

2,2,3,3-Tetrafluoronickelacyclopentanes Generated via the Oxidative Cyclization of Tetrafluoroethylene and Simple Alkenes: A Key Intermediate in Nickel-Catalyzed C–C Bond-Forming Reactions

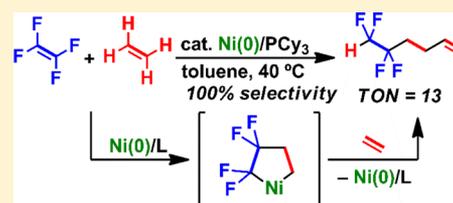
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Supporting Information

ABSTRACT: Oxidative cyclization of tetrafluoroethylene (TFE) and ethylene with Ni(0) resulted in the formation of a five-membered nickelacycle. In the presence of PPh₃ as an auxiliary ligand, the partially fluorinated five-membered nickelacycle was isolated and the structure was determined by X-ray analysis. This nickelacycle was found not only to react stoichiometrically with enones to give a cross-trimerization product but also to be a key reaction intermediate in the Ni(0)-catalyzed cotrimerization of TFE and ethylene, leading to 5,5,6,6-tetrafluoro-1-hexene.



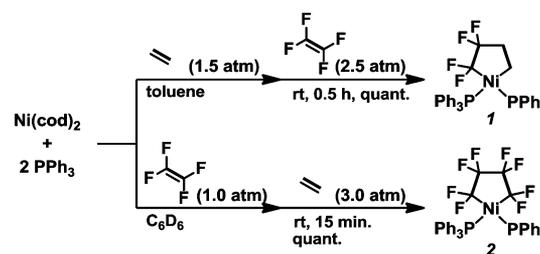
Oxidative cyclization with low-valent transition-metal species has received increasing attention as a straightforward and environmentally benign route to the construction of a C–C bond between varieties of two unsaturated compounds. The generated five-membered metallacycles are assumed to be key reaction intermediates in multicomponent coupling reactions as well as in cycloaddition reactions.^{1,2} The transition-metal-catalyzed trimerization reaction of ethylene to 1-hexene, which is used as a comonomer with ethylene to produce linear low-density polyethylene (LLDPE), has been proposed to proceed via oxidative cyclization of two ethylenes.^{3,4} Since α -olefins can be copolymerized with ethylene to afford polymers with improved properties, it is worthwhile to develop such an oligomerization leading to α -olefins with a terminal functional group.⁵ Nevertheless, selective cotrimerization reactions between ethylene and other alkenes have rarely been investigated. Limited reactions between ethylene and styrene are known to be catalyzed by chromium species.^{6,7} We also demonstrated the Ni-catalyzed cotrimerization reaction of an enone and two ethylenes to give a 1,6-enone derivative.^{8,9}

Recently, our efforts have focused on the development of a novel strategy for utilizing tetrafluoroethylene (TFE; CF₂=CF₂) as a starting material for the synthesis of valuable organofluorine compounds, since conventional usage of the industrially economical TFE has been mostly limited to the production of poly(tetrafluoroethylene) and copolymers with other alkenes.¹⁰ In the course of our recent studies on transformations of TFE,^{11–13} we reaffirmed that oxidative cyclization between TFE and an unsaturated compound with Ni(0) might be a key reaction step in C–C bond formation reactions.^{11c,13,14} A limited number of reports have focused on five-membered nickelacycles generated via the oxidative cyclization of TFE with other unsaturated compounds^{15,16a}

and on their applications to catalytic transformations.¹⁶ On the basis of the aforementioned early study employing ethylene and styrene with chromium,⁵ it is possible that the five-membered nickelacycle generated via the oxidative cyclization of TFE and ethylene with Ni(0) may serve as an intermediate for the cotrimerization of TFE and ethylene. Herein, we report the stoichiometric reactions of TFE and ethylene with Ni(0). In the presence of PPh₃, oxidative cyclization of TFE with ethylene took place to give a five-membered nickelacycle, which was found to further react with ethylene to afford a cotrimerization product. We also established a novel nickel-catalyzed cotrimerization reaction between ethylene and TFE.

