COPPER-CHALCOGEN COMPLEXES AND NANOPARTICLES IN CATALYTIC FORMATION OF C-X (X = C, N, O) BONDS WITH TERTIARY AMINES

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by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

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Dedicated to my beloved parents

CERTIFICATE

This is to certify that the thesis entitled, **"COPPER-CHALCOGEN COMPLEXES AND NANOPARTICLES IN CATALYTIC FORMATION OF C-X (X = C, N, O) BONDS WITH TERTIARY AMINES"** being submitted by **Mr. SONU GUPTA** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. Sonu Gupta has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

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ABSTRACT

Chapter 1 An overview of the various types of coupling reactions such as C-H functionalization and cross dehydrogenative coupling reactions has been provided. The importance of single source precursor route in the synthesis of copper chalcogen nanoparticles, and role of pincer complexes in catalysis has been highlighted. Heterogeneous catalysts stabilized by graphene oxide have been discussed.

Chapter 2 Copper chalcogenide nanoparticles (Cu_2S) synthesized for the first time from a single source precursor, CuSPh act as highly efficient and reusable heterogeneous catalyst for regioselective amination of *N*,*N*-dimethylbenzylamines with various azoles. The reaction involves N−H/C−H cross-dehydrogenative coupling (CDC) and demonstrates wide functional group tolerance. It provides a highly selective access to N^1-alkylated benzotriazoles, N^2-alkylated 1,2,3-triazoles & 4-phenyl-1,2,3-triazoles, and *N*-alkylated carbazoles in 70-89% yields under solvent free conditions. The Cu_2S nanocatalyst has been characterized by PXRD, XPS, SEM-EDX and HR-TEM analysis. Mechanistic studies suggest the reaction to follow a radical pathway and involve an iminium ion intermediate.

Chapter 3 Copper chalcogenide nanoparticles (Cu_7S_4) supported on graphene oxide (GO) have been synthesized for the first time from Cu_2S, and used as highly efficient heterogeneous catalysts for oxidative *ortho*-selective C–H aminomethylation of phenols with *N*,*N*-dimethylbenzylamines. The NPs (30–80 nm) have been characterized by HRTEM, SEM-EDX, PXRD, FTIR, Raman, ICP-AES and XPS analyses. The NP catalyzed sp2–sp3 cross dehydrogenative coupling (CDC) features a broad substrate scope, excellent functional group tolerance, high yields, use of an inexpensive and reusable copper catalyst, mild conditions, and no need for pre-functionalization of substrates.

Chapter 4 The use of copper selenide nanocatalyst for an efficient and regioselective cross-dehydrogenative coupling (CDC) of tertiary amines with terminal alkynes in the presence of *tert*-butyl hydroperoxide as the oxidant is demonstrated for the first time. The catalyst comprising of unique $Cu_6Se_{4.5}$ nanoparticles synthesized from a single source precursor CuSePh, is required in much lower amount (1 mol%), and is recyclable up to four reaction cycles with slight loss in activity. The reaction can be executed in the absence of solvent, is applicable to aromatic, benzylic, and aliphatic tertiary amines, and furnishes propargylamines in moderate to good yields.

Chapter 5 Cross dehydrogenative coupling of unactivated tertiary amines and unactivated terminal alkynes have been catalyzed efficiently with the help of thermally stable, moisture and air insensitive Cu(I) complexes, [Cu**L**Br] **(C1** and **C2),** **L**= (E N E) of pincer ligand, 4,5-bis((phenylthio/seleno)methyl)acridine (**L1**/**L2)** at a low reaction temperature of 60 ^{o}C only. The **C1** and **C2** also affected catalytic oxidative cleavage of benzylic (C-N) bond of *N*,*N* dimethylbenzylamines yielding benzaldehyde under aerobic and solvent-free conditions. A low catalytic loading of 1.0 mol% was good enough to bring about these conversions. Reaction was highly selective, and over-oxidation to acid did not take place. **L** was synthesized by treating of *in situ* generated PhS/SeNa with 4,5-bis(bromomethyl)acridine under N_2 atmosphere. The complexes (**C1/C2**) were prepared by reacting $CuBr.SMe_2$ with **L1**/**L2** in CH_2Cl_2 for 12 h at room temperature. The ligands and their complexes were characterized by elemental analyses, ^{1}H, ^{13}C{^{1}H} and ^{77}Se{^{1}H} NMR (**L2** and **C2** only), HR-MS and single-crystal X-ray diffraction. The bond distances (Å) in **C1**/**C2** were found to be consistent with the earlier reports. In both complexes **C1** and **C2,** ligands **L1** and **L2**, coordinated with the metal in a pincer mode furnishing two six-

membered chelate rings. The geometry of donor atoms around Cu in the complexes is distorted tetrahedral.

