



Swiss Science Concentrates

A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

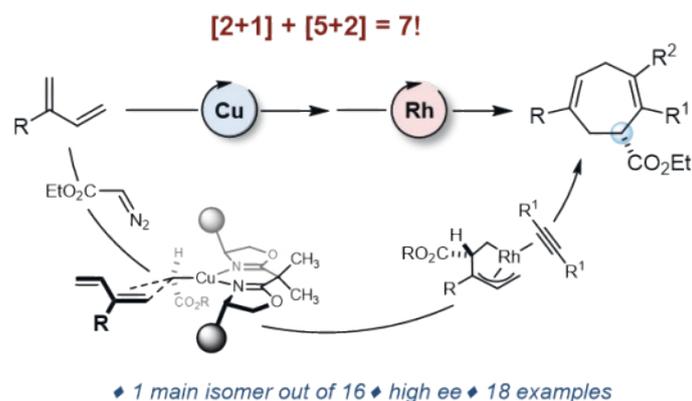
Access to Optically Active 7-Membered Rings by a 2-Step Synthetic Sequence: Cu-Catalyzed Stereoselective Cyclopropanation of Branched 1,3-Dienes/Rh-Catalyzed Stereoconvergent [5+2] Cycloaddition

M. Garbo, C. Besnard, L. Guénée, and C. Mazet*, *ACS Catal.* **2020**, *10*, 9604–9611.
University of Geneva

7-Membered rings are widespread motifs in biologically active molecules and hence synthetic chemists have developed a number of strategies for their preparation. The transition metal-catalyzed [5+2] cycloaddition of vinylcyclopropanes (VCPs) and a π -system is one of the most powerful tools to generate complex 7-membered rings. However, the development of enantioselective versions remains a major challenge. The authors developed a 2-step catalytic sequence to access a range of cycloheptadienes bearing a tertiary stereocenter with high regio- and enantioselectivities. In the first step, the Cu-catalyzed cyclopropanation of branched dienes delivers VCPs with excellent regio- and enantioselectivity, but modest *cis/trans* diastereoselectivity. In the second step, the Rh-catalyzed [5+2] cycloaddition of these VCPs with alkynes affords preferentially one 7-membered ring in a stereoconvergent manner, thereby correcting this apparent limitation.

Authors' comments:

"This sequential combination of two independent semi-predictive stereochemical models applied to an underexplored substrate class provides expedient access to optically active, polyfunctional, 7-membered carbocycles that would be difficult to prepare by existing methods."



Deoxygenative Fluorination of Phosphine Oxides: A General Route to Fluorinated Organophosphorus(v) Compounds and Beyond

D. Bornemann, C. R. Pitts, L. Wettstein, F. Brüning, S. Küng, L. Guan, N. Trapp, H. Grützmacher*, and A. Togni*, *Angew. Chem. Int. Ed.* **2020**, doi: 10.1002/anie.202010943.
ETH Zurich

Fluorinated organophosphorus(v) compounds are highly desirable structures due to their versatile applications in both organic and inorganic chemistry. However, their synthesis traditionally requires the handling of pyrophoric P(III) derivatives and toxic fluorinating agents. The authors describe a mild deoxygenative fluorination (DOF) protocol employing phosphine oxide substrates in combination with oxalyl chloride and KF. The method shows a broad scope and generates a variety of fluorinated phosphorus compounds of general structures R_3PF_2 , R_2PF_3 , and RPF_4 . In addition, hexafluorophosphate salts were accessible, and the DOF was successfully transposed to other group 15 elements to provide fluorinated arsenanes and stibanes. Moreover, the method allowed the synthesis of difluorophosphonium salts $[Ar_2PF_2]^+$ $[B(C_6F_5)_4]^-$, the chemistry of which is still largely unexplored.

Authors' comments:

"The two senior authors have spent 25 years together at ETH, but this is their first joint paper. This collaborative work could fulfil the dream of many synthetic chemists: Discovering new reactivity! All's well that ends well!"

