ ^1H Chemical shifts are relative to internal Me_4Si; ^{19}F chemical shifts are in p.p.m. from external CCl_3F.

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