Intermolecular Association of Biphosphines

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Summary Dramatic changes in the n.m.r. spectra of symmetrical biphosphines in polar media indicate the formation of aggregates with P–P donor–acceptor bonds.

TRICO-ORDINATE phosphorus molecules with substituents of different electronegativities can associate to give semi-polar species (I), which often exist only as intermediates.[1]

$$R^1_3P^{+}\text{—}P^{-}R^2_3 \longleftrightarrow R^1_3P{=}PR^2_3 \qquad (1)$$

We now present evidence that similar interaction can lead to association of symmetrical biphosphines $R^1R^2P{\cdot}PR^1R^2$ (R^1, R^2 = Me, Ph) in which the two phosphorus atoms have the same substituents.

The ^1H n.m.r. spectrum of Me_4P_2, in media of low polarizability is a characteristic triplet given by the $[A_6X]_2$ spin system which has been analysed[2] to give $^1J_{PP} = -179{\cdot}7$ Hz, $^2J_{PH} = +2{\cdot}9$ Hz, and $^3J_{PH} = +11{\cdot}3$ Hz. However, we find that addition of dichloromethane or other solvents of high dielectric constant leads to progressive line broadening and finally collapse of the triplet to a single line with a minimum width at half height of 1·5 Hz when the mixture contains *ca.* 14% of the biphosphine (see Figure). Further addition of dichloromethane leads to an increase in linewidth and eventual partial reappearance of the triplet structure. The biphosphine MePhP·PMePh behaves similarly, and collapse of the two methyl triplets arising from the diastereomers of this compound is followed by merging of the two separate resonances. Rather more fine structure is resolved in the very dilute solutions. The unsymmetrical biphosphine $Me_2P{\cdot}PPh_2$ does not behave in this way, but in dichloromethane and other solvents always gave a methyl resonance consisting of a double doublet arising from coupling to two inequivalent ^{31}P nuclei. However, the methyl resonance of a mixture of Me_4P_2 and Ph_4P_2 in dichloromethane was a singlet of width at half height 4 Hz, and ^1H - $\{^{31}P\}$ double resonance experiments showed that this was associated with two distinct ^{31}P frequencies corresponding to chemical shifts of 59 and 16 p.p.m. to high field of H_3PO_4. These are close to the chemical shifts of the separate biphosphines.[3] After several days the spectrum changed to that of authentic $Me_2P{\cdot}PPh_2$, *i.e.* a double doublet.

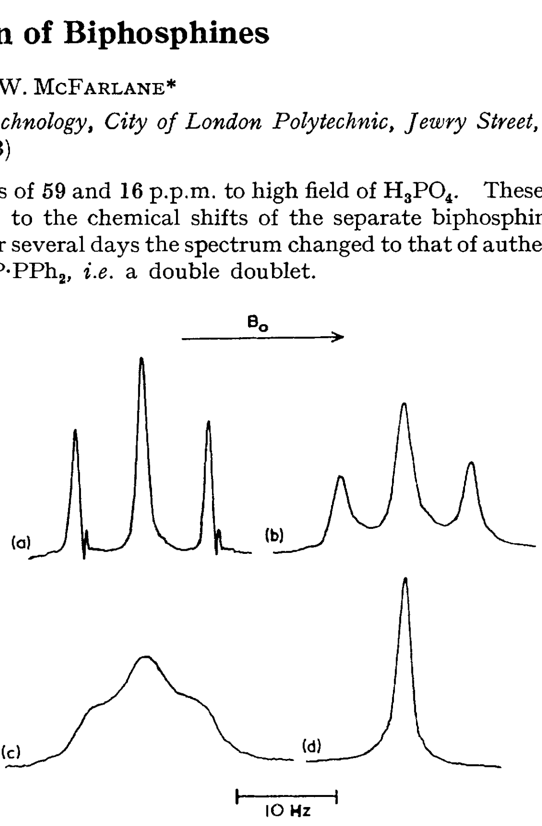
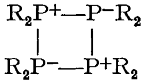
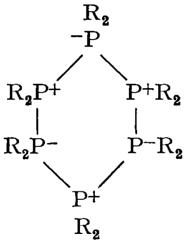


FIGURE. 60 MHz *proton spectra of mixtures of* Me_4P_2 [
(*a*) *neat* Me_4P_2; (*b*) 80% Me_4P_2; (*c*) 72% Me_4P_2; (*d*) 14% Me_4P_2.

The foregoing behaviour is consistent with slow dynamic intermolecular association of the symmetrical biphosphines in dichloromethane to give species such as (II) or (III) which will be stabilised by *dπ–dπ* interaction between the phosphorus atoms, and by a polar medium. This type of association has been postulated[4] to account for the instability of $Me_2P{\cdot}P(CF_3)_2$. Owing to the large (*ca.* 200 Hz) coupling between the directly bound phosphorus atoms any methyl resonance of (II) would be an approximate quintet with a splitting of $\frac{1}{4}(^2J_{PH} + 2{\cdot}^3J_{PH} + {}^4J_{PH})$. Reasonable estimates of the coupling constants are: ${}^2J_{PH}$, -10 Hz; ${}^3J_{PH}$, $+6$ Hz; ${}^4J_{PH}$, 0; so the actual splitting would be small and a broad singlet would be observed. Alternatively, the large J_{PP} would lead to spin exchange between the phosphorus nuclei during the chemical exchange. In the very dilute solutions there would be less association and the normal spectrum of the monomer will reappear. In the mixture of Me_4P_2 and Ph_4P_2 most of the methyl groups will be in species $[(Me_4P_2)]_n$, but some will be in $[(Me_4P_2)_{n-1}\cdot Ph_4P_2]$ and so their resonance will be affected by irradiation at two ${}^{31}P$ frequencies.



(II)



(III)

Even in non-polar media this type of association will occur to some extent, and since dissociation can occur by cleavage of either set of alternate P–P bonds there is a facile route for the formation of $Me_2P\cdot PPh_2$ from Me_4P_2 + Ph_4P_2, and for the epimerisation of MePhP·PMePh. In the light of this, conclusions drawn from high temperature studies[5] about the energy barrier to inversion at phosphorus in biphosphines may need revision. The calculation of separate values of ${}^2J_{PH}$ and ${}^3J_{PH}$ in Me_4P_2 involves consideration of line shapes,[2] and since these depend on the precise composition of the sample such results must be viewed with caution. This type of association will also affect the mechanism of reactions involving biphosphines.

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