सार

अध्याय 1 विभिन्न प्रकार के युग्मन प्रतिक्रियाओं का अवलोकन जैसे कि C-H क्रियाशीलता और पार-निर्जलीकरण युग्मन प्रतिक्रियाएं प्रदान की गई हैं। कॉपर-चाल्कोजन नैनोकणों के संश्लेषण में एकल स्रोत अग्रदूत मार्ग का महत्व, और उत्प्रेरण में पिंसर परिसरों की भूमिका पर प्रकाश डाला गया है। ग्राफीन ऑक्साइड द्वारा स्थिर किए गए विषम उत्प्रेरक पर चर्चा की गई है।

अध्याय 2 कॉपर-चेल्कोजेनाइड नैनोकणों (Cu_2S) को एक एकल स्रोत अग्रदूत CuSPh से पहली बार संश्लेषित किया गया, विभिन्न एज़ोल्स के साथ N, N-डाइमिथाइलबेंज़ाइलएमीन के अत्यधिक कुशल और पुन: प्रयोज्य विषम उत्प्रेरक के रूप में कार्य करता है। प्रतिक्रिया में N-H / C-H पार निर्जलीकरण युग्मन (CDC) शामिल है और व्यापक कार्यात्मक समूह सहिष्णुता को प्रदर्शित करता है। यह N1-अल्काइलेटेड बेंज़ोट्रायज़ोल्स, N2-अल्काइलेटेड 1,2,3-ट्रायज़ोल्स और 4-फ़िनाइल-1,2,3-ट्रायज़ोल्स, और N-अल्काइलेटेड कार्बाज़ोल्स में 70-89% विलायक मुक्त परिस्थितियों में अत्यधिक चयनात्मक पहुंच प्रदान करता है। Cu_2S नैनोउत्प्रेरक को PXRD, XPS, SEM-EDX और HR-TEM विश्लेषण द्वारा चित्रित किया गया है। यंत्रवत अध्ययन एक रेडिकलाइज़ेशन मार्ग का अनुसरण करने और एक इमीनियम आयन मध्यवर्ती को शामिल करने की प्रतिक्रिया का सुझाव देते हैं।

अध्याय 3 ग्राफीन ऑक्साइड (GO) पर सपोर्टेड कॉपर-चेल्कोजेनाइड नैनोकणों (Cu_7S_4) को पहली बार Cu_2S से संश्लेषित किया गया है, और N, N-डाइमिथाइलबेंज़ाइलएमीन के साथ फिनोल के ऑर्थो-चयनात्मक C-H एमिनोमिथाइलेशन के लिए अत्यधिक कुशल विषम उत्प्रेरक के रूप में उपयोग किया गया है। नैनोकणों (30-80 nm) को HR-TEM, SEM-EDX, PXRD, FTIR, Raman, ICP-AES और XPS विश्लेषण द्वारा चित्रित किया गया है। नैनोकण उत्प्रेरित sp^2-sp^3 पार निर्जलीकरण युग्मन (CDC) एक व्यापक सब्सट्रेट गुंजाइश, उत्कृष्ट कार्यात्मक समूह सहिष्णुता, उच्च पैदावार, एक सस्ती और पुन: प्रयोज्य कॉपर उत्प्रेरक का उपयोग, माइल्ड परिस्थितियों, और सब्सट्रेट के पूर्व-कार्यात्मककरण की कोई आवश्यकता नहीं है।

अध्याय 4 एक कुशल और रेजिओसेलेक्टिव कॉपर सेलेनाइड नैनोउत्प्रेरक का उपयोग पार निर्जलीकरण युग्मन (CDC) के लिए तृतीयक एमाइन के साथ टर्मिनल अल्काइन का, तथा ऑक्सीडेंट के रूप में पहली बार *tert*-butyl हाइड्रोपरऑक्साइड की उपस्थिति में प्रदर्शन किया गया है। एकल स्रोत अग्रदूत, CuSePh से संश्लेषित अद्वितीय $Cu_6Se_{4.5}$ नैनोकण उत्प्रेरक, बहुत कम मात्रा (1 मोल%) में आवश्यक है, और गतिविधि में मामूली नुकसान के साथ चार प्रतिक्रिया चक्रों तक पुनर्नवीनीकरण प्रतिक्रिया होती है। प्रतिक्रिया को विलायक की अनुपस्थिति में निष्पादित किया जा सकता है, यह एरोमैटिक, बेंज़िलिक, और एलीफैटिक तृतीयक अमाइन पर लागू होता है, और मध्यम से अच्छे यिल्ड्स में प्रोपार्जीलअमीन्स प्रस्तुत करता है।

