Intramolecular Isomerisation in Six-co-ordinate Bis(bidentate) Phosphorus Anions

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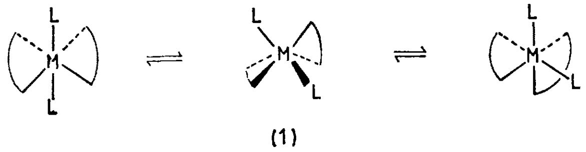
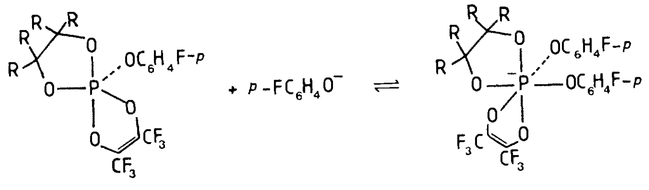
Summary Isomerisation *via* trigonal twist processes is proposed to account for the variable temperature n m r spectra of some six-co-ordinate bis(bidentate) phosphorus anions

INTRAMOLECULAR *cis–trans* isomerisation in bis(bidentate) octahedral species *via* trigonal prismatic intermediates (**1**) is well established in transition metal chemistry.[1] Previous work[2] on the racemisation of amine salts of optically active tris(bidentate) phosphorus anions has shown that these are acid-catalysed processes involving P–O bond fission. We now present data on permutational isomerisation in six-co-ordinate bis(bidentate) phosphorus anions which are most readily interpreted in terms of trigonal prismatic intermediates.

Treatment of the phosphorane (**2**; R = Me), δ_P −36·9 p.p.m., in tetrahydrofuran at room temperature with 1 equiv. of sodium *p*-fluorophenoxide established the equilibrium shown with the thermodynamically stable *cis*-anion[3] (**3**; R = Me), δ_P −110·1 p.p.m.† At −101 °C the ^{19}F n.m.r. spectrum of (**3**; R = Me) showed signals at δ −0·49 and −0·75 (CF_3) and −60·2 and −61·7 p.p.m. (p-FC_6H_4O). The signals due to the trifluoromethyl groups coalesced reversibly at −77 °C ($\Delta\nu$ 25 Hz, ΔG^* 9·7 kcal mol^{-1}‡) whereas those due to the *p*-fluorophenoxy-groups coalesced at 34 °C ($\Delta\nu$ 145 Hz, ΔG^* 14·5 kcal mol^{-1}). In the corresponding *cis*-anion (**3**; R = H), δ_P −105·5 p.p.m., the free energies of activation for equivalence of the trifluoromethyl groups and the *p*-fluorophenoxy-groups were 17·2 ($\Delta\nu$ 73 Hz, T_c 80 °C) and 16·5 ($\Delta\nu$ 21 Hz, T_c 50 °C) kcal mol^{-1} respectively. In both cases, at temperatures above the higher coalescence temperature, separate signals were present for the trifluoromethyl groups of the phosphorane (**2**) and anion (**3**) (R=Me, $\Delta\nu$ 95 Hz at 72 °C; R=H, $\Delta\nu$ 73 Hz at 151 °C) showing that dissociation of (**3**) to give (**2**) is slow on the n.m.r. timescale over the relevant temperature ranges.


(1)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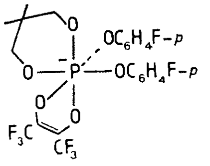
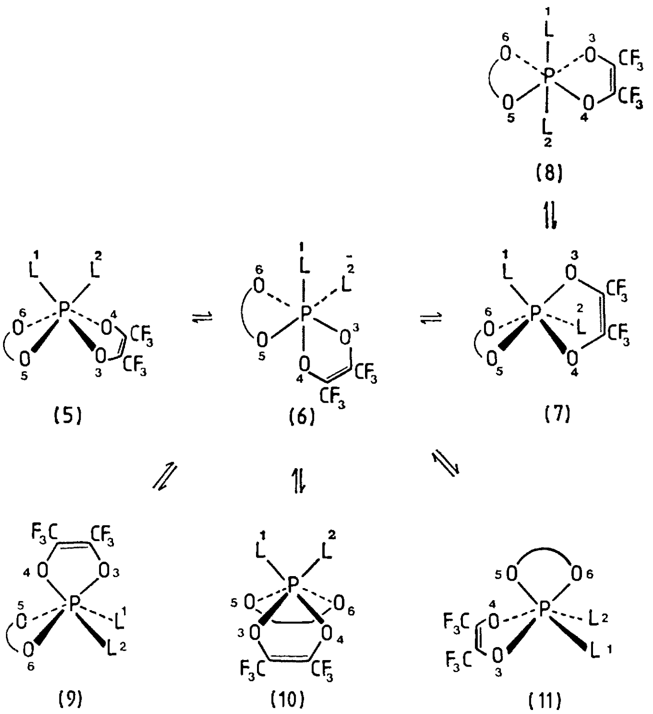

