N-heterocyclic carbene stabilized threecoordinate Cu(I) complexes

M.Sc. Thesis

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DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE

MAY 2022

N-heterocyclic carbene stabilized threecoordinate Cu(I) complexes

A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree of

Master of Science

by

Sujitaben gamit



DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE MAY 2022



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby commit that the work which is being proposed in the thesis entitled **N-heterocyclic carbene stabilized three-coordinate Cu(I) complexes** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY INDORE**, is an authentic record of my own work done during the time period from August 2021 to May 2022 under the supervision of Dr. Abhinav Raghuvanshi, Assistant Professor, IIT Indore. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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This is to confirm that the above statement made by the candidate is right to the best of my/our knowledge.

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ACKNOWLEDGEMENTS

This thesis could not have been accomplished without a great deal of guidance and support. I would like to sincerely thank those people who provided me with everything I needed during these months in which this project lasted. I wish to express my feeling to those whose support and motivation made it possible to present my research work in the form of a dissertation.

First of all, I would like to thank my thesis supervisor **Dr. Abhinav Raghuvanshi** for valuable guidance, suggestions and supervision, and constant encouragement throughout my research work. Further, I would like to thank my PSPC members, **Dr. Shaikh M. Mobin** and **Prof. Rajneesh Misra**, for their valuable suggestions and support. I am highly obliged to take the opportunity to sincerely thank all the faculty members, seniors (research scholars), SIC staff of **IIT INDORE** for their help and cooperation during this dissertation work. I wish to express my special thanks to the lab mates. Despite your own project, you never hesitated to answer my questions to help me out with the project's motto. All the things that you were willing to share with me were highly inspiring, not only for this specific project but also for the communication practice in general as well.

I want to extend my thanks to my batch mates who were always there and never let me down during these M.Sc. days. Last but not least, I would like to pay sincere gratitude to my loving parents for their continuous help and moral support throughout my project work. Dedicated to....

My Family

ABSTRACT

In this project, effectiveness of substituents existing on the ligands on the photophysical property of heteroleptic copper(I) complexes bearing both Nheterocyclic carbenes (NHCs) and phenanthroline based ligands have been studied. Two N-heterocyclic carbene copper chloride (NHC-CuCl) ligands, IMes-CuCl, and Ipr-CuCl [IMes-CuCl = 1,3-bis(2,4,6-trimethylphenyl) imidazolium copper chloride. IPr-CuCl = 1.3-bis(2.6diisopropyl)imidazole-2-ylidene copper chloride, complexes has been prepared. We delineate the synthesis of tri-coordinated copper complexes bearing bidentate phenanthroline based ligands in good yield from (IPr)Cu(Cl). In the thesis, synthesis of three coordinated NHC-copper(I) complexes; [(IPr)Cu(dafo)]PF₆ (1), [(IMes)Cu(dafo)]PF₆ (2), $[(IPr)Cu(phendione)]PF_6(3)$ and $[(IMes)Cu(phendione)]PF_6(4)$ (IPr = 1,3bis(2,6-diisopropylphenyl)imidazole-2-ylidene, IMes = (1E,2E)-dimesityle ethane-1,2-diimine, dafo = 4,5-diazafluoren-9-one, phendione = 1,10phenanthroline-5,6-dione, PF_6 = Hexafluorophosphate have been explained. All the complexes have been characterized by NMR and Mass spectroscopic techniques. In addition, the photophysical properties were also studied.

TABLE OF CONTENTSLIST OF FIGURESxivLIST OF SCHEMESxviLIST OF ACRONYMSxviiLIST OF NOMENCLATURExviii

CHAPTER 1: INTRODUCTION

1. General Introduction	1-4

CHAPTER 2: EXPERIMENT METHOD

2.1. General procedures for Synthesis of precursors	
2.1.1. Synthesis of (1E,2E)-N,N`-bis-(2,6-diisopropylphenyl)ethane-1,2	
diimine	5
2.1.2. Synthesis of (1E,2E)-dimesitylethane-1,2-diimine	6
2.1.3. Synthesis of 1,3-Bis-(2,6- diisopropylphenyl) imida-	
Zoliumchloride	7
2.1.4 Synthesis of 1,3-dimesityl-1H-imidazol-3-ium chloride	7
2.1.5. Synthesis of 1,3-Bis-(2,6-diisopropyiphenyl)imidazole-2-ylidene	;
copper chloride	8
2.3. GENERAL PROCEDURE FOR SYNTHESIS OF LIGANDS	
2.3.1. Synthesis of 1,3-Bis-(2,6-diisopropyiphenyl)imidazole-2-ylidene	
copper chloride	9

2.3.2. Synthesis of mesityl carbene copper chloride	9
2.3.3. Synthesis of 4,5-diazafluoren-9-one	10
2.3.4. Synthesis of 1,10-phenanthroline-5,6-dione	10
2.4. PROCEDURE FOR SYNTHESIS OF COMPLEXES	
2.4.1. Synthesis of complex [(IPr)Cu(dafo)]PF ₆ (1)	11
2.4.2. Synthesis of complex [(IMes)Cu(dafo)]PF ₆ (2)	12
2.4.3. Synthesis of complex [(IPr)Cu(phendione)]PF ₆ (3)	13
2.4.4. Synthesis of complex [(IMes)Cu(phendione)] $PF_6(4)$	14
CHAPTER 3: RESULTS AND DISCUSSION	
3.1. Synthesis and characterization of complexes	15-38

