

**SYNTHESIS OF PALLADIUM(II)-N-HETEROCYCLIC CARBENE VIA
TRANSMETALATION OF SILVER(I) COMPLEX AND ITS CATALYTIC
ACTIVITY IN EPOXIDATION OF ALKENE**

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UNIVERSITI TEKNOLOGI MALAYSIA

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ACTIVITY IN EPOXIDATION OF ALKENE

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TO MY BELOVED FAMILY ESPECIALLY MY FATHER

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In the name of Allah, Most Gracious, Most Merciful. Praise be to Allah, the Cherisher and Sustainer of the worlds; Most Gracious, Most Merciful; Master of the Day of Judgement.

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ABSTRACT

A series of new silver(I)- and palladium(II)-N-heterocyclic carbene complexes of 1-benzyl-3-ethylbenzimidazolium iodide, 1-benzyl-3-(2'-nitrilebenzyl)benzimidazole bromide, 1-benzyl-3-(2'-methyl)propylbenzimidazolium bromide, 1-benzyl-(3'-methyl)butylbenzimidazolium bromide, 1-benzyl-3-hexylbenzimidazolium bromide were successfully synthesized. The respective N-heterocyclic carbene (NHC) precursors were prepared by the reaction of 1-benzylbenzimidazole with ethyl iodide, 2-bromomethylbenzotrile, 2-methylpropylbromide, 3-methylbutyl bromide, and *n*-hexyl bromide in dioxane at 90 °C. Further, these halide salts were converted into their hexafluorophosphate counterparts by the salt metathesis reaction using KPF₆ in methanol. Bis-NHC silver(I) complexes having hexafluorophosphate counterion were yielded (48.4-67.2%) by the reaction of NHC precursors with silver(I) oxide in acetonitrile/methanol at room temperature. Subsequent reactions of the silver(I) hexafluorophosphate complexes with [PdCl₂(CNCH₃)₂] in dichloromethane/methanol afforded the bis-NHC palladium(II) complexes in good yield (48.3-76.4%) *via* carbene transfer method. All new complexes were fully characterized by various techniques such as CHN analysis, single crystal X-ray diffraction and spectroscopic methods such as FTIR and ¹H and ¹³C NMR. Additionally, in case of silver(I) complex, the bis-[1-benzyl-3-(2'-nitrilebenzyl)benzimidazole] silver(I) hexafluorophosphate was characterized by single crystal X-ray diffraction technique. Preliminary catalytic studies show that the nitrile-functionalized palladium(II)-NHC complex is highly active in the oxidation of 1-octene as well as styrene in aqueous hydrogen peroxide as oxidizing agent at 70 °C. All the palladium(II) complexes oxidized both the aforementioned olefins efficiently to their corresponding oxidized products with 47 to 58% conversions. However, selectivity towards epoxy products was relatively low in the range of 7-10%. Major product in the oxidation of 1-octene was the 1,2-octanediol, while 2-octanone is the minor product.

