

Highly Active Cross-Metathesis of Tetrafluoroethylene with a Seven-Membered N-Heterocyclic-Carbene–Ruthenium Catalyst

Kenta Mori, Midori Akiyama,* Ko Inada, Yutaka Imamura, Yuichiro Ishibashi, Yusuke Takahira, Kyoko Nozaki,* and Takashi Okazoe

Cite This: *J. Am. Chem. Soc.* 2021, 143, 20980–20987

Read Online

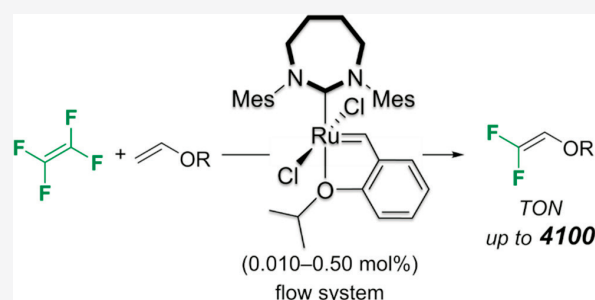
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: A drastic increase in catalyst turnover number (TON) was accomplished in the cross-metathesis of tetrafluoroethylene (TFE) and vinyl ethers. Under a continuous flow of TFE, catalyst **Ru7**, which contains a seven-membered N-heterocyclic carbene (NHC) ligand, reached a TON of 4100; this is 2 orders of magnitude higher than the highest hitherto reported value. Mechanistic studies revealed that the expanded NHC successfully destabilizes the stable intermediates with a difluorocarbene structure, which strongly promotes the reaction.



INTRODUCTION

Tetrafluoroethylene (TFE) is an economical feedstock for the industrial production of poly(tetrafluoroethylene) and copolymers with other olefins.¹ Despite its potential as a synthon to prepare fluorinated compounds (Scheme 1a), its use has mostly been limited to the production of polymers.² In 2011, Ogoshi et al. started reporting reactions to substitute one of the four fluorine atoms of TFE with a carbyl or boryl substituent; namely, a palladium-catalyzed cross-coupling reaction,^{3–5} a lithium-salt-promoted monoalkylation,⁶ and the copper-catalyzed monofluoroborylation of TFE⁷ have been developed. TFE has also been used for the construction of tetrafluoroethylene-bridging structures via the nickel-catalyzed selective coupling of TFE and other unsaturated compounds^{8–10} or the 1,2-addition of copper reagents to TFE.^{11–13} In 2013, Baker et al. investigated the reaction of TFE with a fluoromethylidene–cobalt complex to afford perfluorometallacyclic products, for which TFE also serves as the source of tetrafluoroethylene-bridging units.¹⁴

Olefin metathesis is a valuable reaction for the transformation of alkenes.^{15–17} 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 (Scheme 1a), which are important structural motifs used in fine chemicals, pharmaceuticals, and agrochemicals, as well as in materials science.^{18–20} Furthermore, they can be used as intermediates to prepare other fluorine-containing structures, such as the *gem*-difluoromethylene (–CF₂–) group, monofluoroalkenes, and fluorinated aromatic compounds.^{18,21,22} Although olefin metathesis is a powerful and versatile catalytic transformation to construct new carbon–

carbon double bonds, fluoroalkenes in which the fluorine atoms are directly connected to the sp²-hybridized carbon atoms remain challenging substrates for this reaction.^{23–27} The limited examples of such transformations are summarized in Scheme 1b. In 2009, Johnson et al. reported that the cross-metathesis of fluoroethylene and 1,2-disubstituted alkenes proceeds in the presence of a ruthenium catalyst with a turnover number (TON) of 2–11.²⁶ Another example is the selective synthesis of *Z*-alkenyl halides via the Mo-catalyzed cross-metathesis of 1,2-dihaloethylenes with successful kinetic stereocontrol, which was reported by Hoveyda et al. in 2016.²⁸ While the present manuscript was under preparation, Bonnaire et al. reported the Ru-catalyzed cross-metathesis and ring-opening cross-metathesis using methyl-2-fluoroacrylate, in which the TON was 175 at the highest.²⁹ It should also be noted that these examples of the metal-catalyzed metathesis of fluoroalkenes afforded only monofluoroalkenes but not difluoroalkenes. A pioneering study by Baker et al. in 2018 is concerned with the stoichiometric metathesis of a Ni–fluorocarbene with TFE (Scheme 1c).³⁰

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 countersubstrate;³¹ unfortunately, the efficiency of this reaction was very low

Received: October 6, 2021

Published: December 3, 2021

