

The Synthesis and Reactivity of PBP-Pincer Perfluororhodacyclopentanes

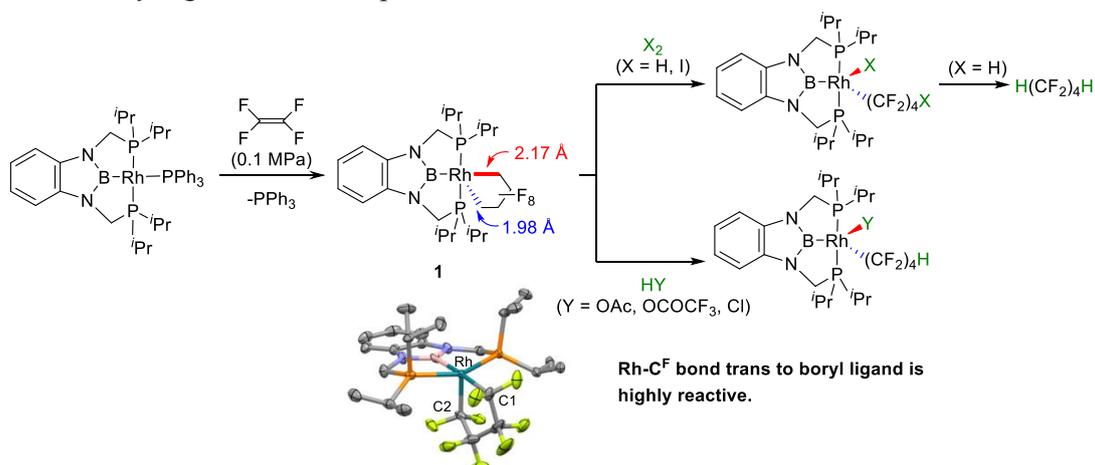
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Keywords: Rh; PBP-pincer; rhodacycle; tetrafluoroethylene; perfluorometallacyclopentane

Oligomerization of tetrafluoroethylene (TFE) has been attracting great attention because of the industrial importance of polyfluoroalkyl building blocks. Although the oxidative cyclization of TFE and low-valent transition metals has been studied for more than half a century, selective oligomerization of TFE is still challenging due to the extraordinary stability of octafluorometalacyclopentane.¹

We employed rhodium complex bearing PBP pincer ligand expecting enhancement of nucleophilicity of the fluoroalkyl group by strong electron-donation from the anionic boryl ligand. The complex $\text{PBPRh}^{\text{III}}(\text{CF}_2)_4$ (**1**) was formed by the oxidative cyclization of the $\text{PBPRh}^{\text{I}}-\text{PPh}_3$ complex with two TFE molecules in 65% yield. Single-crystal X-ray crystallographic analysis revealed that **1** has a square pyramidal geometry, and the Rh–C bond trans to boryl ligand (2.17 Å) is largely elongated compared to the Rh–C bond at the apical position (1.98 Å).

The hydrogenolysis of **1** proceeded under mild conditions (room temperature, 1 atm of H_2) affording 1,1,2,2,3,3,4,4-octafluorobutane in 89% yield, which demonstrated high reactivity of **1** compared to the precedented example with Ni complexes (at 100 °C, under H_2 pressure of 68 atm).² The iodinolysis and the protonolysis of **1** also proceeded selectively at ambient temperature. The high nucleophilicity of Rh–C^F bond can be attributed to the strong effect of boryl ligand in the PBP pincer skeleton.³



- 1) T. A. Manuel, S. L. Stafford, F. G. A. Stone, *J. Am. Chem. Soc.* **1961**, *83*, 249. 2) K. A. Giffin, L. A. Pua, I. Korobkov, R. T. Baker, *Polyhedron* **2019**, *157*, 458. 3) Y. Masuda, M. Hasegawa, M. Yamashita, K. Nozaki, N. Ishida, M. Murakami, *J. Am. Chem. Soc.* **2013**, *135*, 7142.