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C-C BOND FORMATION WITH N-HETEROCYCLIC CARBENE COMPLEXES

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Bornova-İZMİR

Hayati TÜRKMEN tarafından DOKTORA TEZİ olarak sunulan **“C-C Bond Formation With N-Heterocyclic Carbene Complexes”** başlıklı bu çalışma E. Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve ....tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET

N-HETEROSİKLİK KARBEN KOMPLEKSLERİ İLE C-C BAĞ OLUŞUMU

Hayati TÜRKMEN
Doktora Tezi, Kimya Anabilim Dalı

Danışman: **Prof. Dr. Bekir ÇETİNKAYA**

151, sayfa

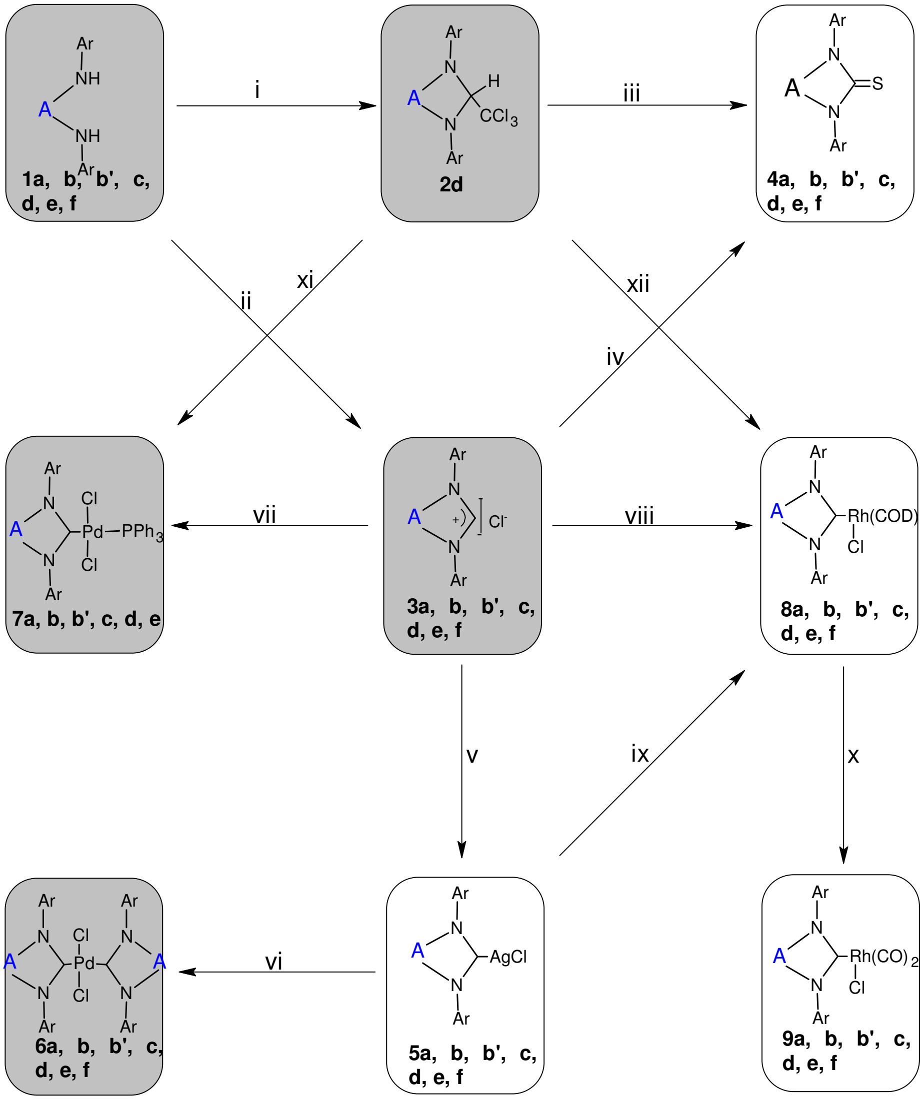
Metal-NHC komplekslerinin homojen katalizde yaygın bir şekilde kunlanılan fosfinlere alternatif olmaları, son zamanlarda büyük ilgi çekmektedir. Çünkü katalitik koşullarda (yüksek sıcaklıkta) P-C bağı kolayca kopmakta ve P atomu havanın oksijeni ile kolayca oksitlenmektedir. Aksine, metal-NHC kompleksleri havanın nemi ve oksijenine karşı çok kararlıdır. Dolayısıyla tepkime ortamında ligant fazlasına gerek yoktur.

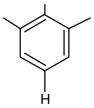
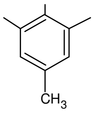
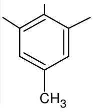
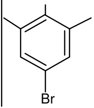
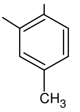
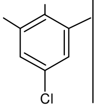
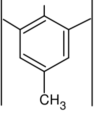
Katalizör tasarımında etkinlik ve seçimliliği artırmak, ürünlerden katalizörün kolay ayrılmasını sağlamak ve katalizörün ömrünü uzun tutmak temel amaçtır. Bu nedenle daha kararlı ve etkin katalizörler hazırlamak amacıyla, imidazolidin halkasının C_4-C_5 konumlarında hidrojen, metil, asenaftil grupları ve azot atomları üzerindeki aril halkasında para pozisyonunda H, CH_3, Br, Cl içeren *N*-heterohalkalı karben öncülleri (**3**) ve bunlardan türeyen Ag(I), Rh(I)- ve Pd(II) kompleksleri sentezlenmiştir (Şema I).

Tez üç bölümden oluşmaktadır. Birinci bölümde *N*-heterohalkalı karben ligandları ve bunların karben kompleksleri üzerindeki çalışmalar özetlenmiştir. İkinci bölümde deneysel çalışmalara yer verilmiştir. Üçüncü bölümde elektronik ve sterik bakımdan farklı imidazolidin ligandları kullanılarak kükürt (**4**), gümüş (**5**), rodyum kompleksleri (**8**, **9**) sentezi, karakterizasyonu ve katalitik incelemeler sunulmuştur. Bu tez çalışmaları sırasında kullanılan bazı imidazolinyum tuzları ve bunlardan türeyen palladyum kompleksleri (**6** ve **7**) ile imidazol halkasının 4,5 pozisyonunda asenaftil grubu içeren imidazoliden türevli öncül ve kompleksleri yayınlandığı için tezde yer almamaktadır. Sadece bu bileşiklerle yapılan katalitik çalışmalar sunulmaktadır.

İmidazolidin türü pek çok metal-NHC kompleksi Şema I deki *v*, v*ii* ve *viii* basamaklarıyla gösterilen üç tepkimeden birisi kullanılarak hazırlanabilir. Özellikle basamak *v*, çok kullanışlı bir metoddur. Burada önce gümüş kompleksi (**5**) sentezlendi ve **5**'in farklı metallerle etkileşimi sonucu diğer NHC kompleksleri hazırlandı. İmidazolinyum tuzu (**3**) bazik karekterli $[Rh(OMe)(COD)]_2$ ile etkileştirilerek rodyum NHC kompleksi (**8**) hazırlandı (viii yöntemi). Metal üzerindeki elektron yoğunluğunu ölçmek için bu kompleksteki siklooktadien ile karbonmonoksit yerdeğiştirme tepkimesi gerçekleştirildi. Çünkü dikarbonil rodyum kompleksinin (**9**) infrared spektroskopisi NHC ligandının σ-elektron verme yeteneğini yansıtmaktadır. Ayrıca, paladyum ve rodyum komplekslerinin katalitik aktiviteleri incelendi. Elektronik ve sterik etkinin katalitik aktivite üzerine etkisi araştırıldı.

Anahtar kelimeler: *N*-heterohalkalı karben, gümüş, palladyum, rodyum, C-C bağ oluşumu.



	a	b	b'	c	d	e	f
A	$(CH_2)_2$	$(CH_2)_2$	$(CHCH_3)_2$	$(CH_2)_2$	$(CH_2)_2$	$(CH_2)_2$	$(C_{12}H_8)$
Ar	 H	 CH_3	 CH_3	 Br	 CH_3	 Cl	 CH_3

Şema 1. Tez çalışması boyunca sen tezlenen bileşikler(1-9). Gölgeli şekildeki bileşikler yayınlanmıştır (**1, 2, 3, 6, 7**).

ABSTRACT

C-C BOND FORMATION WITH N-HETEROCYCLIC CARBENE COMPLEXES

Hayati TÜRKMEN
Ph. D. Thesis in Chemistry

Supervisor: **Prof. Dr. Bekir ÇETİNKAYA**

151 pages

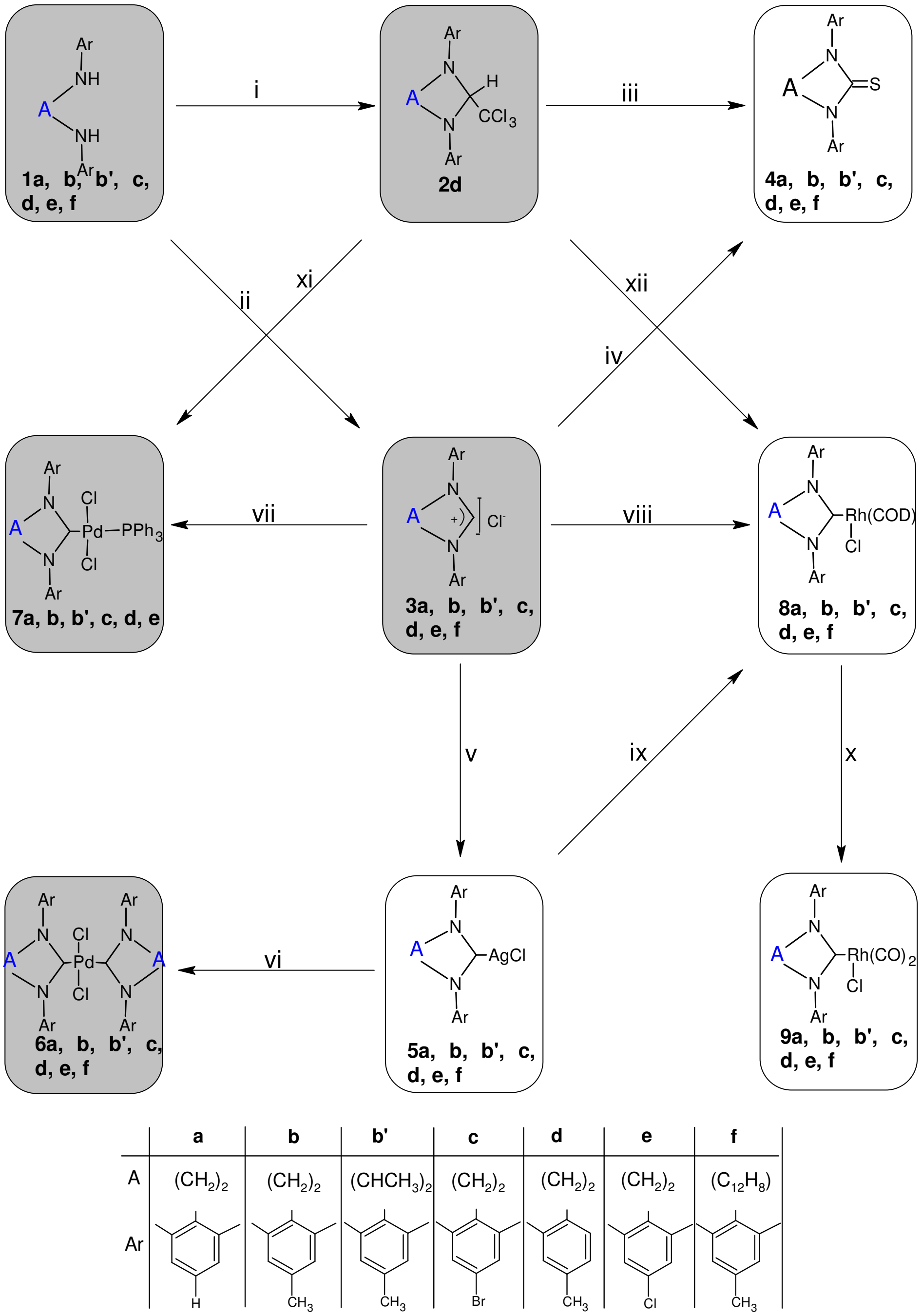
Metal-NHC complexes have recently attracted considerable attention as possible alternatives for the widely used phosphine complexes in homogeneous catalysis. This is because, P-C bonds can easily be cleaved under catalytic conditions (high temperature) and the P atom is easily was oxidized with oxygen of the air. In contrast, metal-NHC complexes are very stable toward moisture and oxygen. Consequently, excess ligands are not used in catalysis.

The fundamental aim in designing the catalyst has been to increase the activity and the selectivity. Easy separation of catalyst from products and increased catalyst life is also a main concern. Therefore, in order to synthesize more efficient and more stable catalysts, *N*-heterocyclic carbene precursors (**3**) and Ag(I), Pd(II), Rh(I) complexes derived from them have been synthesized. These compounds contain hydrogen, methyl, acenaphtyl groups on C_4-C_5 positions of the imidazolidine ring and H, CH_3, Br, Cl, at the *p*-position of the aryl ring on the nitrogen atoms (Scheme 1).

This thesis consists of three parts. The first part is a concise review on *N*-heterocyclic carbene (NHC) ligands and their complexes. In part II the experimental details are given. In part III the synthesis, characterization and catalytic studies of thione (**4**), silver (**5**), rhodium (**8**, **9**) complexes by using various imidazol ligands of different electronic and steric properties (Scheme 1) are described. Some (shaded in scheme 1) imidazolidinium salts and their palladium complexes (**6** and **7**), imidazolyilidene precursor bearing acenaphtyl group on 4,5 position of imidazole ring synthesized during this study have been published. Therefore, they were not included. Only the catalytic studies of these compounds were presented.

Many metal-NHC complexes, such as imidazolidine, can be prepared using one of the three reactions shown via *v*, *vii* and *viii* in Scheme I. Particularly step *v* is a frequently used method. Firstly, silver complexes (**5**) were synthesized in this step and other NHC complexes were prepared via the reaction of different metals with **5**. Rh-NHC complex was also obtained through reaction of imidazolinium salt (**3**) via basic character of $[Rh(OMe)(COD)]_2$ (step viii). In order to measure electron density on metal, substitution reaction was performed between cyclooctadiene in this complex with carbonmonoxide group. Because IR spectrum of obtained dicarbonyl rhodium complexes (**9**) were taken as σ-donor ability of NHC ligand. The catalytic activities of synthesized palladium and rhodium complexes were examined. The effect of electronic and steric effect on catalytic activity was investigated.

Keywords: *N*-heterocyclic carbene, silver, palladium, rhodium, catalysis, C-C bond formation.



Scheme 1 Compounds (1-9) have been synthesized during the study of thesis. The compounds indicated in shaded frame were recently published (**1, 2, 3, 6, 7**).

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ABBREVIATIONS

Abbreviations		**Explanations**
Ad	:	Adamantyl
ADMET	:	Acyclic diene metathesis
Ar	:	Aryl
cat.	:	Catalyst
COD or cod	:	1,5-cyclooctadien
Coe	:	Cyclooctane
CM	:	Cross metathesis
Cp	:	Cyclopentadienyl
Cp*	:	Pentamethylcyclopentadien
DAB	:	1,4-diazobutadiene
Dba	:	Dibenzlydeneacetone
DMSO	:	Dimethyl sulfoxide
Ero	:	Electron-rich olefin (enetetramine)
Et	:	Ethyl
EtOH	:	Ethyl alcohol
GC	:	Gas Chromatography
Hz	:	Hertz
IMes	:	1,3-dimesityl-imidazol-2-ylidene
IR	:	Infrared spectroscopy
L	:	Ligand
m.p.	:	Melting point
Me	:	Methyl
MeCN	:	Acetonitryl
Mes	:	Mesityl, 2,4,6-trimethylphenyl
NHC	:	*N*-heterocyclic carbene
NMR	:	Nuclear Magnetic Resonance
PCy_3	:	Cyclohexylphosphine
Ph	:	Phenyl
PhMe	:	Toluene
PPh_3	:	Triphenylphosphine
Pr	:	Propyl
R	:	Alkyl
RCM	:	Ring closing metathesis
ROMP	:	Ring opening metathesis polymerization
RT	:	Room temperature
Tert	:	Tertiary

Abbreviations		**Explanations**
THF	:	Tetrahydrofuran
Tmeda	:	*N*,*N*,*N*',*N*'-tetramethylethylenediamine
X	:	Halogen
S	:	Singlet
D	:	Doublet
T	:	Triplet
M	:	Multiplet
Q	:	Quartet
η	:	Hapticity
α	:	Alpha
β	:	Beta
δ	:	Delta
μ	:	Bridged ligand
Å	:	Angstrom

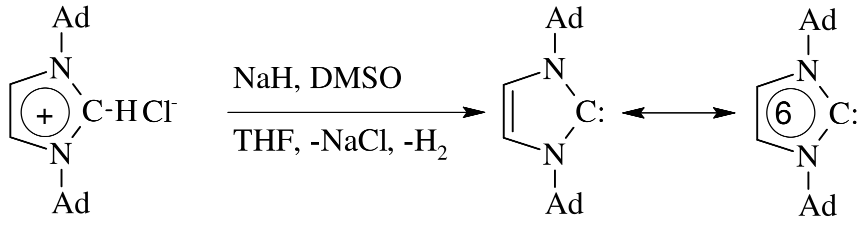
1. INTRODUCTION

1.1. Carbenes

A carbene is a neutral molecule which features a divalent carbon with only six electrons in its valence shell. The desire to prepare isolable carbenes can be traced back to the early nineteenth century, when the quadrivalency of carbon had not yet been established. Many chemists including Dumas (1835) and Nef (1895) embarked in a bold attempt to synthesize methylene, the simplest carbene (CH_2), through the dehydration of methanol. During this period, it appeared that the fascination with carbenes evolved into an obsession for many chemists based on emotional, rather than empirical grounds.

Carbenes have been subject to numerous computational studies, most of them now obsolete as a result of better experimental, as well as computational data. However, the highly reactive nature of carbenes made the goal of isolating them seem unattainable.

In the early 1960s Wanzlick *et al.* recognized that the electron rich imidazole nucleus would be capable of stabilizing a carbene centre at the 2-position between the two nitrogen atoms (Wanzlick, 1962). His fundamental work provided a valuable foundation that led to the isolation of the first stable diaminocarbene. This goal was finally realized in 1991 when Arduengo *et al.* described the synthesis and structure of the aromatic 1,3-diadamantylimidazole-2-ylidene, **1;** a colourless, crystalline and thermally stable solid obtained through the deprotonation of 1,3-di-adamantylimidazolium chloride, **1HCl,** with sodium hydride in the presence of catalytic amounts of DMSO (scheme 1.1) (Arduengo *et al*, 1991). In the last decade, our understanding of carbene chemistry has increased dramatically with the isolation of *N*-heterocyclic diaminocarbenes (NHC's) (Hermann *et* al, 1997, Bourissou *et* al**,** 2000) and advances in the synthesis of persistent triplet carbenes (Tomioka ,1997).

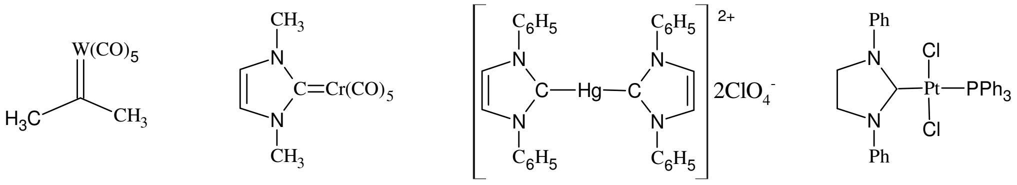


1 HCl **1**

Scheme 1.1. Synthesis of the first stable N-heterocyclic carbene, 1.

1.2. Origins of Diaminocarbene Chemistry

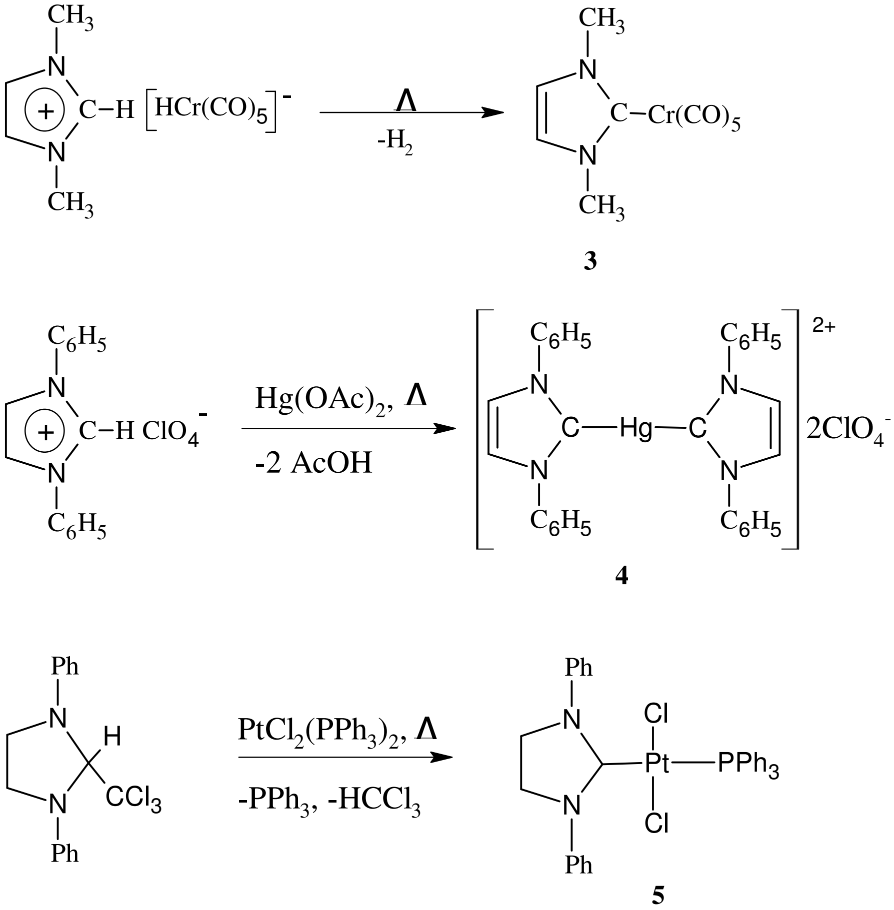
We witnessed the introduction of carbenes into inorganic chemistry in 1964 with the synthesis of **2** (figure 1.1), the first authenticated metal-carbene complex by E. O. Fischer and co-workers (Fischer, *et al*, 1964); a compound belonging to a class of reagents with a steadily increasing number of applications in carbon-carbon bond formation.



2 **3** **4** **5**

Figure 1.1. Notable carbene-metal complexes.

Shortly after, Öfele (Öfele**,** 1968), Wanzlick, (Wanzlick *et al*, 1968) and Lappert in dependently synthesized compounds **3-5,** respectively (figure 1.1). These carbene complexes featured diaminocarbenes attached as ligands to metal centres and were obtained by deprotonating imidazolium salts (scheme 1**.** 2) or C=C bond cleavage of ero (Lappert *et al*, 1971).



Scheme 1.2. Formation of N-heterocyclic carbene complexes.

Although compounds **3-5** were highly unusual at that time, it took several years for these reports to receive the recognition they deserved.

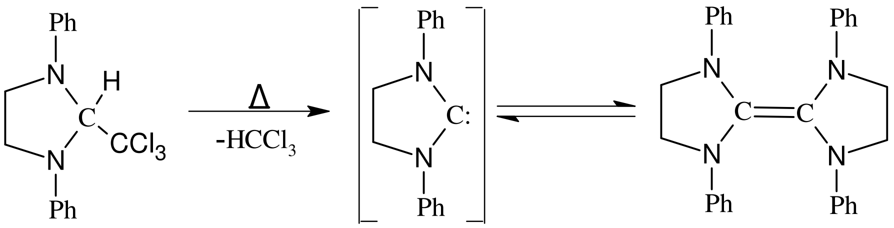
1.2.1. Wanzlick's Contributions

Wanzlick paved the way toward the isolation of the first stable carbene, with his attempts to synthesize imidazole-2-ylidenes, **6** and imidazolidin-2-ylidenes, **7** (Figure 1.2).

6 **7**

Figure 1.2. Imidazole- and imidazolidin-2-ylidene.

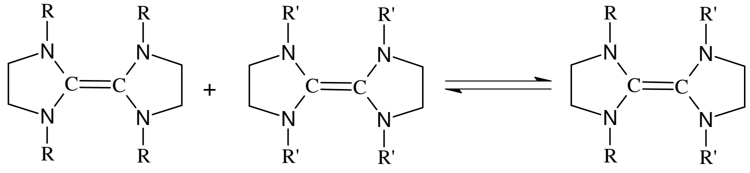
Wanzlick's studies focused primarily on carbenes of type **7**. He attempted the synthesis of N,N'-diphenyl-imidazolidin-2-ylidene (R= Ph) through the thermal elimination of chloroform (Wanzlick *et al*,1961). But isolated only the carbene dimer **8.** No unambiguous proof for the presence of a carbene was provided (scheme 1.3). However, the unusual reactivity of **8** led Wanzlick to the conclusion that it exsists in equilibrium with the carbene**.**



8

Scheme 1.3. Synthesis of enetetramines.

The lack of explicit evidence for this equilibrium prompted a study by former group member K. Hatano, in which mixtures of enetetramines were investigated by multinuclear NMR studies (^{1}H, ^{13}C) at elevated temperatures in sealed tubes (Denk *et al,*1999). The rapid and statistical formation of metathesis products of type **11** has been interpreted by as evidence for this equilibrium (scheme 1.4) (Hahn *et al*, 2000).

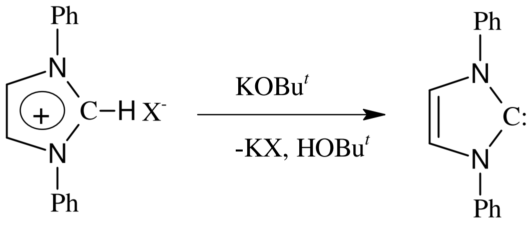


9 **10** **11**

	R	R'
11	Me	Et
11	Et	i-Pr
11	i-Pr	Me
11	Ph	p-Tol

Scheme 1.4. Olefin metathesis.

In 1970, Wanzlick successfully demonstrated that imidazolium salts can be deprotonated by potassium *tert*-butoxide to afford the corresponding imidazole-2-ylidenes, which in a most unfortunate turn of events were only trapped as metal complexes but not isolated (scheme 1.5) (Wanzlick *et al*, 1970). Using the same reaction conditions almost two decades later, Arduengo synthesized and isolated the first stable carbene, **1** (Arduengo *et al*, 1991), which led to a resurrection of the interest in the area of low valent main group compounds.



12.HX **12**

Scheme 1.5. Deprotonation of Imidazolium Salt.

1.3 Electronic Structure of Carbenes

Carbenes can be either linear or bent, each geometry corresponding to a varying degree of s, p hybridization. The linear geometry implies an sp-hybridized carbene center with two nonbonding degenerate orbitals (p_z and

p_y). Bending the molecule breaks this degeneracy and the carbon atom adopts an sp^2-type hybridization: the p_z orbital remains almost unchanged (it is usually called p_π), while the orbital that starts as pure p_y orbital is stabilized since it acquires some s character (it is therefore called σ) (figure 1.3) (Bourissou *et al*, 2000).

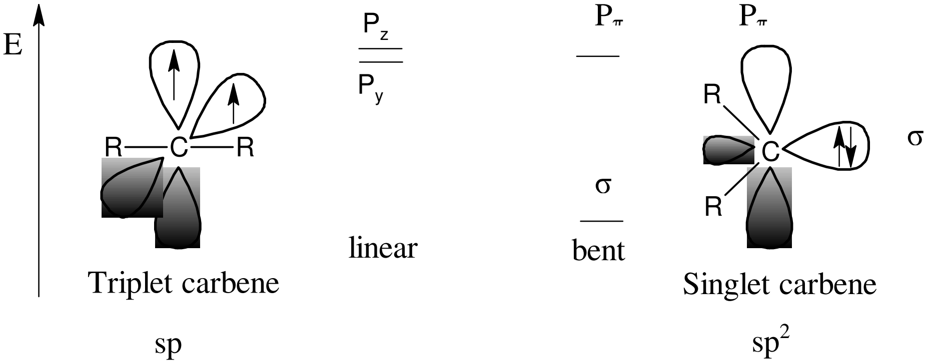


Figure 1.3. Electronic structure of carbenes.

The linear geometry is an extreme case and most carbenes are bent, hence their frontier orbitals are systematically called σ and p_π. Understanding the ground-state multiplicity of carbenes is necessary in order to gain insight into their reactivity. The singlet carbene features a filled and a vacant orbital, hence, it should possess some ambiphilic character. As sextet species, carbenes are highly electron deficient, yet, singlet carbenes possess a lone pair of electrons similar to that of carbanions. Triplet carbenes possess two singly filled orbitals and may be considered as diradicals, although the interaction of two unpaired electrons on the same carbon atom gives rise to some peculiarities (Bourissou *et al*, 2000).

