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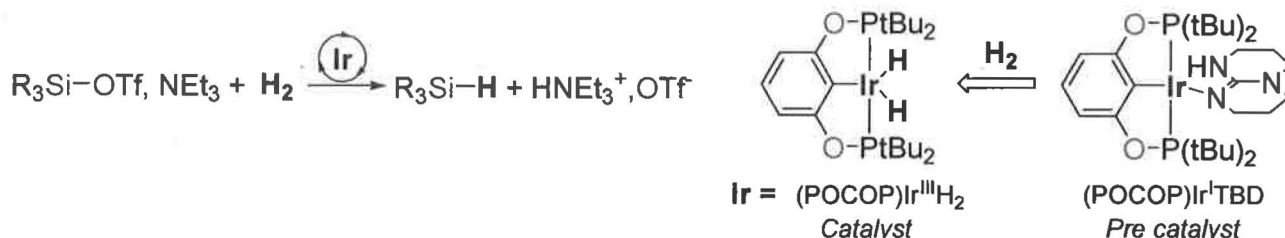
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# Catalytic hydrogenolysis of silyl triflates to hydrosilanes using iridium pincer complexes

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Hydrosilanes are convenient reductants for a large variety of organic oxygenated substrates and they have been successfully applied in the conversion of bio-based materials<sup>1</sup> and CO<sub>2</sub>.<sup>2</sup> At present, hydrosilanes are produced *via* energy intensive processes<sup>3</sup> and they generate, after use, silicon oxides wastes such as siloxanes, which are difficult to recycle. These limitations call for the development of catalytic processes able to transform Si-O bonds in siloxanes and derivatives (silyl halides and triflates) into Si-H hydrides.

Very recently, the groups of Shimada<sup>4</sup> and Schneider<sup>5</sup> reported for the first time the hydrogenolysis of some silyl halides and triflates with iridium(III) catalysts and ruthenium(II). Following these preliminary reports, we studied the catalytic hydrogenolysis of R<sub>3</sub>SiOTf (R = Me, Et, Ph) species in the presence of a base, by the dihydride complex (POCOP)IrH<sub>2</sub> (See figure above). Syntheses and crystal structures of some isolated Ir(I) and Ir(III) complexes will be presented as well as their role in the R<sub>3</sub>SiOTf to R<sub>3</sub>SiH transformation.

The new (POCOP)Ir<sup>I</sup>(TBD) complex, which splits H<sub>2</sub> to (POCOP)Ir<sup>III</sup>H<sub>2</sub> at a low pressure, is a pre-catalyst in the hydrogenolysis of Si-OTf linkages. It can be easily obtained from (POCOP)IrHCl, using the TBD guanidine. To the best of our knowledge, such spontaneous reductive elimination by a weak base of an iridium(III) hydro-chloride species is novel.

The kinetic and thermodynamic profiles of the reaction were examined by means of spectroscopic and DFT studies. The mechanism reveals that rate determining step is the hydride transfer from (POCOP)IrH<sub>2</sub> to the silyl triflate. The base (e.g. NEt<sub>3</sub>) is required to drive the thermodynamics of the reaction, by promoting the regeneration of iridium hydrides intermediates, in the presence of H<sub>2</sub>.

## References

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