CHAPTER 4: CONC	LUSION 39

REFERENCES	40
------------	----

LIST OF FIGURES

Figure 1. ¹ H NMR spectrum of 1a in CDCl ₃	15
Figure 2. Mass spectrogram of 1a in MeOH	16
Figure 3. ¹ H NMR spectrum of 2a in CDCl ₃	17
Figure 4. Mass spectrogram of 2a in MeOH	17
Figure 5. Plausible mechanism got synthesis of imine	18
Figure 6. ¹ H NMR spectrum of 1b in CDCl ₃	19
Figure 7. Mass spectrogram of 1b in MeOH	20
Figure 8. Mass spectrogram of 2b in MeOH	20
Figure 9. Plausible mechanism got the synthesis of imidazolium	
Chloride	21
Figure 10. 1H NMR spectrum of 1b in CDCl ₃	22
Figure 11. Mass spectrogram of 1c in MeOH	23
Figure 12. ¹ H NMR spectrum of 2c in CDCl ₃	24
Figure 13. Mass spectrogram of 2c in MeOH	25
Figure 14. ¹ H NMR spectrum of 3c in CDCl ₃	26
Figure 15. Mass spectrogram of 3c in MeOH	26
Figure 16. ¹ H NMR spectrum of 4c in CDCl ₃	27
Figure 17. Mass spectrogram of 4c in MeOH	28
Figure 18. ¹ H NMR spectrum of complex 1 in CDCl ₃	29
Figure 19. Mass spectrogram of complex 1 in ACN	30

Figure 20. ¹ H NMR spectrum of complex 2 in CDCl ₃	31
Figure 21. Mass spectrogram of complex 2 in MeOH	32
Figure 22. ¹ H NMR spectrum of complex 3 in CDCl ₃	33
Figure 23. Mass spectrogram of complex 3 in ACN	34
Figure 24. ¹ H NMR spectrum of complex 4 in DMSO-D ₆	35
Figure 25. Mass spectrogram of complex 3 in ACN	36
Figure 26. Excitation spectrum of complex 1	36
Figure 27. Emission spectrum of complex 1	37
Figure 28. Excitation spectrum of complex 2	37
Figure 29. Emission spectrum of complex 2	38

SCHEMES

Scheme 1. Synthesis of (1E,2E)-N,N⁻-bis-(2,6-diisopropylphenyl)ethane-1,2-diimine

Scheme 2. Synthesis of (1E,2E)-dimesitylethane-1,2-diimine

Scheme 3. Synthesis of 1,3-Bis-(2,6- diisopropylphenyl) imidazoliumchloride

Scheme 4. Synthesis of 1,3-dimesityl-1H-imidazol-3-ium chloride.

Scheme 5. Synthesis of 1,3-Bis-(2,6-diisopropyiphenyl)imidazole-2ylidene copper chloride

Scheme 6. Synthesis of mesityl carbene chloride

Scheme 7. Synthesis of 4,5-diazafluoren-9-one

Scheme 8. Synthesis of 1,10-phenanthroline-5,6-dione

Scheme 10. Synthesis of [(IPr)Cu(dafo)]PF₆

Scheme 11. Synthesis of [(IMes)Cu(dafo)]PF₆

Scheme 12. Synthesis of [(IPr)Cu(phendione)]PF₆

Scheme 13. Synthesis of [(IPr)Cu(phendione)]PF₆

ACRONYMS

CH ₃ CN	Acetonitrile
CDCl ₃	Chloroform-D
DMSO-D ₆	Deuterated dimethyl sulfoxide
EtOAc	Ethyl acetate
CH ₃ OH	Methanol
Me	Methyl
Μ	Molar

NOMENCLATURE

cm	Chemical shift
cm	Centimeter
٥C	Degree Celsius
mL	Milliliter
mmol	Millimole
nm	Nanometer
π	pi
rt	Room temperature

CHAPTER 1

INTRODUCTION

1.1 General Introduction

The development of advanced photoactive materials has been a hot research topic since it has a wide range of applications in organic light-emitting diodes (OLEDs),¹ photosensitizers, sensors, bioimaging, and electron transfer agents in photocatalytic reactions.² The various applications lead to the enhancement of such energy-saving research or new technologies that demand emissive materials that do not lead to the degradation of natural resources. The first generation of OLEDs incorporated emitters following the fluorescence process that could achieve only 25% of the internal quantum efficiency (IQE). The second-generation emitters involve the phosphorescence process that can achieve 100% IQE. However, these emitters require the presence of heavy metals like platinum, iridium, etc., for efficient phosphorescence. For example, transition metal complexes of 4d and 5d, mainly Ru^{II}, Re^I, Os^{II}, Ir^{III,} and Pt^{II} are used for phosphorescent emitters.³

Due to the high cost of noble metals and limited resources, third-generation emitters were introduced in the past 12-15 years that involve thermally activated delayed fluorescence termed TADF. For a molecule to show TADF, it requires a process called reverse intersystem crossing (RISC), where triplet exciton can be converted into singlet exciton when the energy difference between triplet and singlet excited is less. When there is a long lifetime of excited triplet state, and there is less energy gap between singlet and triplet state, RISC can occur at room temperature. This leads to populating S₁ from T₁ and finally, S₁ \rightarrow S₀ transition leads to emission, this process is termed TADF.⁴



Figure 1. Three generations of OLEDs



Figure. 2. Organic TADF and metal-based DF materials.