Species	Number of covalent bonds	Number of valence electrons
Carbonions	3	8
Radicals	3	7
Carbenium ions	3	6
Carbenes	2	6

Table 1.1. Simple intermediates in the chemistry of carbon compounds.

The carbene ground-state multiplicity is related to the energy gap between the σ and p_π orbitals. A large σ- p_π separation favours the singlet state; Hoffmann determined that a value of at least 2 eV is necessary to impose a singlet ground state, whereas a value below 1.5 eV leads to a triplet state (Gleiter *et al*, 1968).

1.3.1 Influence of Substituents on the Electronic Structure of Carbenes

The magnitude of the σ- p_π separation is infiuenced by the nature of the substituents on the carbene carbon and it can be analyzed in term of electronic and steric effects.

1.3.2 Electronic Effects

Electronic effects can be divided into inductive and mesomeric effects. The importance of inductive effects for the stabilization of carbenes was recognized early (Irikura et al, 1992). It is now well established that σ-withdrawing substituents favour the singlet state. They inductively stabilize the pπ orbital by increasing its s character but leave the pπ orbital relatively unperturbed; this increases the magnitude of the σ- pπ separation. Consequently, σ-donating substituents reduce the σ- pπ gap and favour the triplet state. Inductive effects dictate the ground state multiplicity of carbenes such as CH_2 or CLi_2.

Mesomeric effects consist of interactions of the carbon p orbitals with the appropriate orbitals (p or π) of substituents and when present, they dominate over inductive effects.

Substituents that interact with the carbene carbon can be categorized as either π –acceptors of π -donors. When both substituents are π -donors (-F, -CI, -Br, -OR, -NR_2) the carbene is predicted to have a singlet ground-state as is the case with the stable diaminocarbenes.

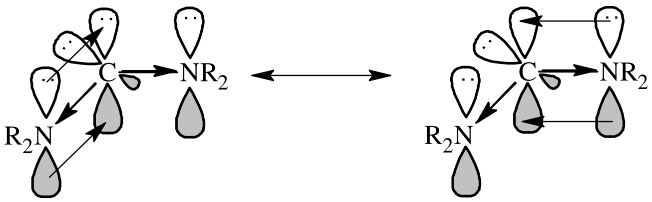


Figure 1.4. Electronic effects of the substituents of diaminocarbenes.

The energy of the vacant p_π orbital is increased by the symmetric combination with the nitrogens lone pairs, but the carbenic σ orbital remains unchanged (figure 1.4). This interaction increases the σ- p_π gap hence favours the singlet ground-state. The mesomeric interaction should lead to a considerable shortening of the carbon-nitrogen bonds. This has been observed for the single crystal X-ray structures of stable amido and diaminocarbenes. The same mesomeric effects apply to describe dialkoxy- and dihalocarbenes (Bourissou *et al*, 2000).

1.3.3 Steric Effects

The effect of sterically demanding substituents on the stability of carbenes is two fold. In the absence of any notable electronic effects, sterics can determine the ground-state multipicity of carbenes.

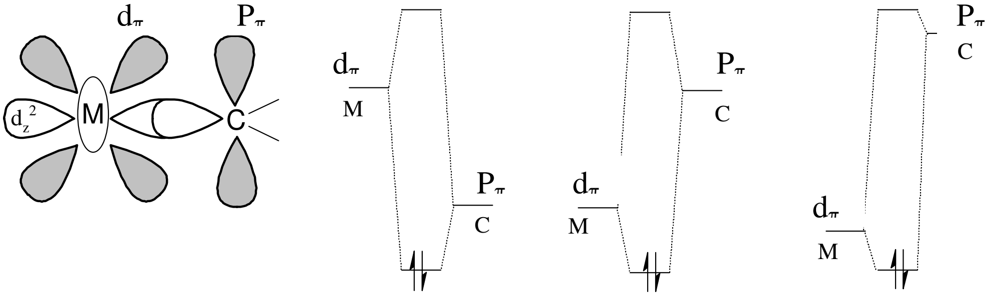
Figure 1. 5. Steric effects of the substituents of carbenes.

The triplet state is favoured when the σ and π orbitals are degenerate, which implies a linear geometry. Moreover, increasing the steric bulk of the substituents will broaden the angle about the carbene centre. Dimethylcarbene has a singlet ground-state and an angle of 111^0 about the carbene centre (Richards *et al*,1995). Di-*tert*-butylcarbene (Myers *et al*, 1986) and diadamantylcarbene (Gano *et al*, 1982) possess triplet ground states with the angles about the carbene centres being 143^0 and 152^0, respectively. The magnitude of these angles has been inferred from electron spin resonance (ESR) measurements (figure 1.5).

The second effect of bulky substituents is kinetic only: They prevent the dimerization (diaminocarbenes) or polymerization (alkyl carbenes) of the carbene.

1.4 NHC ligand properties

Although the metal carbene bond in Schrock and Fischer carbene complexes are both described as double bond, they differ by the polarity of the electron density. This difference arises from the difference in energy between the dπ orbital of the metal and the pπ orbital of the carbene (Figure 1.6). If the dπ orbital is lower in energy than the pπ orbital, the metal carbon bond is polarised δ- on the metal and δ+ on the carbene and it is a Fischer carbene complex. Contrary, if the dπ orbital is higher in energy than the pπ orbital, the metal carbon bond is polarised δ+ on the metal and δ- on the carbene and it is a Schrock carbene complex. A particular example of Fisher carbenes are NHCs which have a pπ orbital of very high energy since their multiple bonding between the carbene atom and the two nitrogen atoms. As a result, the pπ orbital does not interact well with the dπ, thus preventing almost any π-backbonding from the metal to the carbene. In the NHC complexes, the metal carbon bond is therefore best represented by a single bond.



Schrock
nucleophilic carbene

Fischer
electrophilic carbene

NHC carbene

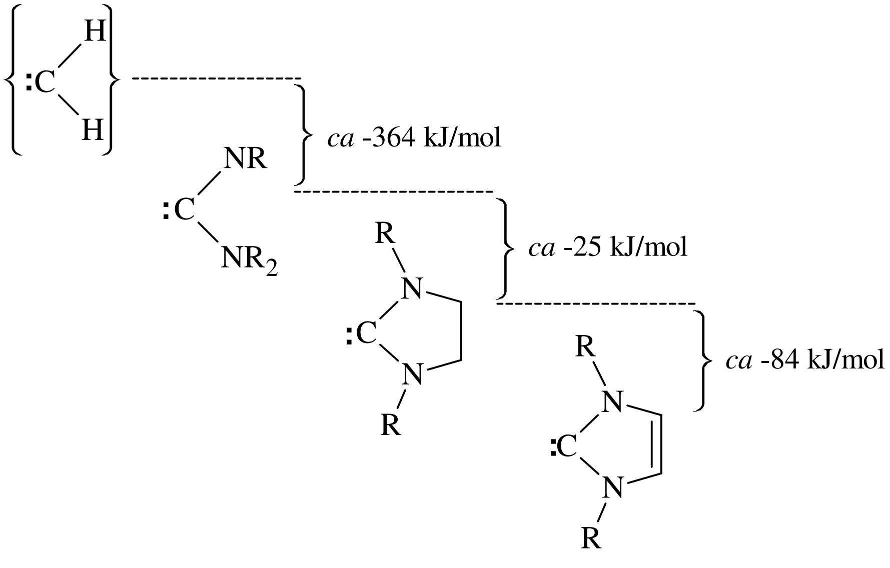
Figure 1.6. Partial molecular diagram for Schrock, Fischer and NHC carbene complexes

The fundamental difference between a typical Schrock alkylidene moiety and an NHC as a ligand is underlined in the crystal structure of [RuCl$_2$(NHC)$_2$ (=CHC$_2$H$_2$Cl)] (NHC = 1,3-diisopropylimidazolin-2-ylidene) where the two types of carbenes are linked to the same metal centre (Weskamp *et* al, 1998). The ruthenium-carbon bond of the Schrock carbene, generally written as a double bond, has a bond length of 1.821(3) Å, whereas the Ru-C bond length to the NHC (2.107(3) Å and 2.115 (3)Å) justifies its representation as a single bond (σ-donor and virtually no π-acceptor).

Measurement of IR carbonyl absorption frequencies of NHC carbonyl metal (Fe, Cr, Rh, Mo and Ir) and their phosphine analogues showed the significantly increased donor capacity of NHC relative to phosphines, even to trialkylphosphines (Köcher *et al,* 1997 and Hermann et al, 2001). Experimental investigations (Weskamp *et al*, 1999), calorimetric studies (Huang *et al*,1999) and experimental calculations (Schwarz *et* al, 2000), agree that the ligand dissociation energy of NHCs from Ru complexes is higher than for phosphines. Further calculations with other metals such as Au, Cu, Ag, Pd and Pt led to similar conclusions (Böhme *et al*,1998 and Green *et al*, 1997).

By analogy to the cone angle defined for phosphines by Tolman (Tolman, 1977) a method to quantify the steric parameters of NHCs has been proposed by Nolan (Huang *et al,* 1999) who described NHCs as "fences" with "length" and "height".

The structural differences for free NHCs and metal complexed NHCs are very small. In ^{13}C-NMR spectra, the signals for the free carbene carbon are usually shifted upfield by about 20-30 ppm upon complexation of the free NHC to a transition metal. Recent results with the bulky substituents at the nitrogen atoms can be regarded as free carbene. Theoretical calculations of what indicate that downhill pathway leads from methylene to isolable heterocyclic carbenes (Scheme 1. 6) (Herrmann and Kocher, 1997).



Scheme 1.6. Downhill energy pathway from methylene to isolabile heterocyclic carbenes.

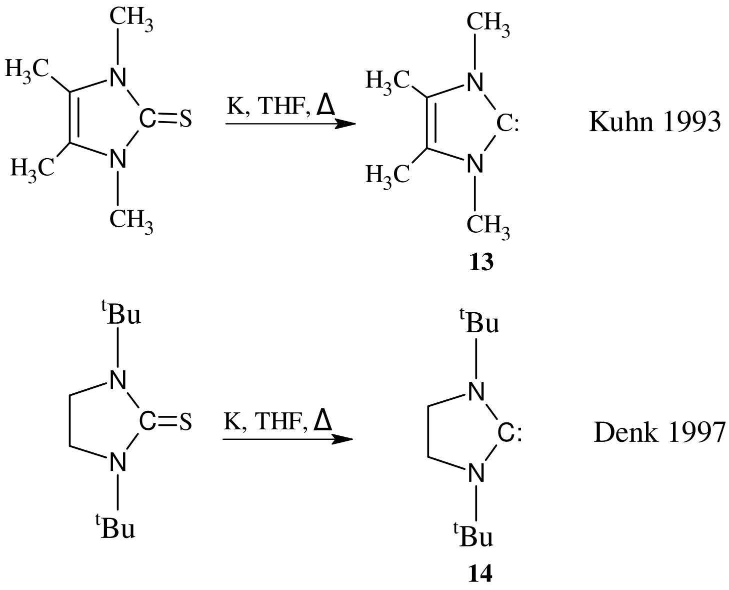
Wanzlick *et al.* recognized that aromatic resonance structures in unsaturated *N*-heterocyclic five-membered rings contribute to carbene stability. Unsaturated *N*-heterocyclic carbenes **5** have the largest singlet-triplet gap (about 356 kJmol^{-1}) of any divalent carbon compounds (Arduengo *et al.,* 1991). They show no tendency to dimerize, which is in contrast to their C-C saturated analogues. The singlet-triplet gap becomes smaller upon saturation of the C-C bond, since five-center six-electron (5c-6e) π delocalization as a stabilizing factor is no longer possible. However, the synthesized carbenes of their C-C saturated analogues stable if the bulky substituents at the nitrogen atoms contained as free carbene. That is to say, C4-C5 backbone effectived only on free carben or dimerization. In addition, C-C saturated *N*-heterocyclic carbenes are expected to be stronger σ-donor ligands than their C-C unsaturated counterparts (Lee *et al*, 2004).

Stable carbenes of all four types shown in Scheme 1.7 have been isolated and characterized, but in organometallic chemistry the trend is that only imidazolylidenes are isolated prior to reaction with a desirable complex precursor.

1.5. Synthesis of Stable Carbenes

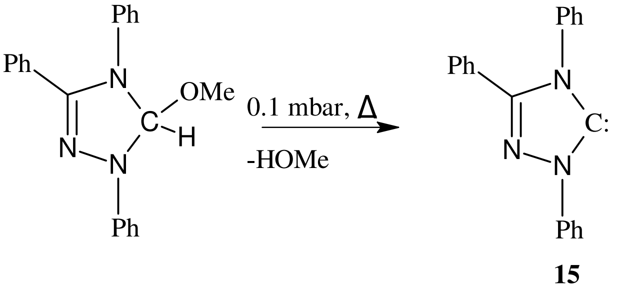
Arduengo obtained 1,3-diadamantylimidazole-2-ylidene, **1,** as a colourless, crystaline solid by deprotonation of 1,3-di-adamantylimidazolium chloride with NaH. In order to obtain reasonable rates for the deprotonation, catalytic amounts of DMSO were added, since the sodium hydride, and in some cases the imidazolium salts, are insoluble in THF (scheme 1.7)**.** Alternatively, stoichiometric amounts of n-BuLi or LDA have been employed by as deprotonating bases, with satisfying results (Denk *et* al, 2000)**.** Herrmann *et al.* showed that deprotonation occurs faster in liquid ammonia as a solvent (homogeneous phase). This method is applicable for a wide range of different carbenes, including nitrogen-, oxygen-containing carbenes, and chiral carbenes (Herrmann *et al*,1996).

Kuhn *et al.* (Kuhn *et al*,1993) devised a method to obtain alkyl-substituted imidazole-2-ylidenes, which relied primarily on the reduction of imidazole-2-thiones with potassium metal; a methodology that was used to obtain the previously unknown imidazolidin-2-ylidenes (Denk *et al*, 1997).



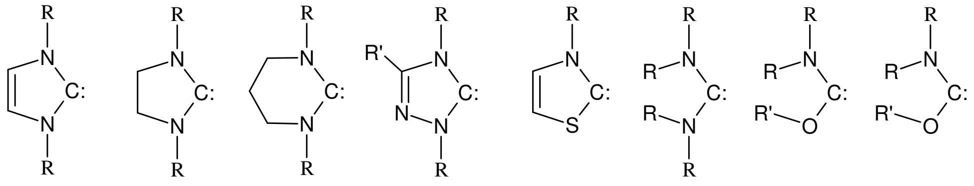
Scheme 1.7. Reduction of imidazole- and imidazolidin-2-thione.

Compound **15** was the first commercially available carbene and was obtained quantitatively from the corresponding 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazole by thermal elimination of methanol under reduced pressure (0.1 mbar) (scheme 1.8) (Enders *et al*, 1995). The 1,1 elimination of methanol is a less general route and takes advantage of the relative lack of volatility of the *N*-heterocyclic carbene, rendered so by the presence of three phenyl substituents on the triazole ring and its lack of symmetry.



Scheme 1.8. Synthesis of 5-methoxy-1,3,4-triphenyl4,5-dihydro-1*H*-1,2,4-triazole.

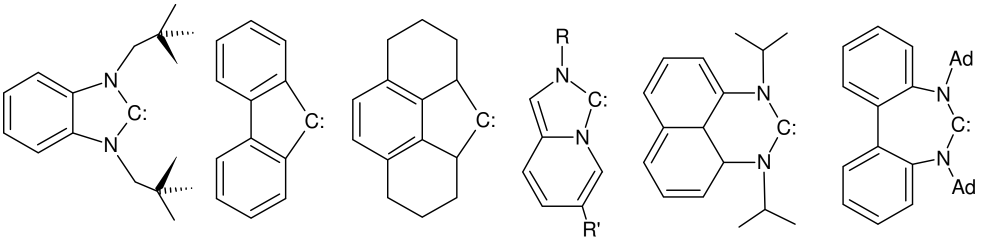
Following these synthetic approaches, a number of stable carbenes have been isolated induding: imidazole-2-ylidenes (**6**), imidazolidin-2-ylidenes (**7**), tetrahydropyrimid-2-ylidenes (**16**), 1,2,4-triazole-5-ylidenes (**17**), 1,3-thiazoie-2-ylidenes (**18**), as well as acyclic diaminocarbenes (**19**), aminoxycarbenes (**20**) and aminothiocarbenes (**21**) (Figure 1.7).



6 **7** **16** **17** **18** **19** **20** **21**

Figure 1.7. Stable carbenes.

As mentioned earlier, the isolation of the stable imidazolin-2-ylidene (**6**) and the saturated imidazolidin-2-ylidene derivative (**7**) sparked renewed interest in the chemistry of N-heterocyclic carbenes and their metal complexes. Initially, the triazole derivative (**17**) and the benzannulated carbene (**22**) were prepared, both containing a diamine-stabilized carbene center as part of a five-membered ring.



22 **23** **24** **25** **26** **27**

Figure 1.8. Polycyclic carbenes

Polycyclic diaminocarbenes derived from four-, five-, six-, and seven-membered *N*-heterocyclic rings (**23**), (**24**), (**25**), (**26**), (**27**) (figure 1. 8) and their metal complexes are also known.

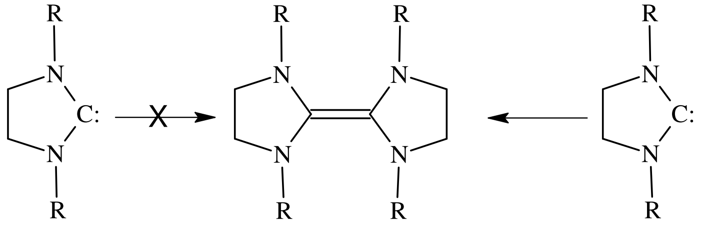
1.6. Structure of Stable Carbenes

All stable carbenes isolated to date bear two π donating substituents with at least one of these being a nitrogen atom. This is due to the efficient stabilizing effects offered by the nitrogen atoms which is by far superior to that offered by oxygen atoms. This has been proven experimentally; indeed, bis(dimethylamino)carbene**,** Me_2N-C-NMe_2, has been characterized by NMR spectroscopy (Alder *et al*,1999) whereas dimethoxycarbene, MeO-C-OMe, has only been characterized in frozen matrices due to its relative instability.

The carbene carbon resonates at rather low fields in the ^{13}C NMR (200 -300 ppm) compared to the cationic precursors, where the ^{13}C NMR of the N-C-N carbon appears between 130- 180 ppm. More precisely, the N-C-N carbon in carbenes of type $\mathbf{7^+}$ resonate in the range of 205- 220 ppm in the ^{13}C NMR, which is 15 -25 ppm upfield from the resonance of the N-C-N carbon of type $\mathbf{7^*}$ carbenes.

The structures of many carbenes have been elucidated by X-ray diffraction studies. The bond angles observed at the N-C-N fragment are between 100 – 110 °**,** which is in very good agreement with that expected for singlet carbenes bearing π donor substituents, i.e., F-C-F =102 ^{0}. The larger N-C-N angle found in the acyclic bis(diisopropylamino)carbene (121.0^0) has been attributed to the increased steric demand around the carbene carbon (Alder *et al*, 1996). The nitrogen atoms in diaminocarbenes are always planar or close to planar and the N-C bond lengths are rather short (1.32 – 1.37 Å)**,** which indicates that they have strong double bond character.

As shown in section 1.3.2 and 1.3.3, carbene centres are highly sensitive to electronic interactions with their substituents. The nature of the stabilization stems from the structure of the molecules as well as their reactivity. While carbenes of type 7* do not require sterically demanding substituents for their stabilization. Denk et al. has shown (Denk et al, 1997) that steric interactions in carbenes of type 7^+play a crucial role in their isolation (scheme 1.9).



7^+
R = Mes
R = ^{t}Bu

11

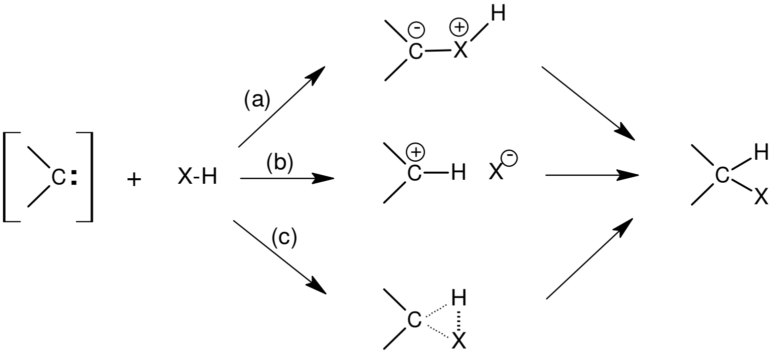
7^*
R = Me
R = Et
R = ^{i}Pr

Scheme 1.9. Dimerization of imidazolidin-2-ylidenes.

The 6π aromatic character of diaminocarbenes of type **7** has been controversial and it gained credibility in 1996 when Apeloig (Apeloig *et al*, 1996) and Frenking (Frenking *et al.*1996) independently investigated carbenes of type **7^+** according to the following criteria: structural, themodynamic, ionization potentials, magnetic properties and π populations. The aromatic character of type **7^+** carbenes was also confirmed by inner-shell electron energy Ioss spectroscopy, the work of Denk *et al.* (Denk *et al.* 1999). Although the aromaticity is less pronounced than in the conesponding imidazolium salt precursors, it brings an additional stabilizing effect that has peculiar effects in the reactivity of carbenes of type **7^+**.

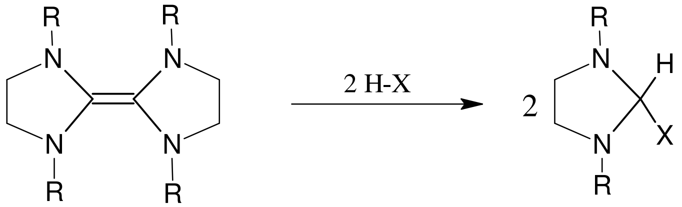
1.6.1. Insertion into polarized H-X bonds

Insertion of transient carbenes into strongly polarized H-X bonds has been discussed primarily in terms of stepwise mechanism: (a) electrophilic attack of the carbene on the heteroatom X, followed by proton transfer (ylid mechanism), and (b) protonation of the carbene to give a carbocation (ion pair), followed by nucleophilic addition (carbocation mechanism) (Scheme 1.10). A concerted process (c) cannot be excluded but has not received definitive experimental support (Kirmse, 1994).



Scheme 1.10. Mechanism of insertion of transient carbenes into H-X bonds.

Çetinkaya reported that bis(1,3-dibenzylimidazolidinilid-2-yliden), **28** was found to react readily with the proton-active compounds (H-X), such as chloroform, phenylacetylene and dimethylamine to give substituted imidazolidines,. These products are formally derived by insertion of the nucleophilic carbene into C-H or N-H bonds (Çetinkaya, 1989).



11

28

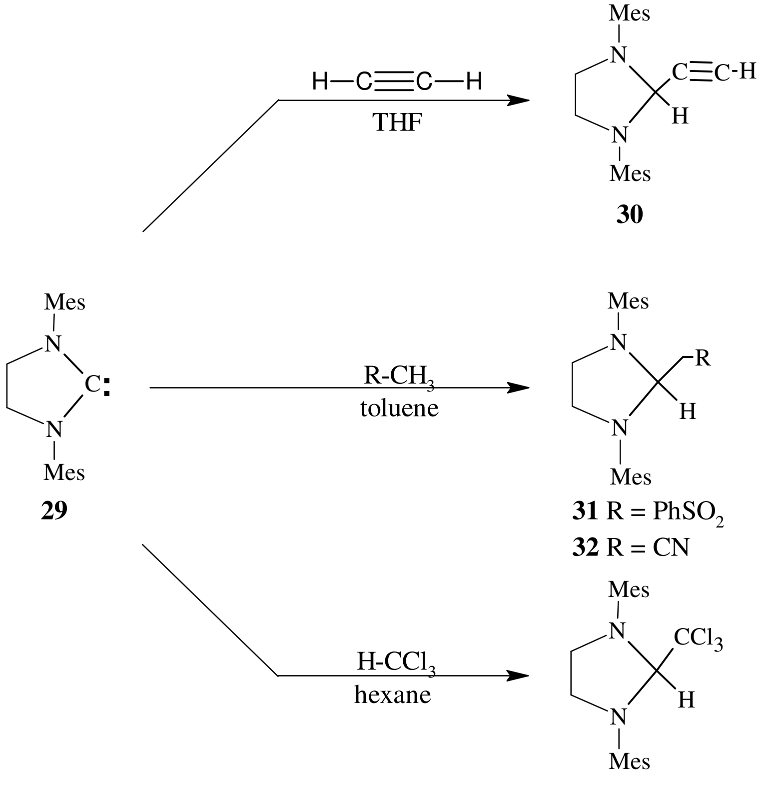
R = alkyl, aryl
R = CH_2Ph

a: $X = CCl_3$
b: $X = C\equiv CPh$
c: $X = NMe_2$

The isolation, in recent year, of stable isolable carbenes has renewed interest in their chemical behaviour (Arduengo, 1999). Among the reactions commonly associated with carbenes is their H-X insertion reaction (X = C, N, O, S etc.). These insertion reactions should be possible for both singlet electrophilic and singlet nucleophilic carbenes. Insertion reactions of imidazol-2-ylidenes, imidazolin-2-ylidenes (4,5-dihydroimidazol-2-ylidenes) or other strongly nucleophilic carbenes have not been widely studied, but a few examples can be found in the literature. Wanzlick *et al.* reported reactions of 1,3-diphenyldihydroimidazol-2-ylidene with acetophenone, benzaldehyde, cyclopentanone, furfural, nitromethane, or various sulfones (Wanzlick *et al.*, 1963; Wanzlick and Schikora, 1960).

Arduengo *et al.* prepared that the carbene 1,3-bis(2,4,6-trimethylphenyl)dihydroimidazol-2-ylidene (**29**) reacts with acetylene in a 1:1 ratio in THF at RT to form the C-H insertion product **30** (Arduengo *et al.* 1999).

Compound **30** is formed quantitatively and is isolated as colourless crystals. Arduengo *et al.* prepared that the insertion of carbene **29** into an α C-H bond of $MeSO_2Ph$ proceeds smoothly at RT in toluene to afford **31** as a colourless solid.



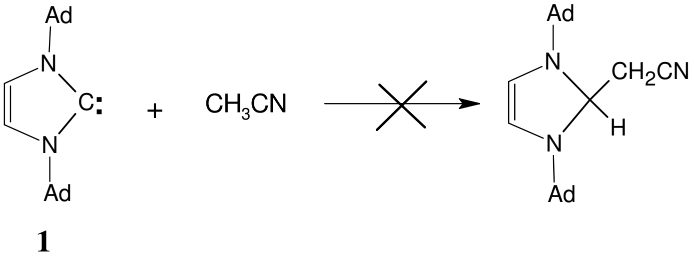
29

30

31 R = $PhSO_2$
32 R = CN

33

In contrast to the reaction between **29** and MeCN, an unsaturated analog of 1,3-di(1-adamantyl)imidazol-2-ylidene (**1**), did not react with MeCN. Interestingly, when imidazol-2-ylidene (**1**) is recrystallised from MeCN or toluene/MeCN, the MeCN solvate of **1** is isolated, but there is no direct acetonitrile imidazolylidene reaction or interaction. **1** C-H insertion reactions of imidazolin-2-ylidenes do occur with acidic C-H bonds.

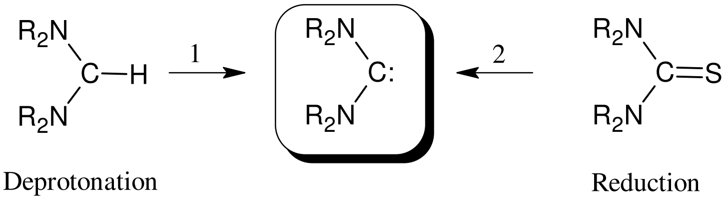


1

Wanzlick and co-workers employed an α-elimination reaction of $CHCl_3$ from 1,3-diphenyl-2-(tricholoromethyl)imidazolidine as an entry point for their work directed toward stable carbenes (Wanzlick and Schikora, 1960; Wanzlick, 1962; Wanzlick *et al.* 1963). Although Wanzlick's work did not succeed in producing a stable imidazolinylidene, the corresponding dimers of the carbenes could be isolated. If transient carbenes were involved in Wanzlick's α-elimination reaction, the reverse of this reaction (the C-H insertion of an imidazolinylidene with $CHCl_3$) may be possible starting with an isolated carbene. After 3 days at RT, carbene **29** added to $CHCl_3$ from a hexane solution to form the imidazolidine **33** (91%).

1.7. Starting Materials for the Synthesis of Diaminocarbene

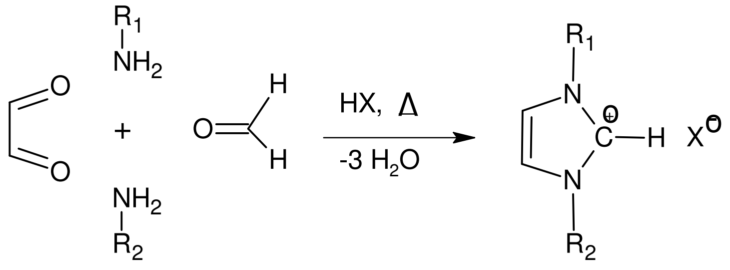
In addition to other applications, thioureas and related carbenium cations are useful starting materials for the preparation of stable carbenes. The main synthetic routes leading to carbenes include: (1) deprotonation of diaminocarbenium salts with strong bases; and (2) the reduction of thioureas with alkali metals (scheme 1.11).