(4)

In the case of the *cis*-anion (**4**), δ_P −128·5 p.p.m. (t, $^6J_{PF}$ 3·4 Hz), formed in a similar equilibrium with the analogous six-membered spirophosphorane, signals due to the trifluoromethyl groups coalesced at 3 °C ($\Delta\nu$ 111 Hz, ΔG^* 13·1 kcal mol^{-1}) whereas those due to the *p*-fluorophenoxy-groups were still separate ($\Delta\nu$ 140 Hz) at 60 °C ($\Delta G^* > 16$ kcal mol^{-1}).

Clearly in the anions (**3**; R = H or Me) and (**4**) separate processes are involved in the equivalence of the trifluoromethyl groups and the *p*-fluorophenoxy-groups. Different energy barriers to the eight possible trigonal twists can account for the data. In the general structure (**6**; L = p-FC_6H_4O) rotation of the trio (243) 60° anticlockwise§ relative to the trio (156) leads to the trigonal prism (**5**) in which the trifluoromethyl groups are equivalent but the *p*-fluorophenoxy-groups are not. On the other hand rotation of the trio (123) 60° anticlockwise relative to (465) gives the trigonal prism (**9**) in which the *p*-fluorophenoxy-groups are equivalent, but the trifluoromethyl groups are not. Of the other possible trigonal twists, (264) clockwise *vs.* (135) to give (**10**), (162) anticlockwise *vs.* (345) to give (**11**), and (243) clockwise *vs.* (156) leading eventually *via* (**7**) to the *trans*-isomer (**8**), give simultaneous equivalence of both sets of fluorines.


(8) (5) (6) (7) (9) (10) (11)

In the *cis*-anions (**3**; R = Me) and (**4**) the trigonal twist to give (**5**) has the lowest energy barrier followed by any of the four to give (**8**), (**9**), (**10**), or (**11**). With the *cis*-anion (**3**; R = H) it may be that the trigonal twist to give (**9**) has the lowest energy barrier. Data on more systems are needed before rationalisation is possible.

Intramolecular isomerisations have been observed in a number of other six-co-ordinate phosphorus anions, *e.g.* in (**12**), δ_P − 106·3 p.p.m., ΔG^* for equivalence of the fluorines

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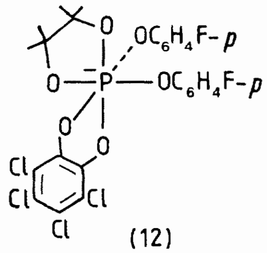
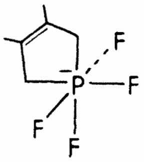
† Positive chemical shifts are to low field of the standards, 85% H_3PO_4 and $PhCF_3$.

‡ 1 cal = 4·184 J.

§ Looking towards phosphorus from the centre of the trio.



(12)



(13)

is 15·5 kcal mol^{-1} ($\Delta\nu$ 113 Hz, T_c 53 °C) whereas in (**13**), δ_P −109·9 p.p.m., ΔG^* for equivalence of the two pairs of fluorines is *ca.* 12 kcal mol^{-1} ($\Delta\nu$ 104 Hz, T_c *ca.* −10 °C). The intramolecular nature of the isomerisation in (**12**) is shown by the retention of PF coupling at 60 °C (t, $^6J_{PF}$ 2·9 Hz) and in (**13**) by the ^{31}P n.m.r. spectrum at 40 °C (quintet, $^1J_{PF}$ 754 Hz).

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