

Dependence of the cone angles of phosphorus-containing ligands in the chemistry of hydride and dihydrogen complexes of ruthenium

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A series of new hydride complexes of ruthenium of the type *trans*-[(dppe)₂Ru(H)(L)][BF₄], dppe = Ph₂CH₂CH₂Ph₂, L = P(OMe)₃, P(OEt)₃, PMe₂Ph, P(OⁱPr)₃ have been prepared and characterized using a procedure similar to the one reported earlier. It was found that the binding ability of the ligand decreases in the order P(OMe)₃ @ P(OEt)₃ > PMe₂Ph > P(OⁱPr)₃ with an increase in the cone angle of the phosphorus ligand. The protonation reactions of the precursor hydride complexes, *trans*-[(dppe)₂Ru(H)(L)][BF₄] result in a mixture of the dihydrogen complex and the homolysis reaction product, the dihydride species for L = P(OMe)₃ and P(OEt)₃. There is strong dependence on the concentration of the acid used for the isolation of either the dihydrogen or the dihydride complex. Similar protonation reactions in the cases of PMe₂Ph and P(OⁱPr)₃ yielded unidentifiable species having a hydride and dihydrogen ligand. P(OⁱPr)₃ ligand in *trans*-[(dppe)₂Ru(H)P(OⁱPr)₃][BF₄] was found to be extremely labile and was readily substituted by H₂ as a consequence of its high cone angle (131°). The syntheses, characterization, and chemistry of these species are presented.