Scheme 1. 11. Synthesis of stable diaminocarbenes.

1.7.1. Carbenium Cations

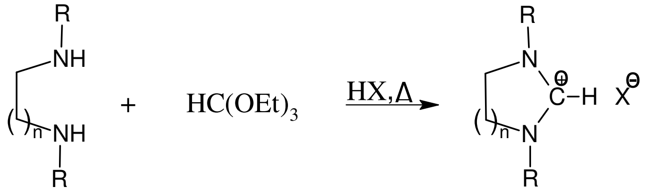
Most of the research on stable diaminocarbenes has been conducted using the unsaturated imidazole-2-ylidenes **6,** mainly because of the ease with which the starting materials *N*-substituted imidazolium salts are obtained. The latter are synthesized through a one-step process patented by DuPont (scheme 1.12) (Arduengo, 1992).



35 HX

Scheme 1.12. Synthesis of substituted imidazolium cations.

Research on saturated imidazolidin-2-ylidenes **7** has not been as widely pursued. This may be due to a lack of good methods for the synthesis of their precursors. For example, there are only three published procedures for the synthesis of irnidazolinium salts and due to their low yields, they are subject to improvement (Rabe *et al*, 1973 and Bildstein *et al*, 1999).



yields 36% -99%

36R HX , n = 1

37R HX , n = 2

Scheme 1.13. Synthesis of imidazolidinium salts: reaction of orthoesters with *N,N'*-dialkyl-α,ω-alkanediamine.

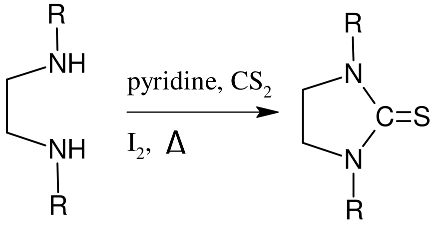
Saba and co-workers (saba *et al.* 1991) found that the reaction of orthoesters with *N,N'*-dialkyl-α,ω-alkanediamine, in the presence of ammonium tetrafluoroborate or ammonium hexafluoro phosphate affords the corresponding imidazolidinium, tetrahydropyrimidinium and tetrahydro-1,3-diazepinium cations good to excellent yields (76 - 99 %) for all R groups, except for the bulky ^{t}Bu (n = 1). For the case of the *tert*-butyl group a 36 % yield isobtained (scheme 1.13).

1.7.2. Thioureas

Thioureas are used in the pharmaceutical sector, various technical applications, and in the synthesis of heterocycles (Mertschenk *et al*, 1995). Denk *et* al. have proven to be good starting materials for diaminocarbenes (Denk *et al.*1999).

A number of diffierent methods are available for the synthesis of thioureas bearing substituents on nitrogen (Bogatskii *et al*, 1983). Thiourea itself is not a good starting material for the synthesis of its N-substituted derivatives because electrophiles react with the sulfur in most cases. A closer examination of the synthetic repertoire reveals serious deficiencies.

Existing methods typically use the highly toxic, and extremely flammable carbon disulfide or the toxic and expensive isothiocyanates R-N=C=S as starting materials not to mention that the standard synthesis from isothiocyanates and amines is restricted to the synthesis of thioureas with the general formula R^1-NH-C(S)-NR^2R^3. In addition, the methods described in the literature are generally incompatible with bulky substituents on the nitrogen atoms. For example, reaction of *N,N'*-dialkyl-ethylenediamines with carbon disulfide and iodine in pyridine, as reaction medium, bears the desired cyclic *N*-substituted thioureas, but the product yields decrease dramatically as the steric bulk of the R substituent on the nitrogen atom increases (scheme 1.14).



38

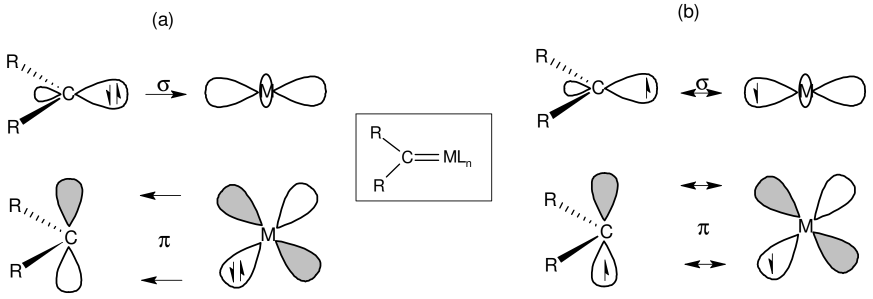
R	%yields
Me	70
Et	60
^{i}Pr	50
^{t}Bu	20

R = Me, Et, ^{i}Pr, ^{t}Bu

Scheme 1.14. Synthesis of imidazolidin-2-thiones.

1.8. Electronic properties of NHC complexes

So far, carbene complexes have been divided into two types according to the nature of the formal metal-carbon double bond (Collman *et al.*, 1987). The metal-carbon bond of Fischer-type carbene complexes is a donor-acceptor bond and formally results from the superposition of carbene to metal σ-donation and metal to carbene π-back-donation (Scheme 1.9a). In contrast, the metal-carbene bond of Schrock-type complexes is essentially covalent and formally results from the interaction of a triplet carbene with a triplet metal fragment (Scheme 1.9b). In relation to these different bonding situations, Fischer complexes are generally formed with a low-valent metal fragment and a carbene bearing at least a π-donor group, whereas Schrock complexes are usually formed with metals in a high oxidation state and carbene ligands bearing alkyl substituents.



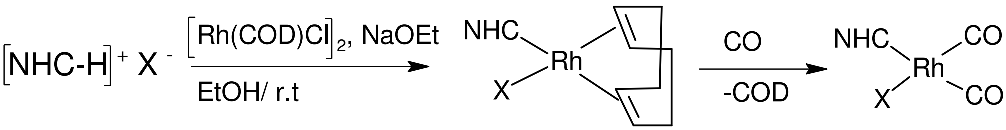
Scheme 1.15. Schematic representations of (a) donor-acceptor bonding in Fischer carbene complexes and (b) covalent bonding in Schrock carbene complexes.

Due to the presence of two π-donor substituents at the carbene center, the N-heterocyclic carbene complexes may be classified, at a first glance, as Fischer-type compounds. However, in contrast to usual Fischer-type complexes, N-heterocyclic carbenes and especially imidazol-2-ylidenes 6 and imidazolidin-2-ylidenes 7 bind to transition metals only through σ donation, π-back-bonding being negligible. Photoelectron spectroscopy coupled with density functional calculations have demonstrated that even for group 10 metals, bonding occurs very predominantly through σ donation from the carbene lone pair (Green et al., 1997). These, peculiar binding properties are easily understandable since the energy of the vacant pπ orbital at the carbene center is considerable increased by the strong N → C π donation. The CO stretching frequencies of mixed carbene-carbonyl complexes also afford interesting information about the electronic properties of N-heterocyclic carbene ligands (Turkmen et al., 2006, Türkmen and Çetinkaya, 2006). The ratio of σ donation to π-back-donation for Fe(CO)4-bonded heteroatom-substituted carbenes increases in the order $:C(OR)R < :C(NR_2)R < :C(NR_2)_2 \approx$ imidazolidin-2-ylidenes ≈ imidazol-2-ylidenes. The π-acceptor ability of diaminocarbene II-IV and VI lies that of nitriles and pyridine. On the basis of solution calorimetric investigations, a relative enthalpy scale has been established for a series of sterically demanding nucleophilic carbene ligands coordinated to the Cp^*RuCl moiety (Huang *et al.*, 1999). Imidazol-2-ylidenes **III** ligands behave as better donors than the best phosphine donor ligands with the exception of the sterically demanding 1,3-di(1-adamantyl)imidazol-2-ylidene.

The X-ray diffraction studies performed on many complexes also reveal the pure σ-donor character of the *N*-heterocyclic carbenes. Indeed, elongated single M-C bonds are generally observed. At the same time, the internal ring angle at the carbon atom is slightly larger in coordinated than in free carbenes, although not as large as that in the related imidazolium salts. Similarly, the C-N bond distances lie between those of the free carbenes and imidazolium salts. These data as a whole suggest that the three- and five-center π-delocalization in the imidazolidin-2-ylidenes **II** and imidazol-2-ylidenes **III**, respectively, be increased by coordination of the carbene center.

By means of theoretical data, IR spectroscopy, and X-ray diffraction data it is possible to compare the electronic properties of NHC ligands, e.g., the σ-donor/π-acceptor quality. One possibility to judge the σ-donor strength of carbene ligands is $\mathrm{p}K_\mathrm{a}$ values suggest strong domors. Besides the influences on the $\mathrm{p}K_\mathrm{a}$ values of substituents in α-position to the acidic proton, there was limited investigation on the effect of the $\mathrm{p}K_\mathrm{a}$ values for diffirent *N*-heterocycles. In comparison to imidazolin-2-ylidenes, their CC-saturated analogues and acyclic carbenes revealed that the latter are the most basic carbenes, whereas imidazolidin-2-ylidines are only slightly more basic than imidazolin-2-ylidenes.

For the experimental determination of the relative σ-donor strength this method is quite extensive. A simple and relatively precise method is indirect measurement of the σ-donor strength by IR spectroscopy. The basicity of carbene ligand is evaluated by the comparison of the υ(CO) infrared data in $\mathrm{Rh(CO)_2X}$(carbene)complexes (Herrmann *et al.*, 2006, Alcarazo *et al.*, 2005, Canac *et al.*, 2005, Chianese *et al.*, 2003, Lavallo *et al.*, 2005). A σ-basic carbene ligand is related to a low stretching frequency (wave number) of the carbon monoxide opposite the carbene.

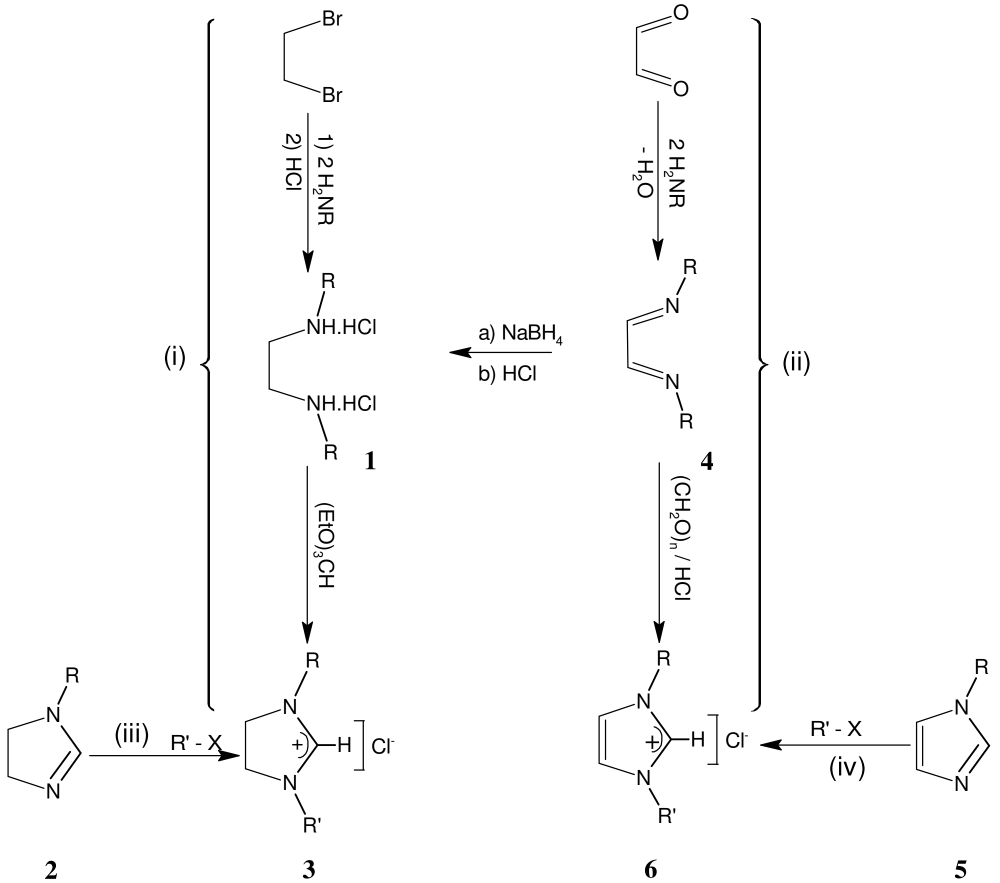


The lower the value of ν(CO), the weaker the C-O bond and this indicates grater back-donation of charge from M to CO.

1.9. Overview of metal NHC chemistry

1.9.1. Precursors for stable carbenes

In many cases the synthesis of NHC complexes starts from *N,N′*-disubstitued azoli(ni)um salts (**IX** and **X**). Imidazolium salts as precursors for imidazolin-2-ylidenes are generally accessible by two ways complementing each other: (i) a multicomponent reaction building up the heterocycle with the appropriate substituents in a one-pot reaction or (ii) quaternasition of the alkyl imidazole .

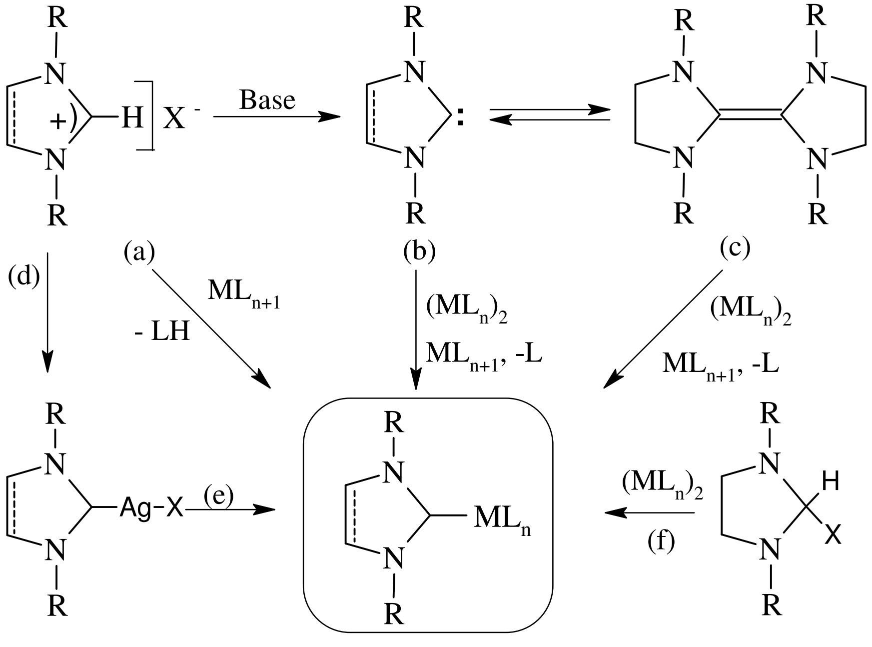


Scheme 1.16. Convenient synthetic routes to imidazolinium salts (**3**) and (**6**). *Reagents and conditions*: (i) a) RNH_2, reflux; b) HC(OEt)$_3$, 140°C; (ii) a) RNH_2, RT; b $NaBH_4$, EtOH, reflux; c) HC(OEt)$_3$/ NH_4Cl; (iii) and (iv) R'X, toluene, 110^0C.

Imidazolium salts that can be prepared by the first procedure, the alkylation of imidazole, are easy to obtain and often used for metal complex synthesis. Potassium imidazolide is reacted with the first equivalent of alkyl halide in toluene to give the 1-alkylimidazole. Subsequent alkylation in 3-position is achieved by addition of another equivalent of alkyl halide (Haque and Rasmussen, 1994; Grimmet, 1997). The reaction of an ortho-ester, e.g., HC(OEt)3, with a secondary bisamine in the presence of an ammonium salt yields imidazolinium salts (X, Scheme 1.3) (Scholl et al., 1999; Saba et al., 1991). The necessary secondary diamines can be generated by a classical condensation-reduction sequence or by applying the palladium-catalyzed Buchwald-Hartwig amination (Cabanal-Duvillard and Mangeney, 1999). The latter reaction offers convenient access to imidazolinium salts with chiral backbones starting from chiral diamines, a number of which are commercially available.

1.9.2. Synthesis of transition metal-NHC complexes

Generally, four major routes were applied for the synthesis of NHC complexes: (a) the *in situ* deprotonation of ligand precursors, (b) complexation of free *N*-heterocyclic carbenes, (c) the cleavage of electron-rich olefins (ero), (d) Metal exchange starting with a silver–NHC complex (prepared by the direct reaction of the imidazolium precursor and Ag_2O) (e) Transmetallation from silver (f) Thermal elimination of H-X from the C2 position (Scheme 1.16).



Scheme 1.17. Major synthetic pathways for the generation of transition metal NHC complexes.

1.9.2.1. Synthetic strategies to NHC metal complexes

The synthesis of a wide range of ligand precursors is relatively straightforward, and many are now commercially available. However, the subsequent deprotonation of the NHC–metal complex is more challenging and can give unexpected results. Many strategies have been employed to prepare NHC–metal complexes, dependent upon the metal centre of interest. NHCs can be introduced as imidazolium salts, as free carbenes or *via* transmetallation routes. Typical methods are given below.

1.9.2.2. C=C bond cleavage of electron-rich olefins

Insertion of a metal into the C=C bond of bis(imidazolidin-2-ylidene)-based electron-rich olefins; successful for the synthesis of noble metalmono-bis(carbene) adducts. The coordination chemistry of electron-rich olefins **39** (Lappert, 1988) containing alkyl or aryl R groups has led to the discovery of their role as precursors of a wide range of transition metal carbene complexes of general formula $(NHC)_2 \rightarrow M(NHC)L_n$ (Lappert *et al.,* 1971) in which L_n represents the sum of all ligands attached to the metal M.

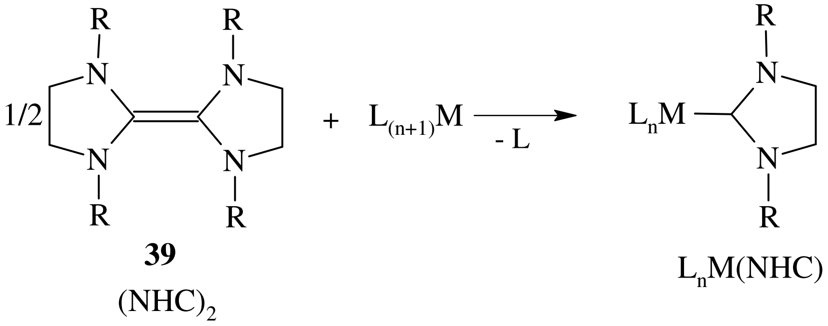
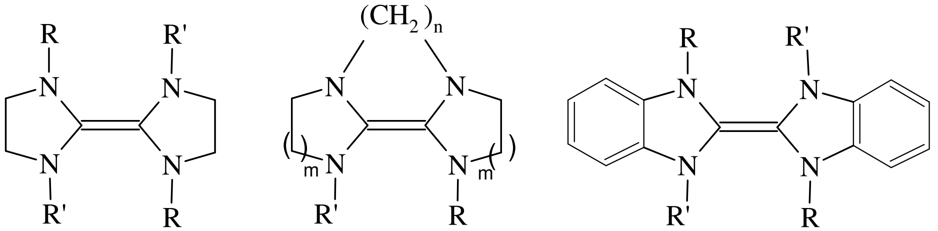


Figure 1.9. Insertion of a metal into the C=C bond

Dimerization of nonstable NHCs such as imidazolin-2-ylidenes is one of the routes used to obtain these electron-rich olefins (Wanzlick and Schikora, 1960). The synthesis of the olefins where R is a primary alkyl group has been accomplished by three general methods: (i) the condensation of *N,N'*-disubstituted ethlenediamines with $CH(OMe)_2NMe_2$ (Winberg *et al.,*

1965) or symmetrical tetraarylenetetramines (**40,** R = an unhindered aryl group, *e.g.* R = Ph) prepared by EtOH elimination from the orthoester $CH(OEt)_3$ (Wanzlick *et al.,* 1963) (ii) the reaction of *N,N'*-dialkylazolinium salts with sodium hydride (Çetinkaya *et al.,* 1992) (iii) elimination of small molecules neutral ligand precursors, *e.g.* $CHCl_3$ elimination (Wanzlick and Schikora, 1960).

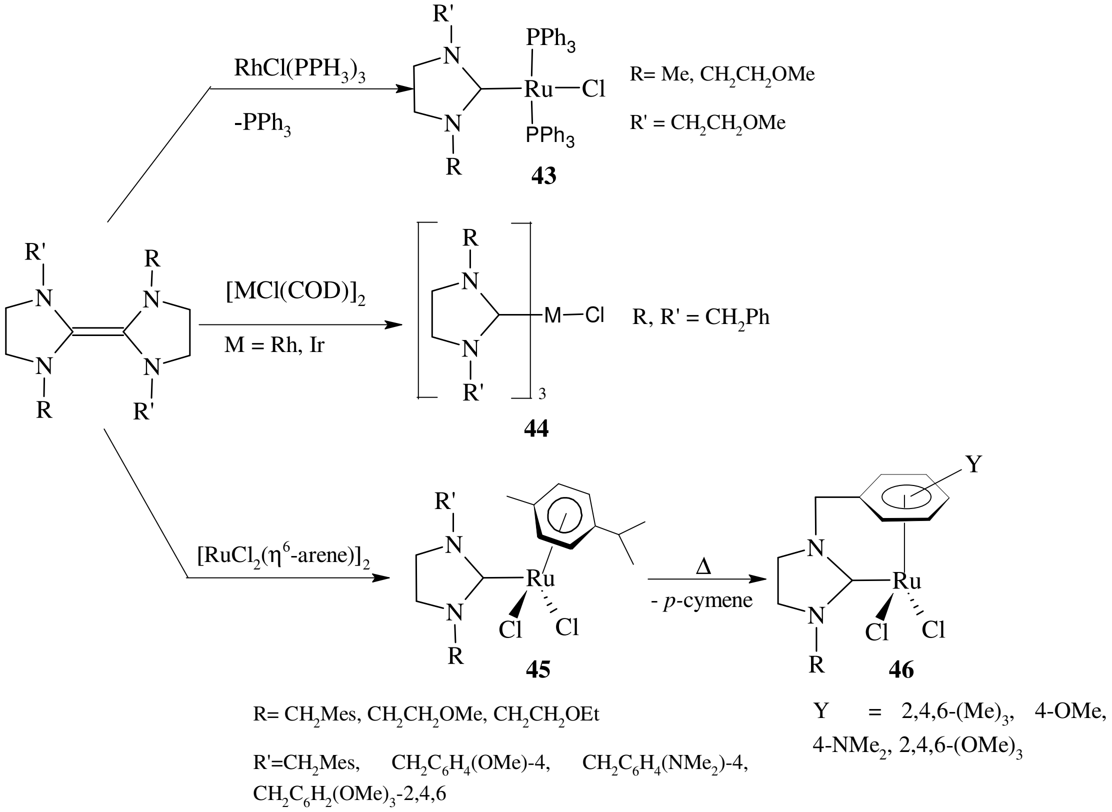


40 **41** **42**

Figure 1.10. Electron-rich olefins

Enetetramines (electron-rich olefins) such as **40**, **41**, and **42** used as (i) sources of carbene transition metal complexes (Çetinkaya *et al.,* 1993; 1994; 1997; 2001; 2003; Lappert, 1988), (ii) powerful reducing agents, especially chlorine atom-abstractors (Çetinkaya *et al.,* 1971; Lappert, 1988; Lappert *et al.,* 1986), or (iii) benzoin catalysts (Lappert and Maskell, 1982). The compounds have an extensive organic chemistry (Hoffmann, 1968; Hocker and Merten, 1972; Roeterdink *et al.,* 1983).

The exchange of phosphine ligands works, *e.g.*, in the Wilkinson catalyst $[Rh(Ph_3P)_3Cl]$, in $[Ru(Ph_3P)_3Cl_2]$ or $[Pt(Et_3P)_2Cl_2]$ (Hitchcock *et al.*, 1978; Cardin *et al.*, 1973; Çetinkaya *et al.*, 1997) and dimeric complexes can be cleaved as well, *e.g.*, $[M(\eta^4\text{-cod})Cl]_2$ (M = Rh, Ir) (Çetinkaya *et al.*, 1993). Imidazolidin-2-ylidene derivatives of rhodium(I) and ruthenium (II), having 2-methoxyethyl substituent on the *N*-atom. $[Rh(NHC)Cl(PPh_3)_2$, $[Rh(NHC)Cl(COD)]$ or $[Ru(NHC)Cl_2(arene)]$ have been prepared by treatment of $[RhCl(PPh_3)_3]$, $[RhCl(COD)]_2$ or $[RuCl_2(arene)]_2$ (arene = *p*-cymene, C_6Me_6) with the *N*-functionalized electron-rich olefins (Çetinkaya *et al.,* 1997).



Scheme 1.18. C=C bond cleavage of electron-rich olefins

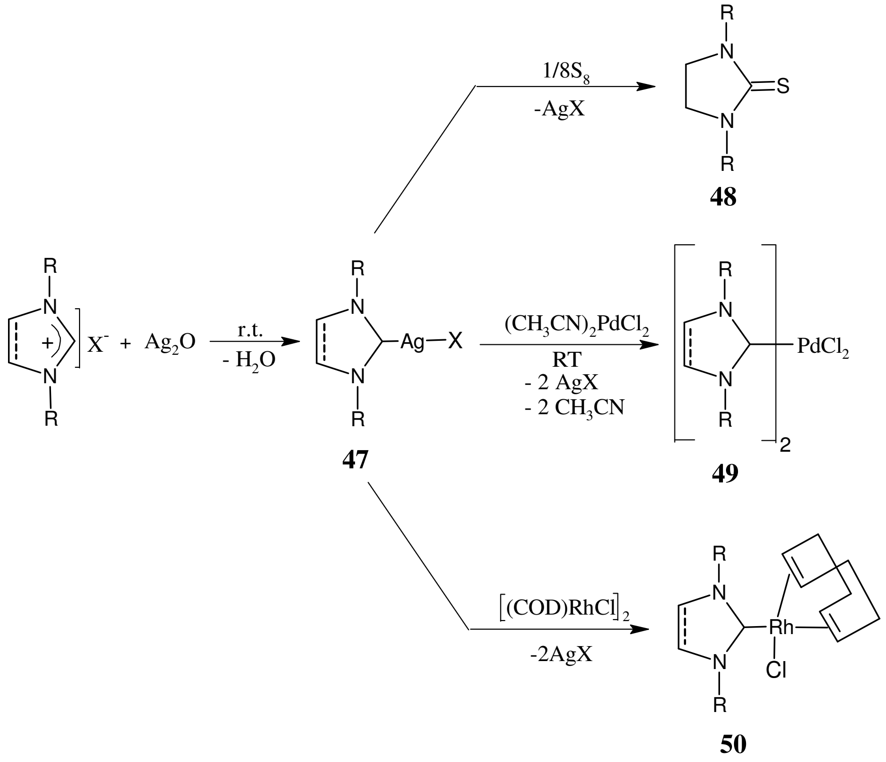
1.9.2.3. Transmetallation from silver

Basic silver(I) oxide Ag_2O is a convenient precursor for silver(I) (NHC) complexes such as **47** (Bildstein *et al*, 1999; Wang and Lin, 1998). The preparation proceeds even at room temperature. The cationic complex precipitates and is therefore easy to purify.

This complex represents a useful NHC transfer agent since it can be used as the NHC source for the preparation of NHC complex of other metals. Similar to Ag_2O, mercury(II) oxide HgO can be used to form Hg-NHC complexes in an ethanol/water mixture.

(NHC)silver(I) complexes can be used to transfer both NHC ligands to [Pd(CH_3CN)$_2$$Cl_2$] or [Au($Me_2S$)Cl] in CH_2Cl_2 at ambient temperature. The silver(I)-NHC complex is not have to be isolated prior to the NHC transfer reaction which makes this method more convenient (Lee *et al.*, 1999).

The silver(I) halide which forms during the transfer can be filtered off the product solution and can be recycled. Under phase transfer conditions this reaction can be run catalytically in silver (*vide supra*). In certain cases it has been advantageous to use a mixture of CH_2Cl_2 and ethanol as the solvent in this reaction (Wang *et al.*, 1999). Hahn *et al.*, studied the reaction of silver(I)-NHC complexes with elemental sulfur (Hahn *et al.*, 2006). The imidazolidin-2-thione **48** was obtained by simple addition of sulfur to a solution of the silver carbene complexes in dichloromethane at ambient temparature. This procedure has been extended to the preparation of a variety of palladium complexes **49** with donor-functionalized NHCs (McGuinness and Cavell, 2000). Due to its convenience and the broad range of complexes accessible, this method is very likely to gain an important role as a synthetic route to NHC complexes. Chianese *et al.* reported the facile syntheses of rhodium complexes **50** of NHCs by transfer from the corresponding silver-carbene complexes (Chianese *et al.* 2003).