It requires a donor and acceptor unit to design the TADF active molecule that has a large molecular orbital separation to avoid mixing of energy states. Most of the organic TADF systems involve either a long bridging ligand or twisted π - systems. While in transition metals compound, there is no such requirement because of the nature of different types of orbitals involved in donor and acceptor units.⁵

Among the photoactive materials of 3d metals, copper holds a particular position. Particularly, Cu(I) having a d¹⁰ configuration is preferred over Cu(II), reducing non-radiative decay due to metal-centered d-d transition.⁶ Also, Cu(I) complexes are very flexible and can show geometries like 4-coordinated tetrahedral, 3-coordinated trigonal planar, and 2-coordinated linear. The presence of bulky substituents on the ligand leads to the formation of 2 and 3-coordinated complexes and also could reduce the non-radiative decay. Also, it has been observed that TADF is mainly seen in photoactive Cu(I) complexes which are heteroleptic in nature.⁷

Sauvage and McMillin discovered the first Cu(I) complex $[Cu(dmp)_2]^+$ (dmp=2,9-dimethyl-1,10-phenanthroline) which showed luminescence at room temperature.⁸ The transition of Cu(I) complexes from excited triplet state to singlet ground state or from ground states to excited triplet state is forbidden due to filled d-orbitals and weak spin-orbit coupling. So, a lack of luminescent properties, especially in mononuclear counterparts was observed. So in the charge recombination process, difficulty in gathering triplet excitons existed. Also, device stability through photochemical reactions and strong saturation effect was hampered by phosphorescence decay which took a longer time. In a recently published work, more efficient Cu(I) complex was obtained by using tridentate phosphine ligand 2,2[']-(phenylphosphinediyl)bis(2,1-phenylene)bis(diphenylphosphine).⁹

For the tri-coordinated compounds, it is essential to insert bulky ligands around the Cu(I) center to inhibit the structural changes in the excited states. This issue can also be tackled by using either a sterically congested bidentate N^N or P^P ligand with a monodentate carbene ligand to give ionic compound or anionic ligands like amine (eg. Carbazole, phenothiazine, etc.), halide, thiol with neutral bulky carbene ligand to give neutral compounds.¹⁰ (Figure 3)



Figure 3. Structures of three coordinate Cu(I) complexes.

In the quest to find mononuclear di and tri-coordinated copper complexes, Thompson et al. reported two luminescent tri coordinate copper complexes having N-heterocyclic carbene or cyclic alkyl amino carbene (CAACs) with phenanthroline and pyridine substituted benzimidazole. Since these complexes have two units, one is NHCs which can act as a sigma donor that strongly binds with the metals, and the second an acceptor unit bearing a phosphine donor or N-donor ligands, the origin of the luminescence mechanism can be metal-ligand charge transfer, triplet charge transfer or interligand charge transfer. In the aforesaid complexes, the origin of luminescence was found to be triplet charge transfer.¹¹

Here, we reported four, three coordinated Cu(I) complexes bearing two different NHC (IPr and IMes) and phenanthroline-based ligands. To get a wide range of color emissions, we can tune the HOMOs and LUMOs energies of the ligands.

CHAPTER 2

EXPERIMENTAL SECTION

2.1 MATERIALS AND INSTRUMENTATION:

Chemicals were used without purification as received unless otherwise indicated. All the complexation reactions were performed under the nitrogen atmosphere because of moisture and oxygen sensitivity. Some ligand synthesis was performed in air and checked by TLC using Merck 60 F254 pre-coated silica gel plate (0.25 mm thickness), and the product was judged under a UV chamber. Mass spectra were obtained through the Bruker Daltonik High-Performance LCMS spectrometer. NMR spectra were obtained on a Bruker 400/500 spectrometer in CDCl₃ or d₆-DMSO operating at 400/500 MHz for ¹H NMR. Chemical shifts are mentioned in delta (δ) units, shown in parts per million (ppm) downfield from tetramethylsilane (TMS). The residual protonated solvent as an internal standard is CDCl₃ showing a peak at 7.26 ppm. The ¹H NMR splitting patterns have been mentioned as 's', singlet, 'd', doublet; 't', triplet, and 'm', multiplet.''. Compounds were named by using Chem draw Ultra 16.0 and NMR data processed by Mestre Nova.

2.2 GENERAL PROCEDURE FOR SYNTHESIS OF PRECURSORS:

2.2.1. (1E,2E)-N,N`-bis-(2,6-diisopropylphenyl)ethane-1,2diimine (1a)

1a was synthesized according to the literature procedure¹²; 2,6diisopropylamine (2 mmol) was added to methanol solvent (4.5 mL). In the above-prepared solution, added 40% glyoxal dissolved in water (1 mmol) and stirred for 18 hours at room temperature. The resulted suspension was purified by washing in cold methanol to give the product 1a.



Scheme 1. Synthesis of 1a

Pale yellow solid; yield 87.22% (8.56 g); LCMS (ESI) m/z calculated for $C_{26}H_{36}N_2$ [M+Na]⁺ 376.1403, obtained 376.1386;¹H NMR (400 MHz, CDCl3): δ 8.11 (s,2H), 7.16 (m, 6H), 2.96 (sept, 4H, J= 6.9 Hz) and 1.20 (d,24H, J = 6.9 Hz)ppm.

2.2.2. Synthesis of (1E,2E)-dimesitylethane-1,2-diimine (2a)

2a was synthesized according to the literature procedure;¹² 2,4,6trimethylamine (2 mmol) was added to methanol solvent (4.5 mL). In the above-prepared solution add on 40% glyoxal dissolved in water (1 mmol). Then, for 18 hours stirred at room temperature. The resulted suspension was purified by washing with cold methanol to give the product 2a.



