Young Career Focus: Professor Yiming Wang (University of Pittsburgh, USA)

Background and Purpose. SYNFORM regularly meets young up-and-coming researchers who are performing exceptionally well in the arena of organic chemistry and related fields of research, in order to introduce them to the readership. This Young Career Focus presents Professor Yiming Wang (University of Pittsburgh, USA).

Biographical Sketch

Professor Y. Wang

Yiming Wang was born in Shanghai, P. R. of China, and grew up in Boulder, Colorado (USA). He graduated with an AB/AM degree in Chemistry & Physics and Mathematics from Harvard University (USA) in 2008 after conducting research in the group of Professor Andrew Myers. After obtaining his Ph.D. under the supervision of Professor Dean Toste at the University of California, Berkeley (USA) in 2013, he conducted postdoctoral research in the laboratory of Professor Stephen Buchwald at the Massachusetts Institute of Technology (USA) as a National Institutes of Health Postdoctoral Fellow. He joined the Department of Chemistry at the University of Pittsburgh (USA) in Fall 2017.

INTERVIEW

SYNFORM *What is the focus of your current research activity?*

Prof. Y. Wang My research group and I are currently interested in the applications of cationic iron catalysis in C–H functionalization chemistry. The functionalization of C–H bonds in hydrocarbons and other simple starting materials is an active area of research in modern organic synthesis that has the potential to lead to shorter and greener synthetic routes. Given the importance of building the framework of carbon–carbon bonds in organic synthesis and the ready availability of unsaturated starting materials, we are particularly interested in applying our approach to the construction of C–C bonds α to nonpolar π-bonds, such as those present in alkenes and alkynes. In general, α-C–H functionalization reactions leading to the installation of carbon-based fragments are not as well developed or as general as those leading to C–O or C–N bond formation, especially for propargylic C–H functionalization. Thus, we hope that our efforts in this area will expand the repertoire of available tools, including catalysts, reagents, and reaction conditions, for these underexplored areas of C–H functionalization chemistry. In addition to this major area of research, we are also interested in new applications of carbocationic intermediates, including vinyl cations.

SYNFORM *When did you get interested in synthesis?*

Prof. Y. Wang I became interested in organic synthesis as a purely intellectual activity when I took Professor David Evans's Advanced Organic Chemistry (Chemistry 206) course during the third year of my undergraduate studies. Although the course was too difficult for me at the time, and I did not do well in it, I came away with a deep impression of the intellectual depth and rigor of the field. More broadly, I gained an appreciation for the power and societal impact of organic syn-

 Synform **2022/02**, A27–A29 • Published online: January 18, 2022 • DOI: 10.1055/s-0040-1720549

thesis during my time working on the synthesis of tetracycline antibiotics in Professor Andrew Myers's group.

SYNFORM *What do you think about the modern role and prospects of organic synthesis?*