Scheme 1.19. Transfer from the corresponding silver-carbene complexes

1.9.2.4. In situ deprotonation

A strong or weak base (such as KH, $LiN(SiMe_3)_2$, KOBu*t*, or NEt_3, NaOAc, Cs_2CO_3) is used to deprotonate an imidazolium salt *in situ*. The *in situ* complexation of the ligand has the advantage of not having to prepare and isolate the free NHC. In cases where the carbene is hardly stable, not yet accessible at all, or difficult to handle, this approach offers the only chance to prepare the desired complex.

1.9.2.5. Oxidative addition

Oxidative addition of an imidazolium cation by activation of the C2–X (X = Me, I, H) bond at low valent or metal hydride precursors.

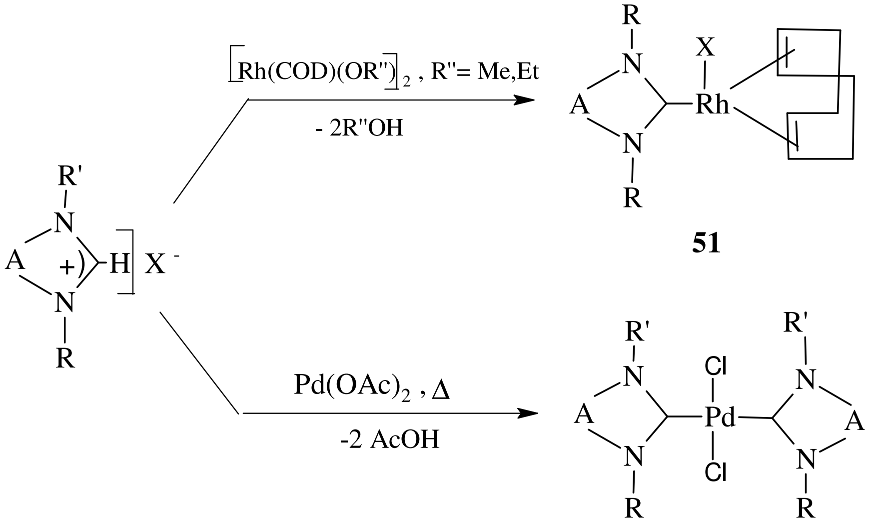
1.9.2.6. Direct metallation

Metallation of an imidazolium salt with a basic metal precursor such as $Pd(OAc)_2$ or $[Ir(COD)(OEt)]_2$. Brönstedt basic anions either on the metal precursor or on the azolium salt can form the desired ligand *in situ* by deprotonation. Commercially available metal acetates, acetylacetonates or alkoxylates, which are also easy to prepare, have been used frequently.

Wanzlick was the first to use an acetate salt in the synthesis of a mercury bis-NHC complex starting from mercury(II) diacetate (Wanzlick and Schoenherr, 1968)(Scheme1.3). There are other examples using the same strategy (Bildstein *et al*., 1998; Chen and Lin, 2000). Exchanging the anionic parts of the mercury precursor and the imidazolium salt, *i.e.*, using $HgCl_2$ and imidazolium acetate, works as well (Schoenherr and Wanzlick, 1970).

More than 25 years later, this method proved to be especially valuable for palladium(II) and nickel(II) complexes starting at the corresponding metal(II) diacetates and imidazolium or triazolium salts (Herrmann *et al*., 1996; Herrmann e*t al*., 1995; Herrmann *et al*., 1997). For palladium, it is possible to apply the *in situ* deprotonation method even without solvent, (Herrmann *et al*., 1996) but using THF or even better DMSO results in enhanced yields of the complexes (Herrmann *et al*., 1999).

The metal of the base functions as the ligand acceptor at the same time. C-deprotonation of azoli(ni)um salts is also feasible with (anionic) carbonylmetalates, which are normally generated through typical Hieber base reactions. Both variants were reported in 1968 for the first time: Wanzlick's homoleptic mercury(II) carbene complex **4** and Öfele's chromium(0) complex **3** were already mentioned. Commercially available metal acetates, acetylacetonates or alkoxylates, which are also easy to prepare, have been used frequently. This route has also been used to prepare complexes from benzimidazolium, pyrazolium, triazolium and tetrazolium salts. The limit of this method is the availability of the appropriate metallate precursors, which is determined by the nature and oxidation state of the central metal atom of the new complex as well as its ligand environment. Palladium(II) complexes were prepared similarly from the metal acetate (Özdemir *et al.,* 2004).



51

52

A	R, R'
CH_2CH_2	$R = R' = CH_2C_6H_2(OMe)_3$-3,4,5
CH_2CH_2	$R = R' = CH_2C_6H_2(Me)_3$-2,4,6
o-C_6H_4	$R = R' = CH_2CH_2OMe$
o-C_6H_4	$R = R' = CH_2CH_2Ph$
o-C_6H_4	$R = CH_2CH_2OMe$, $R' = CH_2CH_2Ph$

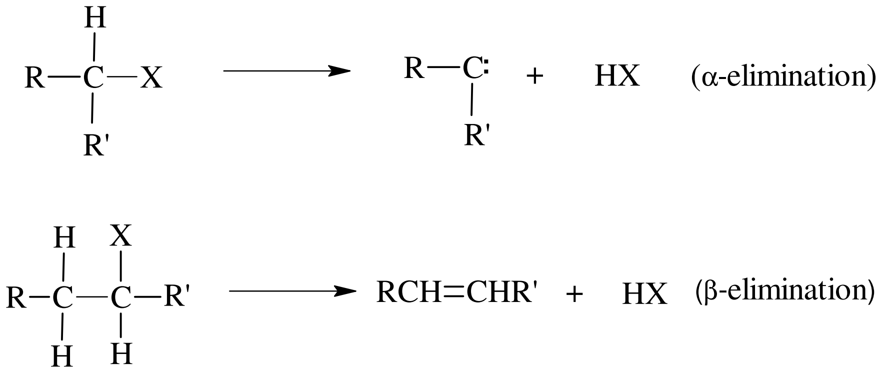
Scheme 1.20. Metallation of an imidazolium salt with a basic metal precursor

A variety of rhodium and iridium complexes were synthesized from easily available μ-alkoxy complexes and azoli(ni)um salts. Using μ-alkoxo complexes of (η^4-cod)rhodium(I) and iridium(I)-formed *in situ* by adding the μ-chloro bridged analogues to a solution of sodium alkoxide in the corresponding alcohol and azoli(ni)ium salts leads to the desired NHC complexes even at room temperature (Köcher and Herrmann, 1997; Çetinkaya *et al.,* 2002; Özdemir et al., 2004). Carbene-complex formation is exclusively effected by proton transfer to the metal-bound alkoxy group.

1.9.2.7. Thermal elimination of H–X from the C-2 position

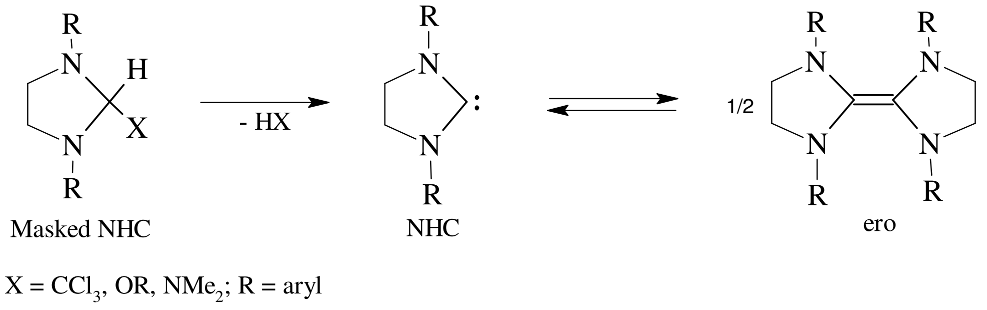
It has been demonstrated that a 2,2-functionalised *N*,*N*-dialkylimidazole, more easily described as an NHC-alcohol or -chloroform adduct can be described as "protected" form of the NHC ligand. For example $[H(CCl_3)C\{NArCH_2\}_2]$ or $[H(C_6F_5)C\{NArCH_2\}_2]$ can be heated to afford $HCCl_3$ or HC_6F_5, and the carbene $C\{NArCH_2\}_2$. To the best of our knowledge, there are no examples of abnormally bound carbenes formed from the Lappert method, addition into an electron rich alkene, from the direct reaction of a free, monodentate NHC with a metal complex, or from the relatively new thermolysis route.

An elimination reaction, the expulsion of another molecule from an organic substrate, can be classified according to the relative placement of the carbon atoms from which elimination occurs.



Scheme 1.21. Elimination reactions

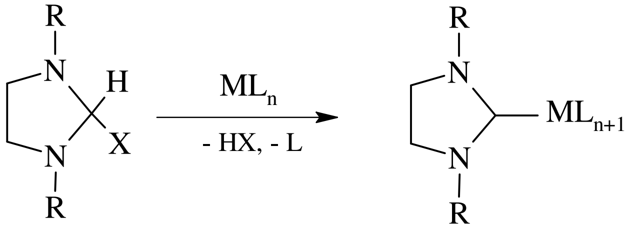
In general, the products of α-elimination (or 1,1-elimination) are unstable divalent species. In the present chapter, attention will be focused on α-elimination, which lead to NHC or ero formation. This type of elimination is affected by heating the masked NHC. However, some of the reactions take place even at RT.



Scheme 1.22. Thermal elimination of H–X from the C-2 position

Prior to work carried out in this study very little has been reported regarding α-elimination from neutral molecules for the synthesis of NHC complexes (Cardin *et al.*, 1973; Gürbüz, 1995; Ergün, 2000).

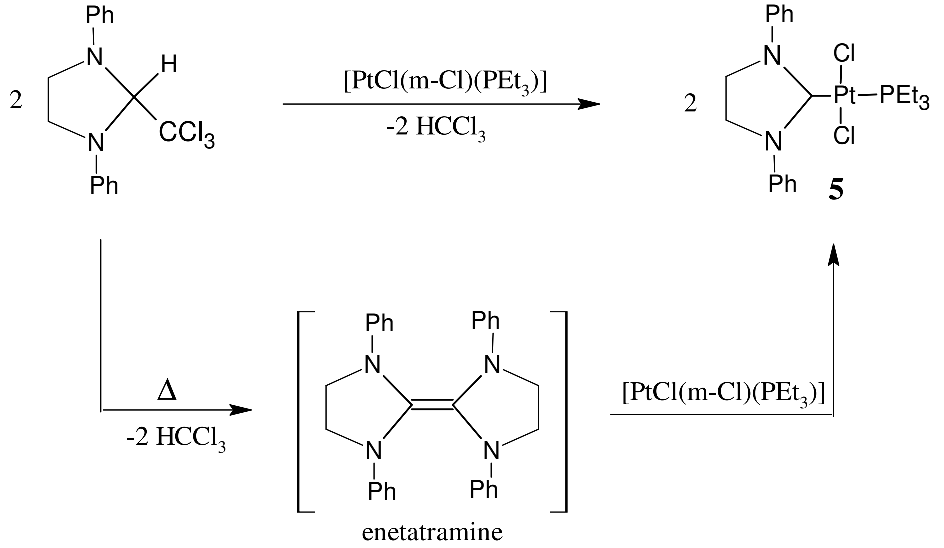
This state described an approach that employs NHC adducts as "protected" forms of the free carbenes. These adducts contain alkoxide or trichloromethyl groups, for instance, and, as illustrated in scheme 1.23. they can eliminate achohol or chloroform to unmask the carbene, which then coordinates to the metal center.



Scheme 1.23. α-elimination from neutral molecules for the synthesis of NHC complexes

Lappert and co-workers had used NHC-chloroform adduct to make $PtCl_2(NHC)(PEt_3)$ complex (Cardin *et al.*, 1973).

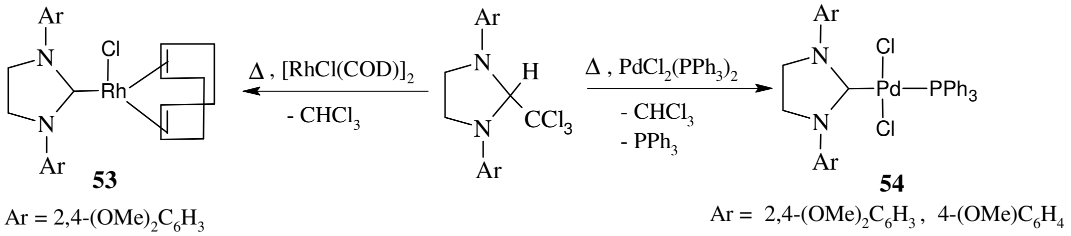
However, in the case of this particular chloroform adduct,1,3-diphenyl-2-(tricholoromethyl) imidazolidine, it is not clear whether the released NHC reacts directly with the platinum precursor or whether 2 equiv. first dimerize to form the enetetramine *in situ* (Scheme 1.7) (Çetinkaya *et al.*, 1998). This ambiguity exits because the free carbene has a strong tendency to dimerize (Hitchcock, 1979) and the enetetramine is known to react with $[(PEt_3)PtCl(\mu\text{-}Cl)]_2$ to provide $(NHC)(PEt_3)PtCl_2$ (Cardin *et al.*, 1973).



Scheme 1.24. Synthesis of NHC complex from 1,3-diphenyl-2-(trichloromethyl) imidazolidine.

The α-elimination has been reported from neutral molecules for the synthesis of NHC complexes (Cardin *et al.*, 1973; Ergün, 2000; Gürbüz, 1995; Grubbs *et al.,* 1999; Günay, 2004).

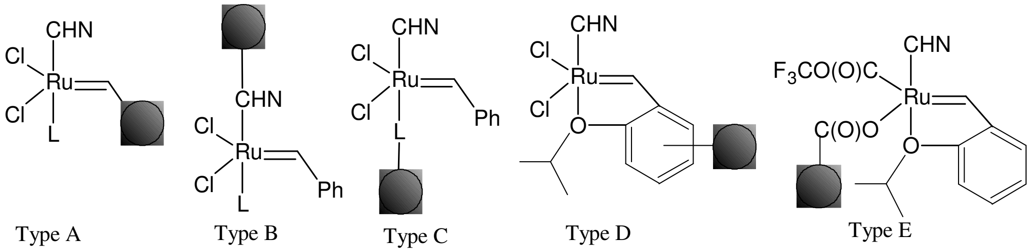
The use of $NHC.CHCl_3$ as NHC precursor has several advantages: (i) $NHC.CHCl_3$ may be easily handled and stored in air. (ii) the desired product is obtained usually in high yield and pure state. Compounds of Rh(I) and Pd(II) can be sytntesized by thermal $CHCl_3$ elimination procedure (Günay, 2004).



Scheme1. 25. Compounds of Rh(I) and Pd(II) can be sytntesized by thermal $CHCl_3$ elimination proced

1.10. Supported N-heterocyclic Carbene Complexes

Recycling is becoming significantly more important chemistry nowadays as environmental harms increase and as resources are becoming scarcer. Chemists continue to develop new catalysts that are more efficient, robust and devise new methods to recover and reuse them. Towards this goal, the immobilization of well known catalysts onto supports often facilitates the recycling of these catalysts. As described above, organometallic NHC complexes, demonstrating their usefulness in the synthesis of complex molecules that have applications ranging from drug precursors to polymers. These vital applications make the NHC ligand a perfect candidate to be supported. However, it must be demonstrated that the catalytic activity of the supported NHC complexes does not change with the nature of the support. Several research groups have made significant contributions towards the synthesis of supported NHC complexes and shown that the catalytic activity is indeed maintained (Buchmeiser, 2004, 2005, hoveyda *et al.,* 2004; Schurer *et al.*, 2000). Over the past five years, NHCs have been grafted onto different supports ranging from monolithic supports to soluble poly(styrene)s (Buchmeiser, 2004, 2005; Schurer *et al.*, 2000). These strategies are described in more details in Figure. Most of these supported systems use ruthenium or palladium as the metal center. However, several examples were published that use rhodium for hydroformylations and the addition of phenyl boronic acid to an aldehyde.



Type A Type B Type C Type D Type E

Figure.1.11. Strategies to tether Ru–NHC complexes onto supports.

N-Heterocyclic carbenes have been supported on a variety of soluble and insoluble polymers ranging from poly(ethyleneglycol) to poly(styrene) resin (Ahmed *et al.,*2000; Varray *et al.*,2003). In 2000, Barrett and coworkers reported the first immobilization of the second generation Grubbs catalyst for olefin metathesis on an insoluble polymeric support (type A) (Ahmed *et al.,*2000). Using vinyl modified poly(styrene) beads as the support, they immobilized the catalyst via the alkylidine. Following this report, Nolan and coworkers published asimilar system using poly(divinyl benzene) as the support.(Jafarpour *et al.*, 2000, 2002). to date (Özdemir *et al.,* 2005). Also in 2000, Blechert and coworkers reported the synthesis and support of the second generation Grubbs catalyst through the *N* -heterocyclic carbene (type B) (Schurer *et al.*, 2000). Contrary to Barrett and Nolan's design, the catalyst is permanently immobilized on the support allowing potentially for a full recovery of the complex after catal-ysis. The support used in this system was a poly(styrene)-based Merrifield resin. Following this report, Blechert and coworkers published also a supported Grubbs–Hoveyda catalyst (typeD) (Connon *et al.*, 2002). To support the Grubbs–Hoveyda catalyst, they used the phenyl carbene to anchor the catalyst onto a poly(ethylene glycol) dimethylacrylamide copolymer resin (PEGA) (Connon *et al.*, 2002). Using the same support, Buchmeiser *et al.* synthesized different supported Grubbs–Hoveyda type catalysts (Buchmeiser, 2003,2004]. Buchmeiser's group reported the first Hoveyda–Grubbs-type catalyst used heterogeneously in a continuous flow reactor (Type E). A new family of NHCs was also synthesized and supported onto poly(styrene)divinyl benzene (PS-DVB) and monolithic supports by Buchmeiser's group. Recently, Kirschning et al. reported the first supported third generation Grubbs catalyst using poly(vinylpyridine) as the support (Mennecke *et al.,* 2005). The catalyst was anchored to the support through one of the pyridines (Type C).

In 2001, Hoveyda et al. introduced the first silica supported NHC complex (Kingsbury *et al.*, 2001). They used a monolith of porous sol–gel as a support that allowed them to remove their catalyst after the reaction giving the final products with high purity. In 2002, Cetinkaya et al. introduced a different silica sup-ported NHC complex (figure1.12). They synthesized three ruthenium NHC complexes for the synthesis of 2,3-dimethylfuran from 3-methylpent-2-en-4-yn-l-ol (Çetinkaya *et al.*, 2001). They were able to show that their catalysts were as active as the small molecule analogue. They demonstrated the possibility to recycle their catalysts in the formation of the furan for up to five cycles with yields around 90% for each cycle.

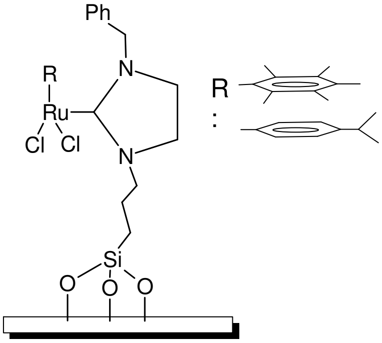


Figure.1.12. Silica supported ruthenium complex by Çetinkaya et al.

The support of Pd–NHC complexes is of utmost importance because of the high activity of these complexes in coupling chemistry. Coupling chemistry is vital in the synthesis of com-plex molecules for the drug and fine chemical industries. Supporting these complexes allows for easy removal of the toxic metal and the possibility of recycling the metal catalysts. Several groups have investigated this topic by supporting palladium complexes on a variety of supports, from poly(styrene) to clay (De Miguel. 2000). However, in contrast to supported Ru–NHC complexes, the literature in this area is limited. The first report of a polymer supported NHC–Pd complexes was provided by Herrmann and coworkers in 2000 (Schwarz *et al.*,2000) They used a di-NHC chelate ligand coordinated to a palladium halide complex (figure 1.13). The authors anchored this complex through the NHC ligand onto an insoluble poly(styrene)-based Wang resin. They studied the catalytic activity of their system for the Heck reaction.

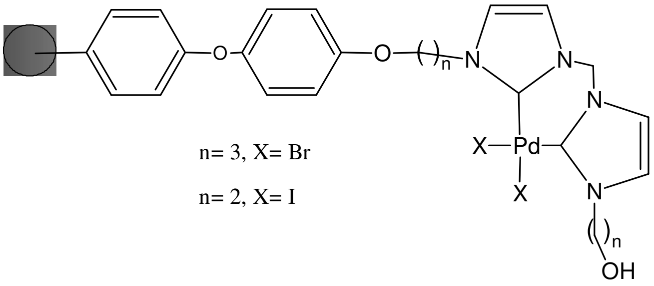


Figure.1.13 Wang resin supported Pd-NHC complexes developed by Herrmann et al.

The most recent report on Pd–NHC complexes supported on insoluble supports comes from Aksın *et al.* who described the immobilization of an NHC–Pd complex matrix onto silica (figure1. 14) (Aksin *et al.*, 2006) system towards the Heck catalysis of aryl iodide with alkyl acrylates and showed that their catalytic system was highly active with nearly quantitative conversions for most of the Heck trans-formations studied. They finally recycled their catalyst three times yielding up to 89% conversions after 26 h for the third cycle.

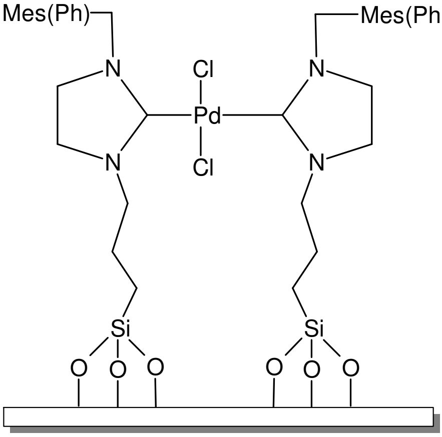


Figure.1.14. Silica supported Pd-NHC complex reported by Aksın.

Finally, in 2005, Özdemir et al. reported the synthesis and immobilization onto silica of a Rh–NHC complex (figure1.15) for the addition of phenyl-boronic acid to benzaldehydes (Özdemir *et al.*, 2005). Using activated and non-activated benzaldehyde, they investigated the activity of their catalytic system and found reasonable yields for the reaction with up to 89% conversion.

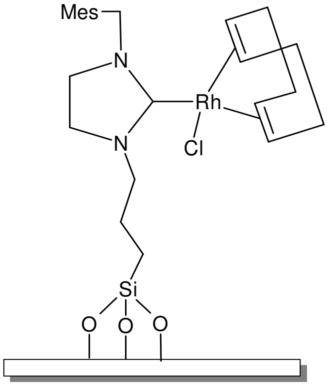


Figure.1.15. Silica supported Rh-NHC complex.

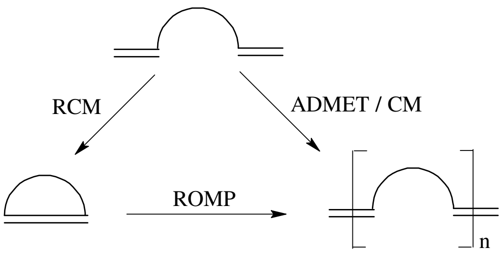
1.11. Applications in Homogeneous Catalysis

N-Heterocyclic carbenes (NHCs) have become universal ligands in organometallic and inorganic coordination chemistry. They not only bind to any transition metal, but also to main group elements such as beryllium, sulfur, selenium, and iodine. Because of their specific coordination chemistry, *N*-heterocyclic carbenes both stabilized and active metal centers in quite different key catalytic steps of organic syntheses, for example, C-H activation, C-C, C-H, C-O, and C-N bond formation. Over the past few years, this chemistry has been the field of vivid scientific competition, and yielded previously unexpected successes in key areas of homogeneous catalysis. The stability of the transition metal complexes of *N*-heterocyclic carbenes is often cited as one of the key advances of these ligands versus their phosphine counterparts.

Nile and Lappert published the first examples of the application of NHCs as directing (Hill and Nile, 1977; Lappert and Maskell, 1984). These results showed the applicability of NHCs as ligands in homogeneous catalysis in principle and were therefore pioneering. The comparisons of spectroscopic and crystallographic data of complexes containing NHCs are comparable to those of trialkylphosphines. More precisely, spectroscopic data assign them an even higher basicity and donor capability (Köcher and Herrmann, 1997). Keeping in mind that even triarylphosphines and trialkylphosphines are not readily interchangeable in most transition metal catalyzed processes, NHCs are less likely to be an alternative in reactions where trialkylphosphines have proven superior. Additionally, due to their strong metal-carbon bond, NHCs have to be considered as typical directing or innocent spectator ligands and are therefore unlikely to be good substitutes for coordinatively labile ligands, which are actively involved in the catalytic cycle by dissociation equilibria (Schwarz *et al.*, 2000; Weskamp *et al.*, 1999).

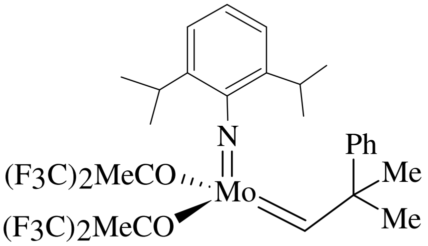
1.11.1. Olefin Metathesis

Olefin metathesis is a carbon-carbon bond-forming reaction that is widely used in both organic and polymer chemistry (Scheme 1.26) (Ivın and Mol, 1997).



Scheme1.26. Olefin metathesis: RCM (ring closing metathesis), ROMP (ring opening metathesis polymerization), ADMET (acyclic diene metathesis), CM (cross metathesis).

Metathesis processes have seen a remarkable level of intense research activity since the development of well defined metal alkylidene catalyst. In particular, Schrock's molybdenum based complex **53** and Grubbs ruthenium catalyst **55** set the standard for catalytic formation of new carbon-carbon olefinic bonds. This reawakened interest in olefin metathesis process during the past decade is largely attributable to the discovery of highly active, well defined molybdenum and ruthenium alkylidene catalyst **53** (Schrock *et al.,*1987; 1990; 1991) and **55** (Grubbs *et al.,* 1995; 1996). Although the ruthenium complex **55** ("Grubbs catalyst") possesses significantly advantages over molybdenum complex **53** in terms of stability and ease of storage and handling, complex **55** displays higher reactivity toward a broad range of sterically and electronically varied substrates. In an effort to improve thermal stability of Ru-catalyst **55**, the groups of Herrmann (Herrmann *et al.,* 1999), Nolan (Huang *et al.,* 1999) and Grubbs (Grubbs *et al.,* 1999) simultaneously reported a new class of alkylidene complexes bearing *N*-heterocyclic carbene (NHC) ligands.



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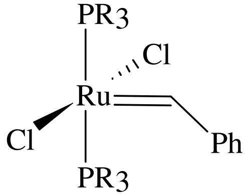
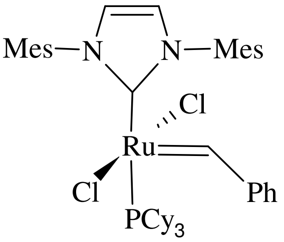


R = Ph **54**
R = Cy **55**

A breakthrough in catalytic metathesis applications was achieved with the second-generation ruthenium-NHC-benzylidene complexes: in **56** (Grubbs *et al.,* 1999; Herrman *et al.,* 1999), **57** (Grubbs *et al.,* 1999), **58** (Grubbs *et al.,* 1999; 2001), **61** (Çetinkaya *et al.,*2003), **62** (Weskamp *et al.,* 1999) and **63** (Huang *et al.,* 1999; Grubbs *et al.,* 1999) are combined with coordinatively more labile ligands such as phosphines or organometallic fragments on the ruthenium center. Complexes **58** and **59** (increased activity profile) have been successfully eployed in a broad range of olefin metathesis reactions ranging from ring-closing metathesis (RCM) (Fürstner *et al.,* 2000) to ring-opening metathesis polymerization (ROMP) (Grubbs *et al.,* 2000) and cross-metathesis (Grubbs *et al.,* 2001; 1999).

Complex **56** containing triphenylphosphines is an active catalyst for olefin metathesis (Grubbs *et al.,* 1995). However, the substitution of the triphenyl phosphines by more electron-donating and sterically more demanding tricyclohexylphosphines is accompanied by a significantly increased stability and catalytic performance (Nguyen *et al.,* 1993).



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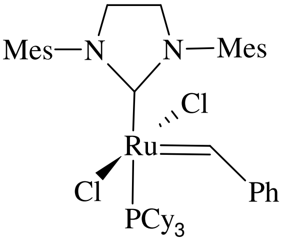

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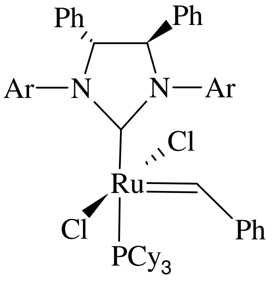
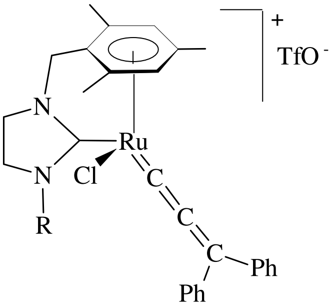


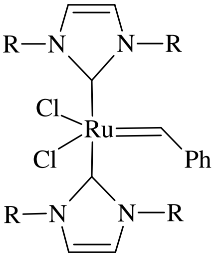
Ar = Mes, 2-MeC$_6$H$_4$, 2-^{i}PrC$_6$H$_4$
58

The chiral imidazolinylidene ruthenium alkylidene complexes **60** have been used for asymmetric metathesis reactions (Grubbs *et al.,* 2001; Hoveyda *et al.,* 2002). Ruthenium-NHC-allenylidene complexes **61** were found to be active and selective catalysis for ring-closing metathesis (RCM) on the nature of the 1,6-dienes (Çetinkaya *et al.,* 2003). Within the NHCs, increased bulk of the substituents at the nitrogen leads to higher activities in a number of metathesis applications. Thus, the 1,3-mesitylsubstituted NHC is advantageous for some applications compared to cyclohexyl or other CHR_2 substituents at the nitrogen (Denk, 1999).



