2nd International Conference

MMM-II

INTERNATIONAL CONFERENCE ON MAIN-GROUP MOLECULES TO MATERIALS-II

DECEMBER 13-15, 2021

(VIRTUAL MODE)

Organised by the School of Chemical Sciences, NISER, Bhubaneswar

ABOUT

The chemistry of main-group elements has been thriving during recent years. While much of the research has been focused on unravelling the preparative methods, reactivity and structure of compounds where the main-group element is in a low-oxidation state or has a low coordination number, there has also been a shift in emphasis in examining the properties of such compounds in applications ranging from photophysical properties to catalysis. This diverse and rich chemistry has prompted us to organize a meeting dedicated to this theme. Fortuitously, many young researchers working in this theme have joined various Indian Institutes during recent years and have been contributing significantly.

It is appropriate that this second meeting (MMM-2020) is being held at the School of Chemical Sciences, National Institute of Science Education and Research, Bhubaneswar, where Organometallics, Catalysis, and Main group chemistry have had a synergistic influence on the growth of Chemistry in general and inorganic chemistry in particular. Some of the recent exciting developments and future challenges in the field will be highlighted in the three-day symposium through several invited lectures by senior and young faculty drawn from across the world. In addition, there will be a vibrant poster session involving young researchers.

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PP-1

Janus-Faced Oxidant and Antioxidant Profiles of Organo Diselenides

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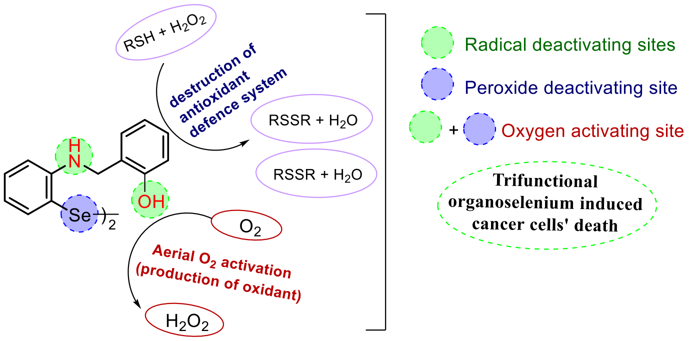
ABSTRACT

Reactive oxygen species (ROS) generated from molecular oxygen inside cancer cells is a new approach to treating cancer and has better cancer-specific cytotoxicity than normal cells.[1] Selenium is one of the essential trace elements for the body to regulate the redox balance. As a result, organoseleniums have been well-established catalysts for the decomposition of oxidants.[2] However, the oxidative properties of the organoseleniums have not been well understood.

In continuation of our work on organochalcogen chemistry, we synthesized the trifunctional organodiselenide, which can activate aerial oxygen towards oxidation of thiols to disulfide in a catalytic manner.[3] The synthesized diselenide shows Janus face as it also catalyzes the reduction of hydrogen peroxide by following the GPx enzymatic catalytic cycle. Therefore, we prepared a series of substituted trifunctional diselenides to modulate its ROS generating properties and GPx and Vitamin E mimicking antioxidant properties.[4] The role of functional groups in these trifunctional diselenides has been explored by optimizing the various transition state involved in O_2 activation using density functional theory (DFT). The screening of these properties against cancer cells suggests that the ROS generating oxidant and antioxidant properties are competing, and the oxidant property is more effective against the cancer cells.



Scheme. Peroxide decomposing, radical chain-breaking antioxidant, and multifunctional oxidant organoselenium

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Spraying Mode Effect on morphological properties of nickel oxide thin films

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ABSTRACT

In this work, we have prepared Nickel oxide (NiO) thin films elaborated by the chemical method of spray pyrolysis on glass substrates at a temperature of 350°C. Using 0.1M aqueous solution of Nickel chloride hexahydrate $NiCl_2.6H_2O$. The effects of spraying mode (with swap and without swap) on the morphological properties of the NiO films were studied. The prepared samples have been analyzed by means of stylus profilometer in order to determine the thickness and morphological properties.

KEYWORDS

Nickel oxide, thin films, Morphology, Surface, profilometry.

PP-3

Octaborane(12) to Icosahedron: A sequential cluster growth

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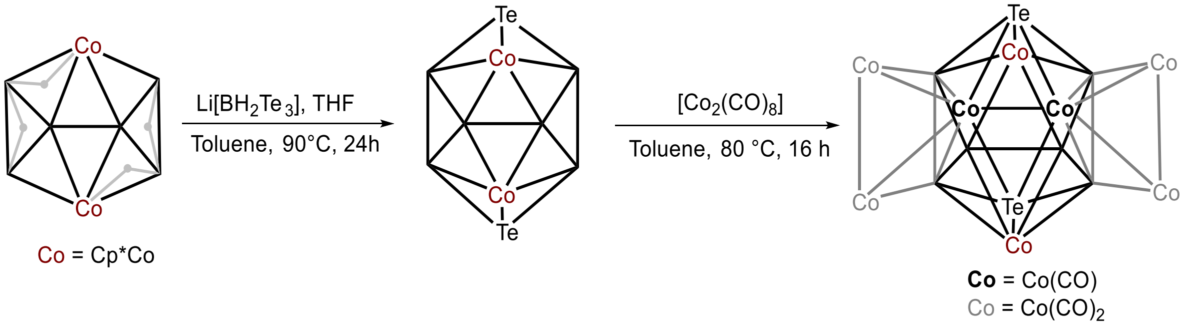
ABSTRACT

Metallaborane chemistry has grown in a pleasing fashion because of their interesting structural, bonding and reaction chemistry. During the last few decades Fehlner *et al.*,[1] Kennedy *et al.*,[2] and we[3] developed various synthetic strategies that led to the emergence of many single cage and condensed metallaborane clusters having unique geometries. In this regard, we have isolated and structurally characterized various edge and face fused icosahedral clusters from the reaction of octaborane(12) $[(Cp^*Co)_2B_6H_{10}]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with various chalcogen based borate ligands $Li[BH_2E_3]$ (E= S, Se and Te) followed by metal carbonyls. These condensed metallaheteroboranes are typically fused through vertices, edges, triangle or square faces. These fused clusters had been employed in the advancement of many electron-counting rules such as Mingos fusion formalism and Jemmis mno rules.[4] The key results of this work will be described.



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Manganese(I) Catalyzed *α*-Alkenylation of Amides and Phosphine Oxides Using Alcohols with Liberation of Hydrogen and Water

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ABSTRACT

α,β-Unsaturated amides and alkenylphophine oxides are valuable class of compounds in organic chemistry. The unsaturated amide functionality is a core motif in various natural products, biologically active compounds, polymeric materials, and pharmaceuticals. Similarly, alkenylphosphine oxides play a vital role as biologically active compounds and are highly useful in agricultural, industrial, and medicinal chemistry. Moreover, *α,β*-unsaturated amides and alkenyl phosphine oxides are useful in organic synthesis and find application in material science. Conventional and reported catalytic methods for the synthesis of *α,β*-unsaturated amides suffer from various drawbacks such as use of excess coupling reagents and use of toxic CO gas whereas conventional synthesis of alkenylphosphine oxides require stoichiometric amount of strong bases and tedious experimental procedures. Herein, an unprecedented manganese pincer-catalyzed direct *α*-alkenylation of amides using alcohols is reported. Aryl amides and methylphosphine oxides are reacted with diverse primary alcohols, which provided the *α,β*-unsaturated amides and alkenylphosphine oxides respectively in moderate to good yields with excellent selectivity.[1-2] Mechanistic studies indicate that Mn(I) catalyst oxidizes the alcohols to their corresponding aldehydes and also plays an important role in efficient C-C bond formation through aldol condensation. This selective olefination is facilitated by metal-ligand cooperation by the aromatization-dearomatization process operating in the catalytic system. Biorenewable alcohols are used as alkenylation reagents for the challenging *α*-alkenylation of amides and phosphine oxides with the highly abundant base metal manganese as a catalyst, which results in water and dihydrogen as the only byproduct, making this catalytic transformation attractive, sustainable, and environmentally benign.

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Multi Substitution at Tetra co-ordinate Six-NHC with Borane center:

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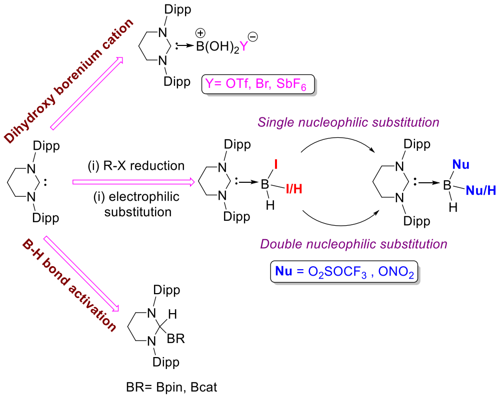
ABSTRACT

The reactivities of six-membered carbenes are cursory in literature, compared to five-membered carbenes. Herein, we have undertaken the reactivity of a variety of boranes with a 6-membered saturated NHC, which has been unexplored so far. The lower HOMO–LUMO gap along with a higher HOMO of 6-SIDipp compared to other typical five-membered NHCs encouraged us to study such chemistry. The stoichiometric reactions of the boranes (BH_3) and halo-boranes ($BRCl_2$) (R = H, Ph) with 6-SIDipp led to mono-SNHC adducts **1**-**3**. Similar adduct formation (**4**) was noticed with 9-borabicyclo [3.3.1] nonane (9-BBN). Further we have prepared 6-NHC-BH_2-X, BHX_2; X= halides Br and I) from the parent 6-NHC borane, **1** by [1] reduction of alkyl halides, R-X and CBr_4 [2] and reaction with electrophiles (like I_2). These NHC-BH_2X and NHC -BHX_2 complexes were further reacted towards various nucleophiles and mono and di substituted by rare tiflates and nitro functional groups. And also, we have prepared 6-NHC stabilized rare dihydroxy borenium cation **14** from **1** by the treatment of 2 equiv triflic acid and **15** via anion exchange of **14** by SbF_6^-. However, the reactions with HBpin with 6-SIDipp led to the oxidative addition of the B-H bond at the carbene carbon (**16**), which is the first example of a B-H bond insertion at the carbene-carbon atom. Similarly, the reactivity of HBcat with 6-SIDipp shows the B-H activation, but the degradation of HBcat forms a tetrahydro pyrimidinium salt with $B(cat)_2$ as a counter-anion (**17**).