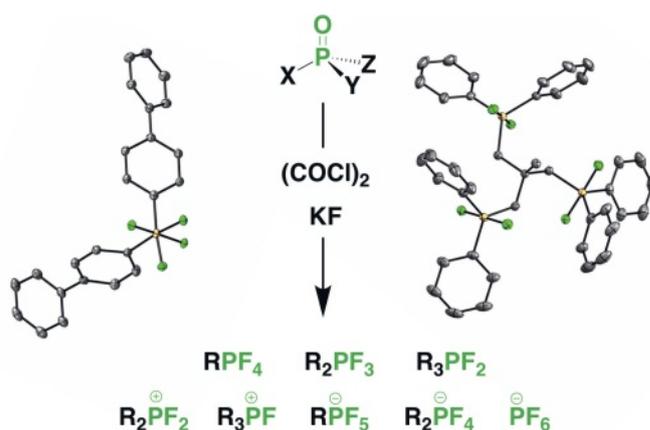
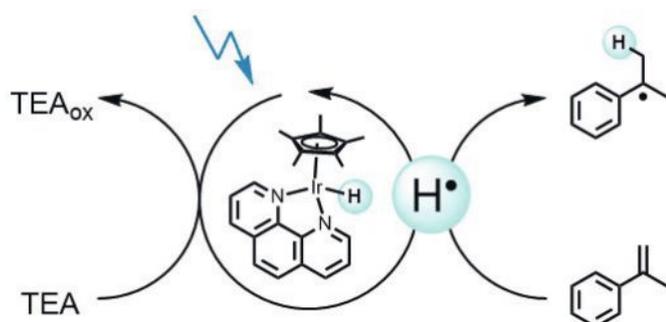


Photo-triggered Hydrogen Atom Transfer from an Iridium Hydride Complex to Unactivated Olefins

M. R. Schreier, B. Pfund, X. Guo*, and O. S. Wenger*, *Chem. Sci.* **2020**, *11*, 8582.

University of Basel

Photoinduced electron transfer (PET) has been demonstrated with many photoactive metal complexes in recent years, and most of the current photochemical studies are based on PET reactivity. Comparatively, research on photo-triggered hydrogen atom transfer (photo-HAT) is underdeveloped. Herein, the authors explored the photo-HAT reactivity of an iridium hydride complex, with the catalytic hydrogenation of PET-inactive olefins as a test reaction. The *in situ*-generated active iridium(II) hydride acts as



an H-atom donor to the olefin upon photoexcitation, whereas a tertiary alkylamine is used as both sacrificial electron and proton source. The evidence for photo-HAT was corroborated by radical clock, H/D isotope labeling and transient absorption experiments. This reaction mode complements the more established PET and thermal HAT pathways and should open new opportunities in photocatalysis.

Authors' comments:

"This work was initiated by Mirjam Schreier and Xingwei Guo. Just recently, Mirjam Schreier received her PhD degree from University of Basel, and she is now working as a teacher at the Fachmaturitätsschule (FMS) Basel. After several years abroad, Xingwei Guo returned to his home country, where he became assistant professor at Tsinghua University in Beijing. Meanwhile, Björn Pfund continues his PhD thesis at University of Basel."

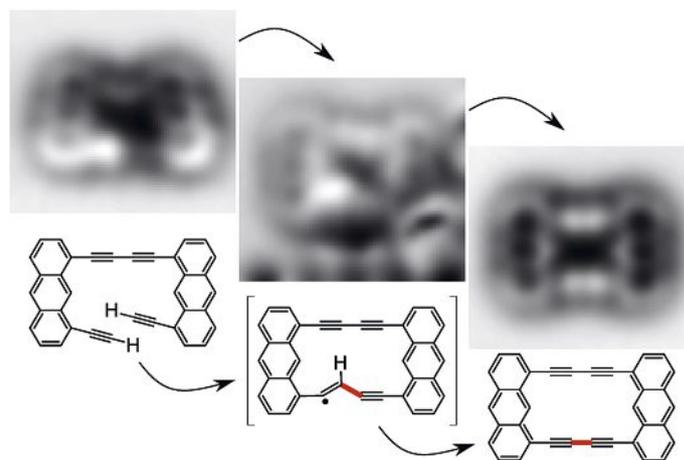
Intramolecular Coupling of Terminal Alkynes by Atom Manipulation

F. Albrecht*, D. Rey, S. Fatayer, F. Schulz, D. Pérez, D. Peña*, L. Gross*, *Angew. Chem. Int. Ed.* **2020**,

doi: 10.1002/anie.202009200.

IBM Research – Zurich, Universidade de Santiago de Compostela

In the past years, on-surface synthesis has emerged as a powerful tool to access novel and elusive molecules, carbon nanoribbons as well as various nanostructures, and to study reaction mechanisms. In particular, on-surface synthesis via atom manipulation



allows inducing reaction steps on individual molecules and to study them in detail. By depositing a tetrayne precursor onto a cold Cu(111) surface partially covered with bilayer NaCl and applying voltage pulses, the authors were able to induce Glaser-type intramolecular coupling. The Glaser coupling precursors and products were directly observed by combined scanning tunneling/atomic force microscopy. This approach allowed visualizing partially hydrogenated intermediates, showing that the C–C bond formation occurred prior to the second hydrogen abstraction.

Authors' comments:

"Glaser-type coupling is desired for the fabrication of complex, atomically defined covalently bonded nanostructures by atom manipulation. Here we demonstrated, as an important step towards this goal, that and how this reaction can be induced within one individual molecule."