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Ruthenium-Catalyzed Olefin Cross-Metathesis with Tetrafluoroethylene and Analogous Fluoroolefins

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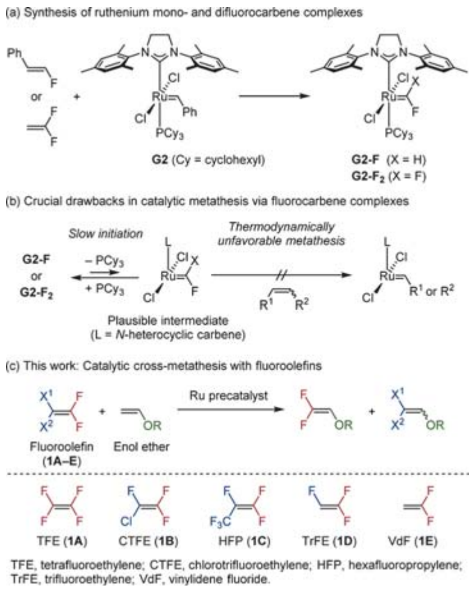
S *Supporting Information*

ABSTRACT: This Communication describes a successful olefin cross-metathesis with tetrafluoroethylene and its analogues. A key to the efficient catalytic cycle is interconversion between two thermodynamically stable, generally considered sluggish, Fischer carbenes. This newly demonstrated catalytic transformation enables easy and short-step synthesis of a new class of partially fluorinated olefins bearing plural fluorine atoms, which are particularly important and valuable compounds in organic synthesis and medicinal chemistry as well as the materials and polymer industries.

Olefin metathesis is one of the most powerful and versatile catalytic transformations to construct a new carbon−carbon double bond, and it has become a widely used synthetic tool in both pure and applied chemistry.[1] Despite ruthenium precatalysts having excellent tolerance toward diverse functional groups, the scarce successes underscore the incompatibility of directly halogenated olefins.[2] Focusing on directly fluorinated olefins, commonly referred to as fluoroolefins, attempts at successful olefin metathesis via fluorocarbene complexes have pointed out two crucial drawbacks in catalytic transformation.[3−8]

Ruthenium mono- and difluorocarbene complexes, **G2-F**[4] and **G2-F$_2$**,[5] respectively, have been prepared previously from the parent benzylidene counterpart **G2** with the corresponding fluoroolefins via stoichiometric metathesis (Scheme 1a). Both complexes showed no phosphine dissociation, a plausible initiation step for catalytic cycles, even at elevated temperatures, based on ^{31}P NMR magnetization transfer experiments, which indicated problematic initiation. Comparison of these catalytic activities for ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (0.33 mol % **G2-F** or **G2-F$_2$**, CD_2Cl_2, 25 °C, 1.25 h) indicated that the initiation of **G2-F$_2$** (only 9% conversion) was much slower than that of **G2-F** (100% conversion), which emphasized the extreme sluggishness of **G2-F$_2$**. Another drawback emerged through density functional theory (DFT) calculations in regard to the Gibbs free-energy profiles of the cross-metathesis of 2-norbornene with several directly halogenated olefins.[6] The results indicated a large contribution of halocarbene ligation, in particular, that of difluorocarbene, to stabilize the whole of the complexes, and this would hinder subsequent turnover. A recent study using coupled cluster theory calculation also predicted that the type of carbene complex involving two electron negative substituents is not likely to be effective for olefin metathesis.[7] These two crucial drawbacks to olefin metathesis explained why no successful catalytic cross-metathesis involving the difluorocarbene complex was reported, whereas there have been a few successes via the monofluorocarbene counterpart (Scheme 1b).[4,8]

Scheme 1. Olefin Metathesis with Fluoroolefins



(a) Synthesis of ruthenium mono- and difluorocarbene complexes

(b) Crucial drawbacks in catalytic metathesis via fluorocarbene complexes

(c) This work: Catalytic cross-metathesis with fluoroolefins

TFE, tetrafluoroethylene; CTFE, chlorotrifluoroethylene; HFP, hexafluoropropylene; TrFE, trifluoroethylene; VdF, vinylidene fluoride.

Fluoroolefins are particularly important and valuable compounds for the synthesis of many commercially successful products in the materials and polymer industries.[9] Thus far, only a limited number of fluoroolefins have been used as monomers because of a lack of suitable, inexpensive methods for their preparation. The use of olefin metathesis involving inexpensive fluoroolefins and a hydrocarbon counterpart will enable easy and short-step synthesis of a wide range of functionalized fluoroolefin monomers for exploitation in polymer chemistry, for example, as well as possible new building blocks bearing plural fluorine atoms in medicinal chemistry. Tetrafluoroethylene (TFE) and its analogues are inexpensive, bulk organofluorine feedstocks and are considered to be suitable starting materials for this perspective.[10]

During our investigations to develop new classes of catalytic transformation with TFE, the simplest perfluoroolefin, we

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