

5th Singapore Inorganic Chemistry Symposium (SICS2019)

**Hosted by the Department of Chemistry
National University of Singapore
Tuesday 2nd July 2019
9.50 am – 4.30 pm @ Uhall, NUS**

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Agilent Technologies

A note from the Singapore Inorganic Chemistry Symposium Organising Committee

I would like to take this opportunity to welcome all attendees and presenters to the 5th instalment of the Singapore Inorganic Chemistry Symposium (SICS). This symposium was established in 2015 in response to a lack of opportunities for young researchers to present their research locally. Of late, funding for students and research fellows to attend international conferences has waned, and regular exposure to the research of other students, as well as the ability to present their own work, is an important component of research training. However, Singapore is home to two of the leading chemistry departments in Asia, with both the chemistry departments at NTU and NUS ranked within the top 5 in Asia and the top 10 globally in the 2018 QS rankings, thus young chemists need only look to their colleagues within Singapore to find world-leading research. As chemists, the influence of our research is only as wide as our ability to communicate this research to other scientists, and to the public at large, and this symposium has become a medium to achieve communication of our science within the national academic arena.

Chemical challenges in Singapore today have become problems that are solved by teams of experts. Not only is problem solving enhanced through multi-disciplinary solutions, but also through multi-institutional approaches. Take the opportunity of this symposium to learn about the wide span of research topics that are addressed through inorganic chemistry, but also make a point to engage in discussion with chemists whom you do not regularly have the opportunity to speak with.

I would also like to acknowledge and encourage the participation of undergraduate chemists at this symposium. This is a prime opportunity for undergraduates to discover the variety of research that is conducted at both NUS and NTU. Furthermore, this is an opportunity to get excited about research, and the potential outcomes of a research career.

Lastly, I would like to thank the sponsors of this year's symposium. Through their support, we are able to make this a free event, and enable access to as many attendees as possible. Our thanks go to Agilent, Tee Hai Chemicals, Strem Chemicals, The Royal Society of Chemistry, Singapore National Institute of Chemistry, the Department of Chemistry at NUS, and the Division of Chemistry and Biological Chemistry at NTU.

Best wishes

Rowan Young
Chair of the 2019 SICS Organising Committee

Event Venue: Lee Kong Chian Wing, Level 2, University Hall, Lower Kentridge Road, NUS

Time	Speaker	Presentation title
Session 1, Chair: Felipe Garcia		
9.50	Felipe Garcia	Opening comments
10.00	Amit Jaiswal	OL1 Lewis Acid Catalysed Carbon-Fluorine Bond Activation and its Functionalisation
10.20	Bin Rao	OL2 Borane-Catalyzed Cross-Metathesis Strategy for Facile Transformation of Cyclic (Alkyl)(Amino)Germynes
10.40	Jun Xiang Ong	OL3 Probing Intracellular Reduction of Anticancer Platinum(IV) Prodrug Complexes
11.00	Dzeneta Halilovic	OL4 Extended corannulenes with variable fluorinated pattern
11.20	Wenbin Wu	OL5 Photo-Induced Thiol Coupling and C-H Activation Using Nanocrystalline Lead-Halide Perovskite Catalysts and Its Light-Mediated Halide Exchange with Haloalkane
11.40	Miloš Đokić	OL6 Selective Carbon-Carbon Bond Cleavage Under Visible Light and Ambient Conditions by Earth-Abundant Vanadium Photocatalysts
12.00	Poster session (Link Bridge)	
12.50	Lunch	
Session 2, Chair: Hendrik Tinnermann		
13.50	Stephen Pang (Agilent)	IL Application of Chemical Resolution for Isobaric Spectral Interferences Control in Inorganic Tandem Mass Spectrometry (ICP-MS/MS)
14.10	Deepshikha Arora	OL7 Semiconductor nanocrystal coordination complexes via facet-to-facet directed oriented attachment
14.30	Ong How Chee	OL8 Modifying Triphenylphosphonium Moieties for Enhanced Mitochondrial Uptake
14.50	Bibhuti Bhusan Rath	OL9 Unusual [2+2] Photo-cycloaddition Reaction in One Dimensional Helical Coordination Polymer
15.10	Tea Break	
Session 3, Chair: Rowan Young		
15.30	Plenary lecture: Professor Eva Hevia	PL Towards a Paradigm Shift in Main Group Polar Organometallic Chemistry
16.15	Rowan Young	Closing remarks and prizes

How to get to the event:



To access University Hall from Kentridge MRT station, catch internal bus services A1 or D2 (free services), or SBS service 95 from Lower Kentridge road bus stop



Event Venue: Lee Kong Chian Wing, Level 2, University Hall, Lower Kentridge Road, NUS

Plenary lecturer: Professor Eva Hevia, University of Bern, Switzerland



Originally from Gijón (Spain), Eva received both her MSci degree in Chemistry and her Ph.D. degree from the Universidad de Oviedo (Spain) in 1998 and 2002 respectively. After a three-year position at the University of Strathclyde (Glasgow, UK) working as a Marie Curie Fellow with Professor Robert Mulvey, in 2006 she took up a Royal Society University Research Fellowship and Lectureship there. Subsequently she was promoted to Full Professor in 2013. Since February 2019 Eva holds a chair in the Department of Chemistry and Biochemistry and the University of Bern, Switzerland.

Elected to the Fellowship of Royal Society of Edinburgh (FRSE), Scotland's National Academy and to the European Academy of Sciences (EurASc), Eva has authored over 130 peer-reviewed papers to date and her research has been recognized with several awards including the 2017 RSC Corday-Morgan Prize, which recognises the most meritorious contributions of chemists working in the UK and the 2019 Organometallic Chemistry Award by the Spanish Royal Society of Chemistry.

Research in her group focuses on polar organometallic chemistry at the crossroads of inorganic, organic, and green chemistry. Some of her recent contributions include the use of cooperative bimetallic compounds for the activation of pharmaceutically relevant organic molecules, as well as the advancement of new methods that replace the use of toxic organic solvents in this chemistry by more sustainable and biorenewable systems.

