

LIQUID STATE STEREOCHEMISTRY OF RH(I)-BISPHOSPHINE-DIENE COMPLEXES. CORRELATION OF CONFORMATIONAL CHIRALITY OF THE COMPLEXES AND THE STRUCTURAL CHIRALITY OF THE LIGAND.

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We report on the liquid state stereostructure and conformational behaviour of (Rh(I)-norbornadiene-BDPP)<sup>+</sup> (1), (Rh(I)-1,5-cyclooctadiene-BDPP)<sup>+</sup> (2) square-planar and the neutral (Rh(I)-norbornadiene-BDPP-Cl) (3) complexes (precursors of homogen catalytic reactions) on the basis of their H-1, P-31 and C-13 NMR spectra. Atoms of the coordinated dienes are sensitive reporters of the conformational changes of the phosphine chelate in solution. In 1 and 2 phenyl rings of the phosphine ligand (BDPP = (2S,4S)-2,4-bis-(diphenylphosphino) pentane) are in a chiral array around the rhodium atom. The structural chirality present in the chelate ring (methyl groups) increase the interconversion barriers of ring inversion. Molecular mechanics calculations indicate 2-3 kcal/mol higher phenyl rotation barrier for BDPP in comparison with its achiral analogue dppp (1,3-bis(diphenylphosphino) propane), nevertheless it is still too low (4-5 kcal/mol) to be observed at 213 K. These planar cationic complexes process  $C_2$  symmetry. The phosphine chelate conformation is *skew* with equatorially disposed methyl groups.

In the P-31 NMR spectrum of the five coordinated species (3) the P atoms are different, furthermore four different, fast rotating phenyl groups could be distinguished when recorded in aromatic solvents or at low temperature in CD<sub>2</sub>Cl<sub>2</sub>. At room temperature in halogenated solvents the P atoms became equivalent and the  $C_2$  symmetry observed for the square-planar species is reestablished. H-1 DNOE experiments prove the existence of a slow exchange process (at 9.39 T) between identical forms and the crosswise identity of the olefinic protons. The latter fact suggest axial-equatorial positions for the phenyls. Surprisingly enough, atoms of the coordinated diene do not show this exchange. No satisfactory explanation has been found for the origin of the phenomenon, however, the generally assumed trigonal-bipyramidal square-pyramidal exchange is rather unlikely. We conclude that the essential role of functional chirality in such bidentate ligands is to make the steric energies of the chiral conformations present in solution different, lack of this "a priori" asymmetry leads to equal amount of left and right rotating optical antipodes.