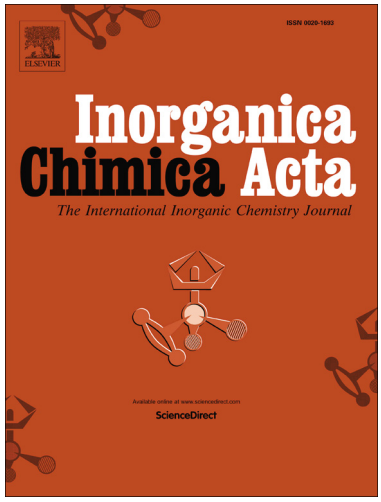

Research paper

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Transfer Hydrogenation of Ketones Catalyzed by Iridium-Bulky Phosphine Complexes

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This contribution is dedicated to Dr. Carlo Mealli in occasion of his 70th birthday.

Abstract

The complexes $[Ir(COD)(PR_3)_2]PF_6$ (R = PPh_3 (**1**); R = PBn_3 = tribenzylphosphine (**2**)), $[Ir(COD)(PBn_3)(PAn_3)]PF_6$ (**3**) (PAn_3 = Tri-orthoanisyl-phosphine) and cis-(P,P)-$[IrH(COD)(PBn_3)\{\eta^2\text{-}P,C\text{-}(C_6H_4CH_2)PBn_2\}]PF_6$ (**4**) are active in the transfer hydrogenation of ketones. However, complex (**3**) gives the best results in conversion toward the alcohol. Interestingly, commercial isopropanol was used as hydrogen source, without any drying treatment. *In situ* generated isopropoxide was used as base. An efficient conversion of a variety of ketones, aromatic or aliphatic, cyclic or linear, including molecules with conjugated or isolated C=C moieties was achieved, thus reporting 12 examples of hydrogenated substrates. Ketones of higher steric hindrance could not be converted under the studied conditions. The experimental evidence indicates that the steric and electronic properties of the substrates are determinant in the observed conversions and performance of the system. For α,β-unsaturated ketones, preference toward the reduction of the C=C bond was observed. However, the system shows chemoselectivity toward the carbonyl group in molecules which also bear an isolated C=C moiety. With the results obtained, a pseudo first-order dependence of the reaction rate on the concentration of ketone was determined. Also, stoichiometric as well as *in situ* tests were performed to shed light into the reaction pathways possibly involved in the catalytic TH of ketones described herein (precursor **3**, base and isopropyl alcohol as hydrogen source).

Keywords: Transfer hydrogenation, hydrogen source, Ir(I) complexes, bulky phosphines, ketones.