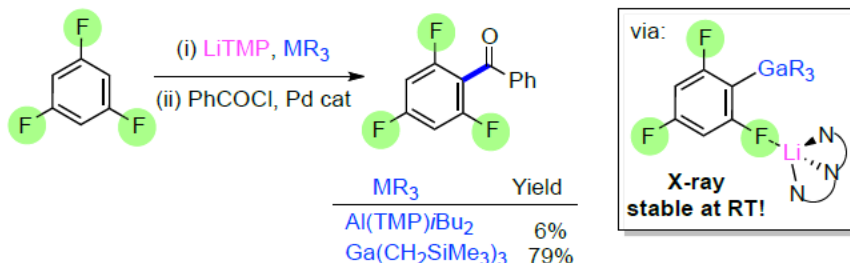
PL: Towards a Paradigm Shift in Main Group Polar Organometallic Chemistry

Eva Hevia^{a,b}

^a Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK ^b Department of Chemistry and Biochemistry, University of Bern, Switzerland

Abstract: Organolithium compounds (*e.g.*, alkyls, aryls and amides) have been and remain pivotal to the development of synthetic chemistry. Staple reagents in academic laboratories and chemical industries worldwide, their extensive utilization reflects their high reactivity and selectivity (notably in directed *ortho*-metallation). However, in many cases this high reactivity can also compromise their functional group tolerance, imposing the use of severely restrictive protocols (*e.g.*, moisture- and oxygen-free organic solvents, inert atmospheres, extremely low temperatures *etc.*) and frequently the lithiated organic intermediates can be unstable and decompose.

This presentation will explore alternative organometallic strategies to overcome some of these major drawbacks faced by standard organolithium reagents. This includes the use of bimetallic combinations for deprotonative metallation reactions, which enable the trapping of sensitive anions. such as fluoroarenes (see Scheme).^[1] Furthermore, the promising use of non-conventional solvent systems such as Deep Eutectic Solvents (DES) in organolithium chemistry will also be discussed,^[2] edging closer towards developing greener and air and moisture compatible methodologies.



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Oral presentation abstracts



OL1: Lewis Acid Catalysed Carbon-Fluorine Bond Activation and its Functionalisation

Amit K Jaiswal¹, Dr. Rowan D Young¹

¹Department of Chemistry, National University of Singapore, 117543, SINGAPORE

Abstract: The significance of fluorinated compounds is largely attributed to the high robustness of C-F bonds¹, constituting an intrinsic challenge for the catalytic activation of C-F bonds in the presence of other groups. Herein, we describe a Lewis acid catalysed carbon heteroatom or carbon-carbon bond formation from aliphatic C-F bonds present in monofluorides and trifluorides that proceeds via pseudohalide intermediate or highly labile 2,4,6 triphenyl pyridines respectively². The reactivity of such intermediates allows a wide range of subsequent functionalisation and good regioselectivity.

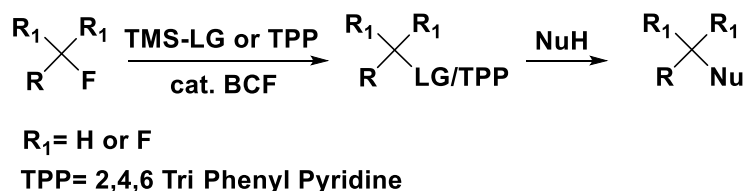


Figure 1 General Scheme of C-F bond functionalisation.

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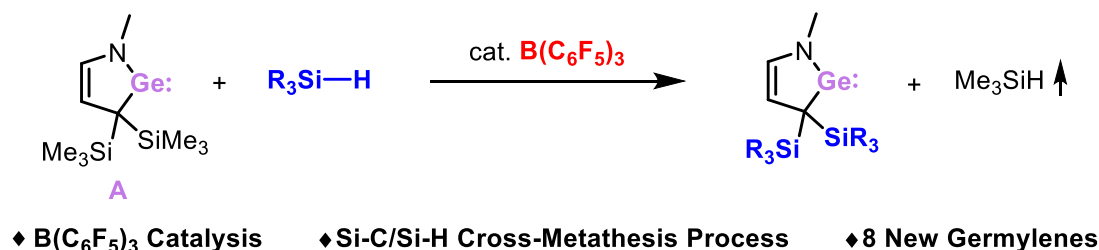
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OL2: Borane-Catalyzed Cross-Metathesis Strategy for Facile Transformation of Cyclic (Alkyl)(Amino)Germynes

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Abstract: Germynes ($\text{R}_2\text{Ge:}$), one member of the group 14 heavier tetrylenes, have been attracting considerable attention because of its diverse application. Conventionally, germynes are prepared by the stoichiometric protocols.^[1] In this presentation, we show that various cyclic (alkyl)(amino)germylenes can be synthesized by a simple and straightforward catalytic process. Triggered by a catalytical amount of Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$, cyclic (alkyl)(amino)germylene (CAAGe) **A** reacts with various hydrosilanes to afford 8 new CAAGes bearing different silyl substituents through a Si-C/Si-H cross-metathesis reaction.^[2] The details of the reaction condition, the scope of the substrates, and a proposed mechanism will be presented.



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OL3: Probing Intracellular Reduction of Anticancer Platinum(IV) Prodrug Complexes

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(2) NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore, 28 Medical Drive, Singapore 117456

Abstract: The application of platinum(IV) prodrug strategy has provided an excellent alternative to overcoming drawbacks associated with conventional platinum(II) drug therapy and is a promising strategy to obtain next-generation platinum drugs. Although many platinum(IV) complexes have been developed, researchers still do not fully comprehend how this new class of platinum drugs are processed at the cellular level. Current approaches to study platinum compounds such as elemental techniques and fluorescence-tagging have their limitations. The use of exogenous platinum-selective fluorescent sensors could potentially help to overcome challenges associated with these methodologies. These platinum-selective fluorescent sensors would provide a direct and efficient method of probing platinum(IV) complexes, allowing us to acquire better understanding of these compounds. Previously, our group developed a platinum-selective rhodamine-based fluorescent turn-on probe equipped with a diethyldithiocarbamate recognition motif to demonstrate the intracellular reduction of a series of platinum(IV) carboxylate prodrugs in cells.^[1] Subsequently, through structure-activity relationship studies, the detection capability of the turn-on probe was enhanced by incorporation of a thiospirolactam.^[2] Herein, we report the first ratiometric probe based on FRET for selective platinum sensing to investigate platinum(IV) anticancer complexes in biological systems.^[3] The ability of the probe to distinguish between platinum(II) species and their parental platinum(IV) prodrug complexes allowed us to apply the probe in cells to study the intracellular activation of platinum(IV) prodrug complexes. The correlation between the amount of active platinum(II) species available after intracellular reduction of platinum(IV) complexes to their cytotoxicity and the role glutathione plays in the reduction of platinum(IV) complexes were investigated.