Scheme 2. Synthesis of 2a

Yellow needles; yield 89.34% (102.6 mg); LCMS (ESI) m/z calculated for $C_{20}H_{24}N_2$ [M+Na]⁺ 315.2038, obtained 315.1832; ¹H NMR (400 MHz, CDCl₃): δ 8.10 (s, 2H), 6.91 (s, 4H), 2.29 (s, 6H), 2.16 (s, 12H)ppm.

2.2.4. Synthesis of the 1,3-Bis-(2,6diisopropylphenyl)imidazolium chloride (1b)

1b was synthesized according to the literature procedure;¹² (1E,2E)-N,N⁻ bis(2,6-diisopropylphenyl)ethane-1,2-diimine (3.22 mmol) and paraformaldehyde (3.22 mmol) in the ethyl acetate was heated at 70 °C and stirred till most of the paraformaldehyde dissolved. Then, a solution of HCl (3.22 mmol) dissolved in ethyl acetate was added to the reaction mixture dropwise with vigorous stirring under N₂ condition, and the reaction was stirred at 70 °C, for 2 hours. The reaction mixture was cooled to -8 °C overnight and with EtOAc and ether to give a grey-white solid.



Scheme 3. Synthesis of 1b

Grey white solid; yield 75.13% (276 g): LCMS (ESI) m/z calculated for $C_{27}H_{36}N_2^+Cl^-$ [M-Cl]⁺ 425.1420, obtained 425.1386; ¹H NMR (400 MHz, CDCl₃) δ 10.04 (s, 1H), 8.14 (d, 2H, J = 1.5 Hz), 7.58 (t, 2H, J = 7.8 Hz), 7.36 (d, 4H, J = 7.8 Hz), 2.45 (sept, 4H, J = 6.8 Hz), 1.30 (d, 12H, J = 6.6 Hz) and 1.25 (d, 12H, J = 6.7 Hz)ppm.

2.2.5. Synthesis of 1,3-dimesityl-1H-imidazole-3-ium chloride (2b)

2b was synthesized according to the literature procedure;¹² (1E,2E)dimesitylethane-1,2-diimine (4.24 mmol) and paraformaldehyde (4.20 mmol) in the ethyl acetate were heated at 70 $^{\circ}$ C and stirred till most of the paraformaldehyde dissolved. Then, a solution of tetramethyl silyl chloride (3.22 mmol) dissolved in ethyl acetate into the reaction mixture dropwise with vigorous stirring under N₂ conditions reaction was stirred at 70 °C, 2 hours. The solution was left undisturbed in an ice bath, filtered, and purified by washing with cold EtOAc and ether. The product was dehydrated suction to give a pale-yellow product.



Scheme 4. Synthesis of 2b

Pale yellow ; yield 78.24% (843.9 mg); LCMS (ESI) m/z calculated for $C_{21}H_{25}N_2^+Cl^-$ [M-Cl]⁺ 305.2030, obtained 305.2012.

2.3 GENERAL PROCEDURE FOR SYNTHESIS OF LIGANDS:

2.3.1. Synthesis of 1,3-Bis-(2,6-diisopropyiphenyl)imidazole-2-ylidene copper chloride (1c)

1c was synthesized according to the literature procedure;¹³ To a vial added IPr.HCl (0.32 mmol), CuCl (0.16 mmol) and K_2CO_3 (0.12 mmol) in acetone (1.0 mL) dissolved in the mixture, at 60 °C for 24 hours stirred the reaction. Then purify through a silica pad, concentrated the solvent over the rotary evaporator, and add hexane to the precipitate that gave the product (IPr)Cu(Cl).



Scheme 5. Synthesis of 1c

White crystalline product; yield 70.13% (576 g): LCMS (ESI) m/z calculated for $C_{21}H_{24}N_2CuCl$ [M+Na]⁺ 486.1534, obtained 486.1024; ¹H NMR (400 MHz, CDCl₃): δ = 1.23 (d, 3 J_{H-H} = 6.9 Hz, 12H), 1.31 (d, 3 J_{H-H} = 6.9 Hz, 12H), 2.56 (sept, 3 J_{H-H} = 6.9 Hz, 4H), 7.13 (s, 2H), 7.31 (d, 3 J_{H-H} = 7.8 Hz, 4H), 7.49 (t, 3 J_{H-H} = 7.8 Hz, 2H).

2.3.2. Synthesis of mesityl carbene copper chloride (2c)

2c was synthesized according to the literature procedure with a slight modification.¹³ To a dry schlenk tube under N₂ condition IMes.HCl (1.03 mmol) was dissolved in THF. Then added Cu₂O (0.81 mmol), and for 4 hours reaction was heated to reflux. After cooling the reaction, then concentrating the solution, the rotary evaporator and added hexane to get the precipitate as white crystalline mesityl carbene copper chloride product obtained.



Scheme 6. Synthesis of 2c

White crystalline; yield 72.56% (102.6 mg): LCMS (ESI) m/z calculated for $C_{20}H_{24}N_2$ [M+K]⁺ 315.2038, obtained 315.1832; ¹H NMR (400 MHz, CDCl₃): δ 8.10 (s, 2H), 6.91 (s, 4H), 2.29 (s, 6H), 2.16 (s, 12H)ppm.

3.2.4. Synthesis of 4,5-diazafluoren-9-one (3c)

3c was synthesized according to the literature procedure.¹⁴ 1,10phenanthroline 5,6-dione (0.076 mmol) and 0.25 M NaOH solution in distilled water were taken The reaction mixture was heated at 100 °C for 4 hours. After the product was filtered and washed with water and the white coloured product was obtained.



