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Frontiers of EOC: Organosilicon Chemistry

Time: Jun.17.2022
Zoom ID: 839 0676 5278
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——Dedicated to the 60th anniversary of Institute of Elemento-Organic Chemistry——

SPEAKERS AND SCHEDULE

01

Donald Watson
University of Delaware
(美国特拉华大学)

(BeijinTime)
9:00-10:00

Title:
Stereoselective Synthesis of Tetrasubstituted Vinyl Silanes Using Silyl-Heck Reactions and the Development of Hiyama Conditions for Their Use in Cross-Coupling Reactions

02

Hajime Ito
Technische Universität Berlin
（日本北海道大学）

(BeijinTime)
10:00-11:00

Title:
General Synthesis of Silylboranes and Their Application in the Synthesis of a Diverse Range of Organosilicon Compounds

03

Martin Oestreich
Technische Universität Berlin
(德国柏林工业大学)

(BeijinTime)
15:00-16:00

Title:
Boring Silicon Chemistry Made Interesting

04

Alejandro Perez-Luna
Sorbonne Université
(法国索邦大学)

(BeijinTime)
16:00-17:00

Title:
Carbon–Silicon Bond-Forming Reactions Mediated by Metals: Our Contribution

01 TITLE

Stereoselective Synthesis of Tetrasubstituted Vinyl Silanes Using Silyl-Heck Reactions and the Development of Hiyama Conditions for Their Use in Cross-Coupling Reactions.

Abstract

We have recently discovered conditions that allow stereoselective synthesis of tetrasubstituted vinyl silanes from internal alkynes, silyl iodides, and organo zinc reagents. These palladium-catalysed processes are believed to proceed via a Heck-like mechanism. Depending on the selection of ligand employed, stereoselectivity for either the cis-addition or trans-addition products can be observed. I will discuss the how this process was discovered and optimized, and the complex kinetic pathways involved in this reaction and how it relates to silyl-Negishi reactions (also discovered in our laboratory). Finally, I also discuss our recent progress of the development of Hiyama conditions that are able to allow cross-coupling of highly-substituted vinyl silanes bearing tetraorgano-silicon centers.

Brief Introduction

Professor Donald Watson is a Professor of Chemistry and Biochemistry at the University of Delaware, USA. He completed this PhD studies at the UC Irvine and postdoctoral studies at both UC Berkeley and MIT. He started his independent academic career at the University of Delaware in 2009.

He started his independent academic career at the University of Delaware in 2009. He was promoted to Associate Professor with tenure in 2015, and Professor in 2018. He also served as Associate Chair for Graduate Studies in his department from 2015-2018. His research program focuses on the development of new synthetic methods, with particular interest in the synthesis of carbon-heteroatom bonds and in transition metal reactivity of main-group electrophiles in cross-coupling reaction. in transition metal reactivity of main-group electrophiles in cross-coupling reaction.

02

TITLE

General synthesis of silylboranes and their application in the synthesis of a diverse range of organosilicon compounds

Abstract

Organosilicon chemistry has a long history of success, but in terms of structural diversity, it falls far short of its homolog, carbon-based molecuels. A search on Reaxys reveals 32 million compounds with sp3 carbons, while sp3 silicon has been synthesized in only 1/30 of that number, 1.2 million. One of the reasons for the lack of synthesis of diverse organosilicon compounds may be the difficulty in generating silicon nucleophilic reagents. Because silicon is a more positive element than carbon, it is more difficult than carbon to put electrons into the silicon center. For example, when chlorosilane is reduced with Li to form a silyl anion, an aromatic substituent is needed on the silicon atom to stabilize the silyl anion. One good way to make a carbon-carbon bond is the reaction of a carbon nucleophile with a carbon electrophile, but due to the difficulty of making silicon nucleophiles, silicon-silicon bond formation is not as flexible as carbon-carbon bond formation.

Tamao and Kawachi reported that silyl nucleophile or silyl anion species could be formed when silylboranes were subjected to Lewis bases in 2001 (Chem. Lett. 2001, 1216). However, the existing silylboranes require silyl nucleophiles generated by the reaction of chlorosilane with lithium, etc.; thus, this can not be a new method for generating silyl nucleophiles.

We have recently focused on the development of a new synthetic method for silylboranes via transition metal-catalyzed borylation of hydrosilanes. Although an Ir catalysis was reported by Hartwig for this reaction in 2008 (Organometallics, 2008, 6013), only a limited number of the silylboranes were synthesized. We then have improved the catalytic activity and reaction scope by using Pt and Rh catalysts (JACS 2020, 14125). The improvement of this reaction has made it possible to synthesize a variety of silylboranes and to generate novel silyl anion species that could not be generated by the known methods. In addition, the iterative and modular synthesis of differently substituted oligosilanes using the newly synthesized silylboranes has been developed.