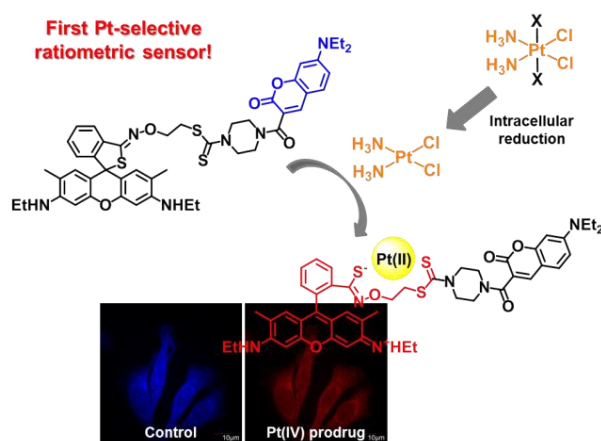


Figure 1. Ratiometric probe based on FRET applied to study the intracellular reduction of platinum(IV) prodrug complexes.

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OL4: Extended corannulenes with variable fluorinated pattern

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Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21-Nanyang Link, 637371, Singapore

Photochemical strategy for the aromatic extension of corannulene scaffold, developed by our group, is a highly practical alternative to the known flash vacuum pyrolysis and metal catalysed processes previously used [1-3]. In this general approach a corannulene-based aldehyde, ylide, or ketone compound is conjugated with an aromatic unit of choice through a Wittig reaction. The resulting stilbene-like precursor can then be subjected to an oxidative photocyclization to yield a corannulene structure with extended π -framework. The mild nature of the developed protocol permits for incorporation of reactive and functional substituents onto the fused aromatic scaffold. Efficient and simple synthesis ensures access to significant amounts of material in a facile manner. In the presentation, we will discuss the development of this strategy for aromatic extension of the corannulene nucleus through synthesis of a large family of fluorinated and curved polycyclic aromatic hydrocarbons with variable fluorinated pattern and their electronic properties [4].

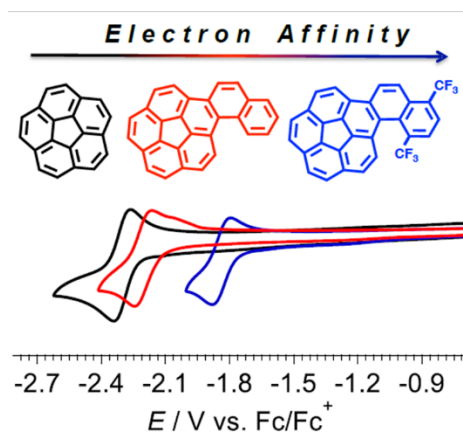


Figure 1. Increase of electron affinity with extension and fluorination comparing with parental corannulene[4].

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OL5: Photo-Induced Thiol Coupling and C–H Activation Using Nanocrystalline Lead-Halide Perovskite Catalysts and Its Light-Mediated Halide Exchange with Haloalkane

Wenbin Wu¹, Ying-Chieh Wong¹, Tian Wang¹, Jun De Andrew Ng^{1,2}, Khoong Hong Khoo^{3,*}, Zhi-Kuang Tan^{1,2,*}, and Jie Wu^{1,*}

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Abstract: We describe the use of nanocrystalline lead-halide perovskites as photocatalysts to catalyze thiol couplings to selectively produce symmetric and unsymmetric disulfides under visible-light conditions. Moreover, a perovskite-catalyzed phosphorylation of tertiary amines via light-driven cross-dehydrogenative coupling has been disclosed. Besides, the photo-activated halide exchange process between perovskite nanocrystals and molecular haloalkanes enables the perovskite luminescence to be controllably shifted across the entire visible spectrum. Employing this halide exchange approach, a micrometer-scale trichromatic patterning of perovskites is demonstrated using a light-source-integrated inkjet printer and tertiary haloalkanes as color-conversion inks.

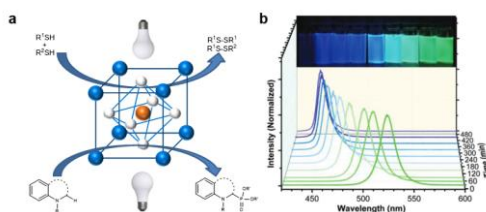


Figure 1 a) CsPbBr₃ perovskite nanocrystals catalyzed thiol coupling and C–H activation; b) PL spectrum in reaction mixtures comprising CsPbBr₃ in CH₂Cl₂.

REFERENCES

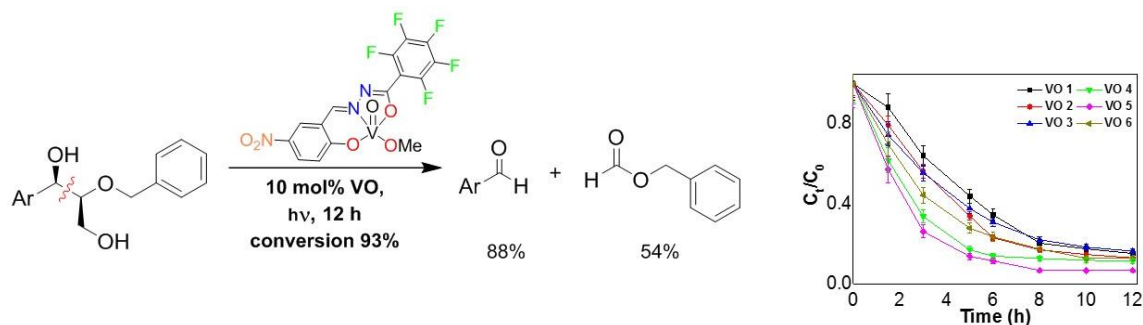
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OL6: Selective Carbon-Carbon Bond Cleavage Under Visible Light and Ambient Conditions by Earth-Abundant Vanadium Photocatalysts

Miloš Đokić¹, Sarifuddin Gazi¹, Kek Foo Chin¹, and Han Sen Soo¹

(1): Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, SINGAPORE

Abstract: Building upon our previous work on selective photocatalytic C–C bond activation in aliphatic alcohols [1], we have recently disclosed a library of new vanadium(V) oxo photocatalysts with enhanced photocatalytic reactivity along with the detailed kinetics and DFT computational studies on lignin model degradation [2]. The studies have revealed that the substrates which generate stabilized, benzyloxy radicals during the reaction, would react significantly faster than the substrates which generate the phenoxy radical. The valuable findings gained from these studies have allowed us to expand the research scope to other important alcohol substrates, such as natural products and active pharmaceutical ingredients (APIs).