Scheme 7. Synthesis of 3c

Pale yellow; yield 87.43% (584.4 mg): LCMS (ESI) m/z solved for $C_{11}H_6N_2O$ [M+Na]⁺ 233.0305, obtained 233.0321;. ¹H NMR (400 MHz, CDCl₃) δ 8.80 (dd, J = 5.0, 1.7 Hz, 2H), 8.00 (dd, J = 7.6, 1.7 Hz, 2H), 7.35 (dd, J = 7.6, 5.0 Hz, 2H).

3.2.5. Synthesis of 1,10-phenanthroline 5,6-dione (4c)

4c was synthesized according to the literature procedure;¹⁵ To a cooled flask of sulphuric acid added 1,10 phenanthroline (0.145 mmol) and KBr (20 mmol) and added solution of HNO₃. The mixture was heated at 90 °C for 2 hours. Then the reaction was cool and neutralize the raction and concentrate the organic layer giving the yellow product obtained.



Scheme 8. Synthesis of 4c

Yellow product; yield 80%, (482.29 mg): LCMS (ESI) m/z solved for $C_{12}H_6N_2O_2$ [M+Na]⁺ 205. 0473, obtained 205.0372. ¹H NMR (400 MHz, CDCl₃) δ 9.13 (dd, J = 5.0, 1.7 Hz, 2H), 8.51 (dd, J = 7.6, 1.7 Hz, 2H), 7.60(dd, J = 7.6, 5.0 Hz, 2H).

2.4. PROCEDURE FOR SYNTHESIS OF COMPLEXES:

2.4.1 Synthesis of complex [(IPr)Cu(dafo)]PF₆(1)

1 was synthesized according to the literature procedure.¹⁶ To a schlenk tube, degassed the ethanol solvent under N_2 condition and then, added IPrCuCl (0.102 mmol) and 4,5 diazafluoren-9-one (0.102 mmol) reaction mixture was heated 80 °C for 15 hours. After adding an aqueous solution of KPF₆, a precipitate was formed. Filtered the precipitate and washed with water to give the yellow product.



Scheme 9. Synthesis of complex 1

Yellow powder; 47.22%, (40.5 mg): LCMS (ESI) m/z solved for $C_{38}H_{42}N_4O$ [M-PF₆]⁺ 633.2110, obtained 633.2649 ; ¹H NMR (400 MHz, CDCl₃) δ 8.59 (s, 1H), 8.05 (s, 1H), 7.74 (s, 1H), 7.51 (s, 2H), 7.37 (t, 2H), 7.31 (d, 4H), 2.56 (m, 4H), 1.29 (d, 12H), 1.24 (d, 12H).

2.4.2 Synthesis of complex [(IMes)Cu(dafo)]PF₆(2)

2 was synthesized according to the literature procedure.¹⁶ To a schlenk tube, in N₂ condition, degassed the ethanol solvent and then, added IMesCuCl (0.123 mmol) and 4,5 diazafluoren-9-one (0.123 mmol) reaction mixture was heated 80 °C for 15 hours. After adding an aqueous solution of KPF6, get the precipitate. Filtered the precipitated and washed with water to give the red product.



Scheme 10. Synthesis of complex 2

Red product; 58.12%, (44.1 mg): LCMS (ESI) m/z solved for $C_{32}H_{30}N_4O$ [M-PF₆]⁺ 549.1237, obtained 549.1710.; ¹H NMR (400 MHz, CDCl₃) δ 8.89 (s, 1H), 7.98 (s, 1H), 7.54 (s, 1H), 7.00 (s, 2H), 6.89 (s, 4H), 1.80 (s, 6H), 1.66 (s, 12H).

2.4.3 Synthesis of complex [(IPr)Cu(phendione)]PF₆(3)

3 was synthesized according to the literature procedure;¹⁶ To a schlenk tube N_2 condition degassed the ethanol solvent and then, added IPrCuCl (0.102 mmol) and 1,10 phenanthroline-5,6 dione (0.102 mmol) reaction mixture was heated 80 °C for 15 hours. After adding an aqueous solution of KPF₆ get precipitated. Filtered the precipitated and washed with water to give the black product.



Scheme 11. Synthesis of complex 3

Black product; 50.12%, (43.8 mg): LCMS (ESI) m/z solved for $C_{32}H_{30}N_4O_2$ [M-PF₆]⁺ 661.2615, obtained 661.2598;¹H NMR (400 MHz, Chloroformd) δ 8.59 (s, 1H), 8.05 (s, 1H), 7.74 (s, 1H), 7.51 (s, 2H), 7.37 (t, 2H), 7.31 (d, 4H), 2.56 (m, 4H), 1.29 (d, 12H), 1.24 (d, 12H).

2.4.2 Synthesis of complex [(IMes)Cu(phendione)]PF₆(4)

4 was synthesized according to the literature procedure;¹⁶ To a schlenk tube in N₂ condition, degassed the ethanol solvent and then added IMesCuCl (0.123 mmol) and 1,10 phenanthroline 5,6-dione (0.123 mmol) reaction mixture was heated 80 °C for 15 hours. After the added an aqueous solution of KPF₆ get precipitate. Filtered the precipitated and washed with water to give the black product.