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PP-6

Hydrogen Bonds with Tetravalent Carbon: Relevance in Structural Biology and C-H Bond Activation through σ-Bond Metathesis

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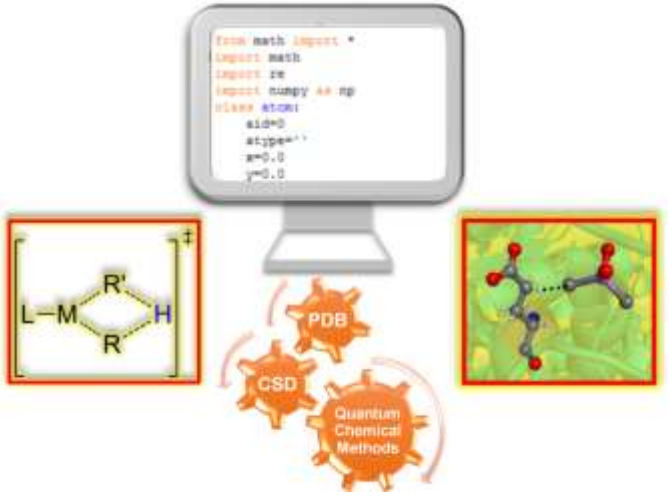
ABSTRACT

Hydrogen bond (H-bond) without lone pair(s) of electrons and π-electrons is a concept developed two to three years ago.[1] H-bonds involving less electronegative tetrahedral carbon are beyond the classical concepts on H-bonds.[2] Herein we present the first report on H-bonds with tetravalent carbons in proteins. Careful protein structure analysis aided with several quantum chemical calculations suggests that these H-bonds are moderate in strength. These C-H···C H-bonds are blue-shifted and are dispersive in nature. We developed an empirical equation to estimate the C-H···C H-bond energy in proteins from the distances between the C- and H-atoms. In proteins, the binding energies range from -5.4 kJ/mol to -14.0 kJ/mol. The C-H···C H-bonds assist the substrate binding in proteins. We also explored the potential role of these carbon-centered H-bonds in C-H bond activation through σ-bond metathesis. To our surprise, these H-bonds contribute almost of similar magnitude as C-H···π H-bonds for C-H bond activation.



```
from math import *
import math
import re
import numpy as np
class atom:
    aid=0
    atype=''
    x=0.0
    y=0.0
```

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PP-7

Chiral AIEgens: Circularly Polarized Luminescence Switching and Stimuli-Induced Sign inversion in Solid state

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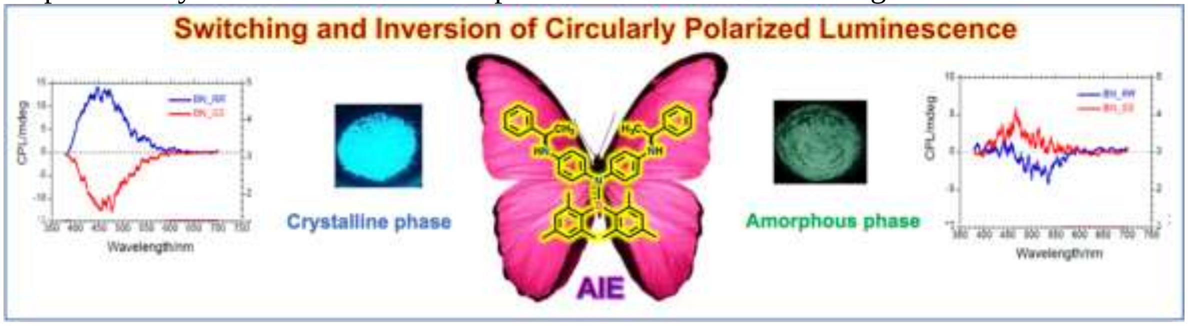
Circularly polarized luminescence (CPL) refers to the chiroptical property of the differential emission between right- and left-handed circularly polarized light from intrinsically chiral fluorophores or fluorophores in chiral environment.[1] Materials that exhibit circularly polarized luminescence are being actively investigated in technologies such as optoelectronics, bio-medical imaging, and security systems, etc. However, the realization of chiral organic molecules with bright luminescence, improved CPL, and switching in the solid-state remains elusive. Our recent efforts are directed towards understanding how the incorporation of the main group elements modify the optical and electronic properties of fully carbon-based systems, the development of molecular probes for the detection and quantification of toxic ions/molecules, and external stimuli-responsive materials.[2] As part of the ongoing program, we study the synthesis and crystalline phase-dependent chiral photoluminescence switching in amino boranes with center-chiral pendent (**BN_RR**, **BN_SS,** and **BN_RAC**). Enantiomerically pure amino boranes **BN_RR** and **BN_SS** show strong luminescence than the racemic compound **BN_RAC**. In contrast, the luminescence enhancement of amorphous nanoaggregates formed from 90% water in the THF mixture was nearly the same for both chirally pure and racemic compounds. Interestingly, a rare event of mechanical pressure-induced color switching and inversion of CPL was observed. Detailed steady-state, time-resolved optical studies, together with microscopic and computational studies, unveil that the chiral ordering in solid-state plays a vital role in controlling their optical properties. This is the first example of B-N-based chiral AIEgens showing both considerably high ϕ_F, g_{lum}, and switchable CPL features to the best of our knowledge.[3] We will also discuss the preliminary results of studies on naphthalimide based chiral AIEgens.



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[3] Manuscript under revision. Manuscript ID: CC-COM-10-2021-006042

PP-8

A Rare Intramolecular Au···H−C(sp^3) Interaction in a Gold(I) N-Heterocyclic Carbene

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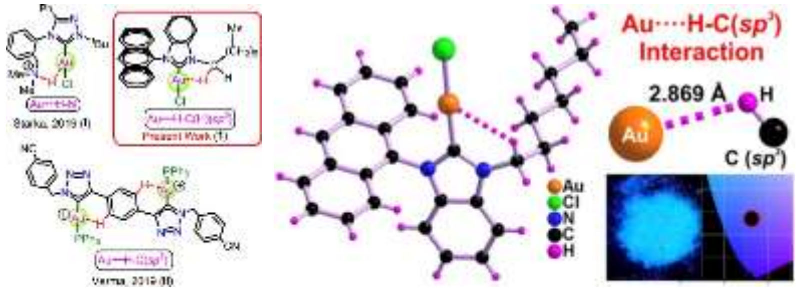
ABSTRACT

For the last few years, several gold carbene complexes with Au···H−C interactions have been demonstrated using both spectroscopic and single-crystal X-ray diffraction studies.[1,2,3] We present here a rare intramolecular Au···H−C(sp^3) hydrogen-bonding interaction and luminescent properties of a gold(I) carbene complex. The Au(I) complex [(**L**)Au(I)Cl] (1), where **L** = N-(9-anthracenyl)-N′(heptyl)benzimidazol-2-ylidene, was prepared, and thermal, emission, and lifetime properties along with a density functional theory study have been considered. X-ray diffraction analysis of single crystals evidenced the solid-state structure of gold complex **1**, which exhibited the expected linear coordination geometry. The n-heptane arm of **L** modulates the hydrogen-bonding interaction between Au(I) and the hydrogen atom of one of the CH$_2$ moieties. The packing of the gold(I) carbene complex shows an interesting one-dimensional column in the solid-state due to intermolecular Cl···H interactions. The blue emission of **1** in the 400−560 nm region has been tentatively ascribed to arise from intra ligand and gold transitions, but the hydrogen-bonding interactions may also make partial contributions.



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Abstract Title-Photocatalytic C–H Thiocyanation of Corroles: Near-Infrared (NIR) Emissive Dyes

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ABSTRACT

A new method of activating corrole macrocycles via *in situ* generated SCN radical has been developed at very mild conditions in room temperature. [1] This photo-redox reaction resulted in the generation of tetrathiocyanatocorroles in good yields. The synthesis of tetrathiocyanatocorroles was never reported earlier. Single-crystal XRD analysis reveals that the insertion of four thiocyanate moieties at the four *β*-pyrrolic positions has imparted significant distortion to the corrole macrocycle. The generated tetrathiocyanatocorroles are different from the parent corroles in many ways. The photophysical properties of the newly synthesized tetrathiocyanatocorroles are dramatically altered from the parent corroles. The absorption feature of these modified corrole derivatives (both position and intensity) bears a nice similarity with the chlorophyll-*a* macrocycle.[2] Thus, these newly synthesized molecules can be considered as spectroscopic model systems for chlorophyll-*a* pigments.[3] The observed absorption and emission spectra of these tetrathiocyanatocorroles certainly point that these newly developed ligand scaffolds and their various metal complexes will have immense potential as pigments in solar cells and also as NIR-emissive dyes.

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Novel Cu^{II} complex of a quinoline based pincer as an advantageous catalyst for C-O cross coupling of unactivated carboxylic acids with alkenes

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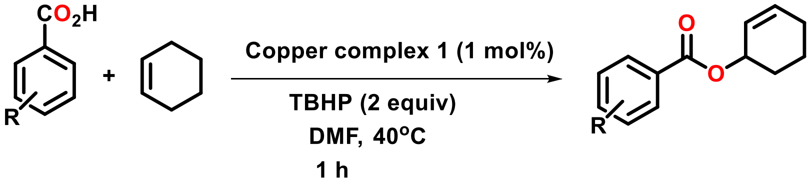
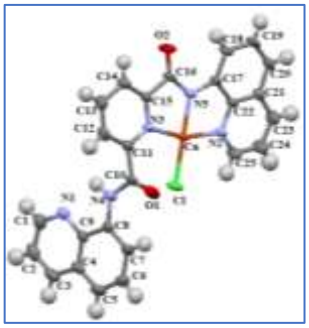
Abstract:

Among the various transition metal catalysed reaction developed so far, the majority of the C-H functionalization reactions rely on expensive and relatively scarce noble transition metals like palladium, rhodium or ruthenium. Thus, the development of new cheap and earth abundant catalyst is one of the major challenges for catalysis research. Keeping this idea in our mind, we have synthesize a novel copper pincer complex using pyridine and quinoline scaffold and its catalytic activity in the cross coupling of acids with alkene to form allylic ester are reported. The complex **1** shows excellent catalytic activity towards cross coupling of a wide variety of aromatic acids with alkenes to form allylic ester in moderate to good yields at ambient temperature (40°C) within very short period of time (1h). Several control experiments along with spectral studies were carried out to characterize the complex **1** and to explore the plausible mechanistic pathways.



Scheme 1: Cross coupling reaction using copper complex **1**



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Synthesis, Crystal Structure and Magnetic properties of a new series of Cobalt-Iron Bimetallic Metal-Organic Framework

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ABSTRACT

A series of Cobalt-Iron bimetallic Hybrid-Framework has been synthesized by one-step hydrothermal synthetic method. The Single-Crystal X-ray studies reveal the formula of the as-synthesized MOFs has chemical formula **[$Co_xFe_{1-x}(C_4H_4N_2)(SO_4)_{0.5}F$]**. The magnetic properties studies predict that the Co-MOF exhibits antiferromagnetic interaction with T_N = 30 K, Fe-MOF exhibits ferrimagnetic interaction with T_C = 20 K; However, by integrating 25% of Fe into the Co-MOF shifts the antiferromagnetic coupling between the paramagnetic centers into ferrimagnetic coupling with a higher T_C value of 58 K.

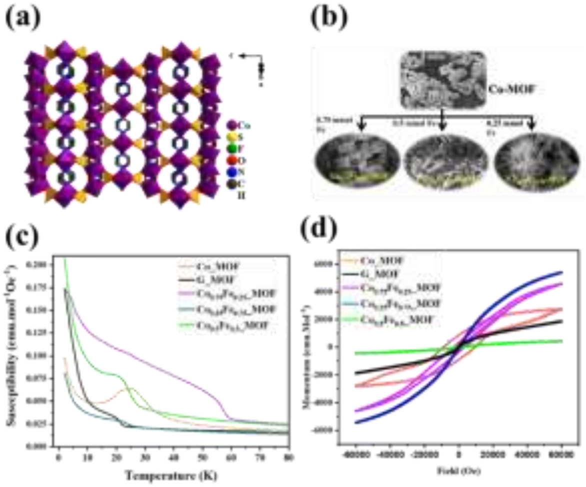

Fig.1. (a) three-dimensional Co-MOF, (b) FESEM morphology, (c) temperature-dependent susceptibility at 100 Oe, (d) isothermal magnetization at 2 K.