Successive treatment of a mixture of Ni(cod)₂ and PPh₃ with ethylene followed by TFE in toluene for 1 h led to quantitative formation of a five-membered nickelacycle, (CF₂CF₂CH₂CH₂)-Ni(PPh₃)₂ (**1**) (Scheme 1). In contrast, before the ethylene treatment, the prior exposure of TFE to the Ni(0)/PPh₃ mixture gave the known octafluoronickelacyclopentane

Scheme 1. Formation of 1 Generated via Oxidative Cyclization of TFE and Ethylene



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(CF₂CF₂CF₂CF₂)Ni(PPh₃)₂ (**2**).^{11c,13g} The X-ray diffraction study of **1** clearly demonstrated that the nickelacyclopentane framework was derived from one TFE and one ethylene unit (Figure 1). One of the structural features is a distorted-square-

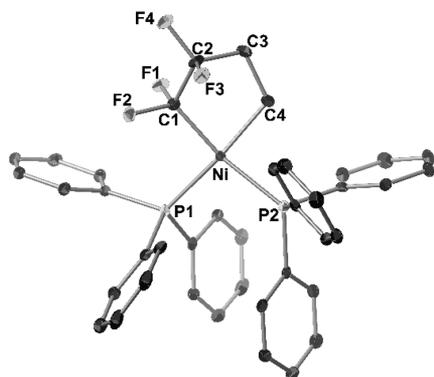
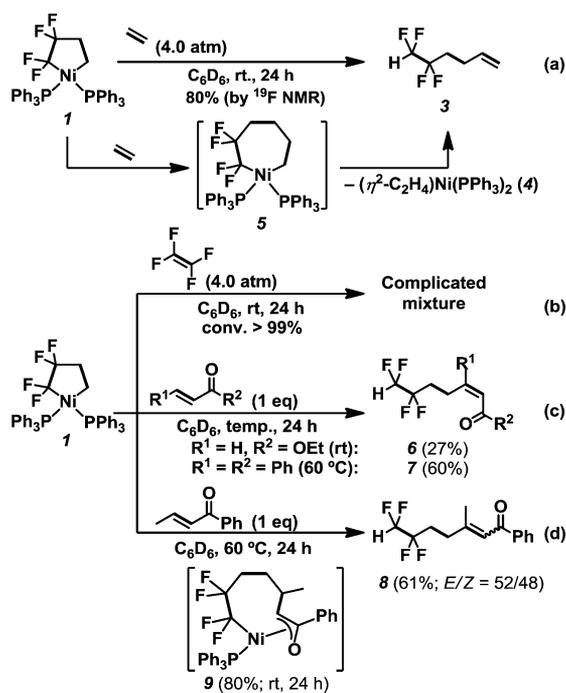


Figure 1. ORTEP drawing of **1** with thermal ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

planar geometry of nickel, as indicated by the sum of the angles around the nickel (363.5°) as well as the difference in bond distances between Ni–C1 and Ni–C4 (1.922(4) and 1.993(4) Å, respectively). Conversely, the Ni–P1 bond length of 2.2182(12) Å was slightly shorter than the Ni–P2 bond (2.2589(12) Å), which reflected the difference in the trans influence between the CH₂ and the CF₂ groups.

When complex **1** was treated with ethylene in C₆D₆ at room temperature for 24 h, generation of 5,5,6,6-tetrafluoro-1-hexene (**3**) was detected in 80% yield (estimated by ¹⁹F NMR analysis; Scheme 2a). In the ³¹P NMR spectrum of the crude reaction mixture, concomitant formation of (η²-CH₂=CH₂)Ni(PPh₃)₂ (**4**) was observed. The cotrimerization product **3** was obtained as the sole product, and neither 3,3,4,4-tetrafluoro-1-hexene nor any C₈ or higher products were detected in the crude product.

Scheme 2. Reactivity of Nickelacycle **1**

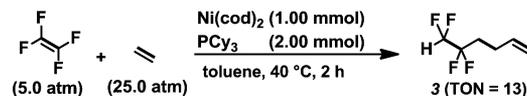


This clearly indicated the following: (a) migratory insertion of ethylene to the Ni–CH₂ bond rather than to the Ni–CF₂ bond in **1** occurred selectively to give a seven-membered nickelacycle intermediate (**5**), although spectroscopic evidence could not be obtained, and (b) β-hydride elimination from **5** would be substantially faster than further ethylene insertion into the Ni–C bonds in **5** (or larger-membered nickelacycles). On the other hand, the reaction of **1** with TFE gave a complicated mixture, albeit with complete consumption of starting complex **1** (Scheme 2b).