Scheme 12. Synthesis of complex 4

Black product; 52.32%, (45.3 mg): LCMS (ESI) m/z solved for $C_{32}H_{30}N_4O_2$ [M-PF₆]⁺ 577.1675, obtained 577.1659.¹H NMR (400 MHz, DMSO-*d*₆) δ 9.63 (s, 1H), 8.27 (s, 2H), 7.58 (s, 1H), 7.20 (s, 4H), 7.00 (s, 2H), 2.35 (s, 6H), 2.12 (s, 12H).

CHAPTER 3

3.1. RESULTS AND DISCUSSION

3.1.1. (1E,2E)-N,N`-bis(2,6-diisopropylphenyl)ethane-1,2-diimine(1a)

3.1.2. (1E,2E)-dimesitylethane-1,2-diimine (2a)

3.1.1. Synthesis of ligand 1a and characterization

1a was synthesized by room temperature stirring of glyoxal and 2,6diisopropylaniline in methanol. The final product was obtained in 96% yield.

Figure 1 shows the ¹H NMR spectrum of 5c from where we can see that a singlet at 8.11 ppm for 2 protons and multiplet at 7.16 ppm for 6 protons in the aromatic region and sept at 2.96 ppm for 4 methyl protons, and a doublet at 1.20 ppm for 24 methyl protons. Thus, from the spectra it is clear that solid obtained is (1E,2E)-N,N⁻-bis(2,6-diisopropylphenyl)ethane-1,2-diimine(1a).



Figure 1. ¹H NMR spectrum of 1a

Figure 2 shows the mass spectrum of 1a, which indicates molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of ligand 1a. The electron impact mass spectra of the ligand were recorded and showed a well-defined base peak of m/z 399.2771 [M+Na]⁺. This could be attributed to $C_{26}H_{36}N_2$.



Figure 2. Mass spectrogram of 1a

3.1.2. Synthesis of ligand 2a and characterization

2a was synthesized by stirring glyoxal and 2,4,6-trimethylaniline in methanol. The final product was obtained in 92% yield.

Figure 3 shows the ¹H NMR spectrum of 2a from where we can see that a singlet at 8.10 ppm for 2 protons and singlet at 6.91 ppm for 4 protons in the aromatic region and a singlet at 2.29 ppm for 6 methyl protons, and a singlet at 2.16 ppm for 12 methyl protons. Thus, from the spectra, it is clear that the solid obtained is (1E,2E)-dimesitylethane-1,2-diimine.



Figure 3. ¹H NMR spectrum of 2a

Figure 4 shows the mass spectrum of 2a, which indicates molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of ligand 2a. The electron impact mass spectra of the ligand were recorded and showed a well-defined base peak of m/z 315.1832 [M+Na]⁺. This could be attributed to $C_{20}H_{24}N_2$.



Figure 4. Mass spectrogram of 2a

Firstly, the aldehyde group takes a proton from solvent methanol with a subsequent nucleophilic attack of amine on aldehydic carbon. Then proton transfer occurs to neutralize amine nitrogen. Then lone pair of nitrogen attacks occur on aldehydic carbon with loss of water. Then deprotonation takes place to yield imine as the product.

Plausible mechanism of the reaction



Figure 5. Plausible mechanism got synthesis of imine.

3.1.3. 1,3-Bis(2,6-diisopropylphenyl)imidazoliumchloride(1b)

3.1.4. 1,3-dimesityl-1H-imidazole-3-ium chloride (2b)

3.1.3. Synthesis of ligand (1b) and characterization

Ligand **1b** was synthesized by heating Synthesis of N,N⁻Bis(2,6diisopropylphenyl)ethanediimine with paraformaldehyde and tetramethyl silyl chloride as shown in Scheme 6. The final product was obtained with an 80.22% yield.

Figure 6 shows the ¹H NMR spectrum of 1b from where we can see that a singlet at 10.04 ppm for 1 proton and doublet at 8.14 ppm for two protons and triplet at 7.58 ppm for two protons, and a doublet at 7.36 ppm for four

protons in aromatic region and sept at 2.45 ppm for four methyl protons and doublet at 1.30 ppm for 12 protons and doublet at 1.25 ppm for 12 protons. Thus, it is clear from the spectra that the solid obtained is (1,3)-bis(2,6-diisopropylphenyl)-1H-imidazolium chloride.



Figure 6. ¹H NMR spectrum of 1b

Figure 7 shows the mass spectrum of 1b, which indicates the molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of the ligand 1b. The electron impact mass spectra of ligand 1b were recorded and showed a well-defined base peak m/z 389.2951 [M-Cl]⁺. This could be attributed to for $C_{27}H_{37}N_2^+Cl^-$.



Figure 7. Mass spectrogram of 1b

Synthesis of ligand 2b and characterization

Ligand **2b** was synthesized by heating (1E,2E)-dimesitylethane-1,2-diimine with paraformaldehyde and tetramethyl silyl chloride, as shown in Scheme 2. The final product was obtained with an 89.22% yield. Obtained solid was characterized by mass spectrometry.

Figure 8 shows the mass spectrum of 2b, which indicates the molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of the ligand 2b. The electron impact mass spectra of ligand 2b were recorded and showed a well-defined base peak m/z 305.2012 [M-Cl]⁺. This could be attributed to for $C_{21}H_{25}N_2^+Cl^-$.



Figure 8. Mass spectrogram of 2b

Plausible mechanism of the reaction

Firstly, protonation of an alcoholic group of paraformaldehyde occurs. Then nucleophilic attack of nitrogen of dimesitylethane-1,2-diimine takes place onto carbon of paraformaldehyde neutralizing oxygen. Then proton transfer takes place with a subsequent attack of nitrogen to form a five-membered ring. Then lone pair of nitrogen attacks to remove oxygen carbocation to give the cyclic five-membered ring as the product.