R = CH_2CH_2OMe , CH_2CH_2OEt , CH_2Mes

59



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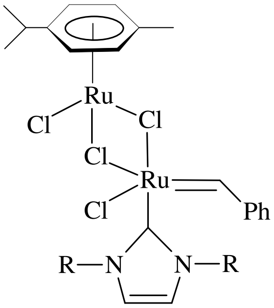


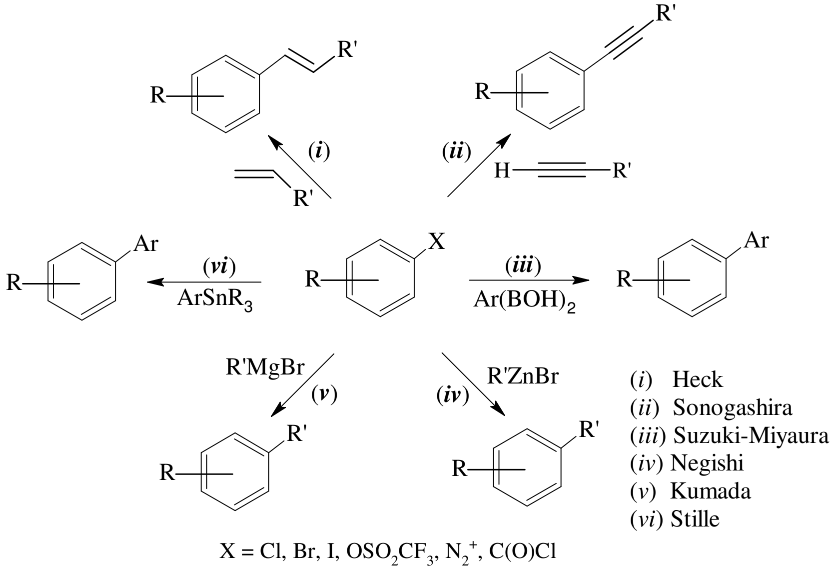
61

Based on these findings, another starting point for modifications besides modifying the labile "coligand" is the NHC ligand itself, especially since there are many more carbenes known and accessible. One of the many possible modifications turned out to be very successful and can-based on its catalytic activity and catalyst lifetime-be considered as the third generation of NHC catalysts in olefin metathesis. The recipe for success is to use NHCs with saturated backbones, *i.e.*, imidazolidin-2-ylidenes (Grubbs *et al*., 1999).

The resulting complexes, *e.g.* **59**, display catalytic activities in ROMP that exceed even the performance of molybdenum-imido system **53**, which has been considered as intrinsically more active than late-transition metal systems, but also more sensitive toward polar functionalities, water, and air. Thus, to combine "molybdenum-like" activity with "ruthenium-like" functional group tolerance has been a goal that has been targeted coming from both the molybdenum and the ruthenium side.

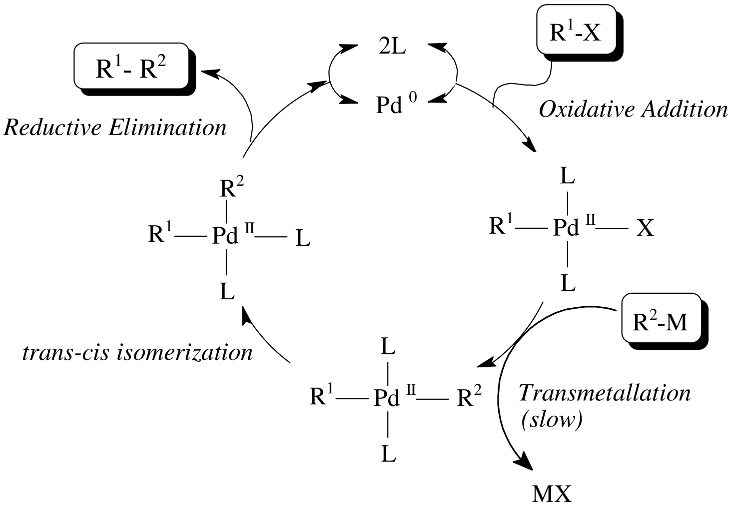
Although discovered quite recently, the types of different groups at nitrogen have already found many applications in ROMP, RCM, and cross-metathesis (Bielawski and Grubbs, 2000; Wright *et al.*, 2000). The higher efficiency of NHCs with saturated backbones compared to their unsaturated analogues can be explained by their higher basicity.

1.11.2. Coupling reactions



Scheme 1.27. Palladium- and nickel-catalyzed C-C bond formations.

A general aim of transition metal-catalyzed organic synthesis is carbon-carbon (C-C) bond formation. In this respect, the Pd-catalyzed coupling reactions *e.g.* Heck-type reactions (***i***) (Heck and Nolley, 1972), the Sonogashira reaction (***ii***) (Sonogashira *et al.*, 1975), the Negishi reaction (***iv***) (Negishi *et al.,* 1977), Kumada-Corriu reaction (***v***) (Kumada *et al.*, 1972) and the Stille reaction (**vi**) (Stille and Milstein, 1979) are available for this purpose(Scheme 1.27), Suzuki-Miyaura cross-coupling reaction which produces biaryls has proven to be the most popular in recent times. Biaryls are building blocks and subunits present in many natural products and have important applications, including use as pharmaceuticals, agrochemicals, and polymer constituents (Bringman *et al.,* 2001). The preference for the Suzuki-Miyaura cross coupling above other Pd-catalyzed cross-coupling reactions is not incidental. The key advantages of the Suzuki-Miyaura coupling are the mild reaction conditions and the commercial availability of the diverse boronic acids that are environmentally safer than the other organometallic reagents. It is worth noting that the palladium catalysts show a broad tolerance towards various functional groups. (Suzuki, 1985; 1994; 1999; Stanforth, 1998). The mechanism of the coupling reactions consists of four main steps (Scheme 1.20) (Moreno-Manas *et al.,* 1996): Oxidative addition of aryl halides to palladium species; transmetallation of aryl borate to form *trans*-diaryl palladium complex; *trans-cis* isomerization of this palladium complex; reductive elimination of the biaryl to regenerate the catalyst.



Scheme 1.28. General mechanism of Suzuki coupling reactions.

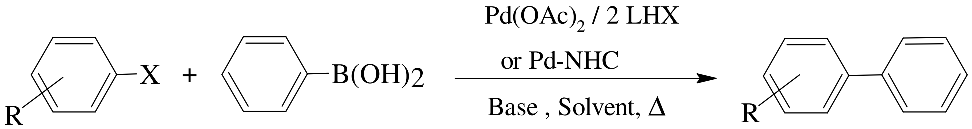
Several parameters affecting the Suzuki coupling reactions are considered. These factors are; solvent effect, substitution group effect, base effect, halogen and ligand effect. Solvents are the most important parameters in organic reactions. As in general organic reactions, appropriately chosen solvent system strongly favours the cross coupling patway. In literature, dioxan, THF, different DMF/H_2O and EtOH/H_2O ratios, toluene and benzene have been used as solvents in Suzuki coupling reactions.

In Suzuki coupling reactions substituent are the most important to influence the activity of the reaction. These groups substantially influence the activity of aryl halide. The reaction is promoted, when electron-withdrawing groups substitute aryl halide. In Suzuki coupling reaction mechanism, first step involves carbon-halide bond cleavage. Carbon-halide bond cleaves more easily when it substitutes with electron withdrawing groups (NO_2, CF_3, CN, etc.) and thereby the reaction proceeds faster as the C-X bond is weakened. This bond will be broken easily and reaction will be faster (Scheme 1.20). In contrast, if this aryl halide group contains an electron donating substituent (CH_3, OCH_3, etc) carbon-halide bond will be stronger. So bond cleavage will be more difficult and reaction would probably proceed slower (Solomons, 2000).

The halogen type also determines the activity of aryl halide towards the Suzuki coupling reaction. The reactivity of the aryl halide component decreases drastically in the order $X = I > Br > Cl$ and electron withdrawing substituents R are required for the chlorides to react (Suzuki, 1999; Gibson *et al.,* 2001; Bedford *et al.,* 2002). Suzuki coupling reaction proceeds via transmetallation in the presence of bases (Scheme 1.20). This procedure does not take place under neutral conditions. This is a characteristic feature of boron chemistry, which is different from that of other organometallic reagents. The most commonly used base in the Suzuki cross coupling reaction is Na_2CO_3 but this is often ineffective with sterically demanding substrates. In such instance, $Ba(OH)_2$ or K_3PO_4 has been used to generate good yields of the cross coupling products. Other bases utilized in the Suzuki cross-coupling reaction include Cs_2CO_3, K_2CO_3, KOMe, TlOH and NaOH (Kotha *et al.,* 2002).

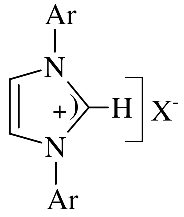
The low reactivity of aryl chlorides in cross-coupling reactions is generally ascribed to their reluctance to oxidatively add to Pd(0) (Littke and Fu, 2002). Current interest focuses on the use of aryl chlorides since they are cheaper and more readily accessible than bromides and iodides (Buchwald *et al.,* 1998). Significant advances have been recently achieved by use of palladacycles (Herrmann *et al.,* 1999; Zim *et al.,* 2000) and especially, by use of bulky and electron-rich tertiary phosphines as catalyst modifiers systems. However, the major drawback of these is that the phosphine ligands are comparatively difficult to make or rather expensive. Furthermore, tertiary phosphines require air-free handling to prevent their oxidation and are susceptibilite to P-C bond cleavage at elevated temperatures (Herrmann, 1996). On the other hand, palladium complexes of *N*-heterocyclic carbene ligands (NHCs), in particular have proved to be excellent catalysts not only for the Suzuki and Heck reaction, but also for Stille and Sonagashira reactions (Herrman *et al.,* 1998; Weskamp *et al.,* 1999; Böhm *et al.,* 2000). The NHC complexes are cost efficient to prepare insensitive to air and moisture and thermally stable in both the solid state and in solution; the carbenes are non-dissociative ligands. However, the development of new ligands or the application of existing ligands in these reactions, particularly those involving aryl chlorides as substrates, is still of considerable importance.

Trudell and co-workers have found that the Suzuki coupling reaction of the arylboronic acids with non-activated aryl chlorides occurs at 80 ^{0}C in high yields if catalytic amounts of $Pd_2(dba)_3$ and the sterically crowded imidazolium salt (LHX) **62** are combined with Cs_2CO_3 in dioxane. Both sterically hindered and electron-rich aryl chloride were found to couple with aryl boronic acids in high yields (Trudell *et al.,* 1999). They later showed that a combination of $Pd(OAc)_2$ and the bis-imidazolium salt **66** gave an air-stable catalytic system, emenable to large-scale synthesis and giving a high yielding cross-coupling reaction of aryl chlorides with arylboronic acids (Zhang and Trudell, 2000). Fürstner has used $Pd(OAc)_2$ and the sterically hindered imidazolium salt (LHX) **63** as the pre-catalyst mixture for the efficient cross-coupling of aryl chlorides with 9R-9-BBN (9-substituted-9-bora bicycle [3.3.1] nonane) derivatives (R= alkyl, aryl, alkynl, cycloporyl) in the presence of KOMe as the base. This protocol is applicable to electron-poor and electron-rich substrates with equal ease (Fürstner and Leitner, 2001).



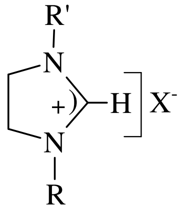
Scheme 1.29. Palladium-catalysed coupling reactions of aryl halides using *N*-heterocarbene ligands

The nature of the NHC ligand on complexes has a tremendous influence on the rate of catalyzed reactions, the use of saturated NHC ligands in coupling reactions is a relatively neglected area. In order to find more efficient palladium catalyst for Suzuki coupling reaction, Çetinkaya *et al.* have prepared from a combination of $Pd(OAc)_2$ and the a series of 1,3-diorganylimidazolinium salts **64** and bridged imidazolinium salts **67** containing a saturated imidazole ring and benzimidazolium salts **65**, perimidinium salts **68** (Scheme 1.21) (Çetinkaya *et al.,* 2004; Özdemir *et al.,* 2005).



62 Ar = 2,4,6-$(Me)_3C_6H_2$

63 Ar = 2,6-$(^iPr)_2$-C_6H_3



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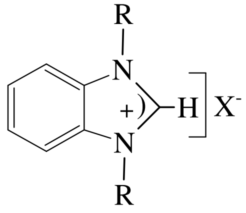

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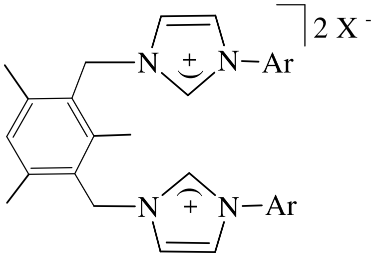

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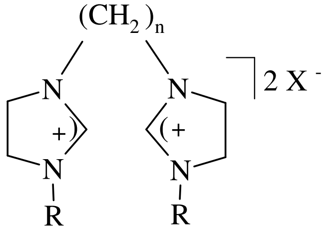
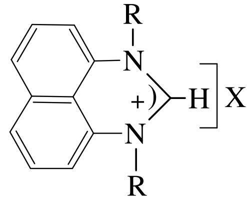


n = 1, 2, 3, 4

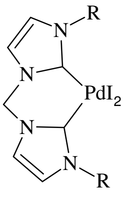
67



68

It has been observed that the in situ formed complexes by deprotonation of the imidazolium salts, leads to significantly better results than use of the preformed carbene complexes (Fürstner and Leitner, 2001).

Herrmann *et al.,* have shown that 4-chloroacetephone and phenylboronic acid can be coupled 1.0 mol% of the Pd(II)-heterocyclic carbene complex **69** at $130^{\circ}C$ (Herrmann *et al.,* 1998), and they have subsequently used the mixed bicyclohexylphosphine complex **70** to catalyse the reaction of phenylboronic acid with various chlorobenzene derivatives (Weskamp *et al.,*1999). They found that, with deactivated aryl chlorides, Cs_2CO_3 is much more effective base than K_2CO_3. Another heterocyclic carbene complex of type **71** has been used for the Suzuki coupling of aryl chlorides, with turnover frequencies up to 552 (Böhm *et al.,* 2000). Çetinkaya *et al.,* have found that the Suzuki coupling of aryl chlorides with phenylboronic acid occurs in high yields if the Pd-NHC complexes **72** containing saturated imidazol backbone are combined with Cs_2CO_3 in DMF / H_2O (1:1) (Çetinkaya *et al.,* 2004).



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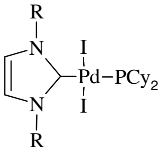

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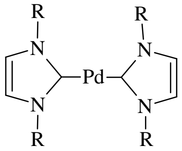

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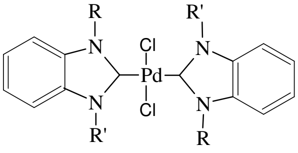

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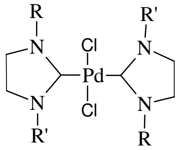
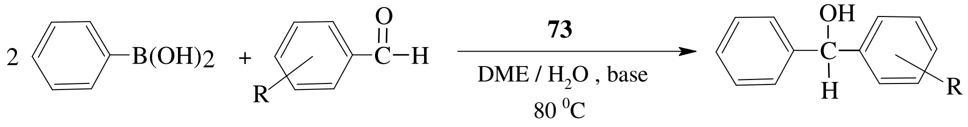
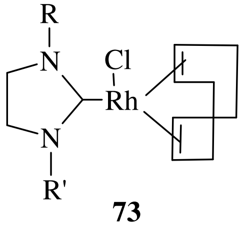


72

Along with palladium, several rhodium-and nickel based catalysts have been used for the carbon-carbon bond formation reaction during the past few years. In this connection, Miyaura *et al.* reported that rhodium catalyzes the addition of aryl and alkenylboronic acids to aldehydes giving secondary alcohols (Sakai *et al.,* 1998). Although Fürstner *et al.* demonstrated the rhodium-catalysed addition of aryl- and alkenylboronic acids to aldehydes in the presence of phosphine and sterically hindered *N*-heterocyclic carbene complex ligands such as **62** and **63** (Fürstner and Krause, 2001). Furthermore, Özdemir *et al.* reported that silica supported and 1,3-disubstituted imidazolidin containing rhodium-*N*-heterocyclic carbene complexes **73a-d**, are an active catalyst for addition of phenylboronic acid to aldehydes (Scheme 1.30) (Özdemir *et al.,* 2004; 2005).



Scheme 1.30. Rh-carbene catalysed addition reactions of phenylboronic acid to aldehydes

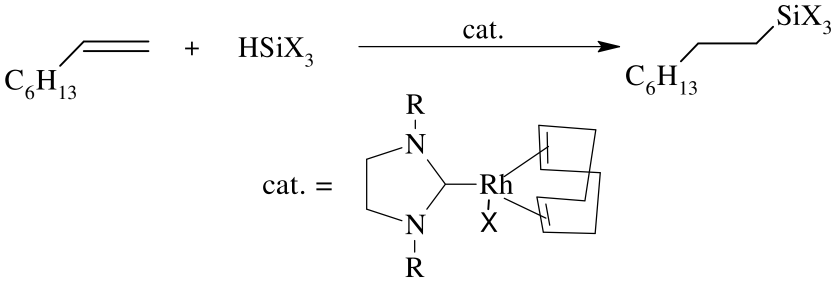


73

a : R = R' = $CH_2C_6H_2Me_3$-2,4,6
b : R = R' = $CH_2C_6H_2(OMe)_3$-3,4,5
c : R = R' = C_5H_9
d : R = CH_2CH_2OMe ; R' = $CH_2C_6H_2(OMe)_3$-3,4,5

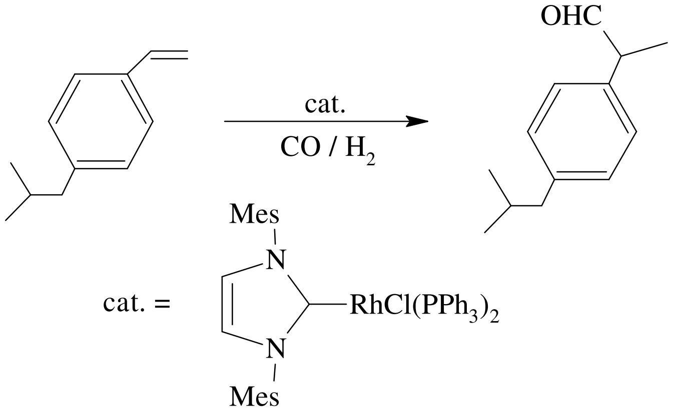
1.11.3. Hydrosilylation

Rhodium(I) and ruthenium(II) complexes containing NHCs have been applied in hydrosilylation reactions with alkenes, alkynes, and ketones. Rhodium(I) complexes with imidazolidin-2-ylidene ligands such as [RhCl(η^4-cod)(NHC)], [RhCl(PPh_3)$_2$(NHC)] and [RhCl(CO)(PPh_3)(NHC)] have been reported to lead to highly selective anti-*Markovnikov* addition of silanes to terminal olefins (Hill and Nile, 1977).



1.11.4. Hydroformylation

Rhodium(I) complexes with 1,3-dimethylimidazolin-2-ylidene ligands were used in the hydroformylation of olefins (Köcher, 1997). However, the activity and selectivity toward formation of branched versus linear aldehyde cannot compete with rhodium-phosphine systems (Cornils and Herrmann, 1998). Similar catalyst systems with the sterically more demanding 1,3-dimesitylimidazolin-2-ylidene give higher branched/linear rations for vinyl arenes (95:5), but the turnover frequency is still low compared to established systems (Chen *et al.*, 2000).



1.11.5. Hydrogenation

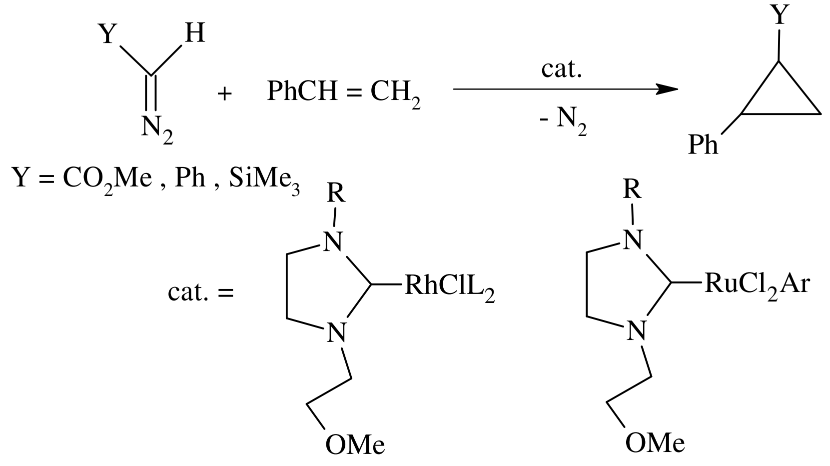
Hydrogenations have not been looked at very intensively so far (Steinbeck, 1998). The results for rhodium complexes containing NHCs with saturated and unsaturated backbones applied to the hydrogenation of dehydroamino acids are far from being comparable to the best phosphine systems. As for hydroformylation, the poor performance illustrates that due to their strong σ-donor capability NHCs do not exhibit the catalyst properties required in these reactions. Usually rhodium complexes containing π-accepting phosphines exhibit the highest activities in these transformations. More basic alkyl-substituted phosphines are, however, reported to be advantageous for certain substrates (Schrock and Osborn, 1970).

1.11.6. Polymerization/oligomerization

Although polymerization plays an important role in today's organometallic catalysis, almost no reports exist about the applications of NHCs in this reaction. Ethylene polymerization catalyzed by a chromium-NHC complex was reported but the efficiency of this catalyst is only moderate (Döhring *et al.*, 2000). After activation with MAO the catalysts produces highly branched PE which contains low- and high-molecular weight fractions. Molybdenum(0) complexes of 1,3-bismethylimidazolin-2-ylidene are reported for the polymerization of methacrylate (Hill and Nile, 1978) and tungsten for the polymerization of diphenylacetylene (Ku *et al.*, 1997).

1.11.7. Cyclopropanation of olefins

Rhodium(I) and ruthenium(II) complexes containing NHCs with hemilabile ether moieties were successfully applied as catalysts for the cyclopropanation of olefins with diazoalkanes (Çetinkaya *et al.*, 1997).



74

R = Me , CH_2CH_2OMe
L = PPh_3 , *cis*-COD

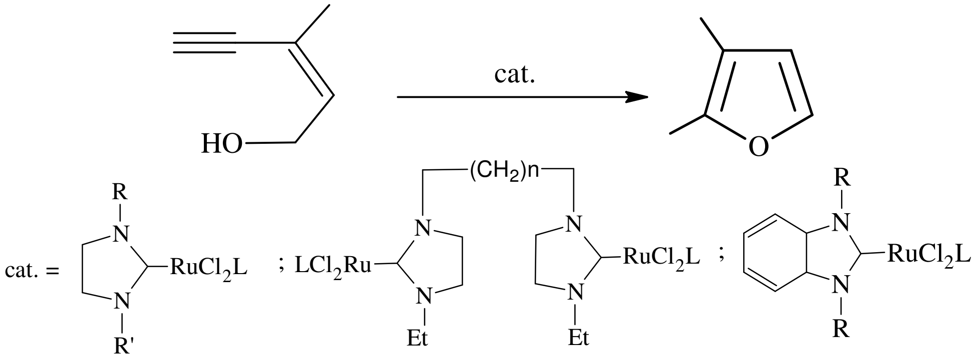
75

R = Me , CH_2CH_2OMe
Ar = C_6Me_6 , *p*-cymene

Scheme.1.31. Cyclopropanation of olefins

1.11. 8. Furan synthesis

Ruthenium(II) systems containing imidazol-2-ylidene have been used to catalyze the synthesis of 2,3-dimethylfuran starting at (Z)-3-methylpent-2-en-4-yn-1-ol (Eq. 1.57) (Çetinkaya *et al.*, 1996; 1997; 2001). The activity of the catalyst strongly depends on the nature of the NHC ligand. Chelated imidazolin-2-ylidenes give the best results for this transformation (Çetinkaya *et al.*, 1997).



76

R = R' = CH_2CH_2OMe
R = CH_2CH_2OMe , R' = Me
R = R' = Et
R = R' = $CH_2C_6H_4NMe_2$-4
L = *p*-cymene , C_6Me_6

77

n = 0 , 1
L = *p*-cymene

78

R = Me , Et
L = *p*-cymene , C_6Me_6

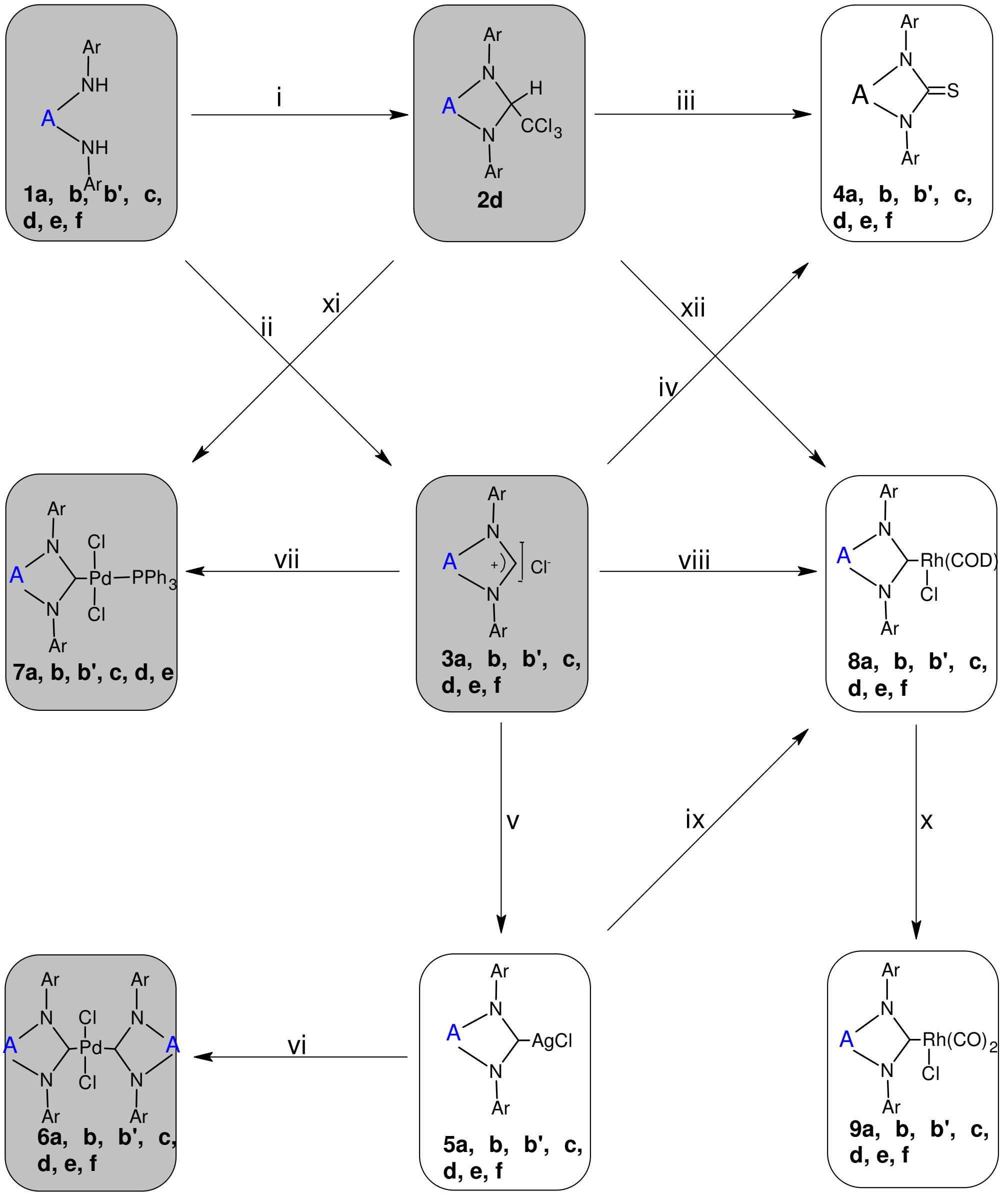
Scheme 1.32. Furan synthesis with Ruthenium(II) complexes

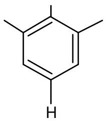
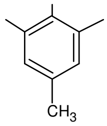
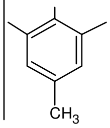
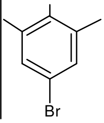
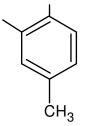
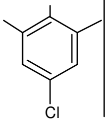
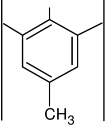
2. EXPERIMENTAL

Reactions involving air-sensitive components performed by using Schlenk-type flasks under argon atmosphere and high vacuum-line techniques. The glass equipment was heated under vacuum in order to remove oxygen and moisture and then they were filled with argon. The solvents were analytical grade and distilled under argon atmosphere from sodium (toluene, diethyl ether, hexane, tetrahydrofuran), P_2O_5 (dichloromethane).