Brief Introduction

Professor Hajime Ito is a Distinguished Professor at Hokkaido University. He was born in Osaka, Japan, in 1968. He completed his PhD in 1996 under the direction of the late Professor Yoshihiko Ito. He then worked as an Assistant Professor at Tsukuba University in corroboration with Professor Akira Hosomi and moved to Institute for Molecular Science. He also joined Professor Kim D. Janda's research group at the Scripps Research Institute as a research associate in 2001. In 2002 he was appointed as an Associate Professor at Hokkaido University, working with Professor Masaya Sawamura. He was promoted to a Full Professor at the same university in 2010. He was also appointed as the vice director and PI of the Institute for Chemical Reaction Design and Discovery (WPI-ICReDD) in 2018.

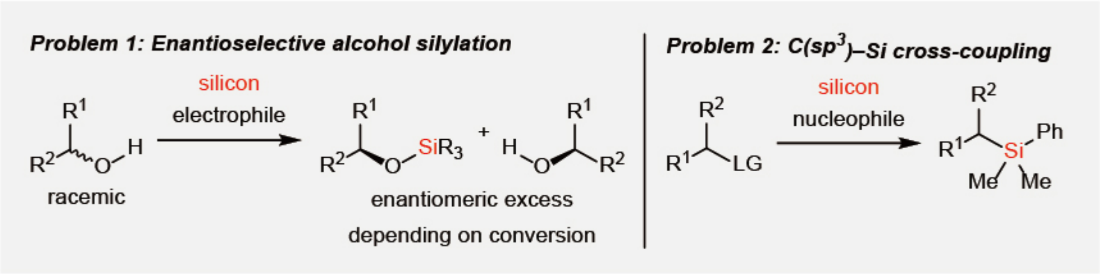
Boring Silicon Chemistry Made Interesting

Abstract

This talk will present solutions to two long-standing problems in silicon chemistry:

1.The (dynamic) kinetic resolution of alcohols by enantioselective silylation1 through transition-metal-catalyzed dehydrogenative Si–O coupling.2,3

2.The formal transition-metal-catalyzed nucleophilic substitution of C(sp3)–LG (w/ LG = leaving group) with silicon (pro)nucleophiles4 by ionic5 or radical mechanisms6...and enantioselective detours.7



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Brief Introduction

Professor Martin Oestreich was born in 1971 in Pforzheim, Germany. He is Professor of Organic Chemistry at the Technische Universität Berlin. He received his diploma degree with Paul Knochel (Marburg, 1996) and his doctoral degree with Dieter Hoppe (Münster, 1999). After a two-year postdoctoral stint with Larry E. Overman (Irvine, 1999-2001), he completed his habilitation with Reinhard Brückner (Freiburg, 2001-2005) and was appointed as Professor of Organic Chemistry at the Westfälische Wilhelms-Universität Münster (2006-2011). He also held visiting positions at Cardiff University in Wales (2005), at The Australian National University in Canberra (2010), and at Kyoto University (2018). Martin recently received the Wacker Silicone Award 2021.

04

TITLE

Carbon–Silicon Bond-Forming Reactions Mediated by Metals: Our Contribution

Abstract

Owing to the relevance of organosilicon compounds for applications in various fields such as medicinal chemistry, fragances or materials chemistry, or as synthetic intermediates, there is a constant demand for silicon-containing building-blocks. In this context, we have been interested in employing our expertise in organometallic chemistry to develop original C–Si bond-forming reactions through metal-mediated processes. We have studied alkyne silylzincation reactions (i.e. the addition of silicon–zinc bonds across carbon–carbon triple bonds) and developed useful methodology for the regio- and stereoselective preparation of functionalized vinyl- and allenysilanes. The implementation of a radical approach relying on zinc-atom transfer reactions was central in this work. In another area of research, we have developed the regioselective iridium-catalyzed C–H silylation of biomass-derived furfural derivatives. Through these examples, this talk will outline different shades of the reactivity of silylmetal reagents. Our efforts to develop the downstream chemistry of the functionalized organosilicon compounds produced in order to illustrate their synthetic value will also be discussed.

Brief Introduction

Doctor Alejandro Perez-Luna is a CNRS Research Director at Sorbonne Université in Paris. He completed a PhD in asymmetric catalysis at Université René Descartes (Paris 5) followed by a postdoctoral fellowship in organometallic chemistry at the University of Geneva. He joined the Institut Parisien de Chimie Moléculaire (IPCM) at Pierre et Marie Curie University (now Sorbonne Université) in 2004 and obtained his habilitation degree in 2012. In the same university, he leads since 2017 the team Reactivité Organometallique et Catalyse pour la Synthèse (ROCS) devoted to metal-mediated synthesis. His recent research activity in this area has focused on combining the radical and polar reactivity of organometallic reagents and on the preparation through original C–Si and C–Ge bond-forming reactions of complex/functionalized organosilanes and organogermanes.