

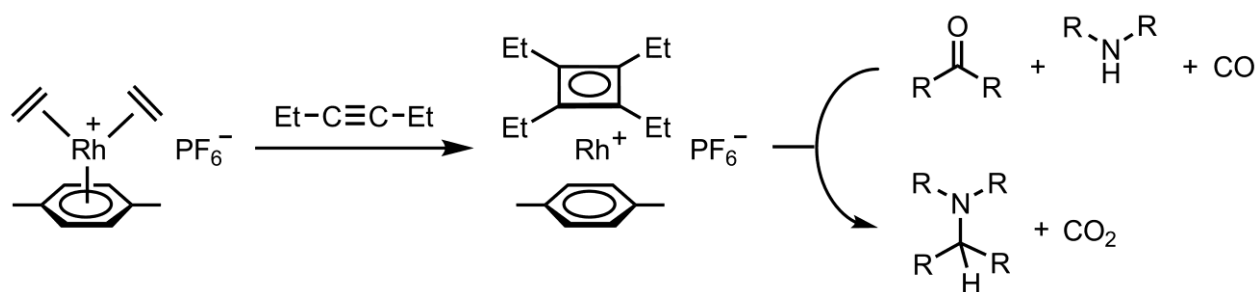
Cyclobutadiene complexes of platinum metals

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Complexes of platinum metals are widely used as catalysts in modern organic chemistry. They are usually equipped with phosphine, carbene or cyclopentadienyl ligands, which help to stabilize the active metal center and to control the selectivity of reactions. At the same time, surprisingly, complexes with cyclobutadiene ligands have not been used in catalysis prior to 2015. Apparently, their application is hampered by their more complicated synthesis, which stems from instability of the cyclobutadiene as a free ligand. The most common method for synthesis of the cyclobutadiene complexes is the dimerization of alkynes in the coordination sphere of a metal. However, this approach suffers from the inherently high reactivity of alkynes, which often leads to formation of oligomerization products [1].

Recently, we have developed a new general method for the synthesis of the cyclobutadiene rhodium complexes [2]. The key idea was to use a metal precursor with only two coordination sites for incoming alkynes in order to suppress the unwanted oligomerization. Indeed, the substitution of two labile ethylene ligands in the rhodium complex $[(C_2H_4)_2Rh(p\text{-xylene})]PF_6$ by 3-hexyne cleanly gave the desired cyclobutadiene complex $[(C_4Et_4)Rh(p\text{-xylene})]PF_6$. This compound provides an access to variety of other rhodium complexes and moreover appeared to be the most active catalyst for reductive amination of aldehydes and ketones in the presence of CO as deoxygenative agent.



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[1] N. V. Shvydkiy, D. S. Perekalin, *Coord. Chem. Rev.* **2017**, *349*, 156–168.

[2] D. S. Perekalin, N. V. Shvydkiy, Y. V. Nelyubina, A. R. Kudinov, *Chem. Eur. J.* **2015**, *21*, 16344–16348.