Semi hydrogenation of alkynes by a novel bimetallic rhodium(I) complex

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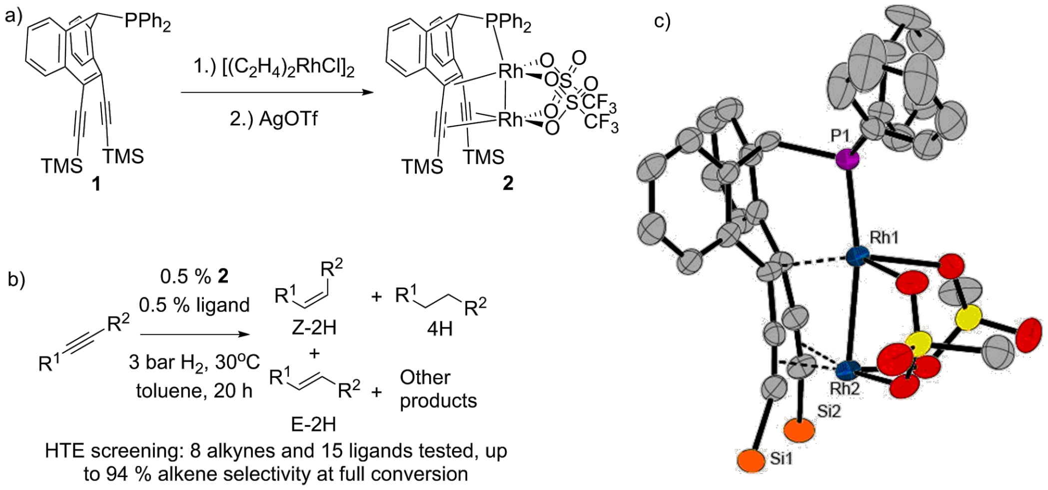
Catalytic semi hydrogenation of alkynes to alkenes is an important process in both academia and industry. Developed in the 50’s, Lindlar’s catalyst (Pd/$CaCO_3$/$Pb(OAc)_2$/quinoline) still remains a privileged system for Z-selective semi hydrogenation reactions. However, the system utilizes a toxic lead additive. Further drawbacks are narrow substrate scope, over hydrogenation to alkenes, Z/E isomerization and double bond migration reactions. [1]

Herein, we report a new bimetallic complex **2** bearing a $[Rh(I)]_2$-mojety. The stabilization of the rhodium-rhodium bond, while leaving two reactive rhodium centers, was achieved by a tailored ligand with olefin/alkyne sites to anchor the two metal centers. The complex **2** was shown to be active in semi hydrogenation of alkynes under very mild conditions. In order to optimize the stability and activity of the complex, high throughput ligand- and substrate screening was performed, leading to a catalyst system able to perform semi hydrogenation reactions with up to 94 % alkene selectivity.



HTE screening: 8 alkynes and 15 ligands tested, up to 94 % alkene selectivity at full conversion

Figure 1. a) Synthesis of a dirhodium complex **2**, b) Conditions for semi hydrogenation reactions, c) crystal structure of **2**. Methyl groups and fluorine atoms omitted for clarity.

[1] A. Fedorov, H. Liu, H. Lo, C. Copéret, *J. Am. Chem. Soc.* **2016,** *138,* 16502.