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Hydrosilylation of Carbonyls and Imines Catalyzed by Cationic Boron and Aluminum Complex

PP-12

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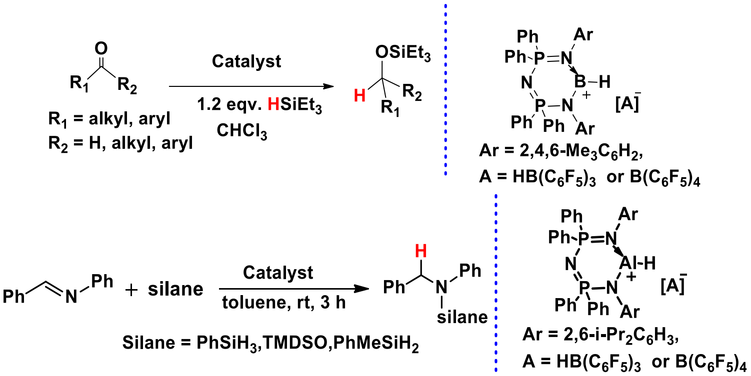
ABSTRACT

Group 13 elements have been a subject of interest for a long decade due to their propensity for Lewis acid activation of various organic molecules, facilitating numerous important chemical transformations [1]. Lewis's acidity, which is crucial property for electrophilic catalysis, is a function of co-ordination number around the metal centre. The three-coordinated B and Al cations are particularly attractive, since they combine the cationic charge and coordinative unsaturation features at the metal center and are thus expected to furnish highly electrophilic reagents. [2,3]

The present work emphasises on the syntheses of monomeric, three-coordinated boron and aluminum cations $[\mathbf{L}B\text{-}H]^+[A]^-$ and $[\mathbf{L}Al\text{-}H]^+[A]^-$ using weekly coordinated anion (A = $[HB(C_6F_5)_3]$ or $[B(C_6F_5)_4]$). The quantitative estimation of Lewis acidity by Gutmann−Beckett method reveals $[\mathbf{L}AlH]^+[HB(C_6F_5)_3]^-$ to be better Lewis acid than $B(C_6F_5)_3$ and $AlCl_3$[3]. The cationic complex of boron is utilized for the hydrosilylation of carbonyl compounds[4] whereas, the cationic aluminum complex is employed for the hydrosilylation of imines. The detailed study of mechanistic aspect for these chemical transformations is commenced via multinuclear NMR investigation, isolation of some key intermediates and DFT calculation.



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PP-13

9-Mesityl-10-methylacridinium Perchlorate Photocatalyst in Cascade Synthesis

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ABSTRACT: Acridinium ions[1] are one of the most primitive classes of hetero-aromatic compounds which have a wide research and industrial applications in the area of photo catalysis, medicinal chemistry, dye, chemosensors, solar cell and photovoltaic applications. Herein, the photocatalytic activity of 9-Mesityl-10-methylacridinium perchlorate (which is commonly known as Fukujumi Dye) has been introduced for cascaded synthesis of dithioacetalizations or thioetherifications[2] from benzyl alcohols and 3-chlorocoumarins from arylalkynoates[3].

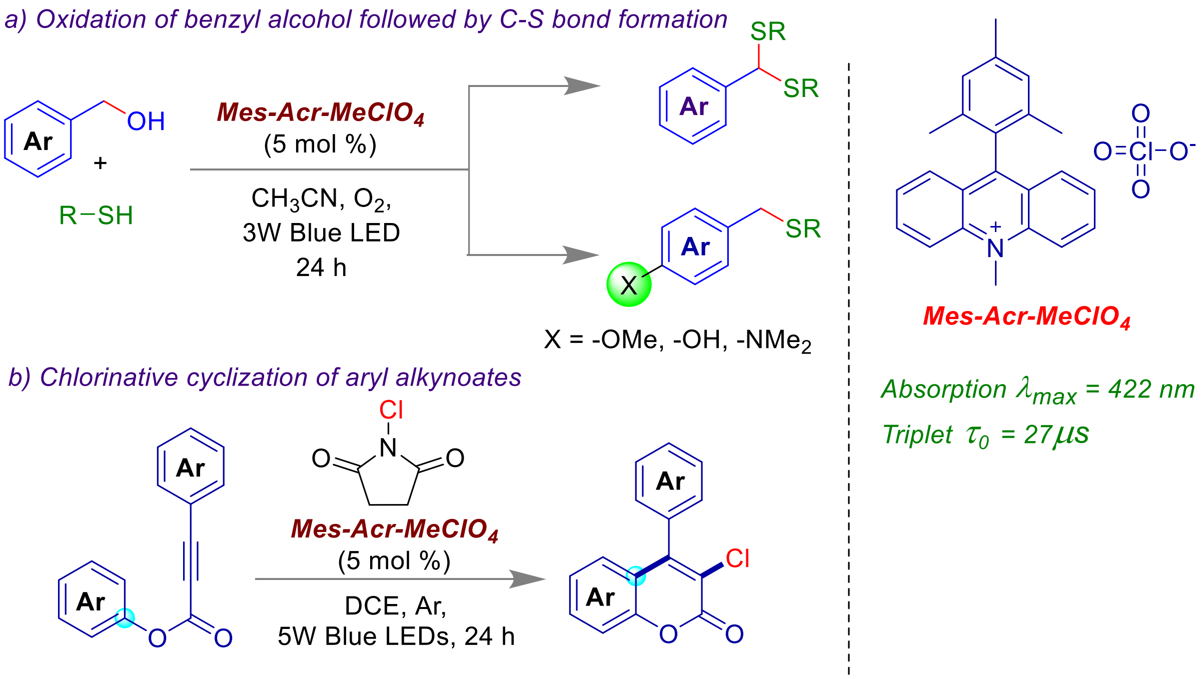

Figure 1. 9-Mesityl-10-methylacridinium perchlorate as Photocatalyst in cascade synthesis.

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Synthesis of Functionalized Quinazolinones via Intramolecular Hydride Reactions

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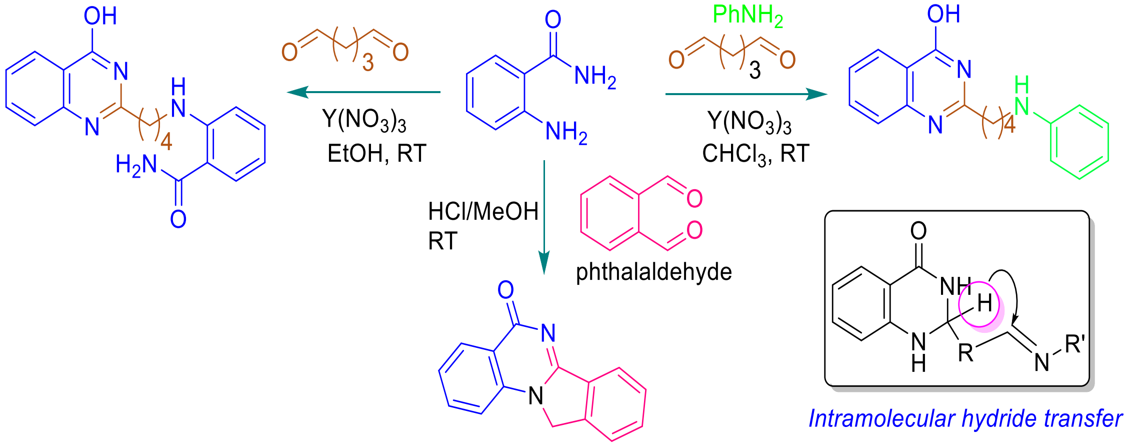
ABSTRACT

A facile intramolecular hydride transfer reaction is developed to synthesize quinazolinones from anthranilamide and dialdehydes under a mild acidic condition at room temperature. Aliphatic and aromatic dialdehyde gives different products. The hydride is transferred from a 2,3-dihydroquinazolin 4(1H)-one moiety to a distal imine functional group. We proposed a hydride transfer mechanism based on the products obtained in a deuterated solvent. The influence of steric and electronic effects of the anthranilamides, and length of the dialdehyde towards the hydride transfer reaction have been investigated. The method is suitable for the preparation of a diverse array of multivalent quinazolinones.



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Carbazole Substituted Amidinato Silylene: Synthesis, Bonding, and Coordination Behavior with Coinage Metals

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ABSTRACT

This work delineates, the synthesis and characterization of a new carbazole substituted amidinatosilylene (1) and its coinage metal complexes are being reported. Before the complexation reactions, we isolated [$PhC(N^tBu)_2Si(Cbz)\rightarrow Co(CO)Cp$] complex to estimate the σ-donating strength of the newly synthesized silylene. Further, several commonly available coinage metal salts were utilized for the complexation reactions to afford structurally diverse coinage metals motifs coordinated with silylene. The solid-state structures of these complexes have been validated by single-crystal X-ray diffraction studies, NMR spectroscopy, and mass spectroscopy. DFT studies were also performed to understand the bonding scenario. Of note, this carbazole substituted silylene consists of a HOMO on its carbazolide moiety, and the HOMO-1 features the silylene character. We also compared the HOMO-LUMO gap of this one with other amidinato silylenes having different N-substitutions. [1]

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PP-16

Acridine N-Heterocyclic Carbene Gold(I) Compounds: Tuning from Yellow to Blue Luminescence

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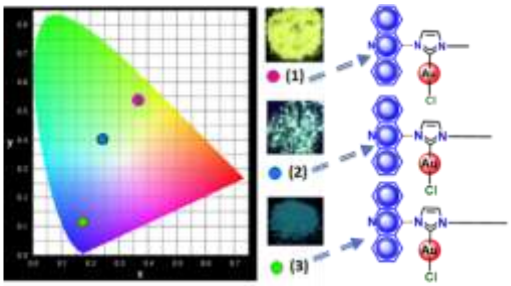
The synthesis of N-heterocyclic carbene (NHC) gold complexes has recently attracted wide attention due to their considerable range of applications, in areas such as luminescent materials and medicinal chemistry, as well as their potential role as new catalysts in gold-catalyzed processes. For several years, NHC-gold materials have found many applications in the field of organic light-emitting diode. In the case of gold–NHC complexes two types of luminescent complexes could be distinguished: molecules showing native luminescence and enhancing luminescent after addition of organic chromophores. Thus we sought to extend our approach to non-chromophoric N-substituent, mainly alkyl chains. In fact, due to their flexible carbon-carbon rotation we expected them to promote unusual solid packing and hence add a novel property to this kind of compound relative to the rigid N substituents. Thus, a comparison of **1-** gold complexes with alkyl chain is explored. The complex **1–3** depicted blue emission in the solution state, while the yellow emission (for **1**), greenish yellow emission (for **2**), and blue emission (for **3**) in the crystalline phase. This paradigm emission shift arises from *n*-butyl to *n*-pentyl and *n*-hexyl in the crystalline state due to the carbon-carbon rotation of the n-alkyl group which tends to promote unusual solid packing. Hence n-alkyl group adds a novel emission property in the crystalline state.[1]



CIE Chromaticity diagram for photoluminescence of **1-3** and photographic images of crystals **1-3**.

