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ABSENCE OF RAPID INTRAMOLECULAR REARRANGEMENT IN THE TETRAHEDRAL COMPLEX $Co(NO)(CO)(PMe_2Ph)_2$

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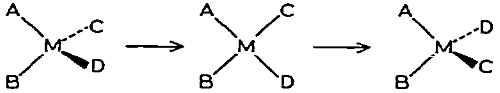
SUMMARY

NMR methods have been used to show that any rearrangement of the tetrahedral complex $Co(NO)(CO)(PMe_2Ph)_2$ through a planar transition state is slow on the NMR time scale.

There has been considerable recent interest in intramolecular rearrangement processes in transition metal complexes. It is suspected, for example, that many trigonal-bipyramidal five-coordinate complexes are stereochemically labile, with ligands interchanging between equatorial and axial positions[1,2].

This paper describes an experiment designed to test the feasibility of an intramolecular rearrangement of a tetrahedral complex through a planar intermediate.



In theory the problem can be approached by studying the racemization of one isomer of an optically active complex MABCD, but this is tedious owing to the difficulty of isolating such a compound in a state of optical purity[3].

A more elegant approach is to study a compound $MABC_2$, where C is the ligand PMe_2Ph. The presence of a plane of symmetry through M and the groups A and B makes the two PMe_2Ph ligands equivalent, but the fact that neither M–P bond lies in this plane of symmetry makes the two methyl groups on a given PMe_2Ph ligand inequivalent. Thus the NMR spectrum of a tetrahedral complex $MAB(PMe_2Ph)_2$ should exhibit *two* resonances for the four methyl groups.

If, however, the complex is undergoing rapid intramolecular rearrangement through a planar intermediate, the effect is to interchange the identities of the two methyl groups on a given PMe_2Ph ligand. Thus, as the rate of such a rearrangement increases, it should first broaden the two methyl resonances and ultimately give rise to one resonance for all the methyl groups in the complex.

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To test this possibility, the tetrahedral complex $Co(NO)(CO)(PMe_2Ph)_2$ was prepared by reaction of $Co(NO)(CO)_3$ with PMe_2Ph in a 1/2.2 molar ratio in 60–80° petroleum ether. The reaction required several days at 60°C. The product was purified by column chromatography on silica gel and recrystallized from 40–60° petroleum ether at −70°. Red crystals, m.p. 42°, were obtained. (Found: C, 51.3; H, 5.55; N, 3.58. $C_{17}H_{22}CoNO_2P_2$ calcd.: C, 51.9; H, 5.64; N, 3.56%.)

The 100 MHz NMR spectrum of $Co(NO)(CO)(PMe_2Ph)_2$ in $CDCl_3$ at 20° showed *two* distinct doublets for the methyl groups at τ 8.43 [J(P–H) 7.5 Hz] and τ 8.54 [J(P–H) 7.5 Hz] respectively. The absence of any further coupling between methyl protons on one ligand with the phosphorus atom on the other is to be expected, since J(PMP′) is very small for tetrahedral complexes of this type[4]. The spectrum remained unchanged up to the boiling point of $CDCl_3$, with no broadening of the methyl resonances. Spectra in dimethyl sulphoxide-d_6 and in nitrobenzene were less satisfactory, but again clearly showed the presence of two types of methyl group. In neither case was there any alteration in the spectrum until the complex decomposed irreversibly at about 100°.

We conclude that, in this tetrahedral complex at any rate, any intramolecular isomerization is slow on the NMR time scale over the whole temperature range studied.

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