Reagents: Glyoxal, ammonium chloride, triethyl orthoformate, mesitylaldehyde, *p*-anisaldehyde, *p*-tolualdehyde, 2, 4, 6-trimethylaniline, 2, 4-dimethylaniline, sodium borohydride, sodium hydride, toluene, tetrahydrofuran, dioxane, hexane, dichloromethane, ethanol, and isopropylalcohol were obtained from Merck. Acenapththenequinone, 4-chloro-2, 6-dimethylaniline were obtained from Alfa Aesar. 4-Bromo-2, 6-dimethylaniline was obtained from Aldrich. Diethyl ether, acetone and methanol were obtained from J. T. Baker. $[RhCl(COD)]_2$ (Chatt and Venanzi, 1957), $PdCl_2(CNMe)_2$ (Chatt and Venanzi, 1957) and $[Rh(OMe)(COD)]_2$ (Uson *et al.*, 1985) were synthesized according to the published procedures.

Instruments: ^1H and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer. J values are given in Hz. Elemental analyses were performed via CHNS-932 (LECO) in TUBITAK Microlab and melting points were determined by electrothermal melting point detection apparatus. IR spectra were obtained by Perkin–Elmer 597 instrument. The measurements for catalytic experiments performed by GC/MS (Thermo-Finnigan on a HP-5 capillary column and with a FID detector) in Ege University Faculty of Science-Department of Chemistry.



	a	b	b'	c	d	e	f
A	$(CH_2)_2$	$(CH_2)_2$	$(CHCH_3)_2$	$(CH_2)_2$	$(CH_2)_2$	$(CH_2)_2$	$(C_{12}H_8)$
Ar	 H	 CH_3	 CH_3	 Br	 CH_3	 Cl	 CH_3

Scheme 2.1. (i) AcOH, Cl_3CCHO, 3 h, RT. (ii) $HC(OEt)_3$, NH_4Cl, 130 °C. (iii) $PhCH_3$, S_8, 4 h, 110 °C. (iv) THF, NaH, 4 h, 65 °C then $PhCH_3$, S_8, 4 h, 110 °C. (v) DCM, Ag_2O, 24 h, RT. (vi) DCM, $PdCl_2(MeCN)_2$, 2 days, RT. (vii) THF, NaH, 4 h, 65 °C then $PhCH_3$, $[PdCl_2(PPh_3)]_2$, 4 h, 110 °C. (viii) $PhCH_3$, $[Rh(OMe)(COD)]_2$, 4 h, 110 °C (ix) DCM, $[Rh(Cl)(COD)]_2$, 4 h, 110 °C. (x) DCM, CO, 0.5 h, RT. (xi) $PhCH_3$, $[PdCl_2(PPh_3)]_2$, 4 h, 110 °C. (xii) $PhCH_3$, $[RhCl(COD)]_2$, 4 h, 110 °C.

2.1. Syntheses of thione derivatives (4).

2.1.1. Synthesis of N,N^1-bis(2,6-dimethylphenyl)imidazolidin-2-thione, 4a.

A 50 mL Schlenk tube was charged with **3a.Cl** (0.314 g, 1 mmol), NaH (0.024 g, 1 mmol) and 10 mL THF. The mixture was stirred for 8 h at 50 °C. The solution was removed in vacuum, then toluene (5 mL) was added and filtered. S_8 (0.033 g, 0.13 mmol) was added to the filtrate and the mixture was heated under reflux for 4h. The solution was cooled to room temperature and hexane (10 mL) was added. The colorless solid was filtered off and then was crystallized from dichloromethane (3 mL) / hexane (6 mL). Yield: 0,226 g; 73%, m.p.: 310-311 °C. Anal. Cal. for $C_{19}H_{22}N_2S$; C: 73.51; H: 7.14; N: 9.02; found C: 73.86; H: 7.36; N: 8.95%.

2.1.2. Synthesis of N,N^1-bis(2, 4, 6-trimethylphenyl)imidazolidin-2-thione, 4b.

This compound was prepared in the same manner as 4**a.** using **3b.Cl$^-$** (0.342 g, 1.0 mmol), NaH (0.024 g, 1.0 mmol) and S_8 (0.033 g, 0.13 mmol). The colorless crystals were obtained. Yield: 0,236 g; 70%, m.p.: 300-301 °C. Anal. Cal. for $C_{21}H_{26}N_2S$; C: 74.51; H: 7.74; N: 8.28; found C: 73.76; H: 7.56; N: 8.35%.

2.1.3. Synthesis of *N,N*¹-bis(4-bromo-2, 6-dimethylphenyl) imidazolidin-2-thione, 4c.

This compound was prepared in the same manner as 4**a.** using **3c.Cl⁻** (0.472 g, 1.0 mmol), NaH (0.024 g, 1.0 mmol) and S_8 (0.033 g, 0.13 mmol). The colorless crystals were obtained. Yield: 0,360 g; 77%, m.p.: 95-96 °C. Anal. Cal. for $C_{19}H_{20}N_2S$; C: 48.74; H: 4.31; N: 5.98; found C: 48.66; H: 4.43; N: 5.66%.

2.1.4. Synthesis of N,N¹-bis(2, 4-dimethylphenyl) imidazolidin-2-thione, 4d.

A 50 mL Schlenk tube was charged with **2d** (0.397 g., 1.0 mmol), S_8 (0.033 g, 0.13 mmol) and 5 mL toluene. The solution was heated under reflux for 4 h. Upon cooling to room temperature, hexane (10 mL) was added into the solution. The solid was filtered off and then was recrystallised in CH_2Cl_2/Et_2O. Yield: 0,217 g; 70%, m.p.: 200-201 °C. Anal. Cal. for $C_{19}H_{22}N_2S$; C: 73.54; H: 7.14; N: 9.02; found C: 73.76; H: 6.86; N: 9.33%.

2.1.5. Synthesis of *N,N*¹-bis(4-bromo-2, 6-dimethylphenyl) imidazolidin-2-thione, 4e.

This compound was prepared in the same manner as 4**a.** using **3e.Cl⁻** (0.337 g, 1.0 mmol), NaH (0.024 g, 1.0 mmol) and S_8 (0.033 g, 0.13 mmol). The colorless crystals were obtained. Yield: 0,272 g; 72%, m.p.: 130-131 °C. Anal. Cal. for $C_{19}H_{20}Cl_2N_2S$; C: 60.16; H: 5.31; N: 7.38; found C: 60.11; H: 5.41; N: 7.18%.

2.2. Syntheses of [AgCl(NHC)] derivatives, 5.

2.2.1. Synthesis of 1,3-bis-(2,6-dimethylphenyl)imidazol-2-ylidene silver(I) chloride, 5a.

Excess Ag_2O (0.276 g, 1.2 mmol) was added to a solution of 1,3-bis(2,6-dimethylphenyl)imidazolidium chloride (0.314 g, 1 mmol) in 25 mL dichloromethane. The mixture was stirred at room temparature for 24 h. After through Celite, the solvent was removed and the crude product dissolved in 25 mL tetrahidrofuran. The volume was reduced to 5 mL and the solution set aside for 24h at -10 °C. The product formed as colorless crystals that were collected by filtration. Yield: 0,336 g; 80%, m.p.: 362-364 °C. Anal. Cal. for $C_{19}H_{22}AgClN_2$; C: 54.51; H: 5.26; N: 6.64; found C: 54.46; H: 5.31; N: 6.69%.

2.2.2. Synthesis of 1,3-bis-(2, 4, 6-trimethylphenyl)imidazol-2-ylidene silver(I) chloride, 5b.

This compound was prepared in the same manner as 5**a.** using **3b.Cl$^-$** (0.342 g, 1.0 mmol). The colorless crystals were obtained. Yield: 0,345 g; 77%, m.p.: 348-350 °C. Anal. Cal. for $C_{21}H_{26}AgClN_2$; C: 56.08; H: 5.83; N: 6.23; found C: 56.25; H: 5.72; N: 6.44%.

2.2.3. Synthesis of 1,3-bis-(4-bromo-2, 6-diimethylphenyl) imidazol-2-ylidene silver(I) chloride, 5c.

This compound was prepared in the same manner as 5**a.** using **3c.Cl$^-$** (0.472 g, 1.0 mmol). The colorless crystals were obtained. Yield: 0,393 g; 68%, m.p.: 298-300 °C. Anal. Cal. for $C_{19}H_{20}AgBr_2ClN_2$; C: 39.38; H: 3.48; N: 4.83; found C: 39.44; H: 3.62; N: 4.87%.

2.2.4. Synthesis of 1,3-bis-(2,4-dimethylphenyl)imidazol-2-ylidene silver(I) chloride, 5d.

This compound was prepared in the same manner as 5**a.** using **3d.Cl$^-$** (0.314 g, 1 mmol). The colorless crystals were obtained. Yield: 0,328 g; 78%, m.p.: 215-216 °C. Anal. Cal. for $C_{19}H_{22}AgClN_2$; C: 54.51; H: 5.26; N: 6.64; found C: 54.61; H: 5.19; N: 6.53%.

2.2.5. Synthesis of 1,3-bis-(4-chloro-2,6-dimethylphenyl) imidazol-2-ylidene silver(I) chloride, 5e.

This compound was prepared in the same manner as 5**e.** using **3e.Cl$^-$** (0.337 g, 1.0 mmol). The colorless crystals were obtained. Yield: 0,303 g; 62%, m.p.: 341-343 ^{0}C. Anal. Cal. for $C_{19}H_{20}AgCl_3N_2$; C: 46.51; H: 4.11; N: 5.71; found C: 46.56; H: 4.21; N: 5.33%.

2.3. Synthesis of [RhCl(COD)(NHC)] derivatives, 8.

2.3.1. Synthesis of (η^4-1,5-cyclooctadiene){ 1,3-bis(2,6-dimethylphenyl) imidazolidin-2-ylidene} rhodium(I) chloride, 8a

A mixture of imidazolinium salt **a** (0.50 mmol, 0.161 g) and [Rh(μ-OMe)(1,5-COD)]$_2$ (0.25 mmol, 0.12 g) was heated under reflux in toluene (5 mL) for 2h. Hexane (15 mL) was then added the precipitate formed was filtered off and cryrstallized from CH_2Cl_2/ Et_2O (1mL /5 mL). Yield:0.263 g, 70%; m.p = 228-230 $^\circ$C (found: C: 61.83, H: 4.88, N: 6.29; $C_{27}H_{35}ClN_2Rh$, calcd.: C: 61.66, H: 6.71, N: 5.33 %).

2.3.2. Synthesis of (η^4-1,5-cyclooctadiene){ 1,3-bis(2, 4, 6-trimethylphenyl)imidazolidin-2-ylidene}rhodium(I) chloride, 8b.

The complex is obtained in anology to **8a** as a yellow crystals. Yield: 0.219 g 79%; m.p = 207-208 $^\circ$C (dec.).

(found: C:48.53, H: 4.08, N: 5.29 $C_{29}H_{39}ClN_2Rh$, calcd.: C: 62.87, H: 7.10, N: 5.06 %).

2.3.3. Synthesis of (η^4-1,5-cyclooctadiene) {1,3-bis(4-bromo-2,6-dimethylphenyl) imidazolidin-2-ylidene}rhodium(I) chloride, 8c.

The complex is obtained in anology to **8a** as a yellow crystals. Yield: 0.184 g 85%; m.p = 223-225 $^\circ$C (dec.).(found: C: 48.53, H: 4.08, N: 5.29; $C_{27}H_{33}Br_2ClN_2Rh$, calcd.: C: 47.53, H: 4.86, N: 4.10 %).

2.3.4. Synthesis of (η^4-1,5-cyclooctadiene){ 1,3-bis(2,4-dimethylphenyl) imidazolidin-2-ylidene} rhodium(I) chloride, 8d.

Yield: 0.168 g, 64%, m.p = 200-202 °C (dec.). (found: C, 61.83, H, 4.88, N, 6.29 $C_{29}H_{39}ClN_2Rh$, calcd.: C, 61.72, H, 6.29, N, 5.33 %).

2.3.5. Synthesis of (η^4-1,5-cyclooctadiene){1,3-bis(4-chloro-2,6-dimethylphenyl)imidazolidin-2-ylidene}rhodium(I) chloride, (8e).

The complex is obtained in anology to **8a** as a yellow crystals. Yield:0.237 g 80%, mp:219- 220 °C (dec.).

found: C, 54.63, H, 5.55, N, 4.93 $C_{27}H_{33}Br_2ClN_2Rh$, calcd.: C, 54.61, H, 5.43, N, 4.72 %.

2.4. Synthesis of [$RhCl(CO)_2(NHC)$] derivatives, 9.

2.4.1. Synthesis of dicarbonyl{1,3-bis(2,6-dimethylphenyl) imidazolidin-2-ylidene}rhodium(I) chloride, 9a.

RhCl(NHC)(COD), **8a**, (50 mg) was disolved in 5mL dichloromethane. Carbon monoxide was bubbled through the solution for 30 min. A color change from orange to pale was observed. The reaction mixture was stirred at room temparature for 2 h. Pentane was added to the mixture and filtrated.

Yield: 40.5 mg, 90%, mp = 175-177 °C (dec.). (found: C, 52.99, H, 4.33, N, 5.83 $C_{21}H_{23}ClN_2O_2Rh$, calcd.: C, 53.24, H, 4.89, N, 5.91 %).

2.4.2. Synthesis of dicarbonyl{1,3-bis(2, 4, 6-trimethylphenyl) imidazolidin-2-ylidene}rhodium(I) chloride, (9b).

The complex, **9b** is obtained in anology to **9a** as a yellow crystals. Yield: 41.9 mg, 92%, m.p = 149-151 °C (dec.). (found: C, 56.86, H, 5.65, N, 5.33 $C_{25}H_{31}ClN_2O_2Rh$, calcd.: C, 56.77, H, 5.69, N, 2.29 %). ^1H NMR (400 MHz $CDCl_3$):

2.4.3. Synthesis of dicarbonyl{1,3-bis(4-bromo-2,6-dimethylphenyl)imidazolidin-2-ylidene} rhodium(I) chloride, (9c).

The complex, **9c** is obtained in anology to **9a** as a yellow crystals. Yield: 43 mg, 93%, m.p = 225-227 °C (dec.). (found: C, 40.11, H, 3.71, N, 4.23 $C_{21}H_{21}Br_2ClN_2O_2Rh$, calcd.: C, 39.94, H, 3.35, N, 4.44 %).

2.4.4. Synthesis of dicarbonyl{1,3-bis(2,4-dimethylphenyl) imidazolidin-2-ylidene}rhodium(I) chloride, (9d).

The complex, **9d** is obtained in anology to **9a** as a yellow crystals. Yield: 37.9 mg, 84%, m.p = 153-155 °C (dec.). (found: C, 53.33, H, 5.01, N, 5.48 $C_{21}H_{23}ClN_2O_2Rh$, calcd.: C, 53.24, H, 4.89, N, 5.91 %).

2.4.5. Synthesis of dicarbonyl{1,3-bis(4-chloro-2,6-dimethylphenyl) imidazolidin-2-ylidene} rhodium(I) chloride, (9e).

The complex, **9e** is obtained in anology to **9a** as a yellow crystals. Yield: 43.9 mg, 96%, mp: 231 °C (dec.). (found: C, 47.00, H, 3.98, N, 5.23 $C_{21}H_{21}Cl_3N_2O_2Rh$, calcd.: C, 46.48, H, 3.90, N, 5.16 %).

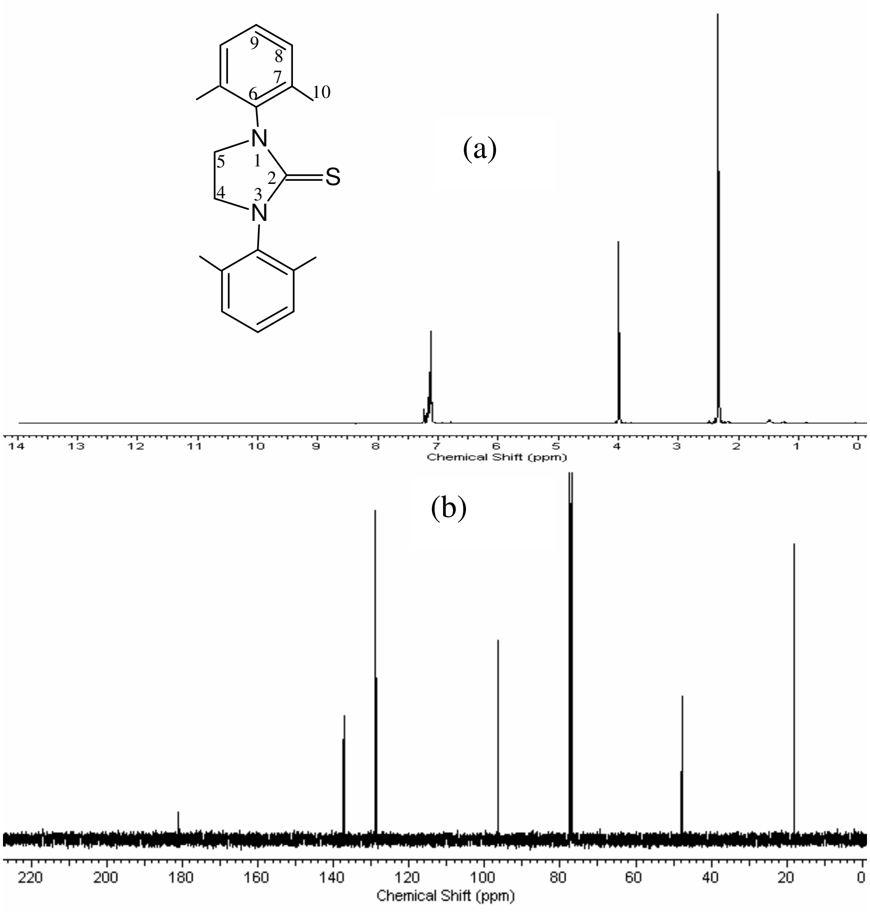


Figure 3.1 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **4a**

Table 3.1. ^{1}H and ^{13}C NMR spectra of **4a**.

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	181.0
4, 5	4.01 (4H, s)	-	47.8
6	-	-	137.1
7	-	-	128.7
8	7.13 (3H, m)	-	128.9
9	7.13 (3H, m)	-	137.3
10	2.36 (12H, s)	-	18.1

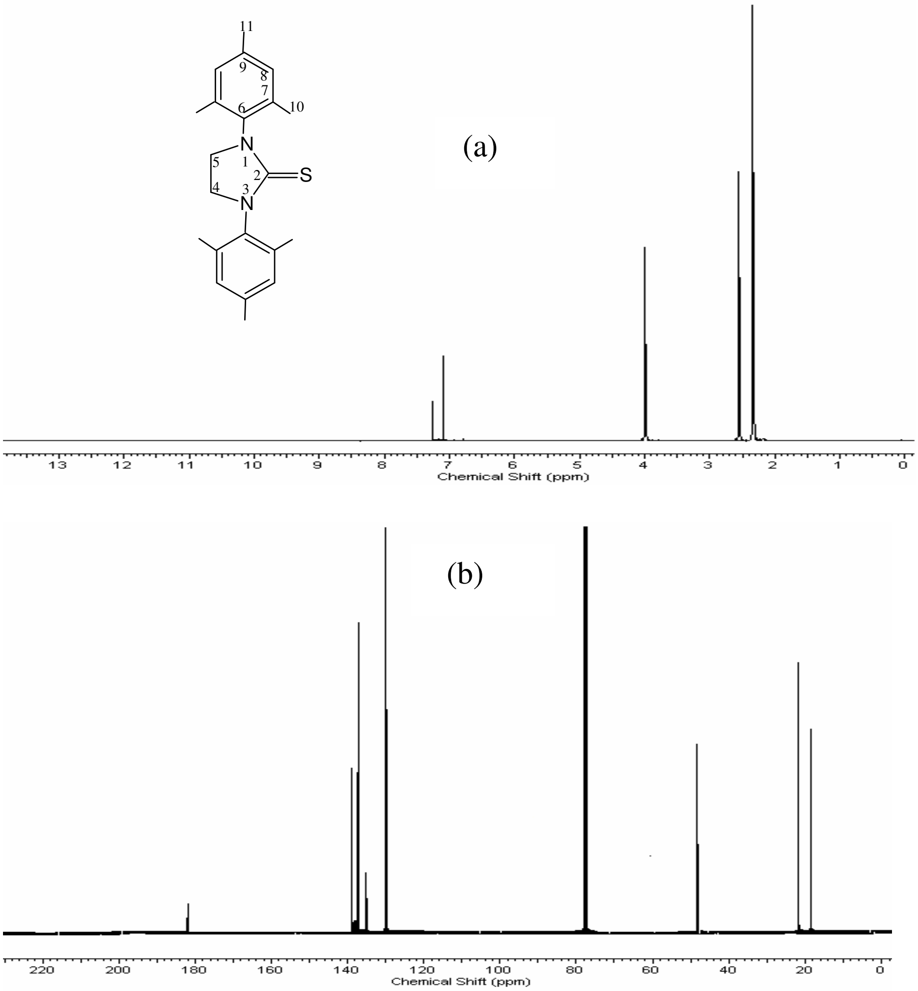


Figure 3.2. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **4b**

Table 3.2. ^{1}H and ^{13}C NMR spectra of **4b.**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	181.3
4, 5	3.99 (4H, s)	-	47.9
6	-	-	138.5
7	-	-	129.7
8	7.12 (4H, s)	-	134.8
9	-	-	136.8
10	2.28(12H, s)	-	21.3
11	2.49 (6H, s)	-	18.0

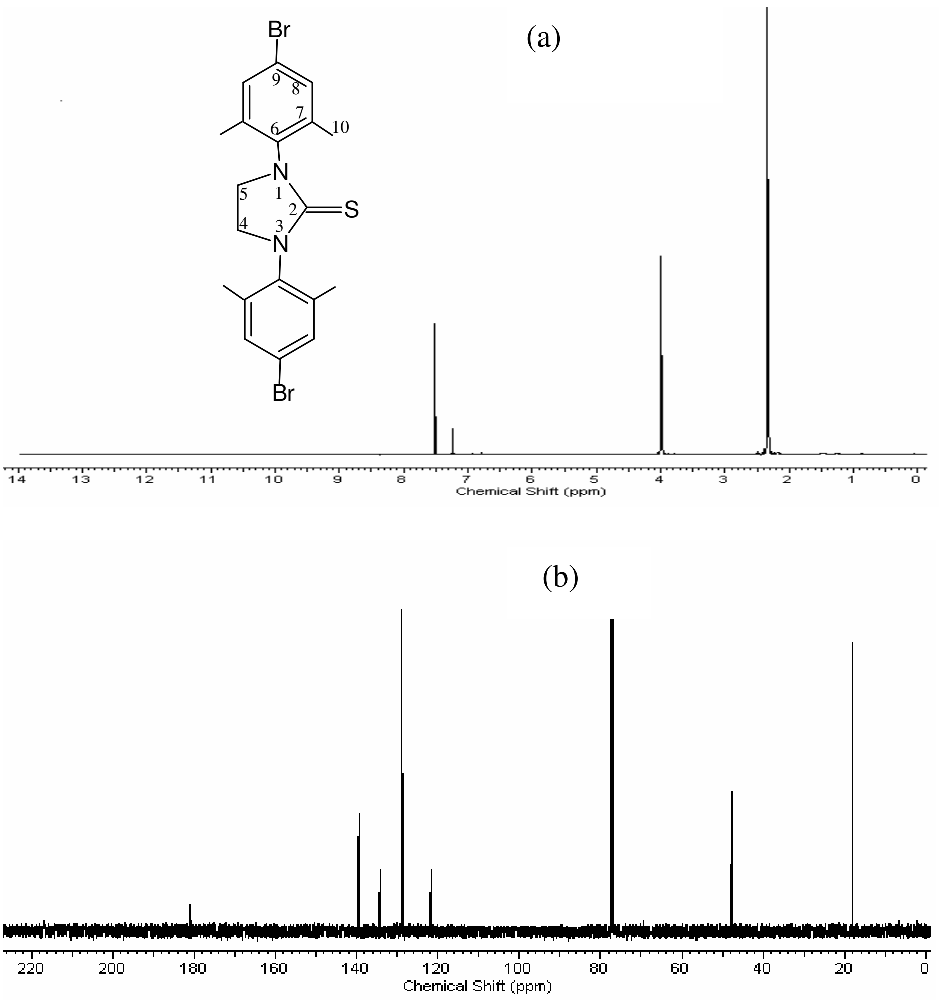


Figure 3.3. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of 4c.