Selective C–C bond cleavage in a model alcohol substrate and kinetics studies with different catalysts.

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Industry Lecture (IL): Application of Chemical Resolution for Isobaric Spectral Interferences Control in Inorganic Tandem Mass Spectrometry (ICP-MS/MS)

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Agilent Technologies, 1 Yishun Avenue 7, Singapore 768923

Abstract: An important development in inorganic tandem mass spectrometry occurred in 2012 with the introduction of the world's first triple quadrupole ICP-MS by Agilent Technologies¹. One critical aspect of inorganic tandem mass spectrometry lies in the application of chemical resolution to overcome spectral interferences². In this presentation, an overview of the application of chemical resolution in ICP-MS/MS is presented including the recent introduction of methyl fluoride as a potential universal reaction cell gas³.

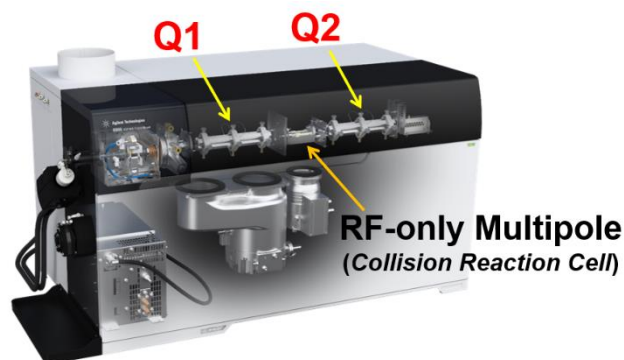


Figure 1. A Modern ICP-MS/MS System (Agilent 8900)

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OL7: Semiconductor nanocrystal coordination complexes via facet-to-facet directed oriented attachment

Deepshikha Arora, Chan Yin Thai

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The idea of colloidal nanoparticles is analogous to ‘artificial atoms’ wherein individual nanoparticles interact and assemble in a controlled manner to form complex structures or ‘artificial molecules’ is still in its infancy. Consequently, complex structural designs which are common in atomic and molecular systems are rare in the colloidal domain. Herein, we report a synthetic methodology to assemble nanoparticles in a stoichiometrically and geometrically controlled fashion via facet to facet attachment of nanoparticle building blocks. We demonstrate that by functionalizing the surface of a Ag_2S domain at the tip of a ZnS nanorod (i.e. a matchstick-like nanoparticle) with dodecylamine (DDA) and then exposing them to octadecylphosphonic acid (ODPA), an acid-base reaction between DDA and ODPA occurs and forms an insoluble alkyl ammonium phosphonate salt. This process effectively strips the DDA selectively from the Ag_2S facets, causing the nanorods to spontaneously fuse via the Ag_2S domains (a process we will call “linking”). The Ag_2S tipped ZnS nanorods linked to form bipods and then tripods at longer reaction times. The angle between nanorods within each tripod was found to be close to 120° , resulting in a nanostructure with trigonal planar geometry. By aging a mixture of bipods and tripods, continued linking between these nanostructures resulted in higher order architectures such as trigonal bipyramidal pentapods or hexapods comprising two trigonal planar tripods in a staggered conformation. When the other tip of the ZnS nanorods is activated via a cation exchange reaction with Ag^+ , leading to the formation of a second Ag_2S domain, the resulting dumbbell-like particles can be linked end-to-end into long nanorod chains.

OL8: Modifying Triphenylphosphonium Moieties for Enhanced Mitochondrial Uptake

Ong How Chee¹, Felipe García¹

(1): Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University (Singapore)

Abstract: The mitochondria is becoming an increasingly attractive target for drug delivery, as aberrant mitochondria has been linked to multiple neurodegenerative and cardiovascular diseases.¹ One method for mitochondrial delivery is to conjugate triphenylphosphonium (TPP⁺) moieties to the cargo, allowing it to accumulate in the mitochondria due to the electric potential. Through the incorporation of additional substituents on the TPP⁺ moiety, the mitochondrial uptake of TPP⁺ compounds can be significantly improved.² This strategy can be applied to bis-TPP⁺ compounds, thus enabling the uptake of highly charged bis-TPP⁺ compounds.³

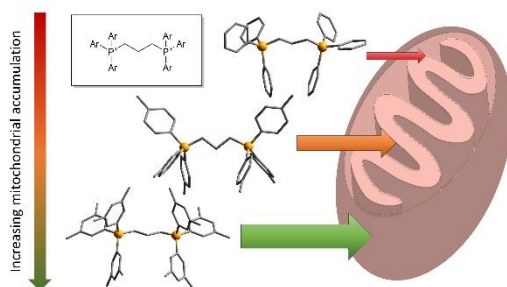


Figure 1 Enabling the uptake of bis-TPP⁺ (PC₃P) through aryl methylation

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OL9: Unusual [2+2] Photo-cycloaddition Reaction in One Dimensional Helical Coordination Polymer

Bibhuti Bhusan Rath , and Jagadese J. Vittal

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Abstract:

In our previous work¹, four helical one dimensional (1D) coordination polymers (CP) were synthesized using trans-5-styrylpyrimidine (5-Spym), triphenylphosphine and silver(I) salts of NO₃⁻ (**1**), BF₄⁻ (**2**), ClO₄⁻ (**3**) and F₃CCO₂⁻ (**4**) anions. The helical chains were aligned in parallel in the solid state such that the 5-Spym arms of the adjacent helical chains were juxtaposed in a *head-to-tail* manner readily to undergo [2+2] photocycloaddition reaction. All the four helical chains underwent [2+2] cycloaddition under UV light quantitatively to 2D coordination polymers. The photodimer obtained from the nitrate salt (**1**) was recrystallized for single crystal X-ray crystallography to confirm the photoproduct (**5**) structurally. Compound **5** has the 2D coordination polymeric structure comprising helical rods connecting the 14cyclobutene rings to form a honeycomb topology. However, the 1D CP of triflate salt was ruled out for photoreactivity due to the orthogonal arrangement of the 5-Spym ligands in the helical chains. But our recent investigation suggests that grinding improves the photoreactivity under UV irradiation. With gradual increase in amorphous content in the grounded samples quantitative photodimerization reaches a maximum 83% in amorphous sample, which is unprecedented. Isolation of the dimerized ligand confirms the dimerization in a *head-to-tail* manner like the previous compounds.