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PP-17

Structural Isomers of Tetra Coordinated Pyrazole-Boron Complexes: Synthesis, Photophysical and Aggregation-Induced Emission properties

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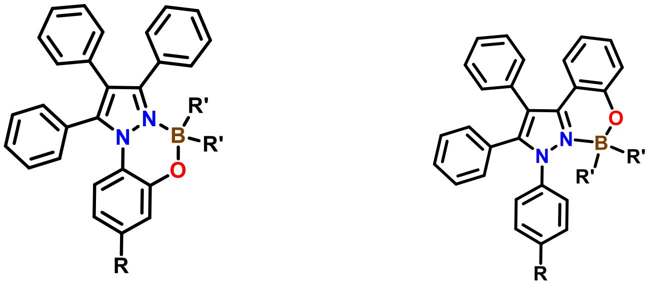
ABSTRACT

Pyrazoles are important class of five-membered heterocyclic compounds and have attracted interest due to their various application in pharmaceutical, and medicinal chemistry.[1,2] Incorporation of various main-group elements like B, P, S, Si, Sn, Se, Te etc., into π-conjugated materials has emerged as an appealing way to fine-tune to optical properties and overcoming the drawbacks of purely organic materials.[3] Especially, tetra coordinated boron compounds have sparked a lot of attention due to their stability, and various application in the field of electron transporting materials, organic light emitting diodes, photo responsive materials and so on.[4] The development of efficient luminescent materials is of great interest for both fundamental research and practical applications. In general, luminescent materials have problem associated with emission in the solid state due to Aggregation Caused Quenching (ACQ), which happens them to use in real world applications. To overcome this problem, researchers have developed a wide range of Aggregation Induced Enhance Emission (AIEE) active luminescent materials enhancing their application in thin film displays, light emitting technology, etc.[5]



R = -H (1)
$-NMe_2$ (2)
$-NPh_2$ (3)
R' = $-C_6F_5$

R = -H (4)
$-NMe_2$ (5)
$-NPh_2$ (6)
R' = $-C_6F_5$

Figure 1: Structure of tetra coordinated AIEE active pyrazole derivatives.

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Benzylation of 5-Aminopyrazoles via *o*rtho-Quinone Methides

PP-18

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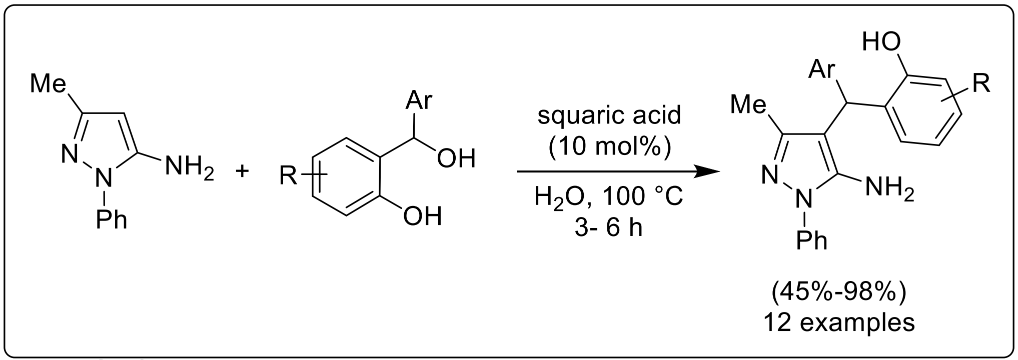
Pyrazoles are versatile heterocycles used in many fields ranging from materials to biomedical applications.[1] Hence, synthesis and functionalization of pyrazoles has gained considerable interest among synthetic community. In literature, several methods have been developed.[2] Despite these methods, developing a new method for functionalization of pyrazole is always needed.

*o*rtho-Quinone methides are useful synthons in organic synthesis. These synthons are generally prepared *in situ* by acid or base mediated transformations from the phenol derivatives.[3] In this presentation, we report a catalytic metal/metal free reaction of 5-aminopyrazoles and *in situ* generated *o*rtho-Quinone methides yielding 4-benzyl substituted pyrazoles in good to excellent.



(45%-98%)
12 examples

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Reactivity of $(TMS)_2N(\eta^1\text{-}Cp^*)Si{=}Si(\eta^1\text{-}Cp^*)N(TMS)_2$ toward the Halides of Groups 13–15

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ABSTRACT

We have demonstrated the unique reactivity of a previously reported disilene $[(TMS)_2N(\eta^1\text{-}Me_5C_5)Si{=}Si(\eta^1\text{-}Me_5C_5)N(TMS)_2]$ (**1**) with the halides of groups 13–15, which resulted in the formation of silicon–E (E = B, Al, Ge, P) bonds. Treatment of (**1**) with Lewis acidic BCl_3 led to the formation of a cationic boron species $[Cp^*BSi(Cl)_2N(TMS)_2)][BCl_3SiCl_3]$. In contrast, the reaction of **1** with BCy_2Cl afforded an oxidative addition product $[(TMS)_2N(\eta^1\text{-}Me_5C_5)Si(BCy_2)(Cl)]$ via the insertion of a Si(II) atom into the B–Cl bond. Extending the reaction with its higher congener led to classical Lewis acid-base adducts, $(TMS)_2N(\eta^1\text{-}Me_5C_5)Si\rightarrow AlCl_3$ and $(TMS)_2N(\eta^1\text{-}Me_5C_5)Si\rightarrow AlBr_3$, respectively. The reaction of $GeCl_2$ with **1** proceeded in a completely different manner and resulted in a hybrid dendrimeric compound $[HGe(Si(Cl)_2N(TMS)_2)_3]$, whereas, with $SnCl_2$, it led to Cp^*SnCl. Lastly, the reaction of Ph_2PCl followed the same pattern like Cy_2BCl and led to the formation of an oxidative addition product $[(TMS)_2N(\eta^1\text{-}Me_5C_5)Si(PPh_2)(Cl)]$ with a Si–P bond.[1]

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PP-20

Oxygenolysis of a series of copper(II)-flavonolate adducts varying the electronic factors on supporting ligands as a mimic of quercetin 2,4-dioxygenase activity

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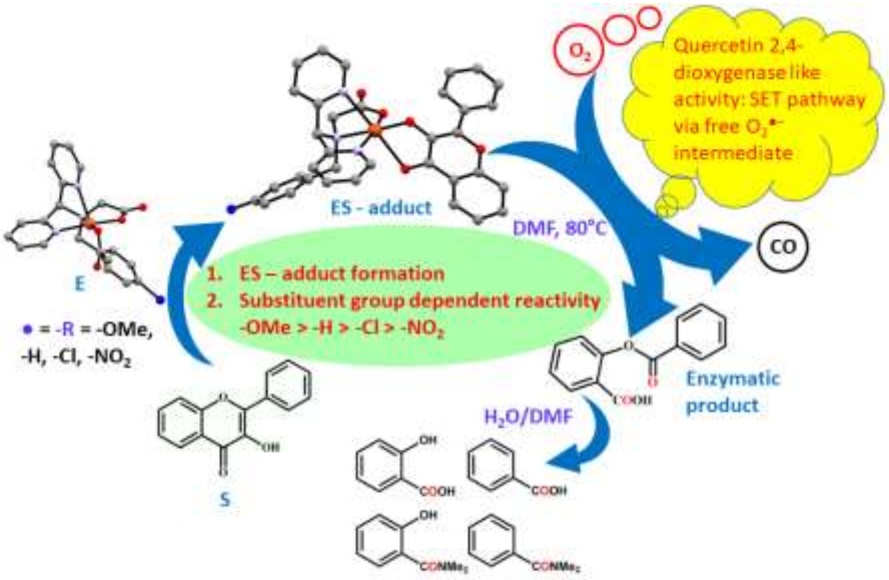
ABSTRACT

Four copper(II)-flavonolate compounds of type [Cu(L^R)(fla)] {where L^R = 2-(*p*-R-benzyl(dipyridin-2- ylmethyl)amino)acetate; R = OMe (**1**), H (**2**), Cl (**3**) and NO_2 (**4**)} have been developed as structural and functional enzyme-substrate (ES) model of Cu^{2+}-containing quercetin 2,4-dioxygenase enzyme. The ES model complexes **1-4** are synthesized by reacting 3-hydroxyflavone in presence of base with the respective acetate-bound copper(II) complexes, [Cu(L^R)(OAc)]. In presence of dioxygen the ES model complexes exhibit enzyme-type oxygenolysis of flavonolate (dioxygenase type bond cleavage reaction) at 80°C in DMF. The reactivity exhibits a substituent group dependent order as OMe (**1**) > H (**2**) > Cl (**3**) > NO_2 (**4**). Experimental studies suggest a single electron transfer (SET) from flavonolate to dioxygen over a valence tautomerism {[Cu^{II}(fla^-)] ↔ [Cu^I($fla^\bullet$)]} to generate the reactive flavonoxy radical ($fla^\bullet$), that reacts further with superoxide radical to bring about the oxygenative ring opening reaction. The SET pathway has been further verified by studying dioxygenation reaction with a redox-inactive Zn^{2+} complex, [Zn(L^{OMe})(fla)] (**5**).



In situ generated chloride, bromide and iodide as catalysts for the oxidation of benzyl halides to benzoic acids in alkaline water using TBHP as oxidant

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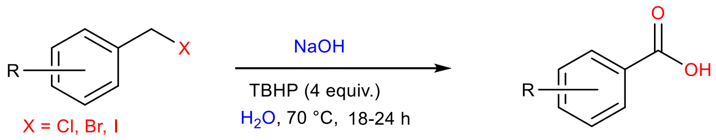
Abstract:

Aromatic carboxylic acids, especially benzoic acid and its derivatives, find extensive use both in academia and industry. Traditionally, carboxylic acids are synthesized by the oxidation of alcohols/aldehydes, and also by the oxidative cracking of unsaturated compounds such as olefins and alkynes. Although a variety of catalytic methods based on transition metals and main group based metal-free catalysts have been developed for oxidation reactions of alcohols, most of these methods suffer from drawbacks, such as the requirement of precious metals, expensive ligands, high temperature, volatile and environmentally unfriendly organic solvents, as well as expensive and toxic additives. Previous work from our group has shown that NaCl can act as a catalyst for the oxidation of alcohols to carboxylic acids. We have now developed an efficient and external catalyst free methodology for the oxidation of benzyl halides to benzoic acids using an inexpensive and green oxidant (TBHP) in aqueous alkaline medium. This protocol offers an excellent way to avoid adding catalysts and involves the in *situ* generated halide ion released from the benzyl halide as the catalyst. A series of carboxylic acids were prepared from benzyl halides in high yields under mild reaction conditions by this method which does not require chromatographic purification. Gram scale reactions for the synthesis of the carboxylic acids in good yields have been successfully carried out using benzyl chloride, bromide and iodide. As an industrial application, the synthesis of a key monomer used for the synthesis of polyethylene terephthalate (PET), i. e., terephthalic acid (PTA), has also been accomplished in good yields.



Scheme 1: Preparation of benzoic acids from benzyl halides.

Keywords: Oxidation 1 • Carboxylic acid 2 • Halides 3 • Aqueous medium 4 • *In situ* generated catalyst 5

PP-22

Synthesis and Functionalization of π-extended B□N Coordinated Phenanthroimidazole Polycyclic Aromatic Hydrocarbons and Study Their Optical Properties

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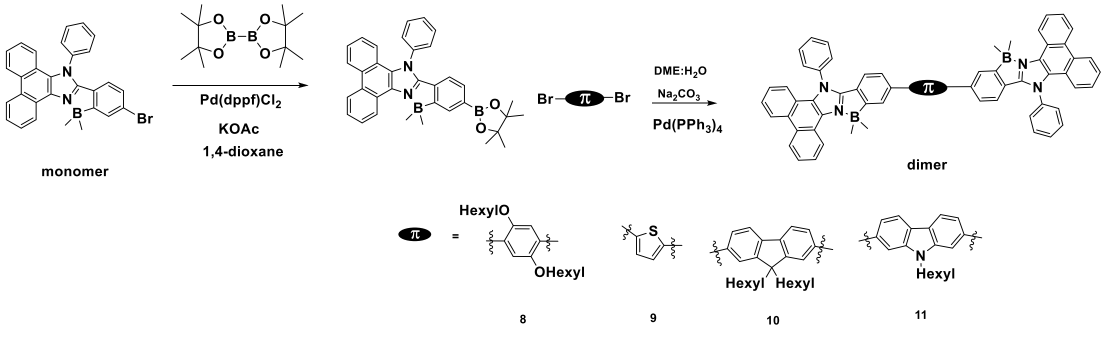
Polycyclic aromatic hydrocarbons (PAHs) are of great interest due to their wide applications in the areas of bioimaging, optoelectronics, organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), dye sensitized solar cell, sensors and so on.[1] But due to their low stability and less fluorescence quantum yields different methods have been developed to tune the electronic properties of these materials. One such approach is the incorporation of tri-coordinate boron into PAHs which increases the luminescence and electron effinity.[2] Modification of PAHs with intramolecular B←N coordination makes the molecules more rigid which increases the conjugation that results in the enhancement of luminescent and electron accepting properties. In 2007 Kawashima and co-workers[3] synthesized highly luminescent azobenzene- or imine-based B←N coordinated boron compounds. Recently, Jakle and co-workers[4] developed a B←N coordinated anthracene derivative which has been used for oxygen sensitization.