ABSTRAK

Suatu siri kompleks karbena N-heterosiklik baru argentum(I) dan paladium(II) dengan 1-benzil-3-etilbenzimidazolium iodida, 1-benzil-3-(2'-nitrilbenzil)benzimidazol bromida, 1-benzil-3-(2'-metil)propilbenzimidazolium bromida, 1-benzil-3-(2'-metil)butilbenzimidazolium bromida, dan 1-benzil-3-heksilbenzimidazolium bromida telah berjaya disintesis. Bahan pemula bagi karbena-heterosiklik (NHC) masing-masing telah disediakan melalui tindak balas 1-benzilbenzimidazol dengan etiliodida, 2-bromometilbenzonitril, 2-metilpropilbromida, 2-metilbutil bromida, dan *n*-heksilbromida, dalam dioksana pada 90 °C. Selanjutnya, garam halida tersebut telah diubah kepada heksafluorofosfat sepadan melalui tindak balas metatesis garam menggunakan KPF_6 dalam metanol. Kompleks bis-NHC argentum(I) yang mengandungi ion lawan heksafluorofosfat telah dihasilkan (48.4-76.4%) dalam tindak balas antara bahan pemula NHC dengan argentum(I) oksida dalam asetonitril/metanol pada suhu bilik. Tindak balas kompleks argentum(I) heksafluorofosfat yang berikutnya dengan $[PdCl_2(CNCH_3)_2]$ dalam diklorometana/metanol telah menghasilkan kompleks bis-NHC paladium(II) melalui kaedah pemindahan karbena. Kesemua kompleks baharu telah dicirikan dengan pelbagai teknik seperti analisis CHN, pembelauan sinar-X hablur tunggal dan kaedah spektroskopi FTIR, dan 1H dan ^{13}C NMR. Tambahan lagi, bagi kompleks argentum(I), pencirian melalui pembelauan sinar-X hablur tunggal telah dilakukan terhadap bis-[1-benzil-3-(2'-nitrilbenzil) benzimidazol argentum(I) heksafluorofosfat. Kajian awal pemangkinan mendapati kompleks paladium(II)-NHC berfungsi nitril menunjukkan keaktifan yang tinggi dalam pengoksidaan 1-oktena dan stirena dengan hidrogen peroksida akueus sebagai agen pengoksidaan pada 70 °C. Kesemua kompleks paladium(II) mengoksidakan masing-masing olefin kepada produk oksida yang sepadan dengan penukaran 47 hingga 58%. Walau bagaimanapun, kepilihan terhadap hasil epoksi secara relatifnya adalah rendah iaitu dalam julat 7-10%. Produk utama bagi pengoksidaan 1-oktena ialah 1,2-oktanadiol, sementara hasil minor pula adalah 2-oktanon.

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LIST OF ABBREVIATIONS

Ag ₂ O	-	Silver(I) Oxide
Ag ₂ CO ₃	-	Silver(I) Carbonate
AgOAc	-	Silver(I) Acetate
C-C	-	Carbon-carbon Bond
C-H	-	Carbon-hydrogen Bond
¹³ C NMR	-	Carbon Nuclear Magnetic Resonance
CH ₃ CN	-	Acetonitrile
C(OMe) ₂	-	Dimethoxy
CCl ₂	-	Chlorocarbide
CDCl ₃	-	Chloroform- <i>d</i> ₆
°C	-	Degree celsius
DCM	-	Dichloromethane
DMSO	-	Dimethyl Sulfoxide (solvent)
Dbp	-	Dibenzylidene acetone
DMSO- <i>d</i> ₆	-	Dimethyl Sulfoxide deuterated
D ₂ O	-	Deuterium Oxide
FTIR	-	Fourier Transformer Infrared
GCMS	-	Gas Chromatography-mass Spectroscopy
mg	-	Milligram
HCT 16	-	Human Cell Tissue (colon carcinoma cell line)
¹ H NMR	-	Proton Nuclear Magnetic Resonance
H ₂ O ₂	-	Hydrogen Peroxide
h	-	Hour
I	-	Zero Spin Quantum Number
IC ₅₀	-	The Half Maximal Inhibitory Concentration
mL	-	Milliliter