Figure 9. Plausible mechanism got the synthesis of imidazolium chloride.

3.1.6. Synthesis of ligand (IPr)Cu(Cl) and characterization

Ligand **1c** was synthesized by reacting of IPr.HCl with CuCl and K_2CO_3 as shown in Scheme 4. The final product was obtained with a 79% yield.

Figure 10 shows the ¹H NMR spectrum of 1c from where we can see that a singlet at 7.13 ppm for two protons and triplet at 7.49 ppm for two protons and a doublet at 7.31 ppm for four protons in the aromatic region, and septet at 2.56 ppm for four methyl protons and doublet at 1.31 ppm for 12 protons and doublet at 1.23 ppm for 12 protons. Thus, from the spectra it is clear that solid obtained is 1,3-Bis(2,6-diisopropylphenyl)imidazole-2-ylidene]copper(I)chloride.



Figure.10¹H NMR spectrum of 1c

Figure 11 shows the mass spectrum of 1c, which indicates the molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of ligand 1c. The electron impact mass spectra of ligand were recorded and showed a well-defined base peak m/z 492.2434 [M+CH₃CN]⁺. This could be attributed to C₂₇H₃₆N₂CuCl.



Figure 11. Mass spectrogram of 1c

3.1.7. Synthesis of ligand mesityl carbene copper chloride and characterization

2c was synthesized by reacting Cu₂O and IMes.HCl under refluxing condition in THF. The final product was obtained in 80% yield.

Figure 12 shows the ¹H NMR spectrum of 2c from where we can see that a singlet at 7.05 ppm for 2 protons and singlet at 6.99 ppm for 4 protons in the aromatic region and a singlet at 2.34 ppm for 6 methyl protons, and a singlet at 2.10 ppm for 12 methyl protons. Thus, from the spectra, it is clear that the solid obtained is mesityl carbene copper chloride.



Figure.12 ¹H NMR spectrum of 2c

Figure 13 shows the mass spectrum of 2c, which indicates the molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of ligand 2c. The electron impact mass spectra of ligand were recorded and showed a well-defined base peak m/z 408.1024 $[M+K]^+$. This could be attributed to $C_{21}H_{24}N_2CuCl$.



Figure 13. Mass spectrogram of 2c

3.1.8. Synthesis of ligand 4,5-diazafluoren-9-one and characterization

3c was synthesized by heating 1,10-phenanthroline 5,6-dione and NaOH in Distilled water. The final product was obtained with 78.22% yield.

Figure 14 shows the ¹H NMR spectrum of 10 from where we can see that a doublet at 8.80 ppm for 2 protons and doublet at 7.35 ppm for 2 protons and doublet at 8.00 ppm for 2 protons. Thus, from the spectra, it is clear that the solid obtained is 4,5-diazafluoren-9-one.



Figure.14 ¹H NMR spectrum of 4c

Figure 15 shows the mass spectrum of 3c which indicated molecular weight of the compound and the resulting fragmentation pattern provided information for elucidating the structure of ligand 3c. The electron impact mass spectra of the ligand were recorded and showed a well-defined base peak m/z 205.0372 [M+Na]⁺. This could be attributed to $C_{11}H_6N_2O$.



Figure 15. Mass spectrogram of 4c

3.1.9. Synthesis of 1,10-phenanthroline 5,6-dione ligand and characterization

5c was synthesized by heating 1,10-phenanthroline and H_2SO_4 and HNO_3 as shown in scheme 11 The final product was obtained in 87.22% yield.

Figure 16 shows the ¹H NMR spectrum of 10 from where we can see that a doublet at 9.13 ppm for 2 protons and doublet at 7.60 ppm for 2 protons and doublet at 8.51 ppm for 2 protons. Thus, from the spectra, it is clear that the solid obtained is 1,10-phenanthroline 5,6-dione.



Figure.16 ¹H NMR spectrum of 5c

Figure 17 shows the mass spectrum of 4c which indicated molecular weight of the compound and the resulting fragmentation pattern provided information for elucidating the structure of ligand 4c. The electron impact mass spectra of the ligand was recorded and showed a well-defined base peak of m/z 233.0321 [M+Na]⁺. This could be attributed to $C_{12}H_6N_2O_2$.



Figure 17. Mass spectrogram of 5c

3.3.10. Synthesis of complex [(IPr)Cu(dafo)]PF6 and characterization

The complex was synthesized by heating IPrCuCl with 4,5 diazafluorene-9one and KPF₆, as shown in Scheme 10. The final product was obtained with a 47.22% yield.

Figure 18 shows the ¹H NMR spectrum of 10, from where we can see that a singlet at 8.59 ppm for 1 proton and singlet at 8.05 ppm for 1 proton and singlet at 7.74 ppm for 1 proton, and a singlet at 7.51 ppm for two protons and triplet at 7.37 ppm for two protons and doublet at 7.31 ppm for four protons in aromatic region and sept at 2.56 ppm for four methyl protons and doublet at 1.29 ppm for 12 protons and doublet at 1.24 ppm for 12 protons. Thus, from the spectra, it is clear that the solid obtained is $[(IPr)Cu(dafo)]PF_{6}$.



Figure.18 ¹H NMR spectrum of complex 1

Figure 19 shows the mass spectrum of 1, which indicates the molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of the complex. The electron impact mass spectra of the complex were recorded and showed 1 well-defined base peak m/z 633.2649 [M-PF₆]⁺. This could be attributed to $C_{38}H_{42}N_4O$.