In this poster, I will present synthesis and characterization of л-extended B←N coordinated phenanthroimidazole dimers and derivatives. These synthesized compounds show excellent luminescence quantum yields in solution and moderate solid state quantum yields. Such properties make these molecules potential candidates for the applications in sensing and optoelectronic devices.



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PP-23

Cobalt(II)porphyrin mediated synthesis of 1,5-diketones via an interrupted-borrowing-hydrogen strategy using methanol as a C1 source

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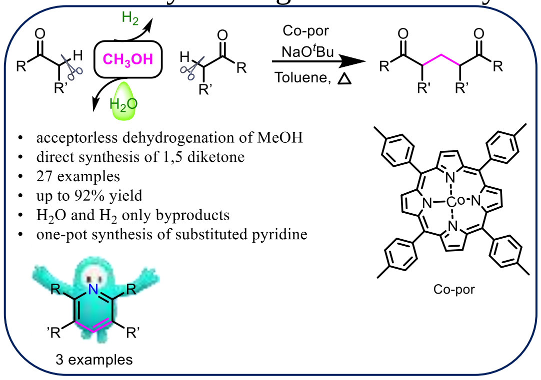
ABSTRACT

A novel cobalt(II)porphyrin-mediated acceptorless dehydrogenation of methanol is reported for the first time. This methodology has been applied for the coupling of a variety of ketones with methanol to produce 1,5-diketones along with H_2 and H_2O as the environment friendly by products. 1,5-diketones have gained attraction due to their potential biological and pharmacological activity,[1] also proven to be invaluable feedstock for the synthesis of many heterocyclic [2] and polyfunctional.[3] This paradigm was also demonstrated for a one-pot synthesis of substituted pyridines using a sequential addition protocol where the 1,5-diketones were generated in situ.[2] From many control experiments including those involving deuterium labelling, it is proposed that protonated cobalt(II)porphyrin methoxide complex acts as an intermediate to generate formaldehyde along with a metal hydride.



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PP-24

Ruthenium Catalyzed α-Alkylation of Ketones using Secondary Alcohols to β-Disubstitued Ketones

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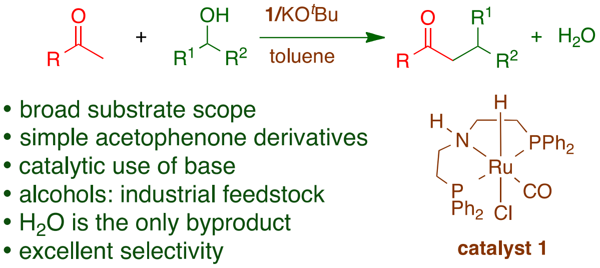
Catalytic coupling of aryl ketones with secondary alcohols gained importance to deliver the -β-disubstituted ketones products in recent years. However, highly hindered arylketones (penta- or tri-substituted) and use of stoichiometric base are prerequisite in known methods to avert the competing side reactions and ensure successful outcome.[1-4] On contrary to previously reported methods, a simple attractive method has been developed where challenging simple acetophenone compounds are effectually reacted with secondary alcohols leading to the selective formation of β-disubstituted ketones (Scheme 1).[5] An assortment of aromatic ketones was successfully diversified with a variety of unactivated secondary alcohols, which served as alkylating agents to provide β-disubstituted ketone products in good to excellent yields. Mechanistic studies and deuterium labeling experiments confirmed that the reaction follows borrowing hydrogen pathway. Notably, this selective and catalytic C-C bond forming methodology requires low catalyst load, catalytic amount of base and produce H_2O as the only by-product, which makes this catalytic method attractive and environmentally benign.



Scheme 1. Selective Catalytic *α*-Alkylation of Ketones Using Secondary Alcohols.

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Transfer Hydrogenation of Aldehydes and Ketones in Air with Methanol and Ethanol by an Air-Stable Ruthenium−Triazole Complex

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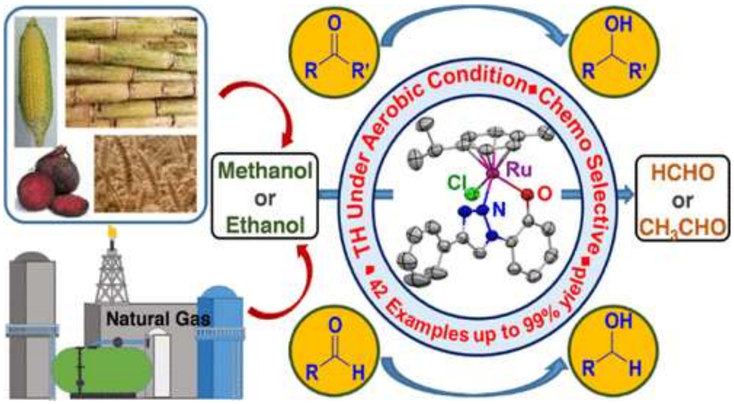
Coordination of 1,4-disubstituted 1,2,3-triazoles with $[(p\text{-cymene})RuCl_2]_2$ followed by dehydrochlorination in the presence of a base resulted in the formation of corresponding ruthenium complexes(1 & 2) respectively[1]. Both were tested for the transfer hydrogenation of aldehydes and ketones in air using ecologically benign and cheap ethanol as the hydrogen source in the presence of a catalytic amount of a base. Air-stable complex 1 was proved to be an active catalyst for the transfer hydrogenation of a wide variety of aromatic and aliphatic aldehydes and ketones bearing various functionalities. Catalyst 1 was also effective for the transfer hydrogenation of carbonyls using the simplest primary alcohol, methanol, under aerobic conditions. Under the present catalytic protocol, labile or reducible functionalities such as nitro, cyano, and ester groups were tolerated. Good selectivity was also observed for acyclic α,β-unsaturated carbonyls. However, this catalytic protocol was not selective for 2-cyclohexen-1-one as both alkene and keto moieties were reduced. The transfer hydrogenations are believed to proceed via a ruthenium-hydride intermediate. Finally, transfer hydrogenation of acetophenone using isopropanol as a commonly used hydrogen source was also performed.



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Zinc Hydride Catalyzed Hydrofunctionalization of Ketones and Chemoselective Hydroboration of Isocyanates

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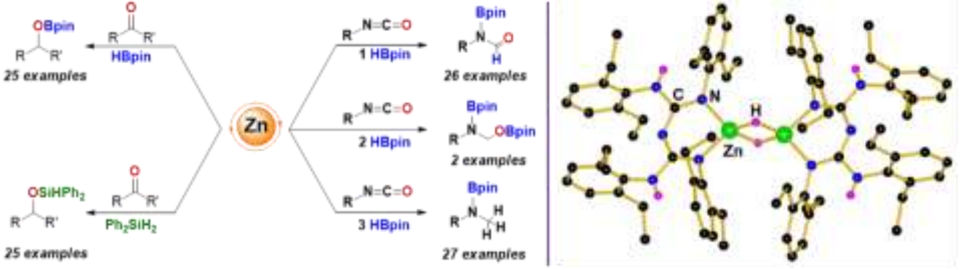
ABSTRACT

A popular NacNac or β-diketiminate analogue, conjugated bis-guanidinate (CBG) stabilized and well-defined dimeric zinc hydride **1**, $[LZnH]_2$; [L = {(ArNH)(ArN)–C=N–C=(NAr)(NHAr)}; Ar = 2,6-Et_2-C_6H_3] has been reported. Next, we have shown that compound **1** catalyzed the hydrofunctionalization of ketones to alcohols.[1] Further, we report that the earth-abundant, cheaper, sustainable zinc catalyzed mono hydroboration (partial reduction) of many organoisocyanates into corresponding N- boryl formamides.[2] A broad range of alkyl and aryl isocyanates undergo chemoselective reduction with HBpin to obtain selectively N-boryl amide, bis(boryl) hemiaminal, and N-boryl methyl amine products.[3] Isocyanates undergo a deoxygenation reduction reaction via hydroboration, in which the C=O bond cleaves, forming N-boryl methylamines.[4] Interestingly, this catalyst covers intra and intermolecular chemoselective hydroboration of isocyanates over several other reducible functionalities like cyano, halide, nitro, and alkene groups. Moreover, a series of control experiments, structurally characterized intermediates, and kinetics suggest that the CBG zinc hydride complex is responsible for all reduction steps.



- ✓ *Wide substrate scope*
- ✓ *Excellent yield*
- ✓ *Low catalyst loading*
- ✓ *Intermolecular chemoselectivity*
- ✓ *Chemoselective reduction*
- ✓ *Hydrodeoxygenation*
- ✓ *Solvent free, Atom economical*
- ✓ *Sustainable catalysis*

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Design and Development of B-N Containing Heteroarenes and Porphyrins: Room-temperature Phosphorescence and Fullerene (C_{60}) Complexation

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ABSTRACT

Organic fluorophores and phosphors have been used vastly in materials science to develop OLEDs, thin-film transistors, photovoltaic devices, lasers, sensors, and smart materials.[1,2] Their emissive property and applicability can be fine-tuned by incorporating main group elements (B, N, O, P, Si, S etc.) in their molecular structure.[3,4] A very promising method to develop new functional material is substituting an isoelectronic B–N units for C=C units in π-conjugated systems producing structural similarities to all-carbon frameworks, but with fundamentally altered electronic and optical properties. Recent decades have witnessed tremendous progress in the field of BN/CC isosterism chemistry.[5] Recently, we demonstrated that B-N/C=C elemental isosterism could be an efficient strategy for the generation of fluorescent materials that show enhanced emission in solid-state over solution state.[6-8] We proved that tetraarylaminoborane (TAAB) is a prototype platform to which electron donors/acceptors are introduced to realize materials with tunable emission colors. Apart from that, developed materials are sensitive to mechanical force, and hence those can find potential applications in security sensors. As part of our ongoing effort to create new functional materials, we have developed two novel B-N systems: 1) *B-N fused polyaromatic hydrocarbons based on phenothiazine moiety (having a tricoordinated boron)*, and 2) *B-N fused with Ni-porphyrin core (having two tetracoordinate boron)*. The structure-property relationship of newly synthesized B-N containing heteroarene and porphyrin systems will be discussed in this poster.