mmol	-	Millimole
M-xylyl	-	Meta-xylyl
MHz	-	Megahertz
NH ₄ PF ₆	-	Ammonium hexafluorophosphate
NHC	-	N-heterocyclic Carbene
O-H	-	Oxygen-hydrogen Bond
O-xylyl	-	Ortho-xylyl
P-xylyl	-	Para-xylyl
Ppm	-	Part per million
PR ₃	-	Try alkyl Phosphine
PtBu ₃	-	Try butyl Palatinum
Pd(CH ₃ COO) ₂	-	Palladium(II) Aetate
[PdCl ₂ (CH ₃ CN) ₂]	-	Bis Acetonitrile dichloro Palladium(II)
[PdCl ₂ (COD)]	-	Palladium dichlorocyclo Octadine
[PdCl ₂ (PhCN) ₂]	-	Dichloro Palladium bis Nitrile Phenyl
Pd-NHC	-	Palladium N-heterocyclic Carbene
PTC	-	Phase Transfer Catalysis
PEPPSI	-	Pyridine-enhanced Precatalyst Prepration, Stabilization and Initiation
PF ₆	-	Hexafluorophosphate
R	-	Alkyl , Aryl , Allyl , Butyl , Mesityl Group
RT	-	Room Temperature
S	-	Sulphur
sym	-	Symmetrical
TMS	-	Tetra Methyl Silane
THT	-	Tetrahydrothiophene
UV-Vis	-	Ultraviolet-visible spectroscopy or Ultraviolet- visible spectrometry
X	-	Halogen
δ	-	Chemical Shifts
Å	-	Angstrom

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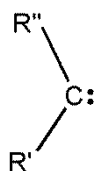
CHAPTER 1

INTRODUCTION

1.1 Research Background

1.1.1 Definitions and Symbolic Representations

Carbenes are a group of molecules, which contain a divalent carbon atom, with two single bonds and a pair of electrons in a non-bonding orbital (Figure 1.1).



R' and R'': alkyl, aryl or
aryl-alkyl

Figure 1.1: General Schematic Representation of a Carbene

Carbenes are known for over 150 years. The alkaline hydrolysis of chloroform reacts through the formation of a reaction transitional with a divalent carbon called dichlorocarbene. Further, the same reaction transitional in Reimer–Tiemann reaction and the transformation of pyrrol to α -chloropyridine in chloroform was proposed [1, 2]. Carbenes can be classified according to the relative energies of

the σ and $p\pi$ orbitals or their reactivity towards metal ions. A large energy gap between the σ orbital and the $p\pi$ orbital gives rise to the formation of singlet state carbene. Secondly, triplet carbenes, which can be considered as diradicals because of their two unpaired electrons. Both, singlet and triplet carbenes are shown in (Figure 1.2).

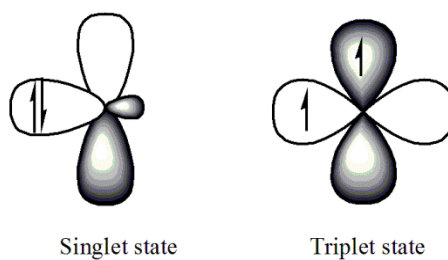


Figure 1.2: Singlet and Triplet Carbenes

1.1.2 Classification of Carbenes

Following is the classification of carbenes based on their reactivity towards metal:

i. Fischer Carbenes:

Fischer and Massbol synthesized this type of carbene for first time in 1964, where it was attached to a metal carrying an electron-withdrawing group(s).

ii. Schrock Carbenes:

These carbene were synthesized by Schrock in 1974 for the first time through a reaction between neopentyl lithium and dichlorotris (neopentyl) tantalium (V). These carbenes are usually formed with high oxidation state with middle and early transition metals such as Ti(IV) and Ta(V) with π -donor ligands.

iii. N-heterocyclic Carbenes:

This is a type of heterocyclic carbenes. It consists of compounds in which the nitrogen-based cyclic ring system has pair of electrons in non-bonding orbital of a carbon atom. NHCs are impartial and two-electron donor ligands with nitrogen heterocyclic core, consisting of imidazole, triazole, pyrazole, tetrazole and benzimidazole amongst others. These have the ability to bond both (hard and soft transition metal ions) through strong chelation. [3]. An azolium salt is shown in (Figure 1.3).

