Co-ordination of Dissymmetric Organophosphines: a Proton Magnetic Resonance Study of Diastereoisomeric Four-co-ordinate Complexes of Nickel(II) and Cobalt(II)

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REPORTS of the ^1H n.m.r. investigation of four-co-ordinate diastereoisomeric transition-metal complexes have recently appeared.[1–3] Thus far these studies have been limited to nickel(II) bischelate complexes,† which usually undergo a planar-tetrahedral interconversion.[3] In the present study, monodentate dihalogenobis(phosphine) complexes of the general type $M[R^1R^2R^3P]_2X_2$, where $M = Co^{II}, Ni^{II}$; $R^1 \neq R^2 \neq R^3 =$ alkyl or aryl; and $X =$ halogen, are examined. The racemic phosphine oxides were prepared by the method of Korpium *et al.*,[4] followed by reduction with lithium aluminium hydride.[5] The complexes were prepared by mixing hot, oxygen-free ethanolic solutions of the phosphine and metal halide and quickly collecting the precipitate, all under nitrogen. The purity of the compounds was checked by elemental analysis and ^1H n.m.r.

The complexes investigated are pseudo-tetrahedral in solution, as determined from their solution magnetic-susceptibilities and u.v.–visible spectra, and exhibit large isotropic ^1H n.m.r. shifts

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† Bis-salicylaldimine and bis-β-ketoamine Ni^{II} complexes.

which enable subtle differences in electronic environment to be distinguished. In complexes of this type each of the two co-ordinating phosphorus atoms represents a centre of dissymmetry and thus the complexes can exist in $++$, $--$ (active), or $\pm$ (*meso*) forms. The ^{1}H n.m.r. spectra of these complexes in deuteriochloroform show a doubling of the resonances assignable to the various chemically equivalent protons. Separate resonances for active and *meso*-forms account for the observed doublings in complexes synthesized from racemic phosphine. The Figure shows the spectra of racemic $Ni[(MPA)P]_2I_2$ and $Co[(BPBz)P]_2I_2$, where (MPA) = methylphenyl-*p*-anisyl and (BPBz) = n-butylphenylbenzyl. For clarity, only the shifted aryl resonances are shown since the presence of unco-ordinated phosphine complicates the intermediate region of the spectrum. Peak assignments were made by comparison with the well-established triphenylphosphine analogues.[6] Active and *meso*-peaks are not identified since the synthesis of the optically active complex has not yet been achieved.

Several paramagnetic racemic phosphine complexes have been synthesized, each showing the expected diastereoisomeric doubling. On the other hand, the corresponding diamagnetic zinc complexes of the same pseudo-tetrahedral structure show no resolvable doublings. Thus it is concluded that this effect, resolved only for the paramagnetic systems, results from differences in the hyperfine interaction constants for active and *meso*-forms. Equation (1)[3] should therefore describe the temperature dependence of the doublet separations ($\Delta\Delta\nu_i$).

$$\frac{\Delta\Delta\nu_i}{\nu_i} = -\Delta a_i \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{6SkT}$$

where $\Delta\Delta\nu_i = |(\Delta\nu_i)_{meso} - (\Delta\nu_i)_{active}|$, $\Delta a_i = |a_{i(meso)} - a_{i(active)}|$, $\Delta\nu_i$ is the isotropic shift of each proton relative to its diamagnetic position, a_i is the hyperfine interaction constant, and the remaining symbols have their usual meanings. The temperature dependence required by the equation is rigorously obeyed in every case.

The diastereoisomeric doublings observed previously for the bischelate Ni^{II} systems were attributed to differences in free-energy change ΔF for the planar–tetrahedral interconversion, *i.e.*, $\Delta F(meso) \neq \Delta F(\text{active})$.[3] In contrast, the doublings in the bisphosphine complexes result from differences in hyperfine coupling constants, *i.e.*, $a_i(\text{active}) \neq a_i(meso)$. This probably results from subtle differences in geometry between active and *meso*-forms which are reasonable in these systems due to the close proximity of the dissymmetric phosphorus atoms, whereas the bischelate complexes have dissymmetric centres removed from the co-ordinating atoms.

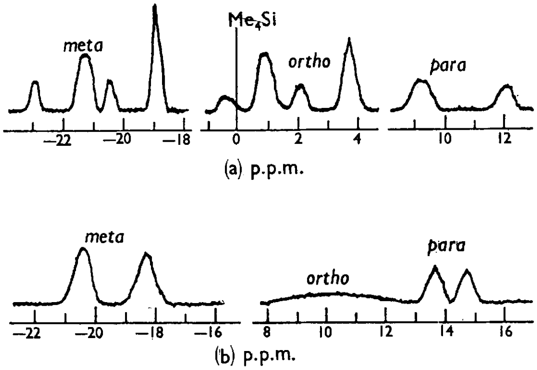

FIGURE. ^{1}H N.m.r. *spectra of* (*a*) Ni(methylphenyl-*p*-anisylphosphine)$_2$I$_2$ *and* (*b*) Co(n-butylphenylbenzylphosphine)$_2$I$_2$ *in* CDCl$_3$ *at* $-5°$.

Temperature studies on these systems reveal Curie behaviour for all doubled resonances between -60 and 50°. Above 50° ligand exchange with unco-ordinated phosphine broadens out the observed peaks. This phenomenon begins at different temperatures for the active and *meso*-diastereoisomers indicating a stereospecific exchange process.

^{1}H N.m.r. spectra of [$^2H_8$]toluene and deuteriochloroform solutions show a significant solvent dependence of $\Delta\nu_i$ and $\Delta\Delta\nu_i$. For example, $\Delta\Delta\nu_{meta} = 1{\cdot}8$ p.p.m. in deuteriochloroform and 2·1 p.p.m. in [$^2H_8$]toluene for Ni[n-butylphenyl-*p*-anisylphosphine]$_2$I$_2$ at 33°. This indicates a subtle solvent effect on the geometry of the complex influencing a_i and Δa_i.

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