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Preliminary communication

Incipient chirality in organometallic triphenylphosphine derivatives

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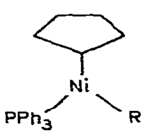
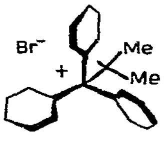
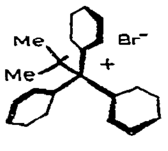
A paper by Thomson, Keeney, Baird and Reynolds recorded the observation that certain alkyl derivatives of triphenylphosphine π-cyclopentadienylnickel(II) with CH_2R bonded to nickel had interesting dynamic NMR properties[1]. At low temperatures the geminal methylene pair became diastereotopic and in (I) ($R = CH_2SiMe_3$) line broadening became apparent below −75°, although a well-resolved low-temperature static spectrum was not observed. This was interpreted in terms of a restricted rotation about the nickel—carbon bond, an explanation which might gain support from the suggestion of substantial hyperconjugation in that bond based on values of H—D coupling constants[2]. We had also observed broadening of the methylene resonance in (I) ($R = CH_2Ph$) between −70° and −105° and of both methylene resonances in (I) ($CH_2CH_2CH{=}CH_2$) between −40° and −100°. In the same temperature range, the corresponding methyl derivative showed a sharp doublet signal. In considering possible explanations, we felt that restricted rotation involving as it must a barrier between rotamers of about 10 kcal·mole^{-1}, would be rather unlikely. An alternative would be an unspecified relaxation effect involving phosphorus. Another, and more attractive, is the possibility of restricted rotation about P—aryl bonds leading to a barrier between enantiomeric conformations which has its origin in H—H repulsion. This is similar in principle to the well-recognised observations of chirality in triarylmethyl carbonium ions, in triarylmethanes and in their heteroatom derivatives[3]. Crystal structure determinations have been carried out on triphenylphosphine, methylene triphenylphosphorane, triphenylalkyl phosphonium salts and triarylphosphine organometallic complexes[4] and in all of these the aryl groups adopt a propellor conformation (C_{3v}) in which each individual molecule is chiral. Alkylnickels related to the present series



(I)



(IIa)



(IIb)

have been examined by X-ray diffraction[5], and here there is deviation from C_{3v} local symmetry which may be dictated by crystal packing forces and not reflect solution conformations. Nevertheless, a chiral local conformation is adopted, and inspection of molecular models suggest a considerable barrier to enantiomer conversion due to H—H interaction.

In order to test the feasibility of this alternative explanation, the low-temperature NMR spectrum of the methyl resonance of triphenylisopropylphosphonium bromide (II) (100 MHz; CH_2Cl_2, $CDCl_3$) and of the methylene resonance of benzyltriphenylphosphonium trifluoroacetate (III) (60 MHz; $CDCl_3$, CD_3OD) were monitored between −50° and −100°. Both resonances showed broadening and coalescence over this range

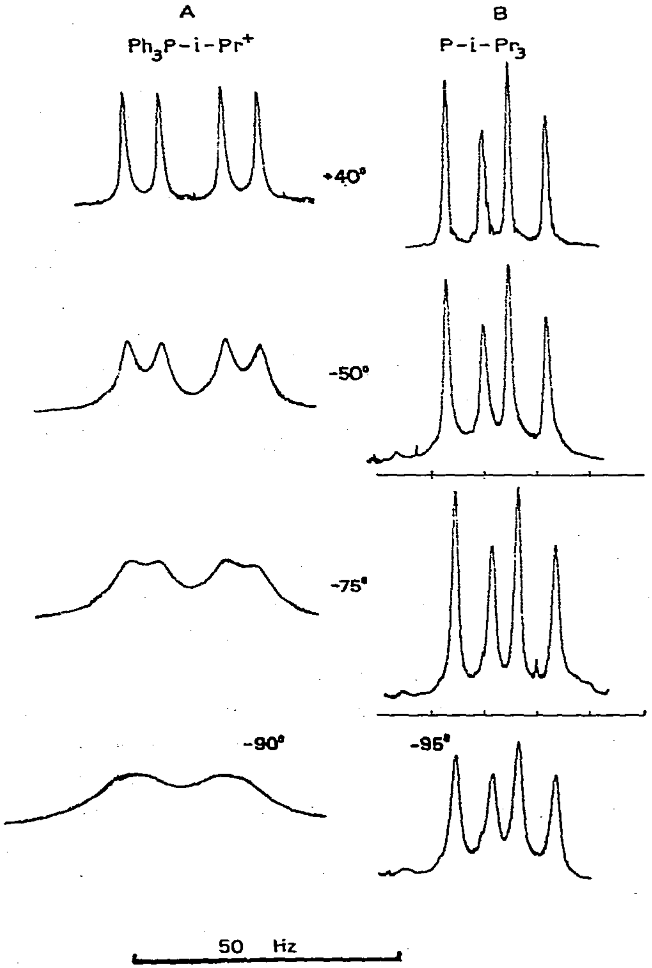


Fig. 1. 100 MHz NMR spectra of (A) $Ph_3\overset{+}{P}$-i-PrBr$^-$ in acetone-d_6 (methyl resonance only) and (B) P-i-Pr$_3$ in acetone-d_6 (methyl resonance only).

whereas the methyl resonance of triisopropylphosphine (100 MHz, C_3D_6O) remained sharp (Fig. 1*). In the latter case restricted rotation effects would be unlikely to operate, for barriers to rotation[6] about C–P single bonds have recently been measured and are such that broadening only occurs below −130°, with $\Delta G^{\ddagger}$ for rotation about 6 kcal·mole^{-1}. Thus triarylphosphine derivatives, and in particular their organometallic complexes must be added to the range of triarylatomic systems in which diastereotopism may be displayed in consequence of an energy barrier to interconversion of enantiomeric conformers.

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*A resolved low-temperature spectrum was not obtained at temperatures where (II) was sufficiently soluble. Making reasonable assumptions for values of $\Delta\nu$ and T_C a value of $\Delta G^{\ddagger} = 9 \pm 1$ kcal·mole^{-1} may be calculated.