Table 3.3. ^{1}H and ^{13}C NMR spectra of **4c.**

Numbers of atoms	*^{1}H NMR (δppm)*	*J (Hz)*	*^{13}C NMR (δppm)*
2	-	-	180.9
4, 5	3.99 (4H, s)	-	47.7
6	-	-	136.3
7	-	-	122.6
8	7.52 (4H, s)	-	128.9
9	-	-	131.9
10	2.33 (12H, s)	-	17,9

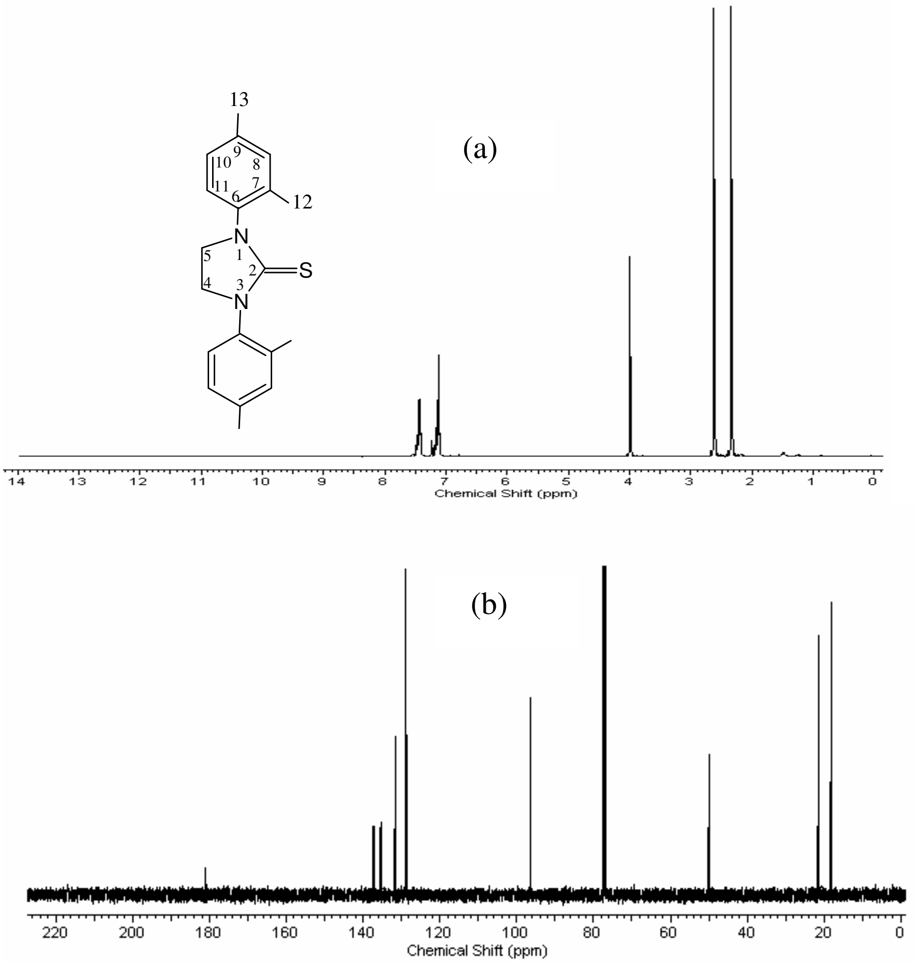


Figure 3.4. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **4d**

Table 3.4. ^{1}H and ^{13}C NMR spectra of **4d.**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	181.6
4, 5	3.91 (4H, s)	-	50.3
6	-	-	138.5
7	-	-	128.4
8	7.05 (2H, s)	-	132.2
9	-	-	97.3
10	7.25(2H, d)	1.96	128.4.
11	6.92 (2H, d)	1.96	136.8
12	2.30(6H, s)	-	18.2
13	2.45(6H, s)	-	21.5

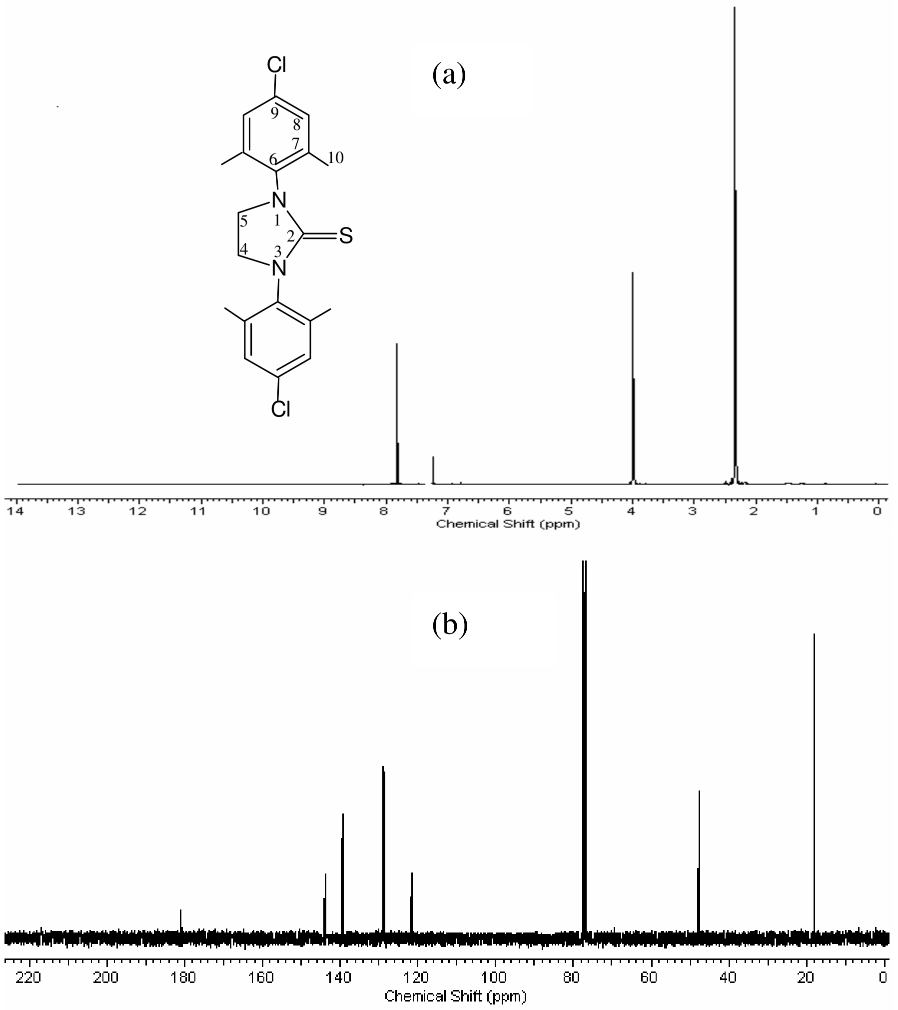


Figure 3.5. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **4e**

Table 3.5. ^{1}H and ^{13}C NMR spectra of **4e.**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	181.9
4, 5	4.09 (4H, s)	-	48.7
6	-	-	138.5
7	-	-	122.8
8	7.60 (4H, s)	-	128.9
9	-	-	143.8
10	2.33 (12H, s)	-	18.9

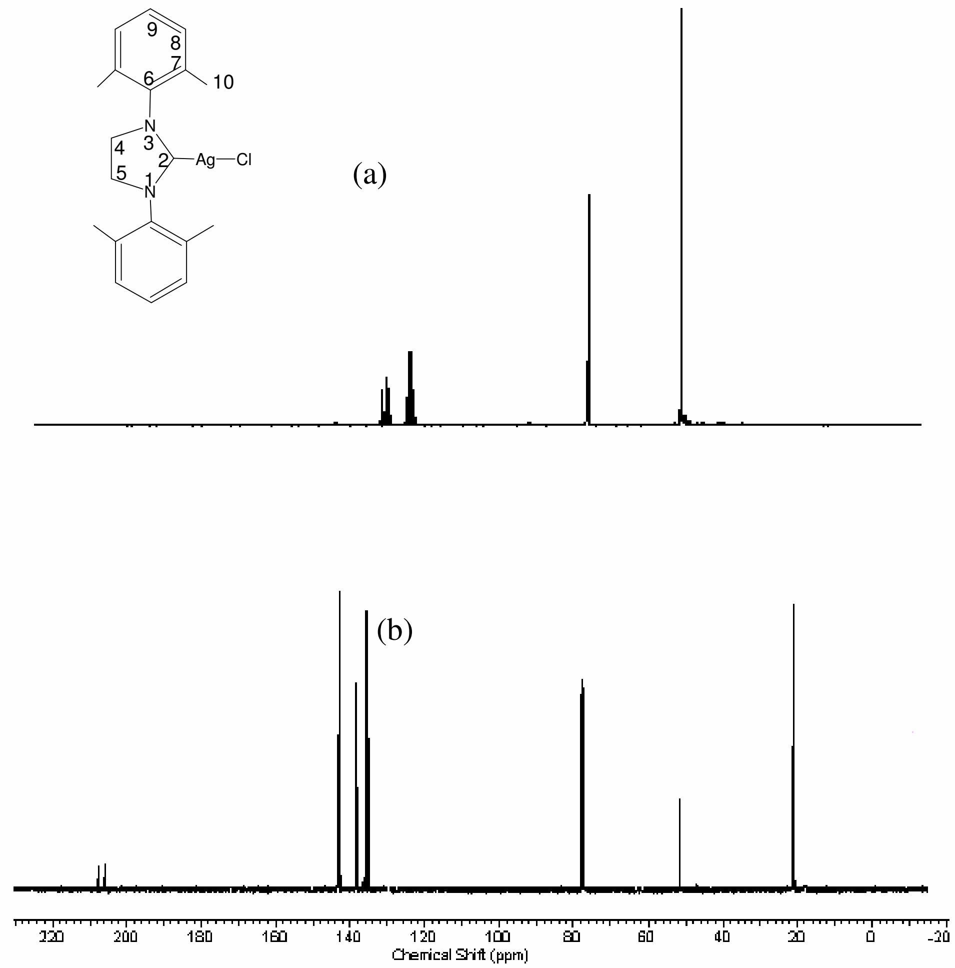


Figure 3.6. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **5a**.

Table 3.6. ^{1}H and ^{13}C NMR spectra of **5a**.

Numbers of atoms	*^{1}H NMR (δppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	48.0	206.5
4, 5	3.89 (4H, s)	-	51.2
6	-	-	138.0
7	-	-	138.6
8	7.66 (4H, s)	1.8	139.0
9	7.20(2H,t)	1.9	142.1
10	2.34 (12H, s)	-	20.3

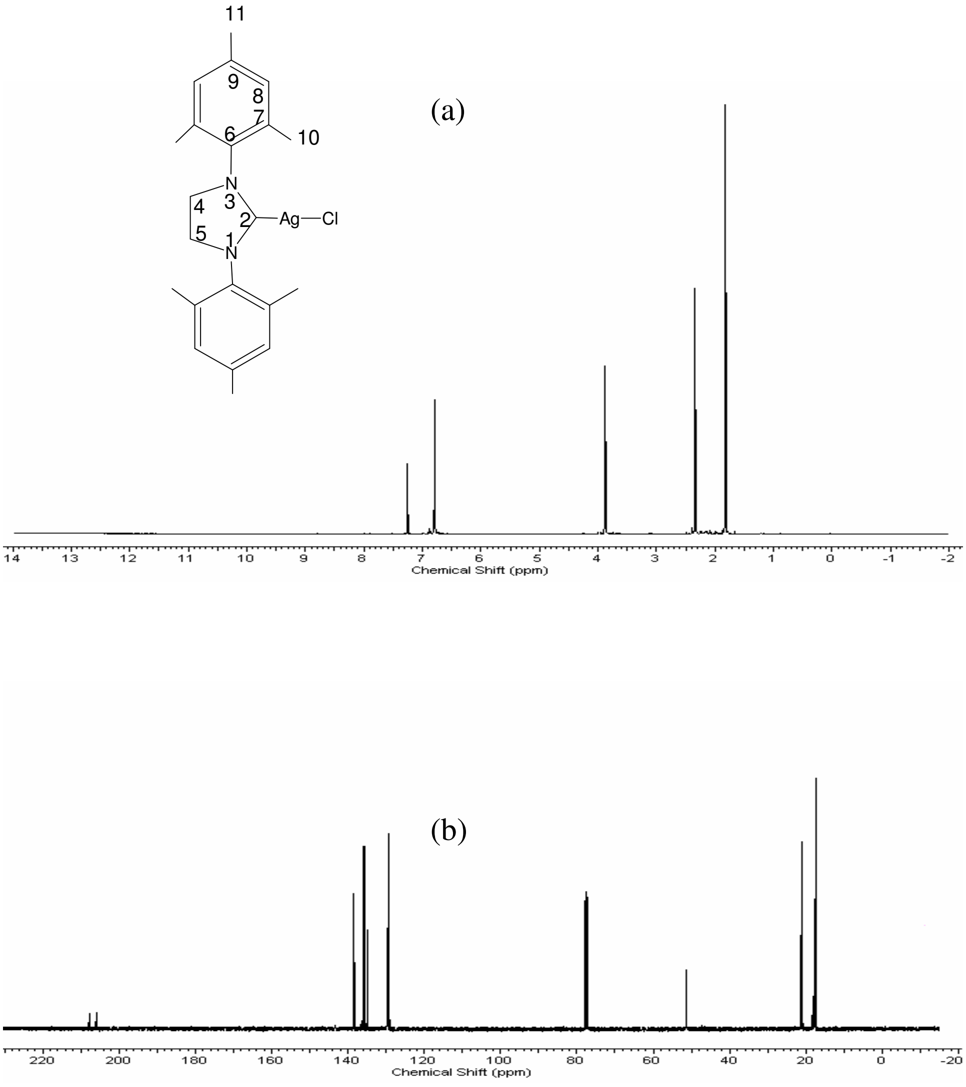


Figure 3.7. (a) 1H NMR, (b) 13C NMR spectra of 5b.

Table 3.7. ^{1}H and ^{13}C NMR spectra of **5b**.

Numbers of atoms	*^{1}H NMR (δppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	192.2, 166.2	206.9
4, 5	3.84 (4H, m)	-	51.4
6	-	-	138.4
7	-	-	129.5
8	7.15 (4H, d)	1.9	134.8
9	7.19 (2H, t)	1.9	135.6
10	2.34(6H, s)	-	17.4
11	1.82	-	21.2

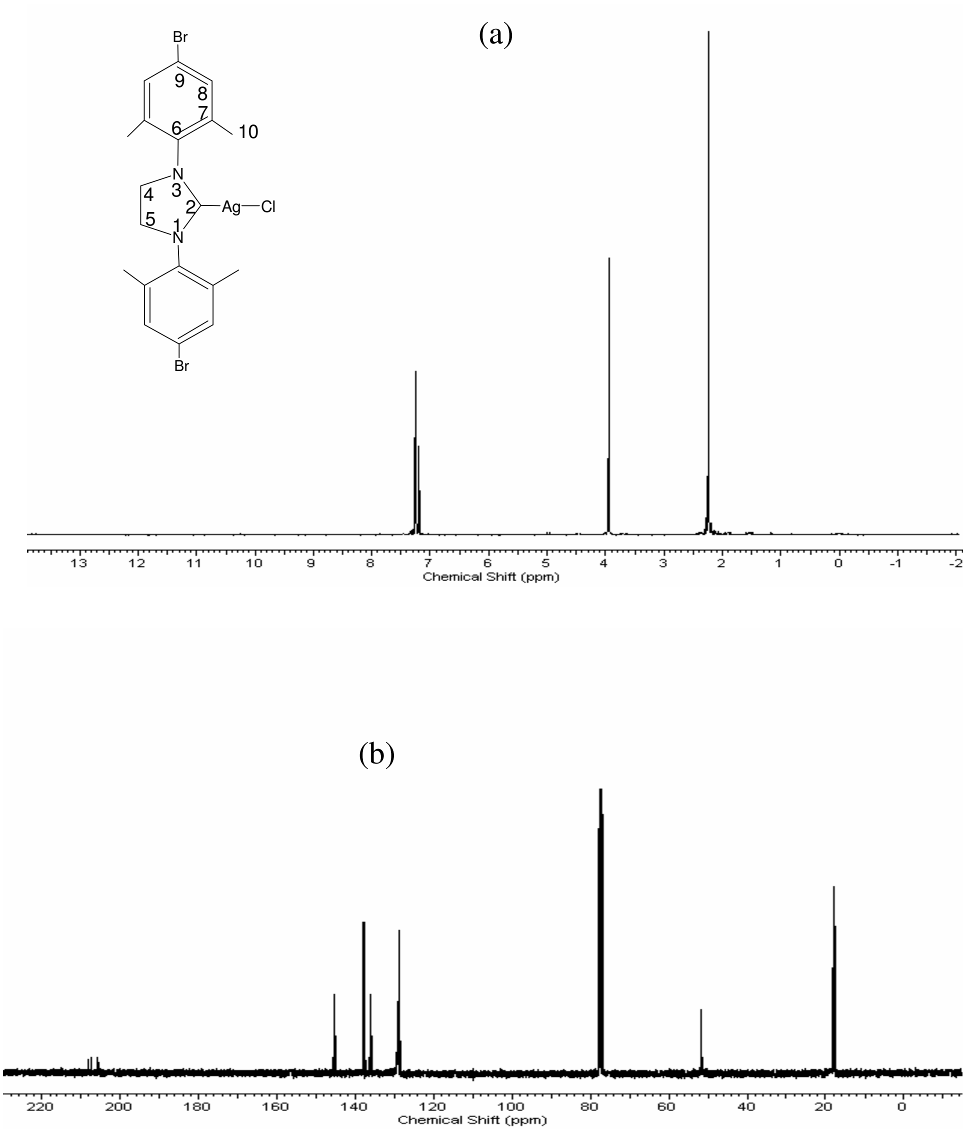


Figure 3.8. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **5c**.

Table 3.8. ^{1}H and ^{13}C NMR spectra of **5c**.

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	195.2, 167.2	206.7
4, 5	3.95 (4H, s)	-	51.7
6	-	-	137.9
7	-	-	129.1
8	7.22 (2H, s)	-	135.9
9	-	-	144.5
10	2.28 (12H, s)	-	18.3

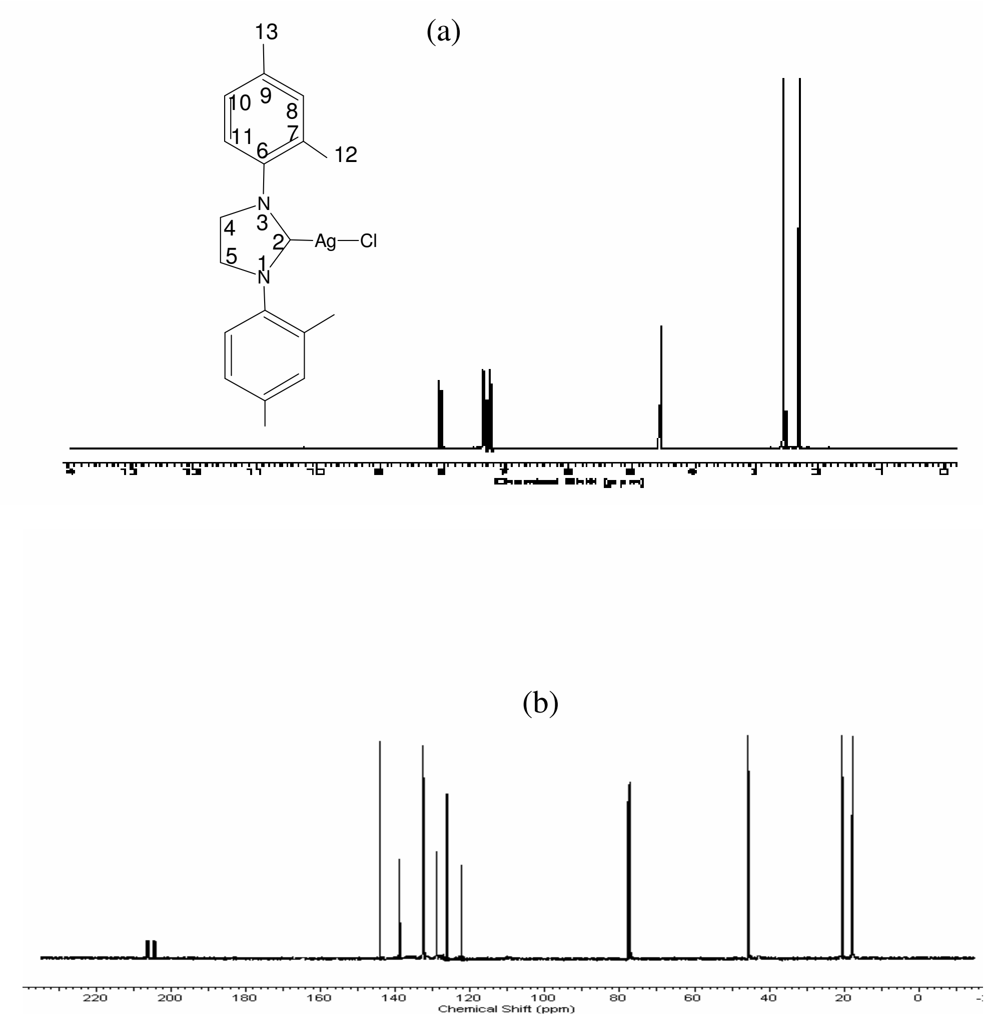


Figure 3.9. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **5d**.

Table 3.9. ^{1}H and ^{13}C NMR spectra of **5d**.

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	192.7, 166.3	205.8
4, 5	4.31 (4H, s)	-	51.4
6	-	-	121.2
7	-	-	135.6
8	7.14 (2H, s)	-	138.4
9	-	-	142.8
10	7.06 (2H, d)	1.9	129.5
11	7.01 (2H, d)	1.9	127.6
12	2.14 (6H, s)	-	17.4
13	2.38 (6H, s)	-	21.2

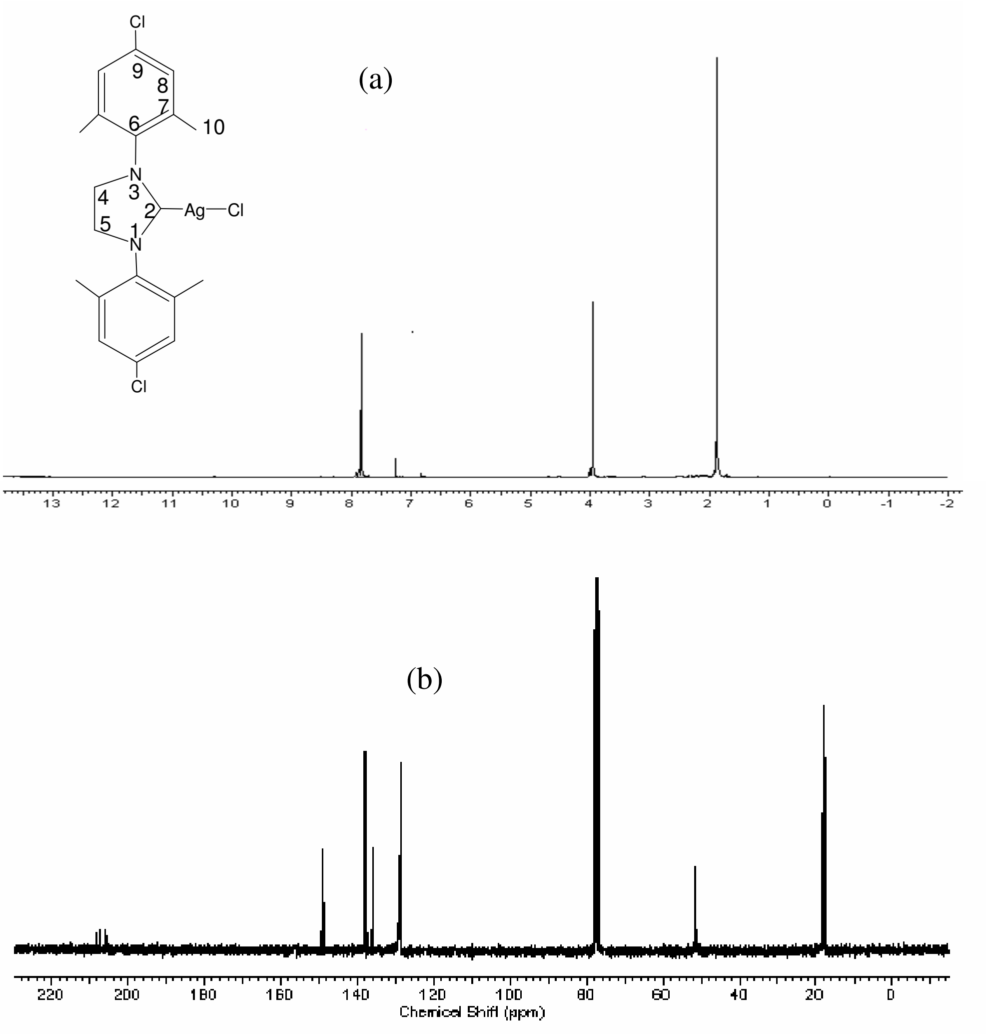


Figure 3.10. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **5e.**

Table 3.10. ^{1}H and ^{13}C NMR spectra of **5e**.

Numbers of atoms	*^{1}H NMR (δppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	196.7, 167.6	205.1
4, 5	3.99 (4H, s)	-	51.6
6	-	-	138.1
7	-	-	138.9
8	7.89 (2H, s)	-	129.6
9	-	-	148.5
10	1.90 (12H, s)	-	19.0

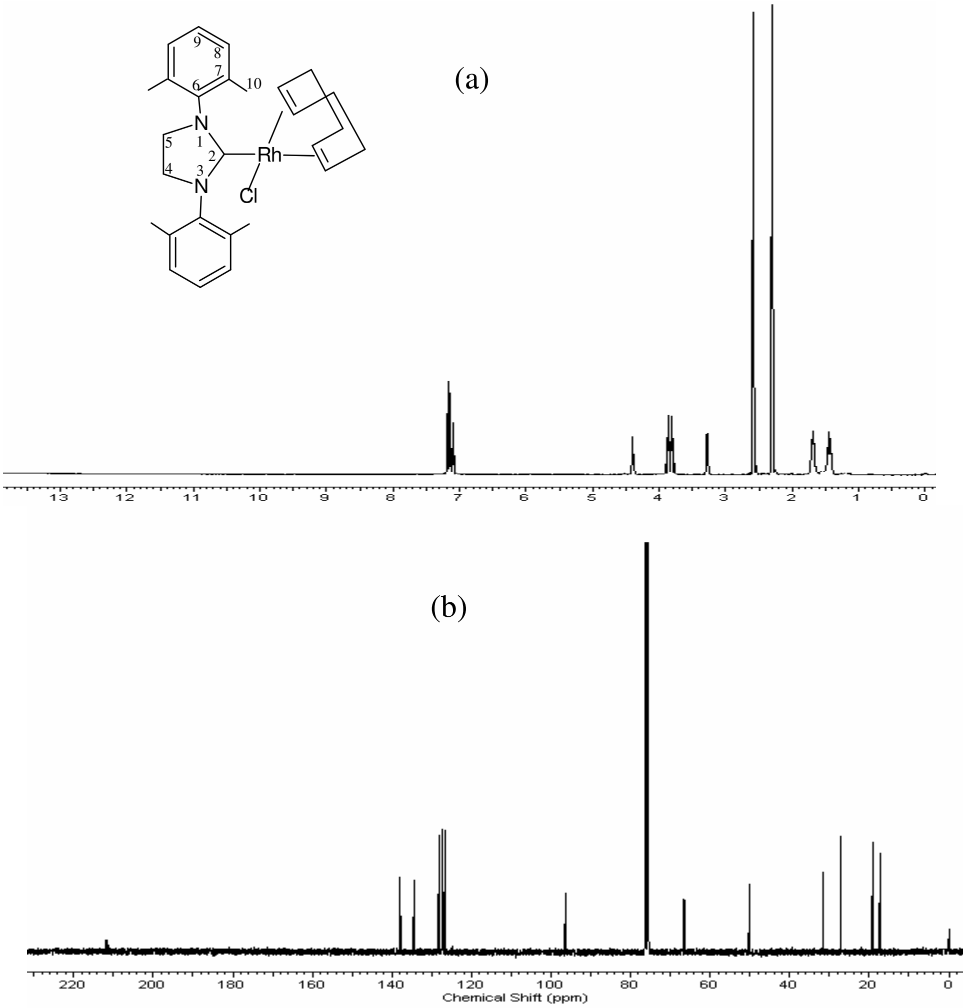


Figure 3.11. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **8a**.

Table 3.11. ^{1}H and ^{13}C NMR spectra of **8a**.

Numbers of atoms	*^{1}H NMR (δppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	48.0	211.8
4, 5	3.84 (4H, m)	-	50.2
6	-	-	126.7
7	-	-	137.9, 137.7
8	7.15 (4H, d)	1.9	128.2, 127.2
9	7.19 (2H, t)	1.9	134.5
10	2.58, 2.30 (12H, s)	-	19.0, 17.4
Others	4. 39 (COD-C*H*, s)	-	96.5
	3.27 (COD-C*H*, d)	0.6	66.5
	1.78 (COD-C*H*$_2$, t)	1.0	31.6
	1.56 (COD-C*H*, t)	1.9	27.1

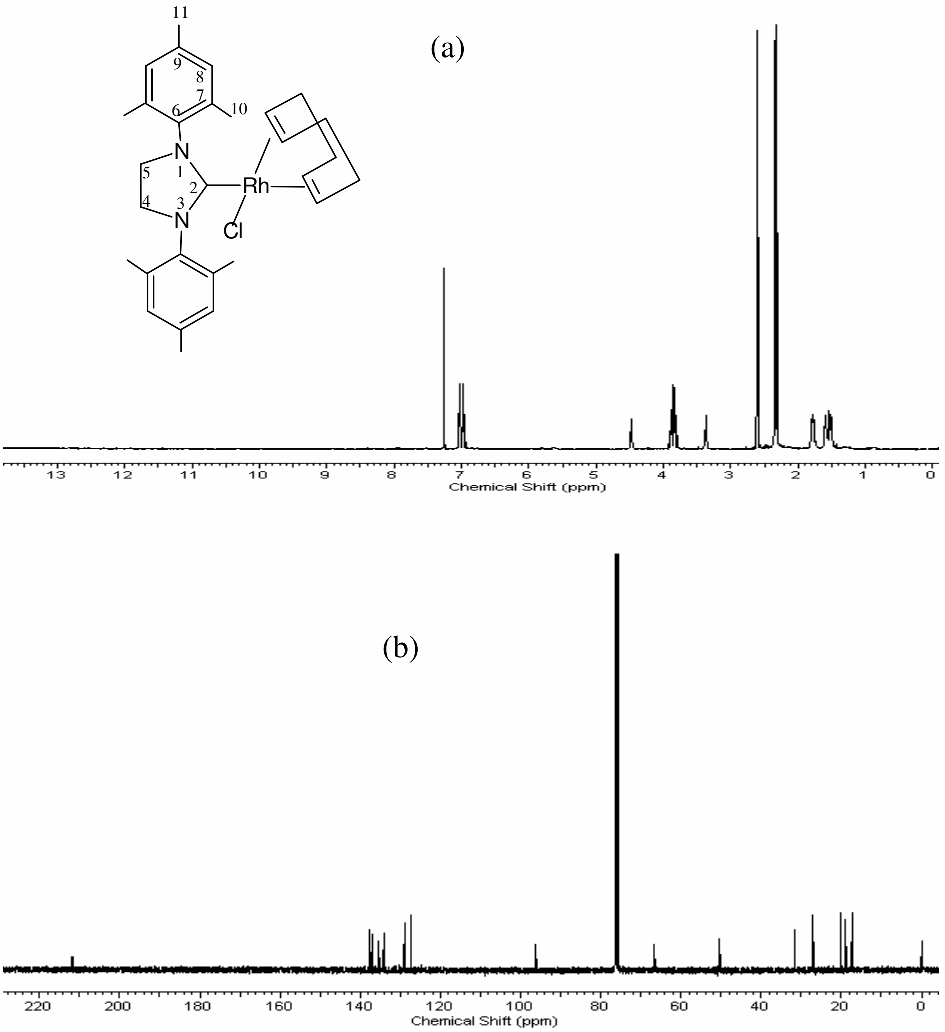


Figure 3.12. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **8b**.

Table 3.12. ^{1}H and ^{13}C NMR spectra of **8b**.

