Highly Active Cross-Metathesis of Tetrafluoroethylene with a Seven-membered NHC-Ruthenium Catalyst

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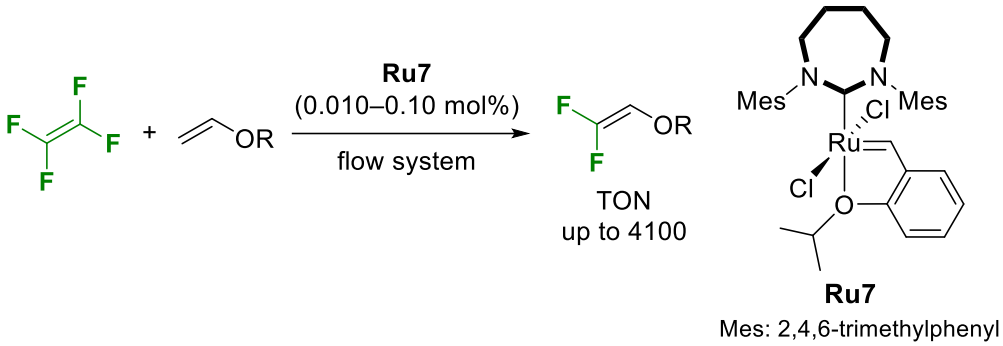
Tetrafluoroethylene (TFE) is an economical feedstock for the industrial production of poly(tetrafluoroethylene) and copolymers with other olefins.[1] If TFE could be employed as a substrate for olefin metathesis, it would serve as a promising difluoromethylene source for the production of 1,1-difluoroalk-1-enes, which are important structural motifs used in fine chemicals, pharmaceuticals, and agrochemicals, as well as in materials science.[2–4]

In 2015, one of the authors (Takahira) and his co-worker achieved the first and so far only cross-metathesis of TFE by employing an alkyl vinyl ether as the counter-substrate;[5] unfortunately, the efficiency of this reaction was very low (TON ≈ 13.4). Here, we report a discontinuous improvement in this catalytic reaction, wherein (i) a continuous-flow system is provided to shift the equilibrium to the desired product, and (ii) a catalyst with a seven-membered NHC ligand (**Ru7**) presents exceptionally high efficiency (Scheme 1). Using the optimized conditions, the TON reaches 4100, which is two orders of magnitude higher than the highest hitherto reported TON. Computational studies suggest that the seven-membered NHC ligand destabilizes the most stable difluromethylidene intermediate more effectively than the conventional five-membered NHC ligand, reducing the relative energy of the highest transition state and thus promoting the reaction.



Scheme 1. Cross metathesis of tetrafluoroethylene and vinyl ethers catalyzed by a seven-membered NHC-Ruthenium catalyst

(1) Okazoe, T. *Proc. Jpn. Acad., Ser. B* **2009**, *85*, 276–289. (2) Zhang, X.; Cao, S. *Tetrahedron Lett.* **2017**, *58*, 375–392. (3) Decostanzi, M.; Campagne, J. M.; Leclerc, E. *Org. Biomol. Chem.* **2015**, *13*, 7351–7380. (4) Ichikawa, J. *J. Fluorine Chem.* **2000**, *105*, 257–263. (5) Takahira, Y.; Morizawa, Y. *J. Am. Chem. Soc.* **2015**, *137*, 7031–7034.