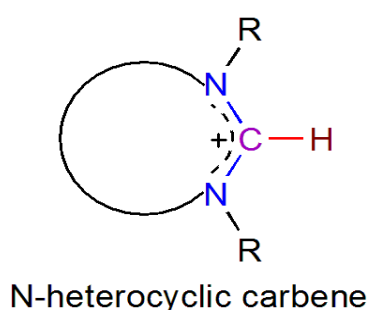


Figure 1.3: Schematic Representation of a NHC.

1.1.3 NHC-Ligands

NHC ligands are of three types i.e. monodentate, bidentate, and polydentate carbenes encompassing at least one N-heterocyclic core. A monodentate NHC ligand has only one carbene carbon donor atom, which can bond to the central metal atom or ion. A ligand having two donor carbene carbon atoms which enables it to bind to a central metal atom or ion at two points is known as bidentate. Some bidentate based silver(I) and mercury(II) complexes of bis-NHC ligands with alkyl, oligo ether and phenylene linkers have been reported by Liu and co-workers in 2012 [4]. Polydentate NHC ligands range in the number of atoms used to bond to a central metal atom or ion. Generally, these NHC ligands formed by the deprotonation of an N,N'-disubstituted imidazolium (or other azolium) salts. NHCs are electronically more flexible, since filled and empty π and π^* orbitals on the NHC ring may donate to the

NHC-metal bond. Electron rich metal atoms may be stabilized through additional back donation of d-electrons of the metal to a π^* orbital of the NHC unit, while electron-deficient metals may be stabilized through the donation of π electrons of the NHC core into an empty d-orbital of the metal atom [5].

Nowadays, NHC-based ligands show a very important role in organometallic chemistry, because of their distinctive complexation behaviours, synthetic versatilities, and vastly tuneable characteristics. These ligands show a high tendency to act as wonderful σ -donor ligands and to make more stable metal-carbene carbon bonds [6]. On the other hand, chiral and immobilized NHC ligands have opened up rather new synthetic ways for preparation of flexible catalytic systems of a high synthetic value in organic and organometallic chemistry. As with other donor ligands such as, phosphines, amines, alkoxys, Schiff bases and so on, substituent group changes let fine-tuning of the steric and electronic properties of the NHC ligands thus, it convenes special entities to the targeted metal complexes [7]. Phosphines were used as ligands in the formerly but due to some disadvantages, such as, the high cost of preparing tertiary (especially chiral) phosphines and their degradative trend in converting to phosphine oxides have only now been addressed by the rich field of NHC ligands used in homogeneous catalysis [8]. In common, metal-carbene carbon bonds those to NHCs do not undergo fast addition or reductive elimination reactions and so NHCs are moderately consistent spectator ligands. Chelating NHC ligands of the pincer type apparently produce stable carbene complexes and thus, have many applications over conventional coordination catalysts [9].

In NHCs, the substituents are associated with atoms one or two bonds away from the donor atom, so that the donor atom itself has the same close situation throughout. So the substituent on the NHC system appears to cause a steric change with only slight changes of the electronic effect. Generally, palladium(II) complexes having NHC ligands have been shown to be wonderful catalysts for many organic reactions, like, Suzuki-Miyaura and Heck cross couplings [10]. Most NHC ligands are synthesized from azolium compounds such as triazolium, imidazolium, thioazolium, and benzimidazolium salts. Unpredicted stability of free NHC would rise mainly from substantial sigma-charge transfer from the carbenic carbon atom to

the more electronegative adjacent nitrogen atoms. Therefore π -donation would only play a small role.

Structural studies can be used to describe the steric effects. It suggests that the large size of the functional group attached to the nitrogen atoms of NHC ligands is significant. Furthermore, the short metal-carbon distances in these complexes result in increased steric congestion around the central metal when linked with tertiary phosphines. Similarly, calculation of % VBur of PR_3 system allows a direct association between these two ligand systems. These calculations have shown that the sterically demanding carbenes are in fact bulkier than $\text{P}(t\text{Bu})_3$ [11]. Effect of ancillary ligands is also required with the steric hindrance of the labile substituents attached to the central metal.