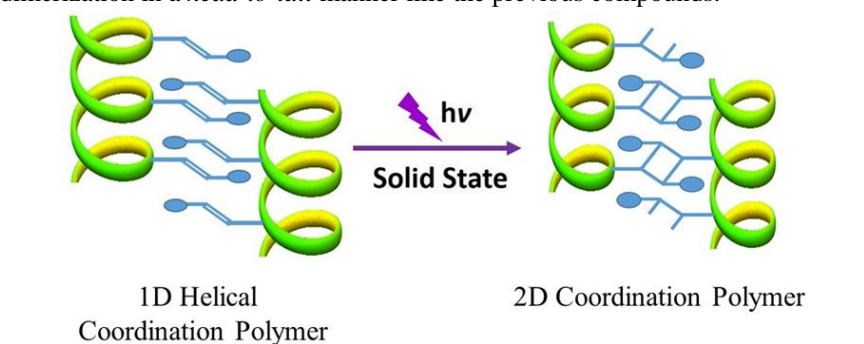
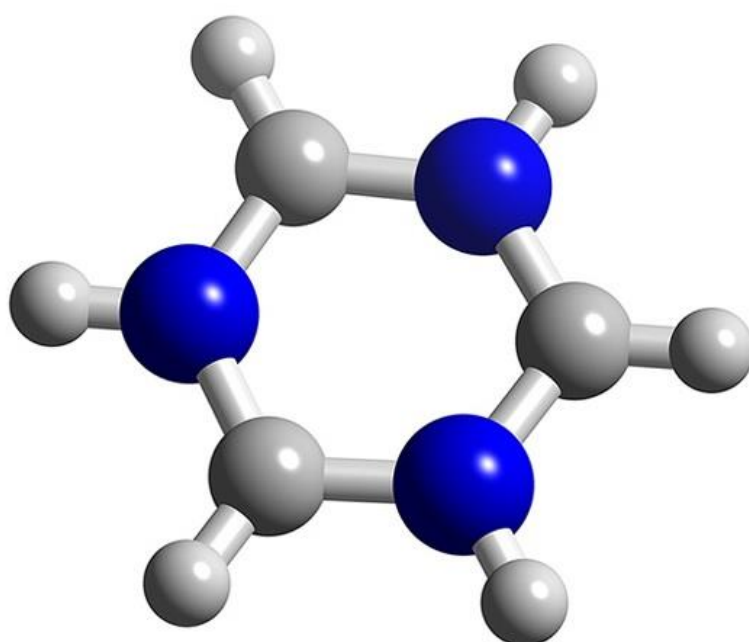


Figure 1. Transformation of 1D helical polymer to 2D CP under UV irradiation

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Poster presentation abstracts



P1: Metal carbonyl complexes – nanoparticle conjugates as CO-release theranostics

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(2): Laboratoire des biomolécules, LBM, Département de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France

Abstract: The fact that carbon monoxide has beneficial effects at low concentration on human body was a great discovery. Among those, anti-inflammatory properties have been demonstrated.^[1] A lot of studies were conducted in order to develop molecules, called CO-releasing molecules (CORMs), able to release and deliver CO in a controlled manner. The CO-release could be achieved thanks to diverse triggers such as enzyme activity, temperature, magnetism and light.^[1] Photoactivation is a particularly interesting trigger because of its modularity: the wavelength, the intensity and the power of the light could be modified.^[2] Furthermore, it is much easier to use than magnetism that requires specific equipment.^[3] The aim of this project is to conjugate photoactive metal carbonyl CORMs onto gold nanoparticles.^[4] The platform will combine tunable CO-release properties and stabilized photoproducts, it will enable the study of their cell uptake, localization and CO-release activity in a biological context using luminescence or SERS, while being non-toxic and decorated for specific delivery.

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P2: Promoting desirable photovoltaic properties in low-dimensional hybrid lead-halide perovskites through crystal engineering

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Abstract:

A tenet of crystal engineering is the directed assembly of molecules in the crystalline state to a structural arrangement that will endow compounds with desired physical and chemical properties. Molecular one- and two-dimensional (1D and 2D) organic lead-halide hybrids are a class of materials that have received much attention in the recent years due to their appealing optoelectronic features. However, as a consequence of their quantum- and electronically-confined inorganic lattices, such low dimensional materials are ill suited to photovoltaic (PV) applications. Herein, we demonstrate that by selection of appropriate organic cations and crystal engineering techniques, the resulting hybrids can be endowed with improved electrical and optoelectronic properties, thereby offering a route by which they might become of practical use.

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P3: Selective monodefluorination and Wittig functionalization of *gem*-difluoromethyl groups to generate monofluoroalkenes

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Abstract: Since 2006, the chemistry of Frustrated Lewis Pairs (FLPs), has advanced greatly in small molecule activations and transformations either stoichiometrically or catalytically.¹ Here we present selective defluorination of *gem*-difluoromethyl groups achieved by FLPs. Screening various triarylphosphines and group 13 Lewis acids as FLP partners, found the combination of P(*o*-Tol)₃ and B(C₆F₅)₃ to be the most suitable choice for clean C-F bond activation and gave activated products in high yield (*e.g.* Figure 1). Cheaper FLP partners (PPh₃ and BF₃.OEt₂) are also feasible for this activation reaction either at room temperature or raised temperature as appropriate. The activated substrates were subject to Wittig reaction protocols to generate a variety of monofluoroalkenes.²

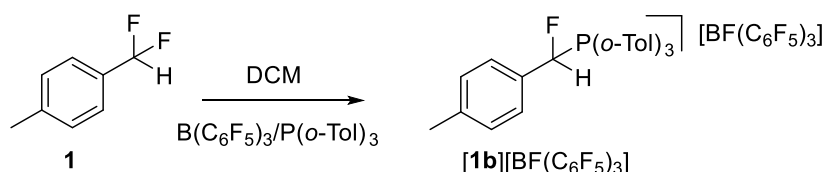


Figure 1 Synthesis of [1b][BF(C₆F₅)₃].