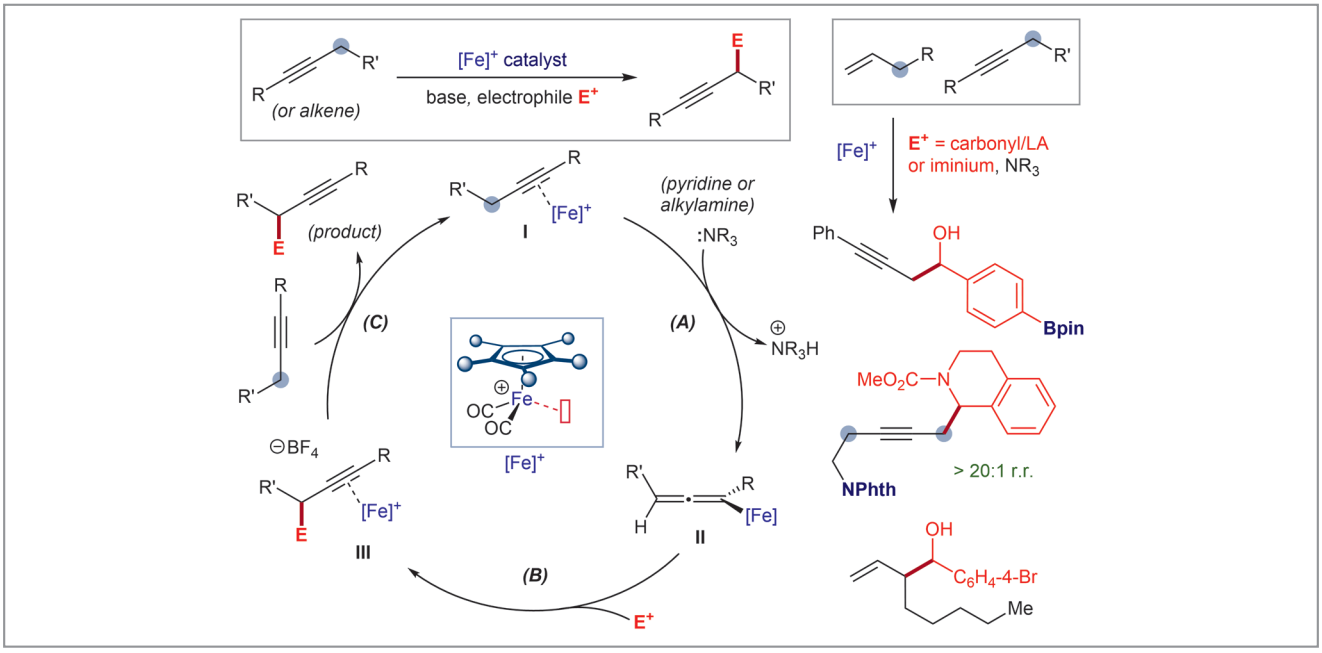
Prof. Y. Wang In my view, the role of organic synthesis has always been both that of a pure science and an applied science. Research in organic chemistry simultaneously satisfies basic human curiosity about the natural world while also playing an immensely impactful role in the development of new medicines and new materials that change society and everyday life. In recent years, developments in organofluorine chemistry, late-stage functionalization, and the synthesis of conjugated materials (to name a few areas) have been driven by demand of the end-users of organic synthesis and ultimately by societal need. At the same time, the proposal of exciting new activation modes for catalysis and the discovery of reactions with novel chemo-, regio-, and stereoselectivities continue to be driven by curiosity as much as applicability.

SYNFORM *Could you tell us more about your group's areas of research and your aims?*

Prof. Y. Wang My research group has worked extensively in the development of cyclopentadienyliron dicarbonyl complexes for the functionalization of C–H bonds α to unsaturated C–C bonds. Much of the intellectual foundations of our work in this area were laid through stoichiometric studies by the group of Myron Rosenblum (Brandeis University) during the 1970s to the 1990s.[1,2] In particular, the reported reactivity of cationic η²-alkene complexes and neutral σ-allyliron species based on the Fp ($CpFe(CO)_2$) fragment led us to believe that catalytic C–H functionalization reactions could be developed using this chemistry.

We proposed a catalytic cycle, shown in Scheme 1, wherein (A) a cationic η² iron–alkyne complex (**I**) first undergoes deprotonation under mild, functional-group-tolerant conditions to afford neutral σ-allenyliron species **II**; (B) reaction of **II** with an electrophile takes place with S_E2' regioselectivity to give a functionalized product still complexed to the cationic iron center (**III**); and (C) iron complex **III** then undergoes ligand exchange to deliver the organic product and regenerate iron complex **I** to complete the catalytic cycle. This was found to be a general strategy that could be applied to the functionalization of alkenes and alkynes with activated carbonyl (oxocarbenium) and iminium electrophiles.[3,4] More recently, using a designer catalyst and well-optimized reaction conditions, this approach was also found to be applicable to the C(sp^2)–H functionalization of allene derivatives (Scheme 2).[5]

More recent work in our group has focused on improving catalyst efficiency, controlling stereoselectivity, and the devel-



Scheme 1 Catalytic cycle for Fe-catalyzed propargylic and allylic C–H functionalization and examples of products obtained under catalytic conditions

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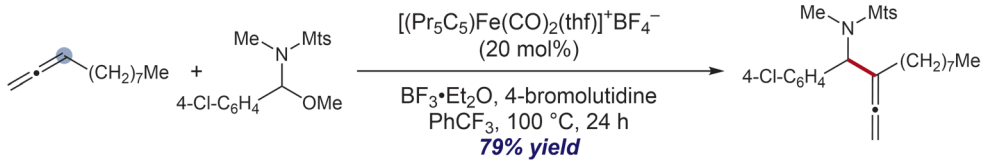


