PALLADIUM CATALYZED CARBON-CARBON BOND FORMATION

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PALLADIUM CATALYZED CARBON-CARBON BOND FORMATION

by

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Department of Chemistry

Submitted

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CERTIFICATE

This is to certify that the thesis entitled, **"PALLADIUM CATALYZED CARBON-CARBON BOND FORMATION"** being submitted by **Miss CHANCHAL PREMI** to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by her. **Miss Chanchal Premi** has worked under my guidance and supervision. She has fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

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

Date:

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Chanchal Premi

ABSTRACT

Chapter 1: An overview of the use of palladium as catalyst in cross-coupling and C-H functionalization reactions has been provided, role of ligands, pre-formed Pd catalyst, and directing group assisted strategy has been emphasized. Heterogeneous catalyst on graphene has been discussed.

Chapter 2: $Pd(OAc)_2$-catalyzed decarboxylative alkylation of unactivated arenes with aliphatic carboxylic acids as inexpensive alkyl source is demonstrated. The alkylation is controlled by the directing group, and is regioselective in nature. It shows high functional group tolerance, and provides mild access to alkylated indolines, 2-phenylpyridines, and azobenzenes under solvent-free conditions in moderate to good yields.

Chapter 3: A palladium catalyzed regioselective *ortho*-acylation of *N*-aryl-1,2,3-triazoles has been discussed under aqueous conditions without the assistance of any surfactant or additive. The reaction takes place with benzylic, heterocyclic, as well as aliphatic alcohols as the acylating reagents, and TBHP as the oxidant. The method provides a mild and easy route for synthesis of triazole substituted aryl, heteroaryl, and aliphatic ketones in excellent yield.

Chapter 4: Palladium nanoparticles (PdNPs) 2–5 nm in size, and preformed by thermal reduction in nitrile-functionalized 3-(3-cyanopropyl)-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate {[CN-bmim]PF_6} act as an *in situ* catalyst for carbon–carbon bond-forming reaction of aromatic and heterocyclic halides with aryl- and vinyltrimethoxysilanes. A variety of biphenyl derivatives, substituted styrenes, and aromatic heterocycles have been synthesized by employing this catalyst. Use of 1-butyl-3-methylimidazolium fluoride as an activator of the organosilanes is shown. The NPs could be reused and recycled up to four times with only a slight loss in catalytic activity.

Chapter 5: A nanocomposite comprising of PdNPs supported on chemically modified graphene (CMG) has been fabricated. The efficacy of CMG-PdNP system as a catalyst towards Heck cross coupling reaction with a variety of functionalized substrates has been demonstrated. Functionalization of reduced graphene oxide with heteroatoms like sulfur and nitrogen enhanced its dispersibility in organic solvents, and also help in stabilizing the active palladium species by acting as a ligand. The CMG-Pd composite exhibits an excellent catalytic activity with a substantially low catalytic loading (0.02 mol %), with the activity sustainable up to three reaction cycles.

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

Å	:	Angstrom
a.u	:	Arbitatry unit
AAPTMS	:	[3-(2-Aminoethylamino)propyl]trimethoxysilane
Ac	:	Acetic
Alk	:	Alkyl
Approx.	:	Approximately
Ar	:	Aryl
BINAP	:	2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene
BMI.PF_6	:	1-*n*-butyl-3-methylimidazolium hexafluorophosphate
Boc	:	*tert*-butyloxycarbonyl
BQ	:	Benzoquinone
^{13}C	:	13Carbon
Cat	:	Catalyst
CMG	:	Chemically modified graphene
CNSs	:	Carbon nanosheets
CNT	:	Carbon nanotubes
cps	:	Counts per second
Cy	:	Cyclohexyl
DCE	:	Dichloromethane
DLS	:	Dynamic light scattering
DMA	:	Dimethylacetamide
DMF	:	Dimethylformamide
DMSO	:	Dimethyl sulfoxide
Dppe	:	Ethylenebis(diphenylphosphine)
EDX	:	Energy-dispersive X-ray spectroscopy

Equiv	:	Equivalent
Et	:	Ethyl
eV	:	Electron volt
^{19}F	:	19 Fluorine
Fcc	:	Face centered cubic
FTIR	:	Fourier transform infrared spectroscopy
G	:	Gram
GL-Pd	:	Graphene ligand-palladium complex
GO	:	Graphene oxide
GSH	:	Thiol-functionalized GO
GS-Py	:	GSH-pyridine ligand
^{1}H	:	Proton
h	:	Hour
Hz	:	Hertz
ICP-MS	:	Inductively coupled plasma mass spectrometry
IL	:	Ionic liquid
i-Pr	:	*iso*-propyl
IPr	:	*N*,*N*'-bis(2,6- diisopropylphenyl)imidazol-2-ylidene
JCPDS	:	Joint Committee on Powder Diffraction Standards
kV	:	Kilovolt
L	:	Litre
M	:	Molar
mg	:	Milligram
MIDA	:	*N*-methyliminodiacetic acid
min	:	Minute
mL	:	Millilitre