1.1.4 Palladium(II)-NHC Complexes

In particular, palladium(II)-NHC complexes can be used as efficient catalysts in various organometallic reactions, and have been successfully applied for olefin oligo/polymerization and metathesis among other reactions. For instance, a series of pyridine-derived palladium(II) complexes of NHC ligands are effective toward ethylene oligo/polymerization reaction [12]. These complexes are very stable to air and moisture, and can be prepared in different oxidation states due to which they could play versatile role in the field of applied catalysis.

Currently, in the field of organometallic chemistry, palladium(II)-NHC complexes can be used in most of C-H, C-N and C-C bond making reactions, especially in the Heck and Suzuki cross coupling as well as other cross coupling reactions like Hyama, Negoshi, O-glycosidation reactions. Although several studies have concentrated on the catalytic activity of these compounds, only Ray et al. have conducted biological studies [13]. In earlier time, Pd(II)-NHC complexes were prepared on two common methods. The reaction of $\text{Pd}(\text{OAc})_2$ and imidazolium salts was one of the first procedures reported to give palladium(II) NHC complexes. The

imidazolium salts are deprotonated in situ through the acetate base that is combined to the palladium salt precursor. In most cases, the reaction involves two equivalents of the ligand per metal center and leads to the formation of $(\text{NHC})_2\text{PdCl}_2$. While this method is relatively common, often giving high yields of both simple and chelating NHC complexes, it needs high temperatures and reduced pressure to remove the acetic acid formed during the reaction [14]. A second common method for the preparation of Pd(II) complexes is the reaction of palladium salts with isolated or in situ produced NHC ligands. While the isolation of free NHC or a reliable means of deprotonation is required, this method is very useful and has afforded many complexes bearing mono-carbene, bis-carbene, chelating carbene, and mixed chelating ligands that consist of at least one carbene [15]. The Pd(II)-NHC complexes can be obtained from three part reactions of 1, 3-dialkylbenzimidazolium halides, potassium tert-butoxide and $\text{Pd}(\text{CH}_3\text{COO})_2$, which can capably catalyse the Suzuki cross-coupling reactions of neutralized aryl chloride substrates [16].

The work by Cavell and co-workers [17], Tilset and co-workers [18], Shreev and co-workers [19], and Gade and co-workers [20], specified the failure of direct metallation to prepare Pd(II)-NHCs. Therefore transmetallation by Ag(I)-NHCs became of general interest. The transmetallation of NHCs from silver(I) to other transition metals has been shown to be a very suitable technique for the preparation of transition-metal NHC complexes, Because silver(I)-NHC complexes can be prepared easily by one-pot reaction. This method was discovered by Wang and Lin [21] and was used to synthesize Pd(II), Pt(II), and Au(I)-NHC complexes. The advantages of this method are that no pregeneration of the free carbene is necessary. The reaction can be conducted at room temperature; but in some cases inert conditions are also mentioned. The transfer of NHC not only depended on the nature of Ag(I)-NHCs, but also on the nature of the receiving metal precursors and the reaction conditions. Before the transmetallation reaction the azolium salt is treated with Ag_2O to form the resultant silver(I)-NHC complex. This silver(I)-NHC complex is then by transmetallation reacted with a species like $[\text{PdCl}_2(\text{COD})]$ or $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ to produce a palladium(II) complex, in which NHC is bound to the metal centre. In NHC migration process, it was initially proposed that the absence of $^{107,109}\text{Ag}-^{13}\text{C}$ coupling in the ^{13}C NMR spectrum and

the labile nature of the Ag(I) complexes caused the effective transfer of NHC from Ag(I)-NHC to Au(I) and Pd(II) [22]. However, later on it was found that Ag(I)-NHCs with non-fluxional Ag-C bonds were also able for NHCs migration [23].