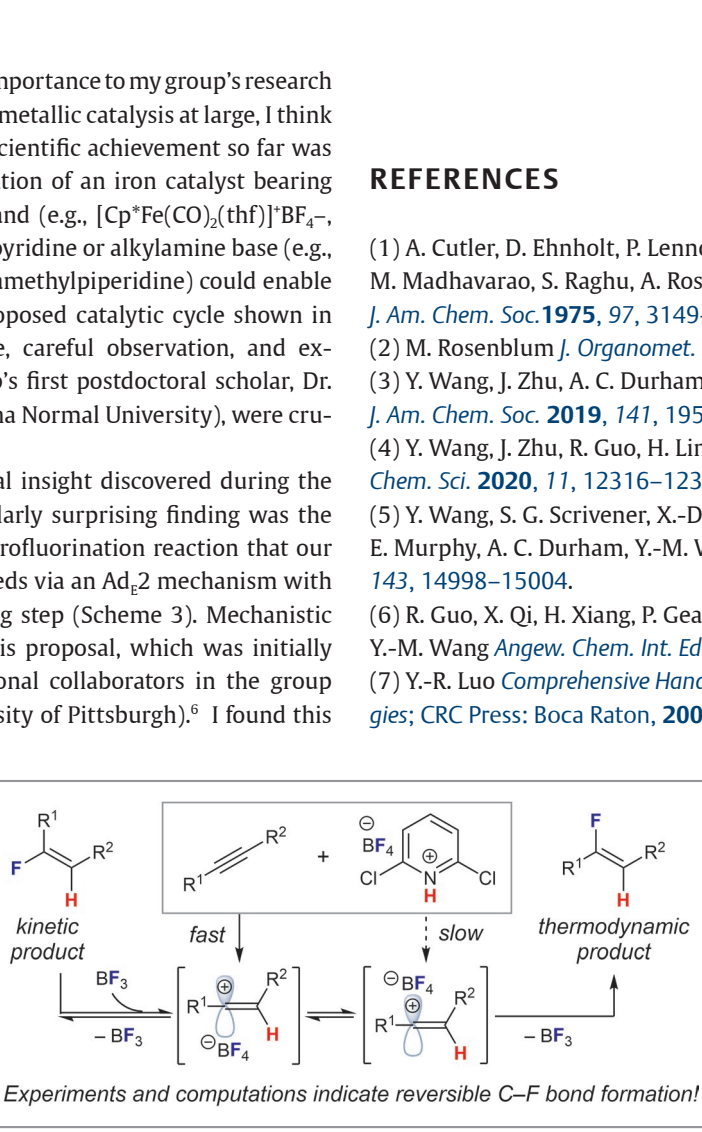
Scheme 2

opment of dual catalytic strategies. We hope to share these results with the synthetic community in the near future.

SYNFORM *What is your most important scientific achievement to date and why?*

Prof. Y. Wang In terms of importance to my group's research program, and perhaps organometallic catalysis at large, I think my group's most important scientific achievement so far was the finding that the combination of an iron catalyst bearing a hindered, electron-rich ligand (e.g., $[Cp^*Fe(CO)_2(thf)]^+BF_4^-$, $Cp^* = C_5Me_5$) and a hindered pyridine or alkylamine base (e.g., 2,4,6-collidine or 2,2,6,6-tetramethylpiperidine) could enable catalytic turnover for the proposed catalytic cycle shown in Scheme 1. The perseverance, careful observation, and excellent intuition of the group's first postdoctoral scholar, Dr. Yidong Wang (Ph.D., East China Normal University), were crucial in making this finding.

In terms of a fundamental insight discovered during the course of research, a particularly surprising finding was the discovery that an alkyne hydrofluorination reaction that our group developed likely proceeds via an Ad_E2 mechanism with a *reversible* C–F bond-forming step (Scheme 3). Mechanistic experiments corroborated this proposal, which was initially suggested by our computational collaborators in the group of Professor Peng Liu (University of Pittsburgh).[6] I found this result (potentially relevant to the development of C–F bond activation reactions) to be highly unintuitive, given the well-known strength of the C–F bonds found in vinyl fluorides ($DH°_{298}$ = 124 kcal/mol in CH_2=CH–F).[7]



Scheme 3 Proposed mechanism for an alkyne hydrofluorination reaction

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 Synform **2022/02**, A27–A29 • Published online: January 18, 2022 • DOI: 10.1055/s-0040-1720549