mmol	:	Millimol
NBS	:	*N*-bromosuccinimide
n-Bu	:	Butyl
NHC	:	*N*-heterocyclic carbene
nm	:	Nanometer
NMR	:	Nuclear magnetic resonance
%	:	Percent
PdNPs	:	Palladium nanoparticles
Piv	:	Pivalic
Ppm	:	Parts per million
PTC	:	Phase transfer catalyst
PTSA	:	*para*-toluenesulfonic acid
PXRD	:	Powder X-ray diffraction
Pym	:	Pyrimidine
rGO	:	Reduced graphene oxide
Rpm	:	Rotation per minute
Rt	:	Room temperature
S.No	:	Serial number
SDS	:	Sodiumdodecasulfate
sec	:	Secondary
SEM	:	Scanning electron microscope
SIPr	:	*N*,*N*'-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene
TBAB	:	Tetrabutylammonium bromide
TBAF	:	Tetrabutylammoniumfluoride
TBAI	:	Tertabutylammoniumiodide
TBHP	:	*tert*-butyl hydroperoxide

t-Bu	:	Tertiary butyl
TEAB	:	Tetraethylammonium borohydride
TEM	:	Transmission electron microscope
Temp	:	Temperature
TEMPO	:	2,2,6,6-Tetramethyl-1-piperidinyloxy
Tert	:	Tertiary
TFA	:	Trifluoroacetic acid
TFE	:	Trifluoroethanol
THF	:	Tetrahydrofuran
TLC	:	Thin layer chromatography
TMEDA	:	*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine
UV	:	Ultra-Violet
Vis	:	Visible
XPS	:	X-ray Photoelectron Spectroscopy
α	:	Alpha
β	:	Beta
μL	:	Microlitre
π	:	Pie
ϒ	:	Gamma

MATERIALS AND METHODS

Physical measurement:

The size of nanoparticles was determined by Malvern DLS nano ZS90. EDX spectra were recorded on ZEISS EVO 50 model QuanTax 200 which is based on the SDD technology and provides an energy resolution of 127 eV at Mn K alpha. Elemental analysis was carried out on Perkin-Elmer 2400 Series II CHNS/O analyzer. HRMS were recorded on micrOTOF-Q ll 228888.10262 using electrospray ionization (ESI) as the ionization method. Inductively Coupled Plasma Mass Spectrometry or ICP-MS on Agilent ICP-MS 7900. NMR spectra (^{1}H and ^{13}C) were measured on a Bruker DPX-300 MHz spectrometer (^{1}H 300 & 400 MHz, ^{13}C 75MHz).

Powder X-ray diffraction (PXRD) data was collected on X-ray diffractometer (Bruker). Raman spectroscopy was performed using the 2.54 eV (488 nm) line of an Ar ion laser on a HORIBA JOBIN YVON Lab RAM HR 800 instrument by placing a pellet on a cleaned glass slide. Scanning electron microscopy (SEM) image was captured with a Zeiss Evo series SEM model EVO 50. The sample was then coated in a sputter coater (EMITECH K 550 x) with a gold layer in vacuum.

Single-crystal X-ray data of compounds was collected on Bruker SMART CCD-Diffractometer using graphite monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). The data integration and reduction were processed with Crys Alis Pro software. The structures were solved by the direct method and then refined on $F2$ by the full matrix least-squares technique with the SHELX-97 set of software using the WinGX (version 1.80.05) program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have been drawn using ORTEP software. Copies of the data can be found free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk.

TEM analyses were performed on Delong instrument, Q imaging Retiga 4000 R by dropping 10µL of dispersed solution in HPLC grade hexane on copper grid. High resolution transmission electron microscope (HRTEM) experiments were conducted in a JEM-2010 FEI TEM with an accelerating voltage of 200 KV. UV-vis spectroscopy was recorded on Lambda

Bio 20, Perkin Elmer. X-ray photoelectron spectroscopy (XPS) was carried out on SPECS, MCD-9, serial number-172-05.01.

Analytical Information:

All the isolated compounds were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy and HRMS using $CDCl_3$ and DMSO as the solvents with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ (ppm) relative to TMS, the coupling constants (*J)* are given in Hz.

Chemicals and reagents:

All reactions were carried out under air in septum covered oven dried round bottom flask/10 mL vial. All the solvents were bought from Aldrich, Spectrochem and Alfa-aesar were used as received. Palladium (II) acetate was purchased from Alfa-Aesar (98% purity). For column chromatography, silica gel (230–400 mesh) from SRL Co. was used. A gradient elution using ethyl acetate-hexane was performed on Merck aluminium TLC sheets (silica gel 60F254).