Relative Signs of N.m.r. Coupling Constants in Phosphines and Phosphine Complexes

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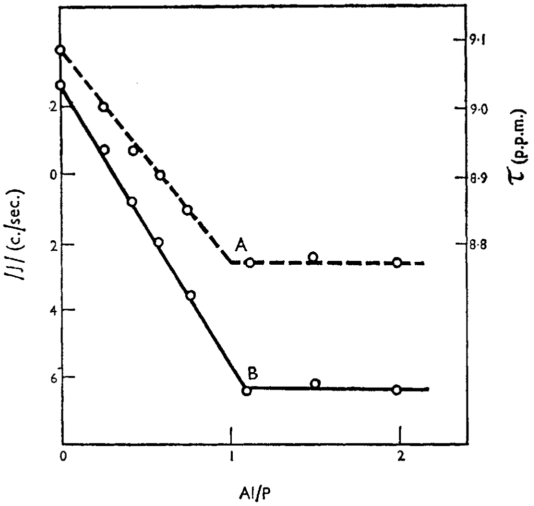
THERE is considerable current interest in the proton magnetic resonance spectra of phosphine complexes with Group III acceptors.[1,2] We have recorded the spectra at 33·5° of benzene or cyclohexane solutions of organoaluminium compounds or triethylboron containing 2M-concentrations of phosphines having the Me–P group. Tetramethylsilane was used as internal reference. The results show that the change in $J_{\text{P–C–H}}$ produced by co-ordination is substantially larger than hitherto has been suspected.

Each spectrum consists of a sharp doublet due to the Me–P group and a number of peaks from other organic groups in the complex. The fact that only one doublet is observed in the spectra of solutions with a deficiency of acceptor shows that exchange between free and complexed phosphine is sufficiently rapid to give averaged values of the chemical shifts and coupling constants.[3] The variation of these parameters with Al/P mole ratio is shown in the Figure for the $Me_3P–AlEt_3$ system. The chemical shift of the methyl protons varies linearly with acceptor concentration until all the phosphine is complexed, and addition of excess of acceptor gives no further change. Such behaviour is expected if dissociation of the complex is small. It is also seen from the Figure that as the Al/P ratio is varied, the observed (averaged) P–C–H coupling constant passes through zero, and this has been confirmed in the ^{31}P-spectra. Thus the coupling constants in the free and complexed trimethylphosphine are of opposite sign.

As a result of this observation several similar systems were examined. The $Me_3P–BEt_3$ system[4] is similar to the $Me_3P–AlEt_3$ system except that the coupling constant is larger in the boron complex. $J_{\text{P–C–H}}$ changes sign on co-ordination in $Me_3P–AlEt_2Cl$, $Me_3P–AlEtCl_2$, Me_3AlPh_3, $Me_2PhP–AlEt_3$, and $MePh_2P–AlEt_3$, but the sign of the P–O–C–H coupling constant does not change in the $(MeO)_3P–AlEt_3$ system. Thus in the phosphine systems the magnitude of the change in $J_{\text{P–C–H}}$ on co-ordination is the sum (rather than



Graph of (A) τ (p.p.m.) and (B) J (c./sec) for P–CH$_3$ in the system Me$_3$P–AlEt$_3$ in cyclohexane.

the difference) of the constants in the free and complexed donor. For $Me_2PhP\text{–}Mo(CO)_3(Me_2PhP)_3$ the exchange rate was too slow to produce averaging.

The small coupling characteristic of Me–P groups appears to be due to the near cancellation of larger terms arising from the Fermi contact mechanism.[5] The sign change presumably arises from a difference in the sensitivity of these terms to the rehybridisation of the phosphorus orbitals produced by co-ordination. If it is assumed that co-ordination produces an effect on $J_{P\text{–}C\text{–}H}$ which is always in the same sense, the kind of study described here can be used to refer the signs of the coupling constants in tertiary phosphines with methyl groups to the signs in Et_3P,[6] Me_2PH, and $MePH_2$.[7]

The shape of the graph of $J_{P\text{–}C\text{–}H}$ against Al/P mole ratio depends on the dilution and the formation constant of the complex; the graph for $Me_3P\text{–}AlEt_3$ becomes markedly curved at a phosphine concentration of 0·2M, and the graphs for 2M-phosphines indicate that the formation constants of the complexes are in the order:—
Me_3PBEt_3, $Me_3PAlEt_3 > Me_2PhPAlEt_3 > MePh_2PAlEt_3$
This is consistent with an inductive reduction in the base strength of the phosphine on replacement of methyl by phenyl groups, and is being studied further in more dilute solutions.

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