अध्याय 5 पार निर्जलीकरण युग्मन (CDC) द्वारा निष्क्रिय तृतीयक अमाइन और निष्क्रिय टर्मिनल अल्काइन को थर्मली स्थिर, नमी और वायु असंवेदनशील कॉपर(I) परिसर, [CuLBr] (**C**1 और **C**2), पिंसर लिगैंड का L = (E N E), 4,5-बिस((फिनाइलथायो/सेलेनो)मिथाइल)एक्रिडिन (L1 / L2) केवल 60 °C की कम प्रतिक्रिया तापमान पर कुशलता से उत्प्रेरित किया गया है। C1 और C2 ने एरोबिक और विलायक मुक्त परिस्थितियों में बेंजाल्डिहाइड का निर्माण करने वाले N, N-डाइमिथाइलबेंज़ाइलएमीन के बेंजोइल (C-N) बंधन के उत्प्रेरक ऑक्सीडेटिव ब्रेकिंग को भी प्रभावित किया है। कम उत्प्रेरक लोडिंग 1.0 मोल% इन रूपांतरणों को लाने के लिए काफी अच्छा था। प्रतिक्रिया अत्यधिक चयनात्मक थी, और एसिड के लिए अति-ऑक्सीकरण नहीं हुआ था। ***insitu*** N_2 वायुमंडल में PhS/SeNa उत्पन्न द्वारा 4,5-बिस(ब्रोमोमिथाइल)एक्रिडिन के साथ उपचारित करके **L** को संश्लेषित किया गया था। $CuBr.SMe_2$ के साथ CH_2Cl_2 में L1 / L2 कमरे के तापमान पर 12 घंटे के लिए प्रतिक्रिया करके परिसर (**C**1 / **C**2) तैयार किए गए थे। लिगेंड और उनके परिसर तात्विक विश्लेषण, ^{1}H, $^{13}C\{^{1}H\}$ और $^{77}Se\{^{1}H\}$ NMR (L2 और **C**2) केवल), HR-MS और एकल-क्रिस्टल एक्स-रे विवर्तन विश्लेषण द्वारा चित्रित किया गया है। **C**1 / **C**2 में बांड की दूरी पहले की रिपोर्टों के अनुरूप पाए गए। **C**1 और **C**2 दोनों परिसरों में, लिगेण्ड्स L1 और L2, पिंसर मोड में धातु के साथ समन्वित होते हैं जो दो छह-सदस्यीय कीलेट रिंगों को प्रस्तुत करते हैं। परिसरों में कॉपर के आसपास दाता परमाणुओं की ज्यामिति विकृत टेट्राहेड्रल है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
δ	chemical shift
ν	frequency
Å	angstrom
nm	nanometer
Ar	Aryl
µL	microlitre
°C	degree centigrade
br	broad signal
n-Bu	*n*-butyl
C_q	quaternary carbon
C−C	carbon−carbon
cm	centimeter
CH_2Cl_2	dichloromethane
$CHCl_3$	chloroform
CH_3CN	acetonitrile
d	doublet
DCM	dichloromethane
DMA	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
e.g.	for example
g	gram
h	hour
HR	high resolution
Hz	hertz
i.e.	that is
kV	kilovolt
m	multiplet
m/z	mass/charge
MHz	megahertz

M^+	molecular ion
M	molar
mmol	millimole
mol	mole
mL	milliliter
m.p.	melting point
NMP	*N*-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
Pd	palladium
Ph	phenyl
n-Pr	*n*-propyl
S	sulfur
Se	selenium
SMC	Suzuki-Miyaura Coupling
t	triplet
q	quartet
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	tetrametylsilane
XRD	x-ray diffraction
EDX	*Energy-dispersive X*-ray spectroscopy
Equiv	Equivalent
^{19}F	19 Fluorine
eV	Electron volt
GO	Graphene oxide
JCPDS	Joint Committee on Powder-
	-Diffraction Standards
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
SMART	Substituted methoxybenzoyl-aryl-thiazole
PXRD	Powder X-ray diffraction
Rpm	Rotation per minute
r.t.	Room temperature

SEM	Scanning electron microscope
TBHP	*tert*-butyl hydroperoxide
t-Bu	Tertiary butyl
TEM	Transmission electron microscope
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy
UV	Ultra-Violet
Vis	Visible
XPS	X-ray Photoelectron *Spectroscopy*
α	Alpha
β	Beta
ϒ	Gamma