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Construction of 3D Mg(II)-Organic Frameworks for Efficient chemical fixation of CO_2 from Air under Environment-Friendly Co-catalyst and Solvent-free Conditions

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Abstract

The immense amount of carbon dioxide (CO_2) emissions has resulted in most serious environmental issues like ocean acidification, extreme weather, species extinction, and global warming[1]. Thus it is highly desirable to develop highly efficient catalytic systems for selective capture and utilization of CO_2 from direct air to tackle the problems of growing CO_2 concentration in the atmosphere. However, the thermodynamic stability and kinetic inertness of CO_2 pose a great challenge for its conversion under mild conditions[2]. Various homogeneous and heterogeneous catalysts have been developed for catalytic conversion of CO_2 into value-added chemicals. In this context, porous metal-organic frameworks (MOFs) have shown great potential for selective capture and conversion of CO_2 owing to their large surface areas and tunable pore size and functionality[3]. However, the number of examples of MOFs known for efficient CO_2 conversion from direct air under solvent/co-catalyst free conditions is limited. In this direction, we have synthesized MOFs based on Mg(II) ion and organic linkers containing basic functional groups for selective capture and chemical fixation of CO_2 from direct air to cyclic carbonates under solvent/co-catalyst free conditions. The synthesis, characterization, gas adsorption and catalytic studies of the MOFs for chemical fixation of CO_2 will be presented.

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Synthesis of sulfur-doped porous carbon for supercapacitor and gas adsorption applications.

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ABSTRACT

Heteroatom-doped porous carbon materials have great potential for both capacitive energy storage and gas sorption applications. This article reports the synthesis of highly porous sulfur-doped carbon from thiophene using an in situ self-doping strategy followed by KOH activation. A series of highly porous sulfur-containing carbon materials with high surface area and pore volume were prepared through variation of activation temperature from 600°C to 900°C and applied as supercapacitor electrodes in alkaline as well as neutral electrolyte and also as adsorbent for CO_2, H_2 adsorption. The material prepared at 800°C presented the highest electrochemical performance with a specific capacitance of $300\ F\ g^{-1}$ at $1\ A\ g^{-1}$ in 6 M KOH because of its high surface area and pore volume. The presence of oxidized sulfur functionality, high surface area, and micro-mesoporous structure were the responsible factors for enhanced storage of gases like CO_2 and H_2. The functionalized carbon showed a good H_2 uptake value of 2.8 wt% under 1 bar pressure at 77 K. CO_2 uptake capacities were found to be 5.6 and 3.3 mmol g^{-1} at 1 bar pressure under the temperature of 273 and 298 K, respectively with a good CO_2/N_2 selectivity of 14.36 and CO_2/CH_4 selectivity of 2.53. This report presents a promising porous sulfur-doped carbon material for cost-effective and efficient gas adsorption and energy storage systems[1].

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PP-30

Simultaneous Mitochondria- and nucleolus imaging through copper(i) complexes with pyrazole-linked triphenylphosphine complexes

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The simultaneous labelling and imaging of mitochondria and nucleolus have attracted great attention because of the involvement of these cellular organelles in critical cellular activities. Therefore, a large number of mitochondria- or nucleolus-labelling probes have been developed throughout the world. However, in the current study, we successfully developed pyrazole-based, copper-linked triphenylphosphine coupled emissive metallo-complexes for the simultaneous visualization of mitochondria and nucleolus in a single run. These complexes were very inexpensive and could be synthesized by a simple one-pot multicomponent reaction scheme. The complexes were very specific, and only a small concentration of 5 μM was found to be sufficient to probe both the organelles efficiently. Additionally, even under a shorter incubation period (half hour), the fluorescence intensity from the cells was appreciable. Also, both the compounds were found to be photostable when torched with 10% of a 100 mW laser for up to 10 min. This is the first report on the development of multifunctional live cell imaging tools for simultaneous mitochondria and nucleolus imaging and within the shortest incubation time of about 30 minutes.

Cobalt Catalyzed Selective Synthesis of Disiloxanes and Hydrosiloxanes

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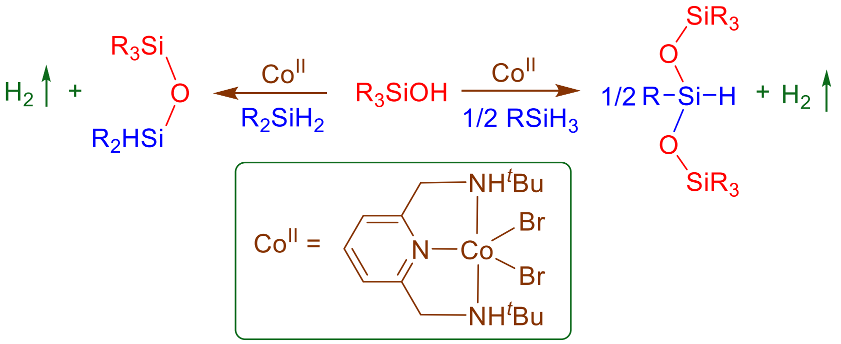
A selective synthesis of symmetrical siloxanes and cyclotetrasiloxanes are attained from reaction of silanes and dihydrosilanes, respectively with water and the reactions are catalyzed by a new NNN^{HtBu} cobalt(II) pincer complex. Interestingly, when phenyltrihydrosilane was subjected to catalysis with water, a siloxane cage consisting of 12 silicon and 18 oxygen centers was obtained and remarkably the reaction proceeded with liberation of 3 equivalent of molecular hydrogen (36 H_2) under mild experimental conditions. Upon reaction of silane with different silanols, highly selective and controlled syntheses of higher order monohydrosiloxanes and disiloxymonohydrosilanes were achieved by cobalt catalysis. The liberated molecular hydrogen is the only byproduct observed in all these transformations. Mechanistic studies indicated that the reactions occur via homogeneous pathway. Kinetic and independent experiments confirmed the catalytic oxidation of silane to silanol and further dehydrocoupling processes are involved in synthesis of symmetrical siloxanes, cyclotetrasiloxanes and siloxane cage compounds, whereas the unsymmetrical siloxane synthesis from silane and silanol proceeded via dehydrogenative coupling reactions. Overall these cobalt-catalyzed oxidative coupling reactions are based on the Si–H, Si–OH and O–H bond activation of silane, silanol and water, respectively. Catalyst cycle consisting of Co(II) intermediates are suggested to be operative.



Scheme 1. Cobalt Catalyzed Selective Synthesis of Disiloxanes.

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Sustainable Approach toward the Construction of Heterocyclic Scaffolds

PP-32

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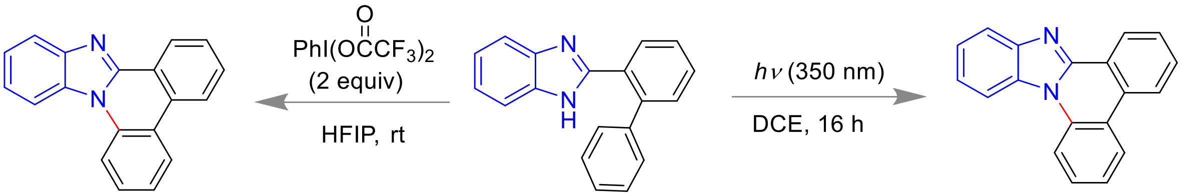
Nitrogen-containing fused heteroaromatic compounds having phenanthridine moiety are ubiquitous in many pharmaceuticals and natural products. Owing to extensive π-conjugation, these types of compounds are utilized as organic semiconductors and luminescent materials. For example, 1,2-disubstituted (hetero)aryl-fused benzimidazoles acts as an electron-transporting and emission functional units. Due to the planarity of the system, phenanthridine moiety shows the ability to bind with human telomere derived g-quadruplexes. Considerable efforts have been paid for developing the methods for synthetic transformations of (hetero)aryl-fused phenanthridines using metal catalyst.



Moreover, this type of methodology suffers from disadvantages like metal contamination in products, reusability of metal catalyst, requirements of multistep paths, etc. We anticipate that our current N-H/C-H arylation method using PIFA in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)[1] and direct photochemical dehydrogenative C-N coupling of unactivated C(sp^2)-H and N(sp^2)-H bonds[2] for the preparation of benzimidazole-fused phenanthridines can be considered as the easiest approach known in literature.

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Isosmaragdyrin with an N_3C_2 core: a) Protonated form with unprecedented anion-arene interaction and b) Stabilization of Organo-Pd(II) complex

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Expanded porphyrins enticed attention due to their miscellaneous prominence in applied and fundamental chemistry.[1] The expanded analogue with five pyrrolic rings concomitant by three *meso* carbon bridges begets smaragdyrin[1.1.0.1.0].[2] The structural isomer of smaragdyrin is acknowledged as isosmaragdyrin[1.1.1.0.0]. It can be obtained by reshuffling the *meso* bridges of smaragdyrin isomer, although, the molecule is unstable in neutral form due to inner steric repulsion.[2] Recently, our group procured isosmaragdyrin in freebase form by incorporating 2,6-di-*m*-phenylpyridine moiety inside the macrocyclic core, which aid in mitigating steric adversary.[3] To date, that is the solitary articulation of stable isosmaragdyrin, but its protonated form is hitherto unexplored. In this poster presentation, I wish to accentuate the spectral and structural characterization of protonated isosmaragdyrin[1.1.1.0.0]. Structural elucidation of protonated form unambiguously revealed an anion-arene interaction (**Figure 1a**) between trifluoroacetate anion and phenyl unit, which is elusive in porphyrin chemistry. Also, the coordination chemistry of isosmaragdyrin core is further explored by Pd(II) complexation. Single crystal X-ray investigation demonstrates that Pd(II) underpins organometallic complex with (N^C)N coordination mode (**Figure 2a**), which construct scantly reported unsymmetrical pincer type complex inside the macrocyclic ring.

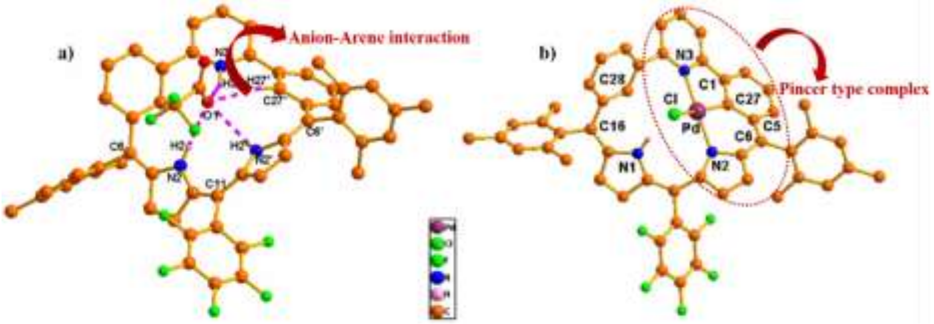

Figure 1: Crystal structure of **a)** Protonated and **b)** Pd(II) complex of isosmaragdyrin[1.1.1.0.0].

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Nickel catalyzed diastereoselective desymmetrization of disubstituted malononitriles: A facile access to α-functionalized aryl ketones

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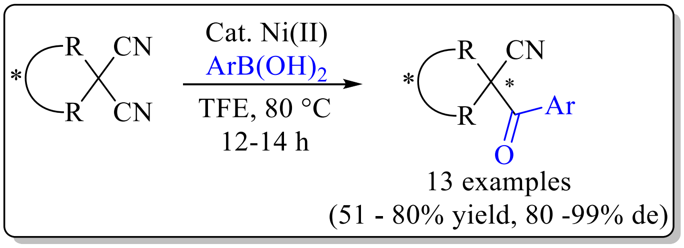
ABSTRACT

Asymmetry is ubiquitous in every part of nature and has a great impact on many fields. In pharmaceuticals, as well as in related industries, asymmetry plays an important role since both enantiomers of a determinate drug do not necessarily have same role.[1] Desymmertization reaction of prochiral or *meso*-compounds is a powerful and useful strategy which allows accessing enantiomerically enriched compounds. Disubstituted malononitriles being a prochiral substrate is an efficient moiety for desymmetrisation.[2] Functionalization of any one of the nitrile groups will lead to quaternary centered nitriles. We have taken prochiral disubstituted malononitrile with an intention of selectively functionalizing one of the nitrile groups by adding aryl boronic acid on the substrate. Under Nickel catalyzed condition, we observed addition of aryl boronic acid to chiral cyclic disubstituted malononitriles, selectively functionalizes only one nitrile group, leading to highly diastereoselective product.