Transmetallation can be used to prepared functionalized Pd(II)-NHCs of different structures. It depending on the nature of the Pd(II) precursor, the reaction conditions, and stoichiometry of the reactants. According to one estimate for the preparation of Pd(II)-NHC complexes among other methods, the Ag-carbene transfer route comprises over 70% of the published results; the free carbene route founds around 20% [24]. Homogenous palladium catalysts provide high turnover number and high activity but they often suffer from difficulty of recycling and separation from the products [25]. The catalytic activity of these complexes can be altered by changing the functional groups present at 1- and 3- positions of azolium salts. The palladium(II)-NHC complexes which are derived from imidazole and benzimidazole core are more reactive in catalytic reactions than others. In general, benzimidazole-based complexes show a main structural difference from their non-benzo-fused nitrogen relatives such as imidazole and its derivatives, even though are very few in numbers. The complexes which are derived from the benzimidazole central core have been used in materials science to limit the compound in metal organic frameworks without altering the porosity and structural order of the metal organic frame [26]. We are also going to use the transmetallation technique to prepare Nitrile-functionalized and non-functionalized alky-aryl, aryl-alkyl disubstituted benzimidazole based unsymmetrically Pd(II)-NHC complexes from the Ag(I)-NHC complexes and use it for the catalytic activity in the epoxidation of alkenes.

1.2 Statement of Problem

NHCs are nowadays probably the most used ligands in organometallic catalysis. Their complexes have superior properties such as high stability combined with an extremely high reactivity. In the present project, it is intended to develop new class of palladium-carbene complexes of benzimidazole-2-ylidines via classical

transmetallation from corresponding silver(I)-NHC complexes. For this purpose, a variety of sterically tuned (benz)imidazole-based NHC proligands have been targeted. Further, palladium(II)-NHC complexes were evaluated for their potential as catalysts in olefin epoxidation reactions using both, 1-octene and styrene, as substrates. Till to date, to the best of our knowledge, no article reporting the use of palladium(II)-NHC complexes as catalysts for the aforementioned catalytic transformation reaction. Therefore, the outcomes of this project will definitely make a milestone in the field of organometallic chemistry as well as catalysis as is going to be reported for the first time.

1.3 Objectives of the Study

Objectives of the study are follows:

1. Synthesis and characterization of various alkyl/aryl/aryl-alkyl disubstituted benzimidazolium salts.
2. Synthesis and characterization of Silver(I)-NHC complexes.
3. Synthesis and characterization of Palladium(II)-NHC complexes *via* transmetallation techniques using Silver(I)-NHC complexes.
4. Evaluation of catalytic activities of Palladium(II)-NHC complexes in the olefin epoxidation reactions with substrates such as, 1-octene and styrene.

1.4 Scope of the Study

In this project, the design, synthesis, spectral and analytical characterization of benzimidazolium-based silver(I)- and palladium(II)-carbene complexes are prepared for catalytic olefin oxidation purposes. The topic of this study is a large section of application in the field of catalysts which covers the elements which are essential for the design and production of active NHC complexes with at least one azolium center. The catalytic performances of palladium(II)-NHC complexes in

oxidation of olefins such as, 1-octene and styrene are planned to perform using the recent results in advanced organometallic chemistry of NHCs as the bases. This study is restricted, but not necessarily, the use of alkyl/aryl/aryl-alkyl substituted benzimidazolium salts with both bromide/iodide and hexafluorophosphate anions for the preparation of palladium-carbene complexes, which are used as olefin epoxidation catalysts.

1.5 Significance of the Research

The project on catalytic studies of novel palladium(II)-NHC complexes is worthy to carry out as it has potential catalytic applications. These ligands and complexes are designed on the basis of structure of active catalysts available in the literature, which definitely enrich the desired outcomes. A series of novel mononuclear silver(I) and palladium(II)-NHC complexes were prepared and characterized. These palladium(II) complexes promote the rate enhancement in the catalytic olefin epoxidation reactions, over the uncatalyzed reaction with multiple catalyst turnovers.

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