Dehydrocoupling of silanes with Ir pincer complexes: Ligand effects on selectivity and activity

The bisphosphinite pincer-ligated Ir complex (POCOP)IrHCl (POCOP) = $2,6-({}^{t}Bu_{2}PO)_{2}C_{6}H_{3}$ (1) selectively dehydrocouples phenylsilane to form a ten-membered cyclosilane product, (PhSiH)₁₀ with high activity. The product selectivity of this catalyst is hypothesized to be based on both the steric and electronic environment around the metal center, which is dominated by the alkyl substituents on the phosphine. Complex **1** has been used to dehydrocouple *o*-tolylsilane, napthylsilane, phenylmethylsilane, diphenylsilane, and mesitylsilane, with decreasing catalytic activity as the steric bulk of the silane increases. To determine the effect of steric bulk on the catalyst, a less bulky bisphosphinite pincer-ligated Ir complex (POCOP)IrHCl, (POCOP) = $2,6-(R_2PO)_2C_6H_3$ (R= ⁱPr) has been synthesized and used in the catalytic dehydrocoupling of primary and secondary silanes. The aryl backbone of the ligand p-X(POCOP)IrHCl (X= COOMe, NMe₂) has also been functionalized to determine the extent that the electronics of the pincer ligand contribute to catalytic activity. Trends in product distribution will be discussed relative to the steric bulk of the silane substrate as well as the coordination sphere of the catalyst.