Nickelacycle **1** was found to be very useful for the stoichiometric preparation of cross-trimerization products of TFE, ethylene, and α,β-unsaturated carbonyl compounds. Both ethyl acrylate and chalcone reacted with **1** to give the corresponding β-disubstituted ketones (**6** and **7**) in 27% and 60% isolated yields, respectively (Scheme 2c).¹⁷ These products could be isolated as a single regioisomer, although the latter reaction required a higher reaction temperature (60 °C). On the other hand, the reaction with phenyl 1-propenyl ketone led to the formation of an *E/Z* mixture of 6,6,7,7-tetrafluoro-3-methyl-1-phenyl-2-hepten-1-one (**8**) in 61% isolated yield (Scheme 2d). In these reactions, the rarity of insertions into the Ni–CF₂ bond was observed. When the reaction was carried out with phenyl 1-propenyl ketone at room temperature for 24 h, a seven-membered nickelacycle (**9**) was generated via the insertion of the ketone into the Ni–CH₂ bond in **1**.¹⁸ Thermolysis of **9** in C₆D₆ at 60 °C yielded **8**. An attempt to apply these stoichiometric reactions to the catalytic formation of the cross-trimerization product failed. One of the reasons for this failure was formation of the oxidative cyclization product derived from TFE and α,β-unsaturated compounds. For instance, using phenyl 1-propenyl ketone, the corresponding oxidative cyclization product [(η¹:η³-CF₂CF₂C(H)MeCHC(O)Ph)Ni(PCy₃)] (**10**), generated in the reaction mixture, did not react with ethylene, presumably due to its stable η³-oxallyl structure.¹⁸

In sharp contrast to the cross-trimerization reactions, the selective cotrimerization reaction of TFE with ethylene, leading to **3**, proceeded catalytically, as anticipated from the regeneration of the Ni(0) complex **4** (Scheme 2a). Thus, optimization of the reaction conditions revealed that exposing TFE (5 atm) followed by ethylene (25 atm) to a toluene solution of Ni(cod)₂/PCy₃ catalyst gave the best results, albeit with a low turnover number of 13 (Scheme 3).¹⁸ On the other

Scheme 3. Ni(0)-Catalyzed Selective Cotrimerization Reaction of TFE with Ethylene

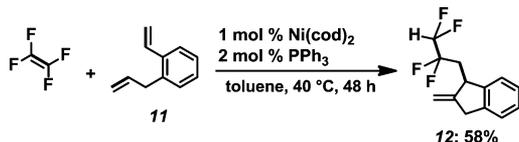


hand, the cotrimerization hardly proceeded in the presence of a catalytic amount of Ni(cod)₂ and PPh₃, which was probably due to the formation of the undesired nickelacycle **2**.¹⁹

Attempts to expand the substrate scope with respect to other simple α-olefins failed; no cotrimerization product was obtained when vinylidene fluoride, chlorotrifluoroethylene, or perfluoropropylene was used in place of TFE. In addition, the use of either 1-hexene or styrene instead of ethylene yielded no cotrimerization products. In contrast, employing 2-allylstyrene (**11**) as a substrate resulted in smooth progress for the catalytic reaction with TFE, yielding a 2-methylene-2,3-dihydroindene

derivative (**12**). An elaborate investigation of the reaction conditions concluded that TFE reacted with **11** selectively in the presence Ni(cod)₂ and PPh₃ (1 and 2 mol %, respectively) to afford **12** in 58% yield (Scheme 4). Excess pressure of TFE

