Mode of Ligand Exchange in a Cyclic Phosphoranyl Radical

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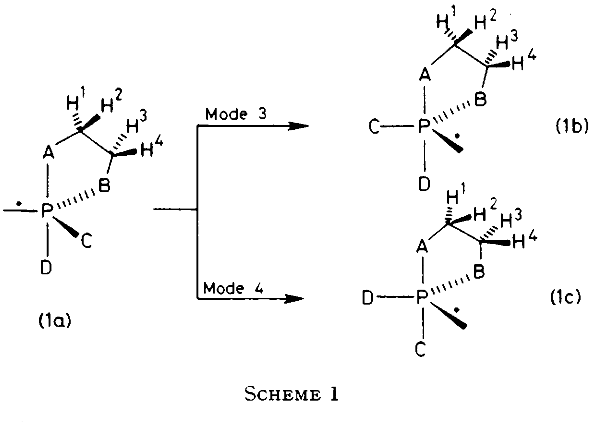
Summary E.s.r. line-shape effects enable the mode of exchange of the apical and equatorial exocyclic ligands to be identified for the trigonal bipyramidal phosphoranyl radical $\overline{\mathrm{OCH_2CH_2O\dot{P}}}[\mathrm{N(SiMe_3)_2}]\mathrm{OSiMe_3}$.

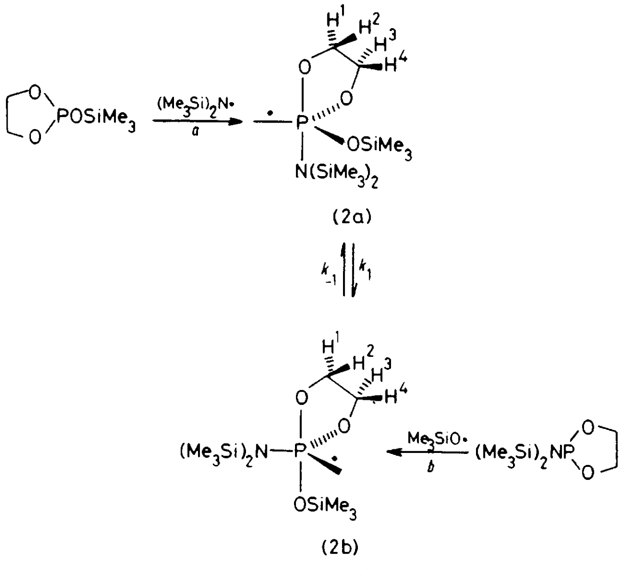
Although it is now established that apical–equatorial ligand exchange takes place very rapidly in certain trigonal bipyramidal (TBP) phosphoranyl radicals,[1] the detailed nature of the exchange process remains to be elucidated. For example,[2] the mode 3 and mode 4 (Musher's[3] notation) rearrangements of (**1a**) cannot be distinguished on the basis of the line-shape effects apparent in the e.s.r. spectrum of (**1**; A = B = MeN, C = D = $\mathrm{Bu^tO}$), although indirect evidence points to the latter permutation.†



Scheme 1

In the mode 4 rearrangement of (**1a**), exchange of H^1 with H^2 takes place at the same time as exchange of the equatorial ligand C with the apical ligand D. This has never been demonstrated directly, since a suitable phosphoranyl radical has not been generated previously.

We now report that the e.s.r. spectrum of the transient radical $\overline{\mathrm{OCH_2CH_2O\dot{P}}}[\mathrm{N(SiMe_3)_2}]\mathrm{OSiMe_3}$ (**2**) shows the



Scheme 2

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† Only one set of enantiomers is shown in Schemes (1) and (2). The spectral changes observed for (**1**) would, of course, be the same if (**1a**) exchanged with the mirror images of (**1b**) or (**1c**). However, it is difficult to envisage any reasonable mechanism for these interconversions.

presence of two isomers, of similar stability, and interconversion of these gives rise to line-shape effects which permit the mode of their exchange to be identified.

The e.s.r. spectra observed during continuous photochemical generation of (**2**) over a range of temperature in liquid ethylene solution are shown in the Figure; identical spectra were obtained from routes *a* and *b* [Scheme (2)].

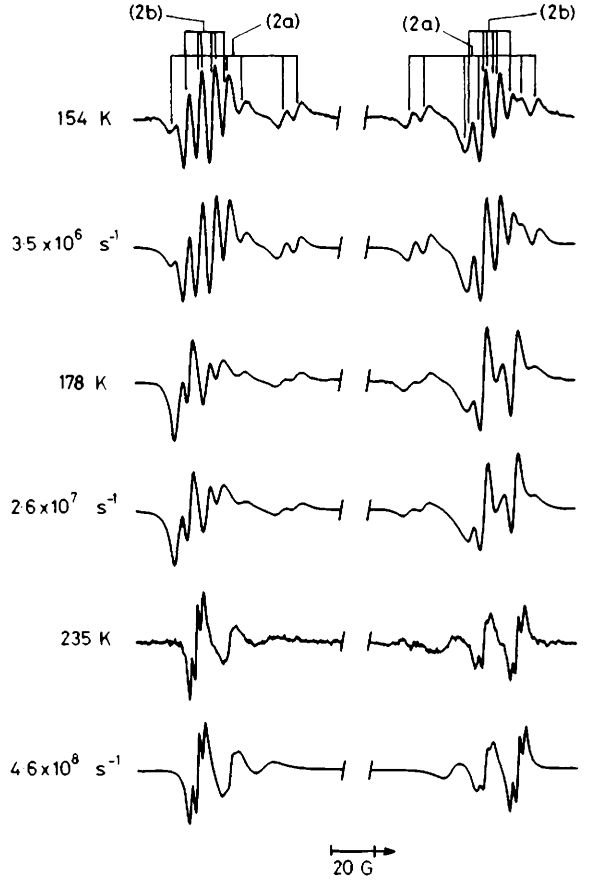


FIGURE. Experimental and computer simulated e.s.r. spectra of the phosphoranyl radical (**2**) in ethylene solvent. Values of k_1 are given alongside the corresponding simulated spectra.