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P4: Oxidative addition of elemental Selenium to 1,4,2,5 diazadiborinine

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Abstract: Since the emergence of Frustrated Lewis pairs (FLP) in 2006¹, the element-element bond activation no longer solely belongs to the domain of transition metal complexes. Following, the FLP concept further developed to encompass main-group ambiphiles (MGA).² Very recently, the group of Wagner has elegantly demonstrated that 9,10-diboraanthracene dianion cleaves the chalcogen-chalcogen bonds of various dichalcogenides E₂R₂ (E = O, S, Se, Te).³ Albeit this area has significantly advanced in recent years, no investigation on the reactivity of aromatic boron heterocycles toward elemental selenium (Se) has been described thus far, which prompted us to study the chemical behavior of diazadiborinine in this respect. In this presentation, we report the synthesis of a novel 1,4,2,5-diazadiborinine **3** and its reactivity toward Se.⁴ When **3** was treated with elemental grey selenium (Se), the oxidative addition of Se proceeded regioselectively at the boron centres of **3** to give a bicyclo[2.2.2] molecule **4** involving a B-Se-Se-B unit, which can be deemed a heavier analogue of dibora-peroxide. The details of the reaction condition, structural features and computational studies will be discussed in the poster session.

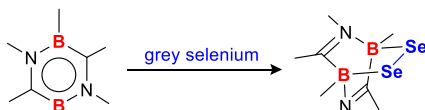


Figure 1 Reaction of **3** with grey Selenium.

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P5: Designing Polymers with Capability to Host Fullerene C₆₀ through Ball-and-Socket type of Aromatic Stacking Interactions

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Abstract: Developing hosts of fullerenes is an active area of research with technological implications [1]. In this context, macrocycles, dendrimers, π -conjugated linear and cyclic oligomers, molecular clips, and self-assembled small molecules have been developed for their fullerene encapsulation properties. Recently, we brought a shift in this paradigm by designing a polymer-based receptor for fullerene C₆₀[2]. This was accomplished by encoding a polymer with the corannulene motif. Corannulene is a non-planar hydrocarbon that can interact with fullerene C₆₀ through concave-convex type of π - π stacking interaction. Therefore, each repeat-unit of the designed polymer contained the necessary information to interact with fullerene C₆₀ through the described 'ball-and-socket' type of specific hosting interaction. However, this initial design involved a tedious monomer synthesis and each repeating unit contained only one corannulene thus limiting the strength of the supramolecular interaction. In this work, we improve upon the practicality aspects of this unique fullerene host family through designing a new monomer based on the vinylcyclopropane motif (Figure 1). The resulting polymers would contain two corannulene units per repeating unit and therefore we also expect significant increase in the association constant between fullerene C₆₀ and the new polymer host. We will discuss these advances in this presentation.

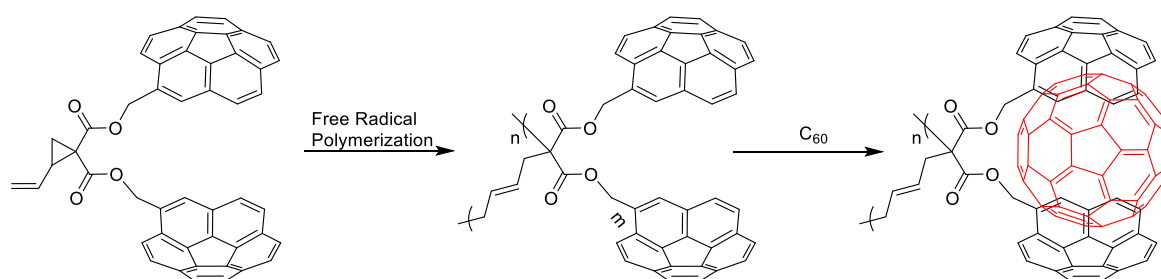


Figure 1. Polymers containing two corannulene units per repeating unit

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P6: Catalytic and Selective C(sp³)-F Bond Activation Using Frustrated Lewis Pair Approach

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Abstract: Monodefluorination of difluoro compounds is achieved using a frustrated Lewis pair (FLP) approach. Sulfides and group 13 Lewis acids were surveyed as FLP components. The combination of tetrahydrothiophene (THT) and B(C₆F₅)₃ yielded the desired defluorination products. These corresponding α -fluoroalkylsulfonium salts prepared are of lower reactivity compared to the reacting difluoride, leading to highly selective monodefluorination. Further the reaction could be rendered catalytically employing sacrificial silane sources, for example TMSNTf₂. The reaction also is feasible with inexpensive and commercially available components, employing for example THT and BF₃·OEt₂. After the successful monodefluorination, the obtained sulfonium salts were transformed into useful product by nucleophilic substitution.

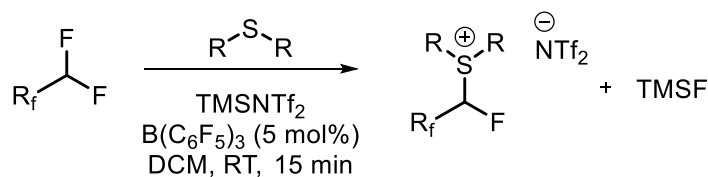


Figure 1 Selective and cat. C-F bond activation using frustrated Lewis pair approach

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P7: Zwitterionic Inorganic Benzene Valence Isomer with σ -Bonding between Two π -Orbitals

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By doping of organic compounds with BN units, a variety of organic/inorganic hybrid benzene derivatives ($B_nC_nN_nR_6$) have been developed over the years.^[1] By comparison, fully B,N-based inorganic benzenes such as borazine derivatives ($B_3N_3R_6$) remains relatively unknown.^[2] In this presentation, we report the synthesis of a 1,4-diazatetraborinane derivative **1** and its chemical reduction. The latter gave rise to zwitterionic inorganic benzene valence isomer **2**,^[3] in which two electrons are delocalized over the four boron atoms, leading to the σ -bonding between two odd-electron B–B π -orbitals. The details of spectroscopic data, the solid-state molecular structures and computational studies of **2**, and the recent relevant results will be presented.