Diverse aryl boronic acids were studied affording the α-cyano ketones in very good yields with >99% *de*. Some of these ketones were transformed into alcohols and amides without losing diastereoselectivity. The detailed study of the desymmetrization of disubstituted malononitriles will be discussed in the symposium.[3]

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PP-35

Efficient α-Alkylation of Arylacetonitriles with Secondary Alcohols Catalyzed by a Phosphine-Free Air-Stable Iridium(III) Complex

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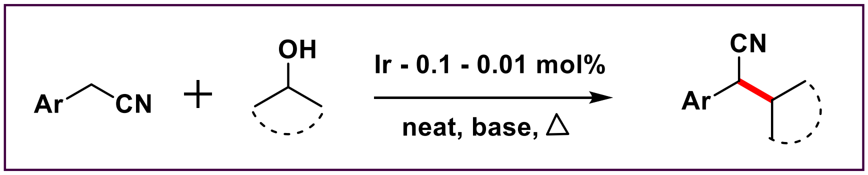
In organic synthesis, the importance of α-alkylation of nitriles is enormous as α-alkylated nitriles are versatile building blocks for the synthesis of varieties of compounds. Direct catalytic alkylation with alcohols is a highly atom-economic protocol and offers a green alternative as water is the only by-product. A large number of metal complexes have been reported with primary alcohols, however, the use of secondary alcohols is limited. During our study, Two groups independently reported catalytic α-alkylation of arylacetonitriles with secondary alcohols[1,2] but elevated temperature, high catalyst loading and base loading, reaction time are few drawbacks there. A well-defined and readily available air-stable dimeric iridium(III) complex catalyzed α-alkylation of arylacetonitriles using secondary alcohols with the liberation of water as the only by product is reported here.[3] The α-alkylations were efficiently performed at 120 °C under solvent-free conditions with very low (0.1−0.01 mol %) catalyst loading. Mechanistic study revealed that the reaction proceeds via alcohol activation by metal−ligand cooperation with the formation of reactive iridium-hydride species.



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Synthesis of α-Methyl Ketones from Allylic Alcohols and Methanol Catalyzed by Palladium

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ABSTRACT

Allylic alcohols play an important role in organic synthesis as alkylating or allylating reagents alternating to carbonyl compounds[1]. Methyl group is one of the chemical motifs occurring in many pharmaceutically and biologically active molecules[2]. Thus, methanol as a methylating reagent by hydrogen borrowing approach is gaining interest as it is a green and renewable C1 source[3]. Selective one-pot conversion of secondary allylic alcohols to α -methyl ketones[4] is a potentially beneficial reaction. We synthesized α-methyl ketones starting from 1,3-diaryl propenols or 1-aryl propenols using methanol as a C1 source in One-pot. Commercially available $Pd(OAc)_2$ used as a catalyst for this one-pot isomerization-methylation reaction, where H_2O is the only by-product. The reaction pathway involves isomerization of allyl alcohol followed by methylation through hydrogen borrowing in these isomerization-methylation reactions, which was supported by mechanistic studies and deuterium labelling experiments.

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PP-37

NaCl as Catalyst and Water as Solvent: Highly E-Selective Olefination of Methyl Substituted N-Heteroarenes with Benzyl Amines and Alcohols

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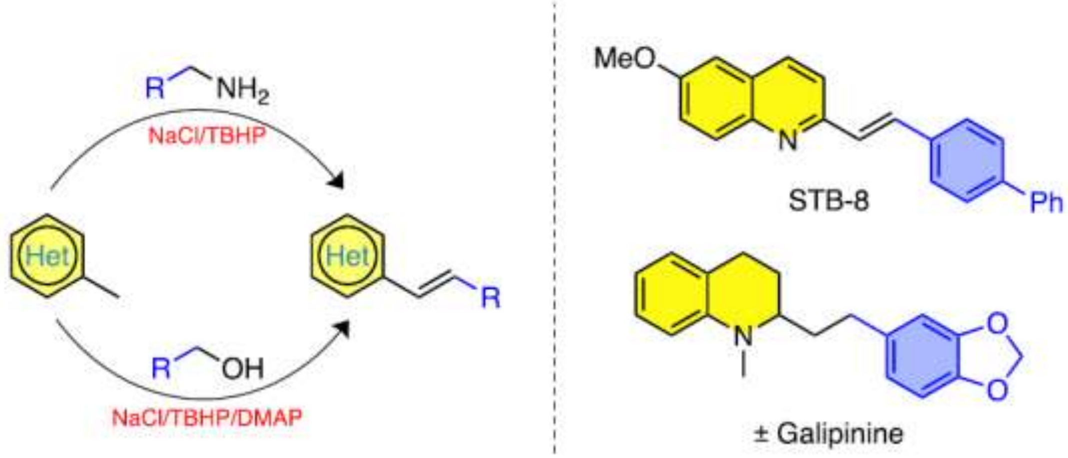
Abstract

E-Selective conjugated olefins are considered as valuable building blocks due to their diverse applications in the synthesis of agrochemicals, pharmaceuticals, and fine chemicals, and they are also structural entities present in several bioactive natural products. Oxidative coupling of benzylamines and alcohols with methyl substituted *N*-heteroarenes such as quinolines and quinoxalines has been achieved using chloride, a sea abundant anion as the catalyst for practical synthesis of a wide range of *E*-disubstituted olefins in aqueous medium. Detailed mechanistic studies and control experiments were carried out to deduce the reaction mechanism which indicated that the *in situ* formed ClO_2^- is the active form of the catalyst. We have successfully carried out a 1g scale reaction using this methodology, and five pharmaceutically relevant conjugated olefins were also synthesized by this method in moderate to good yields.

Synthesis of STB-8, an in vivo specific staining agent for β-amyloid plaques found in the brain cells of patients with Alzheimer's disease. The STB-8 unit is also present in the core structure of 2E10, another imaging agent for amyloid deposits. The core structures of the drugs, Montelukast and UCF 501, which are used for the treatment of asthma/seasonal allergies and malaria, respectively, were also synthesized using this present method. In addition, we were able to isolate (±)-Galipinine in 53% overall yield using the olefin percussor.

Keywords: Metal-free· chloride catalyzed· main-group catalysis· oxidative coupling



Scheme 1: Oxidative olefination of methyl substituted *N*-heteroarenes with benzyl amines and benzyl alcohols using NaCl catalyst in aqueous medium

Air and Water Stable Germacarbonyl Compounds

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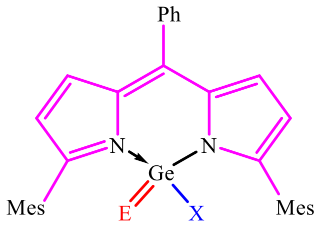
ABSTRACT

Germacarbonyl compounds are the germanium analogs of carbonyl compounds; they require an inert atmosphere for their stability.[1-4] As the isolation of air and water stable germylenes was achievable,[5-6] the synthesis of germacarbonyl compounds that are stable under ambient conditions was attempted. Accordingly, the isolation and characterization of air and water stable germacarbonyl compounds **1-8** are reported here (Chart 1). The isolated germacarbonyl compounds are germanones **1** and **5**, germacarboxylic acids **2** and **6**, germaesters **3** (Figure 1) and **7**, and germaamides **4** and **8** containing Ge=E bonds (E = S and Se). These compounds were synthesized by reacting the corresponding functionalized germylenes with elemental sulphur/selenium. Further details will be presented in the poster.



E = S; X = Ph (**1**), OH (**2**), OEt (**3**), N(TMS)$_2$ (**4**)
E = Se; X = Ph (**5**), OH (**6**), OEt (**7**), N(TMS)$_2$ (**8**)

Chart 1. Structure of compounds **1-8**

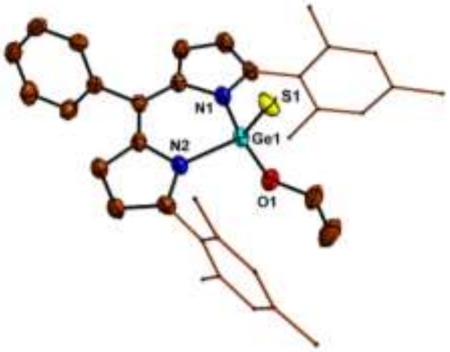


Figure 1. Molecular structure of compound **3**

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PP-39

Cyanosilylation of Aldehydes using Stannylene Cyanide

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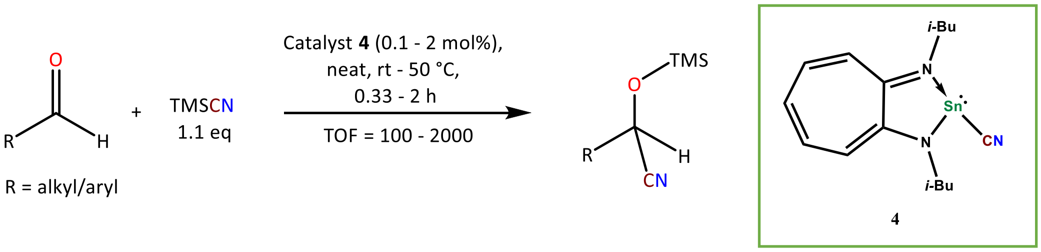
ABSTRACT

Catalysis using main group compounds is an important area of research in modern main group chemistry.[1] Earlier, we showed the use of germylene cyanide as a cyanosilylation catalyst,[1a] and here we demonstrate that cyanosilylation can also be achieved using a stannylene cyanide **4**. The first example of stannylene cyanide [(L)SnCN] (**4**) was synthesized through the substitution reaction of either stannylene amide [(*i*-Bu)$_2$ATISnN(SiMe$_3$)$_2$] (**2**) or stannylene pyrrolide [(*i*-Bu)$_2$ATISnPy] (**3**) with an excess of trimethylsilyl cyanide (L = aminotroponiminate (ATI)). Compound **4** catalyzes the cyanosilylation of a variety of aldehydes (Equation 1); *p*-formaldehyde got cyanosilylated in 30 min at room temperature in the presence of 0.1 mol% of compound **4** with a TOF of 1960. The cyanosilylation of benzaldehyde at 50 °C using 0.5 mol% of compound **4** took 20 min for more than 99% conversion. Additional details of the work will be provided in the poster, along with the mechanistic studies.



Equation 1. Cyanosilylation of aldehydes catalysed using compound **4**.

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Germylene and Stannylene Isocyanides

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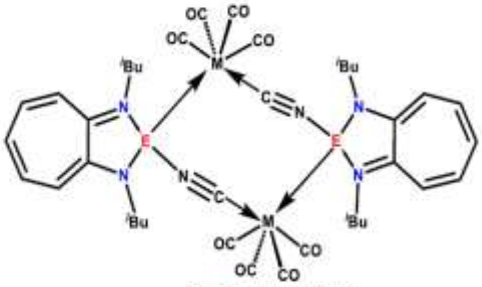
ABSTRACT

Isocyanides (RNC) are the isomers of cyanides (RCN); in the former and latter, the carbon of the R group is attached to nitrogen and carbon of the NC and CN groups, respectively. [1] Heavier tetrylene isocyanides should have E-NC bonds and their chemistry is hardly explored (E = Si, Ge, Sn, Pb). [2] Recently, we have succeeded in isolating germanium and tin tetrylene isocyanides as their transition metal complexes [(ATI)E(NC)→M(CO)4]2 (E = Ge; M = Mo **3**, W **4** and E = Sn; M = Mo **5**, W **6**) (ATI = Aminotroponiminate); these results will be presented in this poster. The first examples of germylene and stannylene isocyanides were synthesized by reacting germylene and stannylene cyanides (ATI)ECN (E = Ge[3] **1**; Sn **2**) with *cis*-[M(CO)$_4$(COD)] (M = Mo, W) (COD = 1,5-cyclooctadiene). Complexes **3-6** have unique 8-membered metallacyclic ring (E = Ge; M = Mo **3**, W = **4** and E = Sn; M = Mo **5**, W = **6**). DFT studies were carried out to support the experimental findings.



