Complexes of heteroscorpionate trispyrazolylborate ligands. Part 10. Structures and fluxional behavior of rhodium(I) complexes with heteroscorpionate trispyrazolylborate ligands, Tp''Rh(LL) (LL = $(CO)_2$ or COD).

Autorzy

Tomasz Ruman

Zbigniew Ciunik

Anna M. Trzeciak

Stanisław Wołowiec

Józef J. Ziółkowski

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Streszczenie

Heteroscorpionate Tp‘ ‘ ligands constructed of two 3-phenyl-5-methylpyrazolyl and a variable third pyrazolyl residue (3-methyl-5-phenyl-, 3,5-dimethyl-, and 3,5-diethylpyrazolyl) coordinate to rhodium(I) in a κ^2 fashion to form Tp‘ ‘Rh(LL) complexes (where LL = COD or $(CO)_2$). One of the two 3-phenyl-5-methylpyrazolyl and the less sterically hindered pyrazolyl coordinate through N(2) atoms, while the axially appended 3-phenyl-5-methylpyrazolyl is in side-on conformation. The Tp‘ ‘Rh(COD) complexes possess C_1 symmetry in the solid state. The energy of activation of the exchange between coordinated and uncoordinated pyrazolyls was estimated from variable-temperature ^{1}H NMR measurements. Two $\Delta G^{\ddagger}$ values were found for heteroscorpionate complexes. The $\Delta G^{\ddagger}_1 - \Delta G^{\ddagger}_2$ depends on a difference in steric demands of competing pyrazoles. For the homoscorpionate $Tp^{Ph,Me}$Rh(COD) complex two rotational isomers were identified by low-temperature ^{1}H NMR spectroscopy, which originate from slow rotation of the dangling 3-phenyl-5-methylpyrazolyl residue. All studied Tp‘Rh(COD) complexes were found to be catalytically active in regioselective polymerization of phenylacetylene.

Słowa kluczowe

Conformation, Ligands, Molecular structure, Molecules, Pyrazolyl

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