At low temperatures, separate signals were observed for (**2a**) [a(P) 885·6, a(N) 24·8, a(1H) 6·8 G, g 2·0024 at 154 K] and (**2b**) [a(P) 909·2, a(N) 6·2, a(1H) 5·2 G, g 2·0020 at 154 K], and the ring proton giving rise to resolvable splitting is assigned[1] as H^1 in (**2a**) and H^2 in (**2b**). At higher temperatures, the e.s.r. signals from (**2a**) and (**2b**) exhibit line-shape effects due to rapid interconversion of the radicals (see Figure), and the spectra could be simulated only by assuming that exchange of apical and equatorial exocyclic ligands takes place at the same rate as exchange of the apical methyleneoxy protons H^1 and H^2.† At the highest temperatures attainable before the onset of rapid fragmentation of (**2**),‡ a spectrum corresponding to the weighted average of the signals from (**2a**) and (**2b**) was detected [$\bar{a}$(P) 895·2, $\bar{a}$(N) 15·0, $\bar{a}(H^1) + \bar{a}(H^2)$ 5·8 G, g 2·0022 at 235 K].

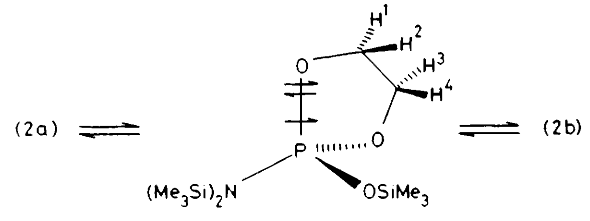
The simulations§ were obtained by making the following simplifying assumptions. (i) Only one ring proton gives rise to non-zero hyperfine splitting and this splitting is independent of temperature. (ii) The nitrogen splittings for (**2a**) and (**2b**), which must have the same sign, are independent of temperature. (iii) The equilibrium constant (k_1/k_{-1}) varies normally with temperature between the directly measured value of 2·1 at 154 K and the calculated value of 1·1, obtained from the average nitrogen splitting, at 235 K.¶ (iv) The difference in the phosphorus splittings of (**2a**) and (**2b**) increases linearly with temperature by 8 G between 154 and 235 K.

The apparent 1:2:1 triplet splitting from the apical methyleneoxy protons in the averaged spectrum of (**2**) arises because (k_1/k_{-1}) is close to unity. Exchange of H^1 with H^2, rather than with H^3 or H^4, was demonstrated by generating the phosphoranyl radicals by addition of $(Me_3Si)_2N\cdot$ to $\overline{OCH_2CD_2OP}OSiMe_3$.[1] Apart from splittings from N and P, the high-temperature averaged spectrum showed a 1:6:1 splitting of *ca.* 3 G confirming (*cf.* ref. 1) exchange of H with H (and D with D), rather than of H with D, and hence of H^1 with H^2 for the unlabelled radicals.

An Arrhenius plot of the rate constants k_1 showed a good fit to the straight line defined by equation (1), and k_1 was 1·2 × 10^8 s⁻¹ at 205 K.

$$\log_{10}(k_1/\text{s}^{-1}) = 12{\cdot}7 - 18{\cdot}2/2{\cdot}303RT \text{ kJ mol}^{-1} \qquad (1)$$

The low barrier for interconversion of (**2a**) and (**2b**) is similar to that estimated from e.s.r. studies of apical–equatorial ligand exchange in other TBP phosphoranyl radicals.[1,2] It appears reasonable[4] that the mechanism of exchange of (**2a**) and (**2b**) involves an intermediate (undetected) trigonal pyramidal isomer (**3**) which has a σ^* electronic structure (Scheme 3).



(3)

SCHEME 3

We have shown previously[1,2] that the apicophilicity (preference for the apical site in a TBP phosphoranyl radical) of an RO group is similar to that of an R_2N group, and the present results show that this similarity extends to the trimethylsilyl-substituted ligands.

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‡ Fragmentation of (**2**) involves β-scission to give $\cdot CH_2CH_2OP(O)[N(SiMe_3)_2]OSiMe_3$. This will be discussed in a full paper.

§ We used the program (no. 209) ESREXN available from Q.C.P.E.

¶ At 150 K, [(**2b**)]/[(**2a**)] remained constant for at least 20 s during the decay of both radicals after interrupting photolysis.

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[2] R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140.
[3] J. I. Musher, *J. Chem. Educ.*, 1974, **51**, 94.
[4] R. S. Hay and B. P. Roberts, *J.C.S. Perkin II*, 1978, 770.