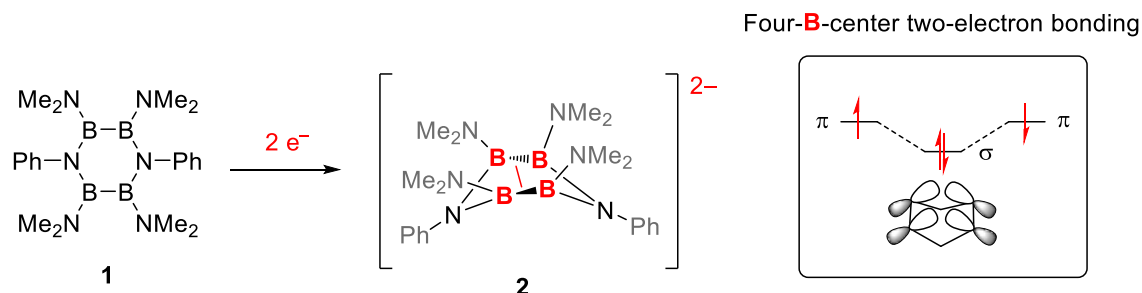


Figure 1 Reduction of a 1,4-diazatetraborinane derivative **1**.

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P8: Determination of ligand donor strength of NHCs using Huynh Electronic Parameter (HEP) and elucidation of effect of anagostic interactions in deduction of ligand donicities

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Abstract: Determination of ligand donor strength is highly sought after because of their significant role in the properties and reactivities of corresponding metal complexes. However determination of electronic effects is less straight forward than sterics and several parameters have been developed over the years to understand the same. The most recent one (HEP) developed by Huynh group involving ¹³C NMR spectroscopy of hetero-bis(carbene) complexes of Pd(II) has proved to be efficient and reliable. Thus a group of such complexes has been prepared, characterized by multinuclear NMR spectroscopy, electrospray ionization mass spectrometry, and X-ray diffraction analysis and their HEP has been determined. NHCs bearing benzhydryl substituents were found to exhibit rare anagostic interactions in both solid and solution state, which interfered with ranking of their donicities by HEP. Finally the HEP and %V_{bur} were mapped to analyse the overall stereoelectronics of the Pd(II)-NHC complexes.

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P9: Large-Stokes-Shifted Infrared-Emitting InAs-In(Zn)P-ZnSe-ZnS Giant-Shell Quantum Dots by One-Pot Continuous-Injection Synthesis

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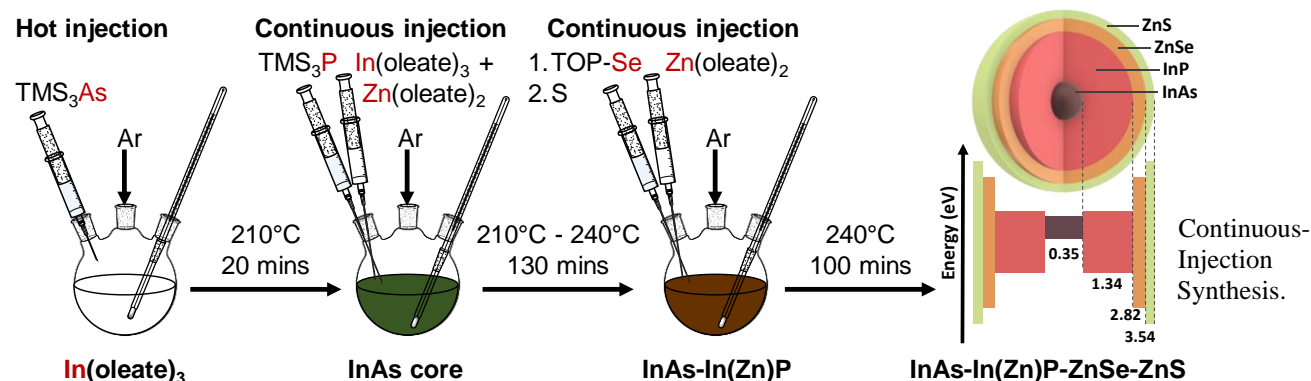
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Abstract: Infrared-emitting materials with large Stokes shift and minimal reabsorption are technologically-important for luminescent solar concentrators and for bio-imaging applications. Here, we describe the synthesis of new InAs-In(Zn)P-ZnSe-ZnS quaternary giant-shell quantum dots (QDs) that possess efficient photoluminescence (PL) in the near-infrared. We employ a convenient one-pot, continuous-injection approach to achieve the controlled-growth of thick In(Zn)P shells around small InAs nuclei. The In(Zn)P shell absorbs strongly across the visible spectrum from 400 to 780 nm, and transfers the excitation to the InAs core for emission at 873 nm, hence providing a significant Stokes shift and minimal absorption-emission spectral overlap. Density functional theory (DFT) calculations reveal a conduction band delocalization and a quasi-type-II band alignment that are responsible for the significant spectral red-shifts during shell growth, despite a tiny core size of ca. 3 nm. The resulting quantum dots are neutral-colored, contain no regulated heavy-metals and are broadly-useful in consumer opto-electronic products and biological applications.

Figure 1 Large-Stokes-Shifted Infrared-Emitting InAs-In(Zn)P-ZnSe-ZnS Giant-Shell Quantum Dots by One-Pot



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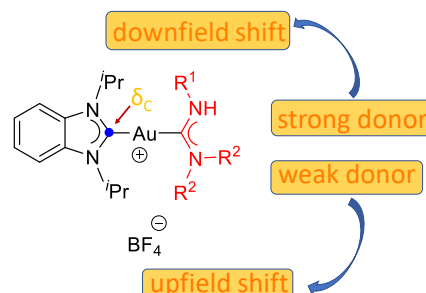
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P10: Assessing the σ -donor Strength of Acyclic Diaminocarbene using Huynh Electronic Parameter

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Abstract: In the current study we have assessed the σ -donor strength of acyclic diaminocarbenes using the Huynh Electronic Parameter (HEP).¹⁻³ For this purpose, we have synthesized mixed N-heterocyclic carbene (NHC)/acyclic diaminocarbene (ADC) complexes of the general formula [Au(ADC)(ⁱPr₂-bimy)]BF₄ (ⁱPr₂-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene). These complexes were obtained in good to excellent yield by nucleophilic attack of secondary amines such as pyrrolidine, piperidine and morpholine on isocyanide complexes of the type [Au(CNR¹)(ⁱPr₂-bimy)]BF₄.