Figure 19. Mass spectrogram of complex 1

3.3.11. Synthesis of complex [(IMes)Cu(dafo)]PF6 and characterization

The complex was synthesized by reaction of IMesCuCl with 4,5 diazafluorene-9-one and KPF₆ as shown in Scheme 11. The final product was obtained in a 58.12% yield.

Figure 20 shows the ¹H NMR spectrum of 2 from where we can see that a singlet at 8.89 ppm for 1 proton and singlet at 7.96 ppm for 1 proton and singlet at 7.54 ppm for 1 proton, and a singlet at 7.00 ppm for 2 protons and a singlet at 6.89 ppm for 4 protons in aromatic region and singlet at 1.80 ppm for 6 methyl protons and a singlet at 1.66 ppm for 12 methyl protons. Thus, from the spectra, it is clear that the solid obtained is [(IMes)Cu(dafo)]PF₆.

Figure.20¹H NMR spectrum of complex 2

Figure 21 shows the mass spectrum of 2, which indicates the molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of the complex. The electron impact mass spectra of the complex were recorded and showed 2 well-defined base peaks m/z 549.1710 [M-PF₆]⁺. This could be attributed to C₃₂H₃₀N₄O.

Figure 21. Mass spectrogram of complex 2

3.1.12. Synthesis of complex [(IPr)Cu(phendione)]PF₆ and characterization

The complex was synthesized by heating Synthesis of IPrCuCl with 1,10 phenanthroline 5, 6 dione, and KPF_{6} , as shown in Scheme 12. The final product was obtained with a 50.12% yield.

Figure 22 shows the ¹H NMR spectrum of 3 from where we can see that a singlet at 8.59 ppm for 1 proton and singlet at 8.05 ppm for 1 proton and singlet at 7.74 ppm for 1 proton, and a singlet at 7.51 ppm for two protons and triplet at 7.37 ppm for two protons and doublet at 7.31 ppm for four protons in aromatic region and sept at 2.56 ppm for four methyl protons and doublet at 1.29 ppm for 12 protons and doublet at 1.24 ppm for 12 protons. Thus, from the spectra, it is clear that the solid obtained is [(IPr)Cu(phendione)]PF₆.

Figure.22 ¹H NMR spectrum of complex 3

Figure 23 shows the mass spectrum of 3, which indicates the molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of the complex. The electron impact mass spectra of the complex were recorded and showed 3 well-defined base peak m/z 661.2598 [M-PF₆]⁺. This could be attributed to $C_{36}H_{42}N_4O_2$.

Figure 23. Mass spectrogram of complex 3

3.1.13. Synthesis of complex [(IMes)Cu(phendione)]PF₆ and characterization

The complex was synthesized by heating Synthesis of IMesCuCl with 1,10 phenanthroline 5,6 dione, and KPF_{6} , as shown in Scheme 12. The final product was obtained with a 52.32% yield.

Figure 24 shows the ¹H NMR spectrum of 4 from where we can see that a singlet at 9.63 ppm for 1 proton and singlet at 7.54 ppm for 1 proton and singlet at 7.00 ppm for 1 proton, and a singlet at 8.27 ppm for 2 protons and a singlet at 7.20 ppm for 4 protons in aromatic region and singlet at 2.35 ppm for 6 methyl protons and a singlet at 2.12 ppm for 12 methyl protons. Thus, from the spectra, it is clear that the solid obtained is $[(IMes)Cu(phendione)]PF_{6}$.

Figure.24 ¹H NMR spectrum of complex 4

Figure 25 shows the mass spectrum of 4, which indicates the molecular weight of the compound, and the resulting fragmentation pattern provided information for elucidating the structure of the complex. The electron impact mass spectra of the complex were recorded and showed 4 well-defined base peak m/z 577.1659 [M-PF₆]⁺. This could be attributed to $C_{32}H_{30}N_4O_2$.

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Figure 25. Mass spectrogram of complex 4

PHOTOPHYSICAL CHARACTERIZATION

The photophysical properties of Complex $[(IPr)Cu(dafo)]PF_6$ were studied in DCM solution at room temperature which shows emission (fig. 27) in the blue region at 447 nm on excitation (Fig. 26) at 361 nm respectively.

Figure.26 Excitation spectrum of complex 1

Figure27 Emission spectrum of complex 1.

The photophysical properties of Complex [(IMess)Cu(dafo)]PF₆ were studied in DCM solution at room temperature which shows emission (Fig. 29) in the blue region at 453 nm on excitation (Fig. 28) at 316 nm respectively.

Figure.28 Excitation spectrum of complex 2.

Figure. 29 Emission spectrum of complex 2

CHAPTER 4

CONCLUSION

In the current work, three-coordinate copper(I) complex with an N-heterocyclic carbene and bidentate (1,10)-phenanthroline 5,6-dione and 4,5-dizafluorene-9-one have been synthesized and characterized. Three coordinate Cu(I)–NHC complexes were obtained in good yields. The IPr and mesityl (IMes) substituted carbene ligand was chosen for the three-coordinate complexes because of the steric nature of the substituent.

Complex [(IPr)Cu(dafo)]PF₆ and complex [(IMes)Cu(dafo)]PF₆ were found to be luminescent at room temperature with emission in blue region at 447 nm and 453 nm on excitation at 361 and 316 nm respectively. And the origin of luminescent is probably due to the ligand centered transitions. Complexes [(IPr)Cu(phendione)]PF₆ and [(IMes)Cu(phendione)]PF₆ were not found luminescent.

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