^{1}H Nuclear Magnetic Resonance Study of the Kinetics of Tetrahedral $\rightleftarrows$ Square-planar Isomerization in Nickel(II) Complexes

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Summary The rates of tetrahedral square-planar interconversion for bisdiphenylmethylphosphinenickel dibromide and di-iodide have been determined from ^{1}H n.m.r. line-widths.

AN unusual characteristic of four-co-ordinated nickel(II) complexes is that the square-planar, diamagnetic, and (pseudo)tetrahedral, paramagnetic, isomers often have sufficiently similar ground-state energies that both conformations are populated in solution at room temperature.[1-5] The thermodynamics of this square-planar ($S = 0$) $\rightleftarrows$ tetrahedral ($S = 1$) equilibrium in solution has been investigated extensively for a large variety of ligands, using absorption spectra, magnetic moments, and ^{1}H n.m.r. spectra.[1-5] It has been concluded that increasing ligand–ligand steric interactions tend to depopulate the electronically more stable square-planar isomer,[1-3] although electronic effects could also favour the tetrahedral isomer.[4,5] However, nothing is known to date about the factors influencing the kinetics of this conformational change. A lower limit to the rate of interconversion[6] of $>10^5$—10^7 sec.$^{-1}$ is obtained for a number of complexes from the fact that only averaged isotopic shifts are observed in the ^{1}H n.m.r. spectra.[1-3] The appearance of separate absorption bands for the two isomers indicates[6,7] that their rate of interconversion is slower than 10^{13} sec.$^{-1}$.

We report that the bisdiphenylmethylphosphinenickel(II) dihalides,[5] $(Ph_2PMe)_2NiX_2$, also participate in this structural interconversion, and that for the first time, the kinetics of this interconversion can be readily determined from the line-widths[8] of the contact interaction dominated isotropic ^{1}H n.m.r. peaks of the ligand. The phenyl proton peaks in $(Ph_2PMe)_2NiBr_2$ in $CDCl_3$ exhibit the same relative contact shifts as previously reported[9] for the fully paramagnetic triphenylphosphine complexes, where the spin density resides in a ligand π-orbital, except that the Ph_2PMe shifts at 30° are only about half those of the Ph_3P complexes. Upon cooling the solution, the contact shifts increase more slowly than predicted by Curie behaviour,[10] and the line-widths increase dramatically down to $-12°$, when the m-H resonance, for example, splits into two separate resonances, one centred at the diamagnetic ligand position, and one centred at approximately the position for the fully tetrahedral Ph_3P complex.[9] Below $-20°$, the contact shifts for all protons in the tetrahedral isomer follow the Curie law.[10] From the coalescence temperature of the m-H peak, we estimate $k = ca.\ 1{\cdot}7 \times 10^3$ sec.$^{-1}$ at $-12°$. Extrapolation of the low-temperature Curie behaviour to 30° indicates that the complex is 58% paramagnetic, which is consistent with the value obtained from solution magnetic moments.[11] Integration of the m-H peak in the square-planar and tetrahedral isomers at $-50°$ yields $40 \pm 10\%$ paramagnetism. The average isotropic shifts are not observed over a sufficiently wide temperature range to allow an accurate determination of the thermodynamic parameters at this time. The determination of the activation energy must await a complete line-shape analysis over a temperature range. The reduced solution magnetic moment[11] of *ca.* 2·3 BM for $(Ph_2PMe)_2NiBr_2$ rules out the possibility that simple ligand exchange is responsible for the line-width effect.[12]

Of particular interest is the fact that for $(Ph_2PMe)_2NiI_2$, although the complex is more paramagnetic (*ca.* 65%) than the bromide in $CDCl_3$ solution, its rate of interconversion is much *faster*; the coalescence temperature for the m-H peak yields $k = ca.\ 2 \times 10^3$ sec.$^{-1}$ at $-55°$. The fact that the iodide complex interconverts more rapidly than the bromide,† although any ligand–ligand steric effects would be greater in the iodide, indicates that the potential barrier to this torsional distortion which gives rise to the structural interconversion is not a simple function of the steric interactions.

In a recent analysis[6] of the symmetry restrictions on the tetrahedral square-planar isomerization for d^8-complexes, Eaton has suggested that one of the reasons for the previous inability to detect this rapid isomerization in other nickel(II) complexes by n.m.r. is that this rearrangement is symmetry-allowed by the Woodward–Hoffman rules. The relative slow kinetics for the present phosphine complexes suggests that such arguments by themselves can be misleading.

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† The relative rates of ligand exchange (ref. 12), Br > I, are opposite to the observed relative rates of structural interconversion, I > Br.

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