E = Ge 1; M = Mo 3, W 4
E = Sn 2; M = Mo 5, W 6

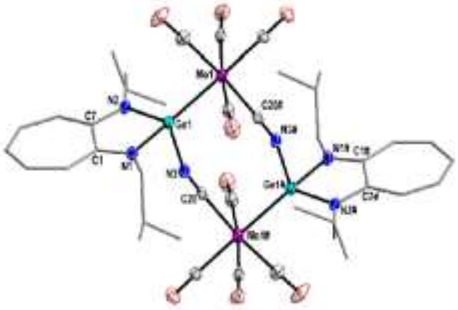


Figure 1: Crystal Structure of compound **3**.

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PP-41

Air and Water Stable Copper Complexes of Germaamides

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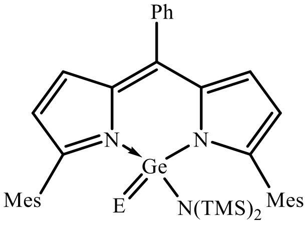
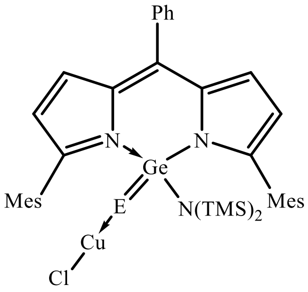
ABSTRACT

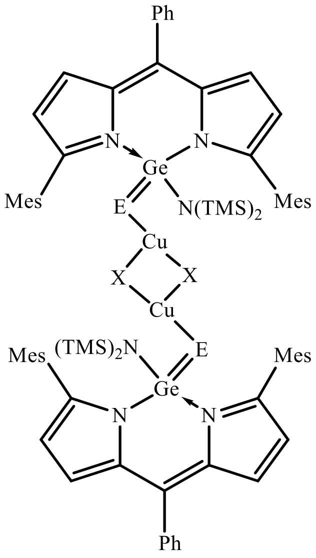
The coordination chemistry of germacarbonyl compounds is in its infancy and fast-growing.[1] Until now, there was no example of an air and water stable metal complex stabilized by germacarbonyl compound. As we were able to isolate air and water stable germaamides recently,[2] their ability to offer metal complexes that are stable under ambient conditions was probed. The germaamides **1** and **2** with Ge=S and Ge=Se bonds reacted with copper(I) halides at ambient conditions in a non-dried solvent to offer a variety of copper(I) complexes **3-8** (halide = Cl, Br, I). These copper complexes air and water stability were proved using ^{1}H NMR spectroscopy. Peerless is the selective binding of thiogermaamide and selenogermaamide towards copper chloride and bromide, respectively, in a copper(I) halide mixture. The poster will offer more details about this work.



E = S (**1**), Se (**2**)



E = S (**3**), Se (**4**)



E = S; X = Br (**5**), I (**6**)
E = Se; X = Br (**7**), I (**8**)

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PP-42

Phosphoramides: Crystallization Induced Room-Temperature Phosphorescence and Chiral Photoluminescence

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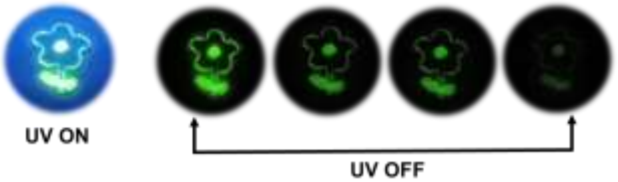
Room temperature phosphorescence (RTP) materials have attracted a lot of research interest owing to their potential applications in organic light-emitting diodes (OLEDs), sensing and time-gated bio-imaging applications.[1] Since the efficiency of RTP heavily depends on the intersystem crossing, in the past, the development of RTP molecules was mainly limited to transition metals complexes.[2] Recently, a large amount of research work has been devoted to developing metal-free organic phosphors because of their low toxicity and environmentally benign nature over their inorganic counterparts. However, organic phosphors exhibit weak luminescence with low quantum yields at ambient conditions because of weak intersystem crossing.[3] Thus, developing organic phosphors with improved ISC and PL quantum yield is an important and challenging area of research.



We have been involved in developing multi-functional molecules by constraining their molecular conformations.[4] From our previous studies, we realized that the conformation of the molecule plays a significant role in controlling the energy and mixing of the electronically excited states, thereby curbing the undesirable intermolecular interactions (π-π interactions), which are detrimental to the PL quantum yield.[5] As part of the ongoing program, we designed and synthesized phosphoramides **TPTZPO**, **TPTZPS** and **TPTZPSe**, considering that the nonplanar heterocycle phenothiazine would enhance SOC by mixing molecular orbitals with different symmetry. Further, covalently linking a P=X (X = O/S/Se) group to phenothiazine can enhance the SOC and intersystem crossing via n-π* interactions. All the compounds show structured fluorescence with a nanosecond lifetime in dilute solutions. In the solid-state, they show dual fluorescence and room temperature phosphorescence (RTP). Both intensity and energy of luminescence depend on the nature of heteroatom attached to the phosphorous center. The detailed steady-state and time-resolved photoluminescence studies and computational calculations show that the phosphorescence of these compounds originates from the triplet n-π* state dominated by phenothiazine moiety. Compounds **TPTZPS** and **TPTZPSe** crystallized in enantiomerically pure form and showed intriguing chiroptical properties in the solid state.

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PP-43

Tuning of phosphorescence emission via substituent modulation in *N*-borylated carbazoles showing engrossing deep blue emission.

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ABSTRACT

Substituting isoelectronic B–N units for C=C units in π-conjugated systems produce novel materials with structural similarities to all-carbon frameworks but fundamentally altered electronic and optical properties.[1] Further, the co-occurrence of excited states with different symmetry (π-π* and n-π*) should facilitate effective spin-orbit coupling and enhance ISC and rISC process.[2] Though BN/CC isosterism known for several decades, however, this concept has not been demonstrated. Recently, by exploiting the BN/CC isosterism and topochemistry our group has developed highly sought-after deep-blue delayed fluorescent materials.[3.a] We have also developed an exciting strategy for the rational design and construction of novel materials by replacing the carbon-carbon double bond in tetraarylethylene systems with an isoelectronic boron-nitrogen unit.[3] For the first time, this approach led to the identification of the intriguing aggregation-induced emission enhancement (AIEE)[3.c] and mechanoluminescence properties of *tetra*-arylaminoboranes (TAAB).[3.d] As part of the ongoing program, we have designed and synthesized a series of N-borylated carbazole derivatives with different substituents on carbazole donor and/or the diarylborane (BAr_2) acceptor moieties. The phosphorescence emission color of these compounds were tuned from green to blue with improved luminescence quantum efficiency by modulating the electronic and steric factors. Interestingly, compounds bearing a smaller number of methyl substituents are strongly emissive than its higher homologue, revealing the effect of the number of methyl substitutions in the emission process. The dynamics of the excited state of aminoboranes have been investigated in polar and nonpolar solvents using the subpicosecond time-resolved absorption spectroscopic technique. The results showed that aminoboranes show stimulated emission before undergoing singlet to intersystem triplet crossing.

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PP-44

Water Stable Germylenes and their Biological Applications

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ABSTRACT

Germylenes require an inert atmosphere for their stability.[1] If they are made stable under ambient conditions, their applications in various fields can be explored; one such domain is bioorganometallic chemistry.[2] Herein, we present the synthesis of air, water, and culture-medium stable germylene hydroxide DPMGeOH (**3**) and its biological applications.[3] Compound **3** shows dose-dependent and cell-type-specific cytotoxicity towards human cancer cell lines (HeLa, MCF7, and Huh7). Its antiproliferative effects on human cancer cell lines MCF7 and Huh7 were marginally better than that of cisplatin, while on HeLa cells, the results are comparable. The cytotoxicity of compound **3** on normal epithelial cells derived from an African green monkey (Vero cells) is minimal and is like that of the currently used anticancer drugs. Further details of the work will be presented in the poster.

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PP-45

Unusual Access to flexible β-diketiminate and Pyridylpyrrolido ligand Based Germanium and Tin Chemistry

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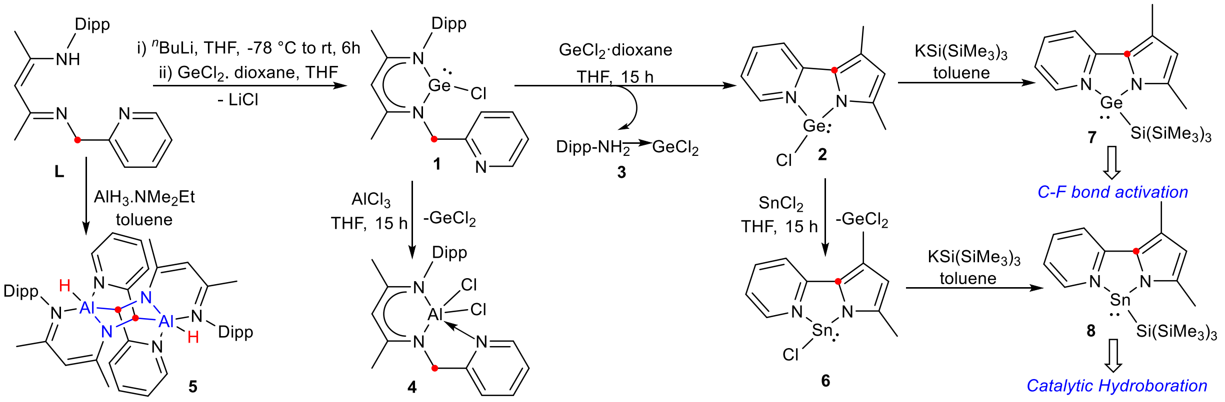
ABSTRACT

A nacnac-based tridentate ligand containing a picolyl group (**L**) was employed to isolate a new chlorogermylene (**1**). The reaction of 1 with another equivalent of $GeCl_2$·dioxane surprisingly gave pyridylpyrrolide-based chlorogermylene (**2**) via C–N bond cleavage and C–C coupling, while with $AlCl_3$, it afforded a transmetalated product, **4**. Similarly, the reaction between **2** and $SnCl_2$ led to the formation of analogous chlorostannylene (**6**) with the simultaneous exclusion of $GeCl_2$. These are very unusual examples of transmetallation between two main-group elements. The reaction of **L** with $AlH_3.NMe_2Et$ led to an unusual cyclohexane type six-membered dialane heterocycle (**5**). Subsequently, **2** and **6** were used as precursors to generate germylene (**7**) and stannylene (**8**) featuring tris(trimethylsilyl)silyl (hypersilyl) moieties. We also prepared tetrafluoropyridyl germylene (**9**) by reacting **7** with C_5F_5N with the simultaneous elimination of $(Me_3Si)_3SiF$ by utilizing the fluoride affinity of the silicon atom. As there is a scarcity of using Sn(II) compounds as single-site catalysts, we investigated **8** as a catalyst towards the hydroboration of aldehydes, ketones, alkenes and alkynes.



Scheme 1: Synthesis of compounds 1-8

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