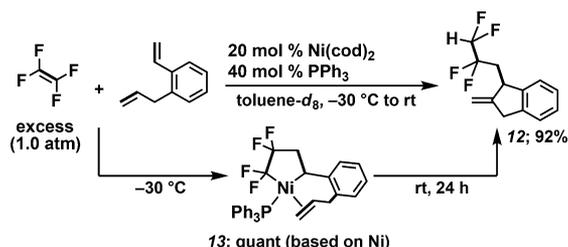
Scheme 4. Ni(0)-Catalyzed Cycloaddition of TFE with 2-Allylstyrene



promoted the formation of the catalytically unreactive **2**, leading to a deactivation of the catalyst. The use of PCy₃ in place of PPh₃ retarded the reaction, since the oxidative addition of a C–F bond of TFE to nickel gradually occurred to yield *trans*-(PCy₃)₂Ni(F)(CF=CF₂) at 40 °C.¹⁶

When the catalytic reaction using **11** was monitored by NMR spectroscopy, a transient intermediate (**13**) was observed at –50 °C (Scheme 5). The appearance of four inequivalent ¹⁹F

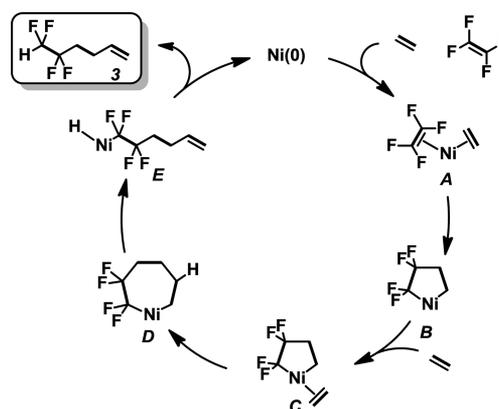
Scheme 5. Observation of the Key Intermediate **13**



resonances as well as the disappearance of those of the vinyl group of **11** in the ¹H NMR spectrum clearly indicated the occurrence of the oxidative cyclization of TFE and the vinyl group. The ³¹P NMR resonance was coupled with two fluorine atoms at the α-CF₂ group at 30.7 ppm (dd, ³J_{PF} = 34.9, 11.1 Hz). In addition, the characteristic resonances assignable to the allyl group coordinated to nickel appeared in the high-field shift region at δ_H 3.64, 4.21, and 4.43 ppm and at δ_C 87.5 and 96.4 ppm. These observations support the formation of **13**, although strict assignment of the ¹H and ¹³C resonances attributable to its aromatic rings was hampered by overlap with the rings of the unreacted **11**. This intermediate and unreacted **11** were fully converted to **12** at room temperature with the concomitant generation of **2**.

On the basis of stoichiometric reactions, the catalytic reaction of TFE with either ethylene or **11** might proceed via a widely accepted mechanism observed in ethylene trimerizations that involves metallacycle intermediates (Scheme 6).⁴ Thus, the simultaneous coordination of TFE and ethylene, or the vinyl group of **11**, to nickel led to an oxidative cyclization between them and yielded a five-membered nickelacycle (**B**) that was similar to **1**. Then, the selective migratory insertion of another ethylene (or the allyl group of **11**) to the Ni–CH₂ bond took place to give a seven-membered nickelacycle intermediate (**D**). Observation of the transient intermediate **13**, corresponding to **C**, could support a rationale whereby the oxidative cyclization of TFE and ethylene occurred prior to that of two units of ethylene. β-Hydride elimination followed by reductive elimi-

Scheme 6. Plausible Mechanism for Ni(0)-Catalyzed Selective Cotrimerization of TFE and Ethylene



nation afforded the cotrimerization product **3** (or **12**) and regenerated a Ni(0) species.

In summary, we have provided the first demonstration of nickelacycles as key reaction intermediates in a selective cotrimerization of ethylene and/or other alkenes, leading to α-olefins with fluoroalkyl chains. The key reaction intermediate generated via the oxidative cyclization of TFE and ethylene with Ni(0) was isolated and structurally determined. Our achievement is significant from the viewpoint of the effective utilization of TFE as a starting material for the preparation of fluorooorganics.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving detailed experimental procedures, analytical and spectral data for all new compounds, and crystallographic data for **1** and **10**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00218.

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Notes

The authors declare no competing financial interest.

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(17) The NMR yields of **6** and **7** were 69 and 64%, respectively. See also the Supporting Information for details.

(18) See the Supporting Information for experimental details, an ORTEP drawing of **10**, and optimization of the catalytic reaction conditions.

(19) No formation of **3** was observed in the catalytic reaction in which the two kinds of gases were pressurized in the reverse order.