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P11: Metal-free Selective Borylation of Arenes by a Diazadiborinine via C–H/C–F Bond Activation and Dearomatization

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(1) Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, SINGAPORE

Abstract: Direct borylation of non-activated aromatic hydrocarbons represents the straightforward synthesis of value-added chemical building blocks from raw materials. Conventionally, metal-containing molecules or metal catalysts have been employed for the borylation reaction.¹ By contrast, the metal-free strategy is still limited, in particular, C–F bond borylation of aromatic hydrocarbons,² remains extremely challenging, and to our knowledge, intermolecular and thermally reversible dearomative borylation is hitherto unprecedented. In this presentation, we show that an annulated 1,3,2,5-diazadiborinine derivative (**1**) selectively activates a C–H bond and C–F bond in arenes, to furnish borylation products under the catalyst-, metal-, and irradiation-free condition. Moreover, **1** readily undergoes a dearomative coupling reaction with polycyclic aromatic hydrocarbons to afford diboration products. The details of the reaction conditions, scope of the substrates, and the proposed reaction mechanism will be presented.³

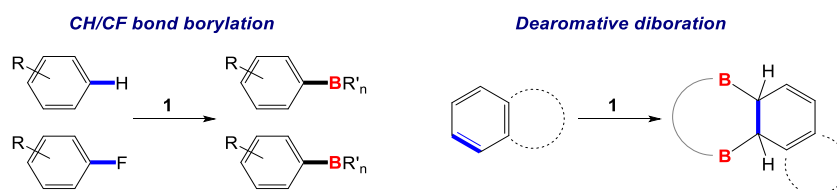


Figure 1 Metal-free borylation of arenes.

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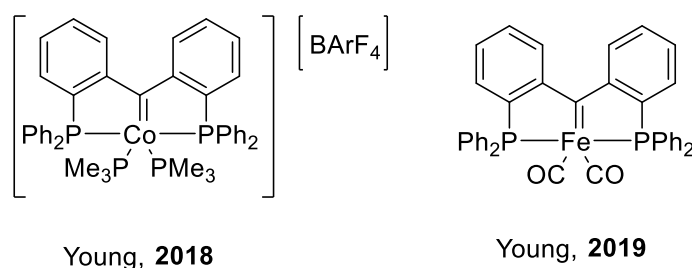
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P12: Synthesis and Reactivity of Base Metal PC_{carbene}P Pincer Complexes

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Abstract: Pincer ligands (i.e. tridentate meridional ligands) form a fundamental scaffold upon which many transition metal complexes are based and have been proved in the development of various bond activation chemistries. In the last decades, pincer ligands are increasingly being used as supports in transition metal catalysis.^[1] But most pincer catalyst are limited with precious metals like Rh, Ru and Ir and earth-abundant metal pincer complexes are rarely reported. In this work, two type of novel base metal PC_{carbene}P pincer complexes are firstly synthesised following with a large scope of reactivity test.



Young, 2018

Young, 2019

Figure 1. The Novel Co(0) PC_{carbene}P Pincer Complex and Fe(0) PC_{carbene}P Pincer Complex.

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P13: Ligand centred reactivity of PCP pincer complexes in dechalcogenation reactions.

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De(T)Ox: A unique ligand centred activation of a plethora of bonds is shown by PC_{carbene}P metal complexes.^{1,2} Amongst the bonds activated are disulfides, carbodiimides and N-oxides. Using N-oxides in the bond activation process yielded the corresponding keto ligand metal complex, which then could be reduced by employing hydrogen gas, silanes or even alcohols. The use of mild reductants also allowed us to render this process catalytic enabling the reduction of several N-oxides with isopropanol under mild conditions with excellent yields. This catalytic system can also be used to enable the oxidation of different alcohols with N-oxides as oxidant with good yields.

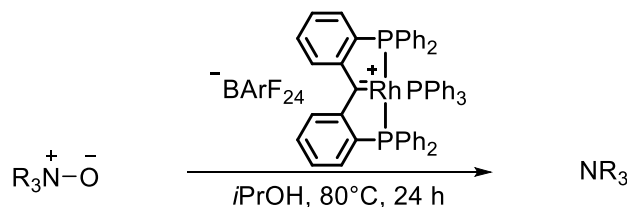


Figure 1 Catalytic deoxygenation of N-oxides.

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P14 Gold Complexes of Expanded-Ring N-heterocyclic Carbenes: Structure, Reactivity and Catalytic Studies

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Abstract: Expanded-ring N-heterocyclic carbenes (erNHCs) are the non-classical type of NHCs derived from six, seven, and eight-membered heterocycles, and recently attracted for their better catalytic activities in transition-metal catalysis. The superior catalytic activity of these class of NHCs belongs to the enlarge N-C-N bond angle and better σ -electron donating ability. In this work, we have prepared a series of [AuBr(erNHC)] and [Au(^tPr₂-bimy)(erNHC)]BF₄ types of Au^I complexes by installing mesityl N-substituted erNHCs on gold metal centre. The synthesized Au^I complexes were reacted with bromine to give respective Au^{III} complexes, which obtained from different reactivity patterns. Finally, the catalytic efficiencies of gold precatalysts analyzed towards hydroamination reaction of alkynes and aromatic amines. Au^I complex [AuBr(8-Mes)] (**3**), bearing eight-membered erNHC found to be the best catalyst for the hydroamination reaction of phenylacetylene and mesityl amine, among the synthesized eighteen Au-erNHC complexes.

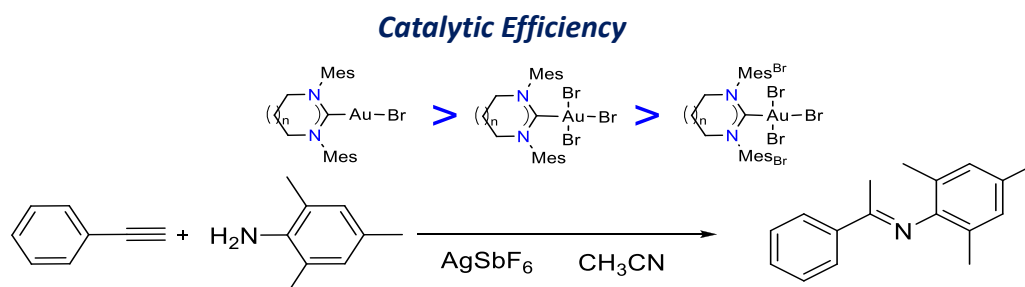


Figure 1. Gold-catalyzed hydroamination reaction of phenylacetylene and mesityl amine.