Numbers of atoms	*^{1}H NMR (δppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	48.0	211.7
4, 5	3.86 (4H, m)	-	50.3
6	-	-	127.3
7	-	-	135.3, 134.1
8	7.32 7.02 (2H, s)	-	137.9, 136.8
9	-	-	128.9
10	2.59, 2.31 (12H, s)	-	20.0, 18.9
11	2.34 (6H, s)	-	17.3
Others	4.47 (COD-C*H*, s)	-	96.2
	3.36 (COD-C*H*, d)	0.6	66.5
	1.78 (COD-CH_2, t)	1.3	31.6
	1.56 (COD-C*H*, t)	1.9	27.1

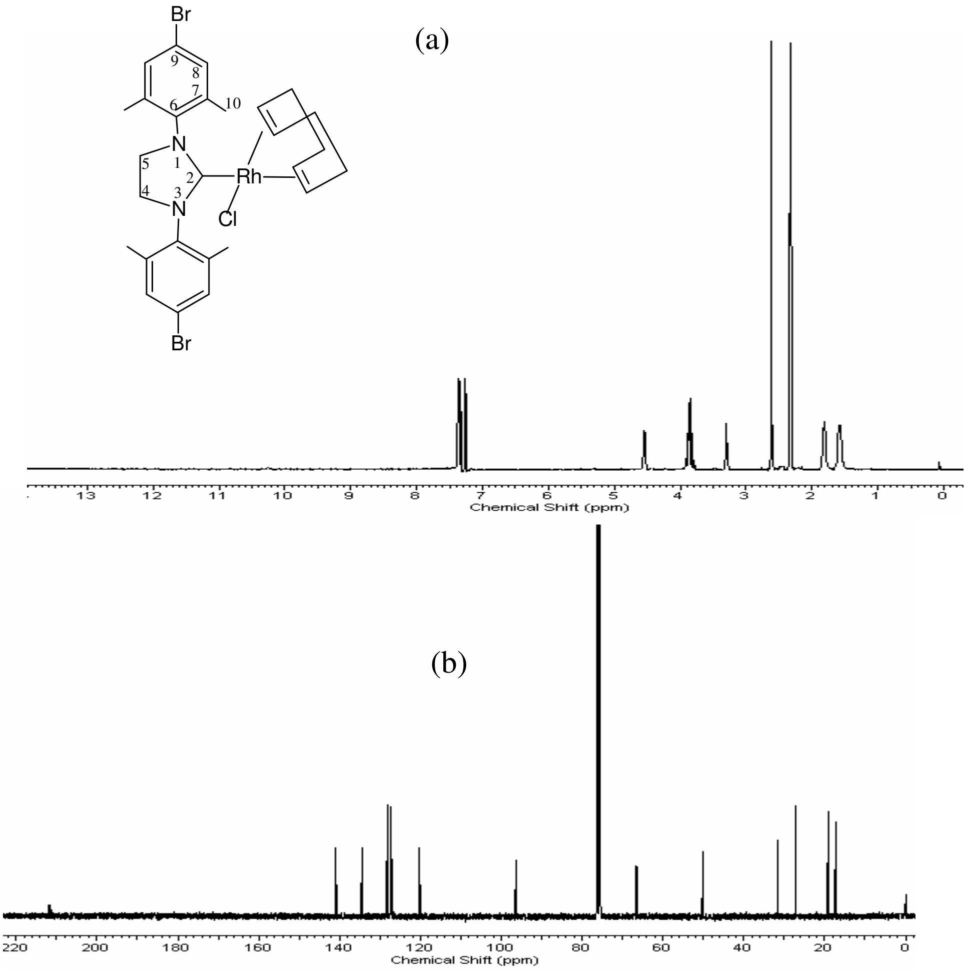


Figure 3.13. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **8c**.

Table 3.13. ^{1}H and ^{13}C NMR spectra of **8c**.

Numbers of atoms	*^{1}H NMR (δppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	48.1	213.8
4, 5	3.81 (4H, m)	-	51.4
6	-	-	122.1
7	-	-	132.0, 130.8
8	7.36 7.32 (2H, s)	-	137.8, 132.4
9	-	-	141.3
10	2.61, 2.32 (12H, s)	-	20.2, 18.7
Others	4.54 (COD-C*H*, s)	-	97.7
	3.29 (COD-C*H*, s)	-	68.1
	1.81 (COD-CH_2, t)	1.3	32.8
	1.56 (COD-C*H*, t)	1.3	28.3

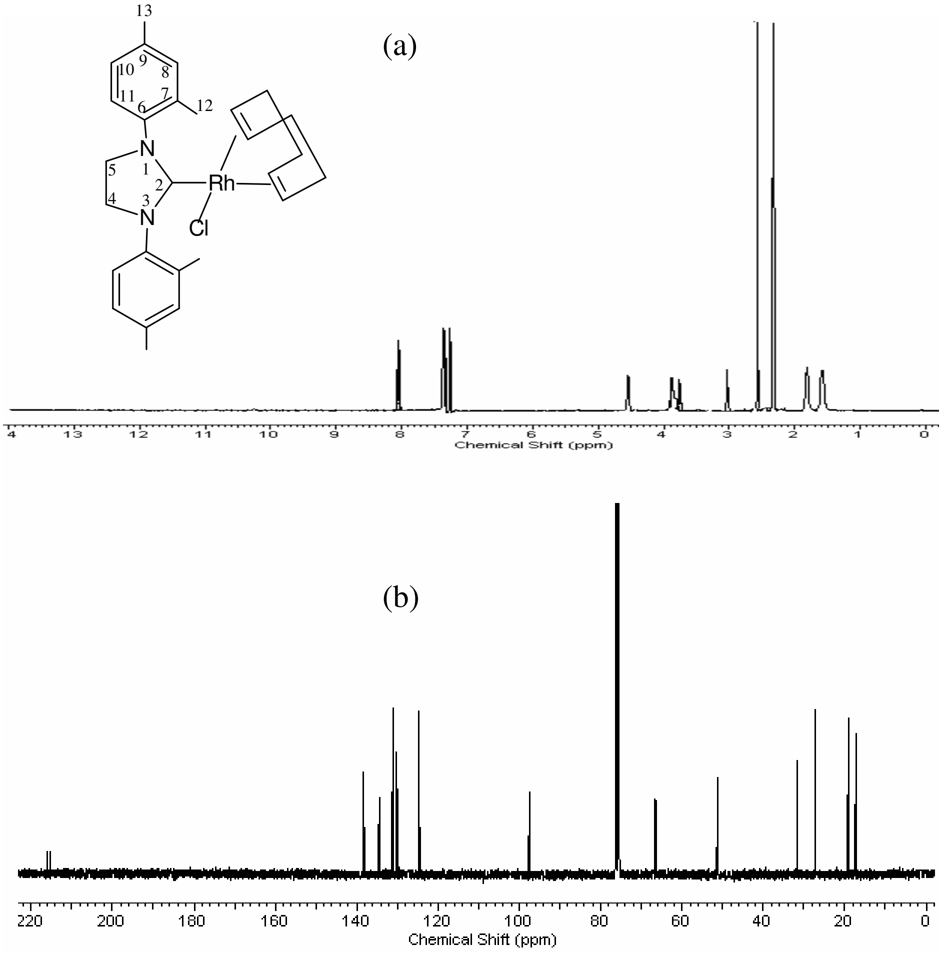


Figure 3.14. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **8d**.

Table 3.14. ^{1}H and ^{13}C NMR spectra of **8d**.

Numbers of atoms	*^{1}H NMR (δppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	49.0	215.2
4, 5	3.89-3.84 (4H, m)	-	52.6
6	-	-	138.0
7	-	-	138.1
8	7.267(2H, s)	-	127.6
9	-	-	134.4
10	7.32 (2H, d)	7.9	131.0
11	8.12 (2H, d)	7.9	131.6
12	2.23 (6H, s)	-	18.7
13	2.40 (6H, s)	-	19.5
Others	4.46 (COD-C*H*, s)	-	97.3
	3.22 (COD-C*H*, s)	-	66.9
	1.81 (COD-CH_2, t)	1.3	31.6
	1.75 (COD-C*H*, t)	1.4	27.1

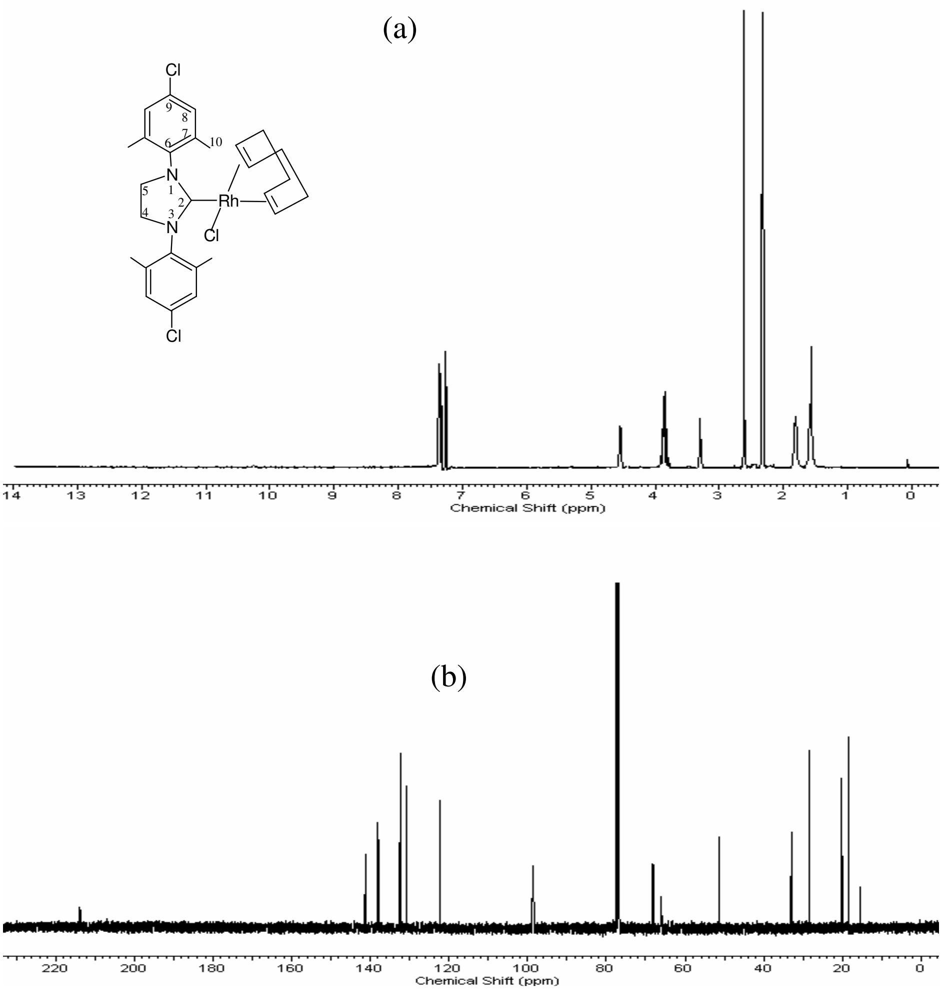


Figure 3.15. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **8e**.

Table 3.15. ^{1}H and ^{13}C NMR spectra of **8e**.

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	48.0	212.5
4, 5	3.79 (4H, m)	-	50.2
6	-	-	120.9
7	-	-	136.6, 136.8
8	7.26 7.28 (2H, s)	-	129.6, 131.1
9	-	-	140.1
10	2.07, 2.53 (12H, s)	-	17.3, 19.0
Others	4.46 (COD-C*H*, s)	-	97.3
	3.22 (COD-C*H*, s)	-	66.9
	1.81 (COD-CH_2, t)	1.3	31.6
	1.75 (COD-C*H*, t)	1.4	27.1

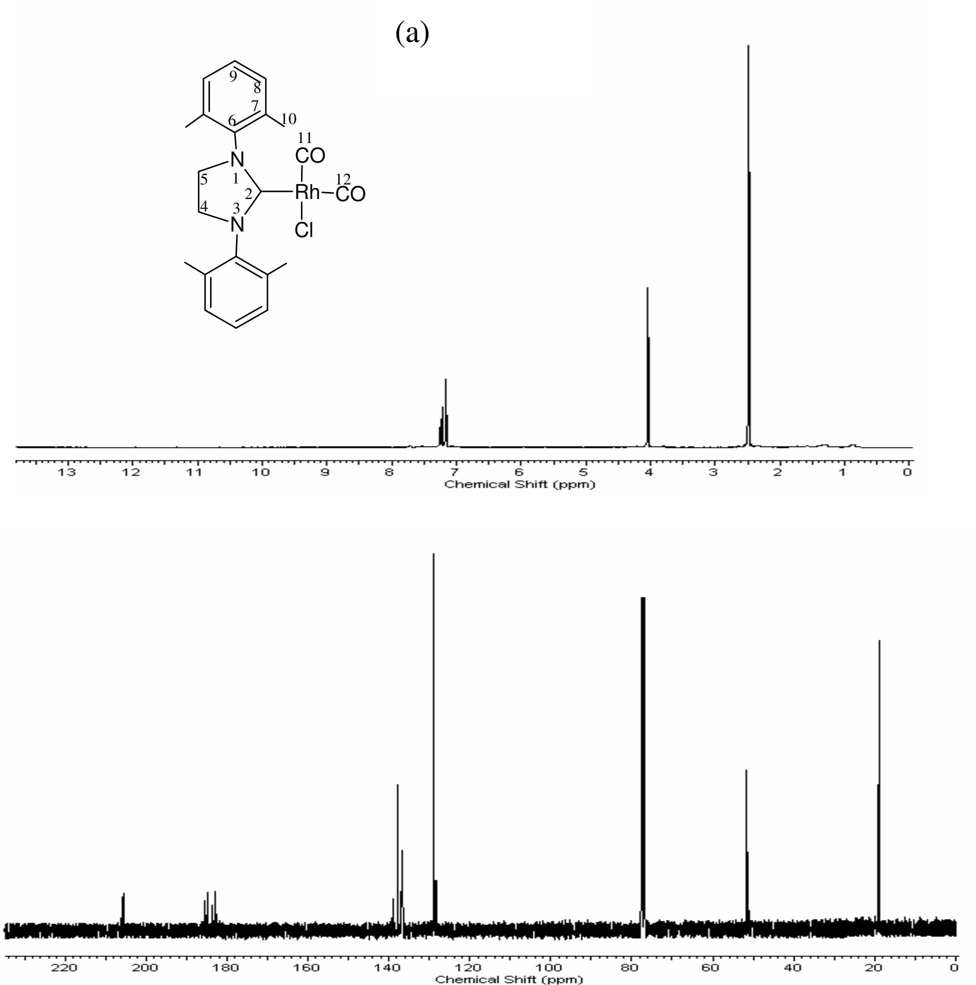


Figure 3.16. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **9a**

Table 3.16. ^{1}H and ^{13}C NMR spectra of **9a**.

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	41.0	205.7
4, 5	4.04 (4H, s)	-	51.7
6	-	-	139.1
7	-	-	128.2
8	7.17 (4H, d)	2.0	131.1
9	7.25 (2H, t)	0.6	137.6
10	2.48 (2H, t)	-	19.1
11	-	53.4	185.1
12	-	74.7	183.2

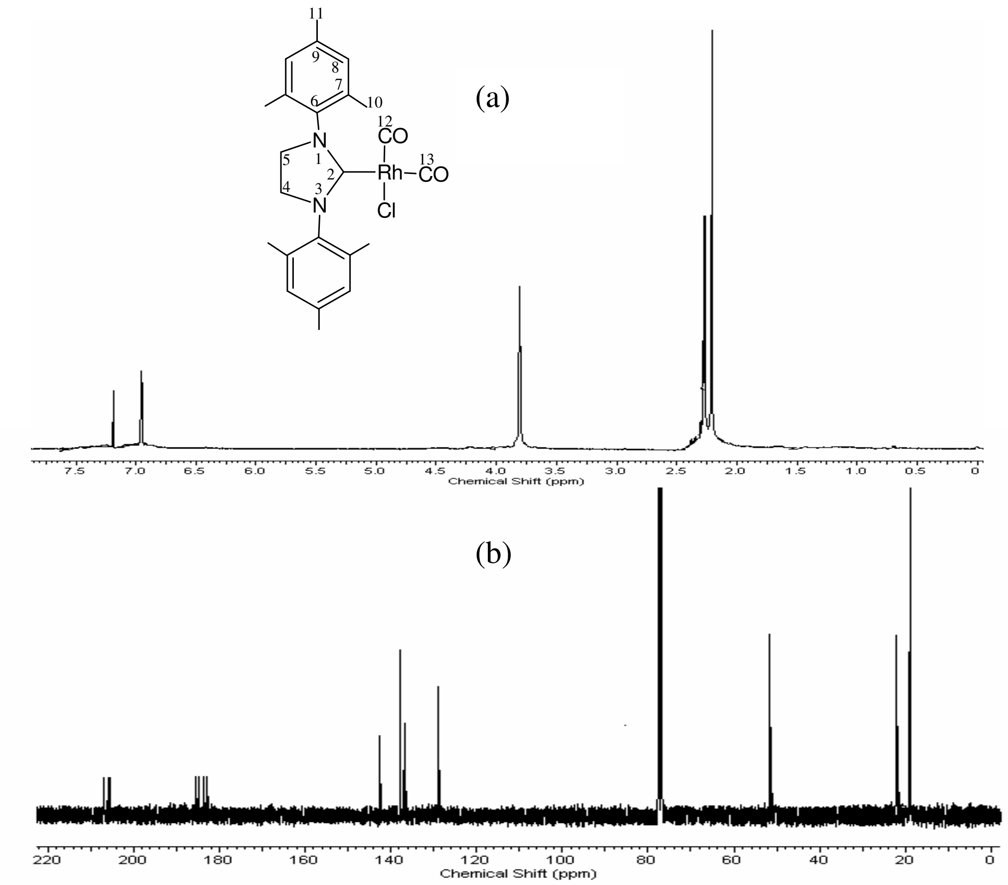


Figure 3.17. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **9b**.

Table 3.17 ^{1}H and ^{13}C NMR spectra of **9b**.

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	41.3	206.8
4, 5	3.79 (4H, s)	-	51.3
6	-	-	129.4
7	-	-	137.0
8	6.91 (4H, d)	-	137.9
9	-	-	142.5
10	2.41(12H, s)	-	19.0
11	2.37(6H, s)	-	21.4
12	-	52.5	185.0
13	-	73.3	182.8

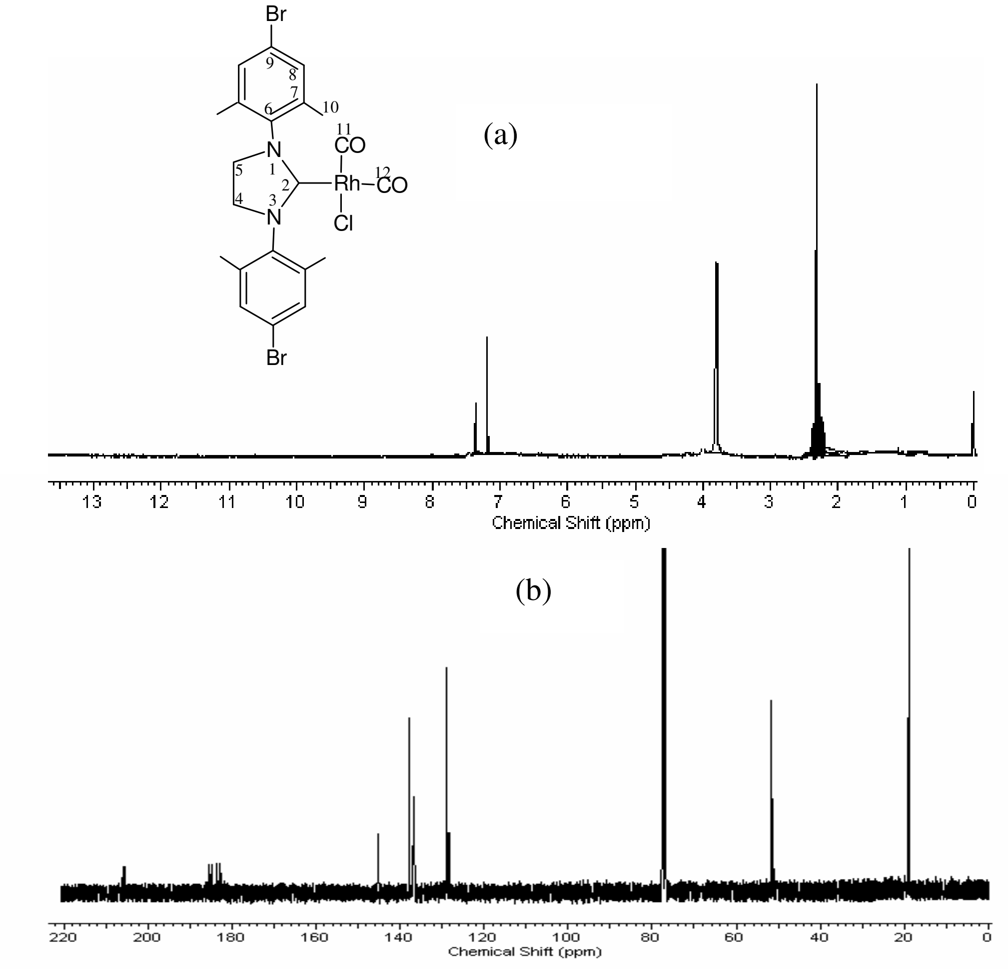


Figure 3.18. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **9c**

Table 3.18. ^{1}H and ^{13}C NMR spectra of **9c.**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	42.0	206.7
4, 5	3.93 (4H, s)	-	52.4
6	-	-	142.0
7	-	-	137.8
8	7.24 (4H, s)	-	128.0
9	-	-	137.0
10	2.48 (12H, s)	-	19.4
11	-	53.1	184.7
12	-	74.0	182.9

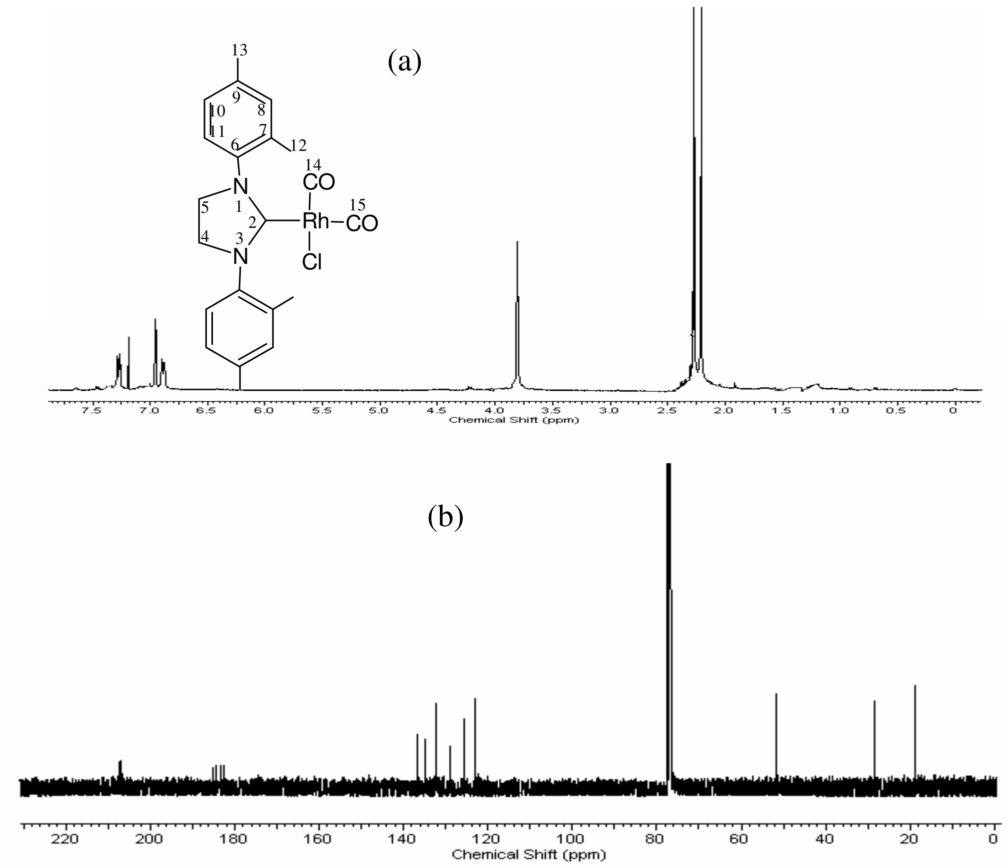


Figure 3.19. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **9d**.

Table 3.19. ^{1}H and ^{13}C NMR spectra of **9d**.

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	41.0	206.8
4, 5	3.81 (4H, s)	-	51.7
6	-	-	139.4
7	-	-	123.1
8	6.95 (2H, s)	-	127.5
9	-	-	131.9
10	7.17 (2H, d)	1.9	137.0
11	7.28 (2H, d)	1.9	137.6
12	2.27 (6H, s)	-	19.0
13	2.21 (6H, s)	-	19.9
14	-	52.9	184.6
15	-	73.7	182.5

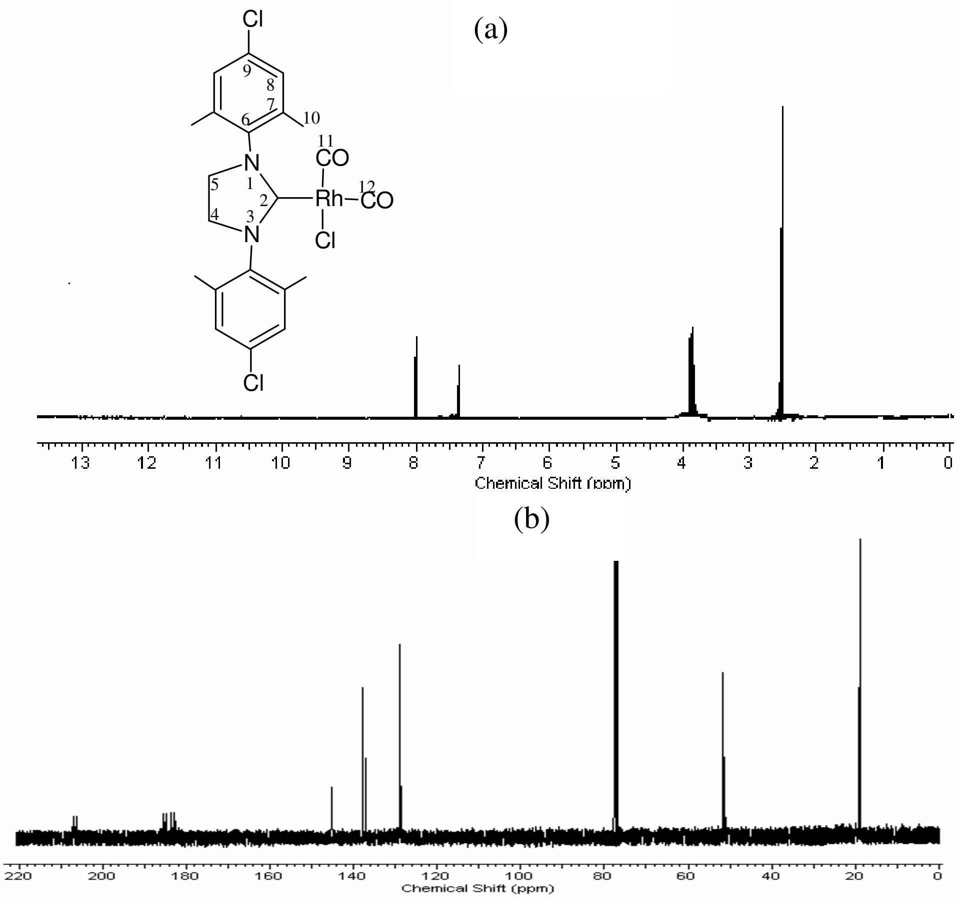


Figure 3.20. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of 9e

Table 3.20. ^{1}H and ^{13}C NMR spectra of **9e.**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	42.0	206.8
4, 5	3.88 (4H, s)	-	51.7
6	-	-	138.0
7	-	-	128.9
8	7.99 (4H, d)	-	137.6
9	-	-	143.8
10	2.51 (12H, s)	-	18.2
11	-	53.3	185.1
12	-	74.0	182.7

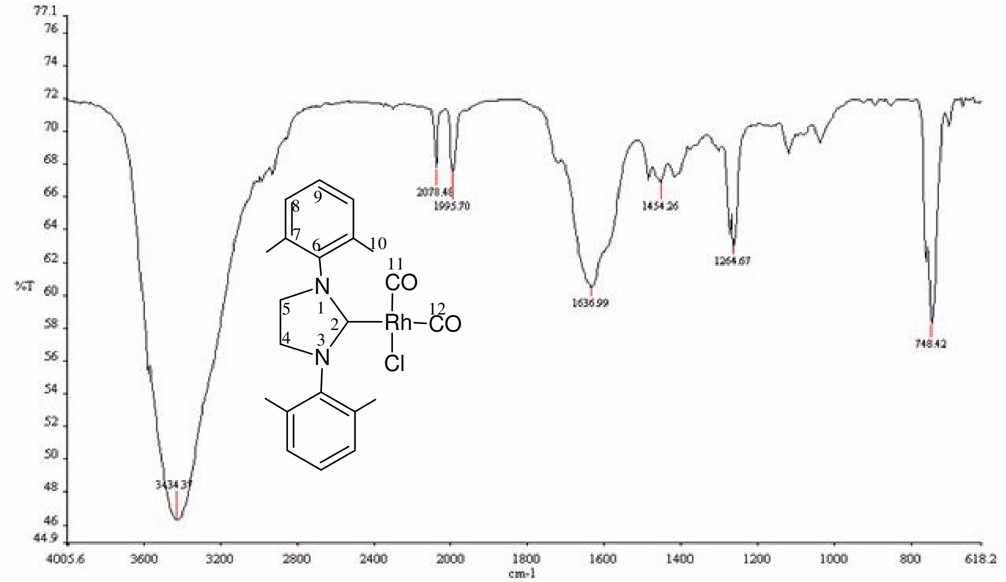


Figure 3.21. IR spectra of **9a**

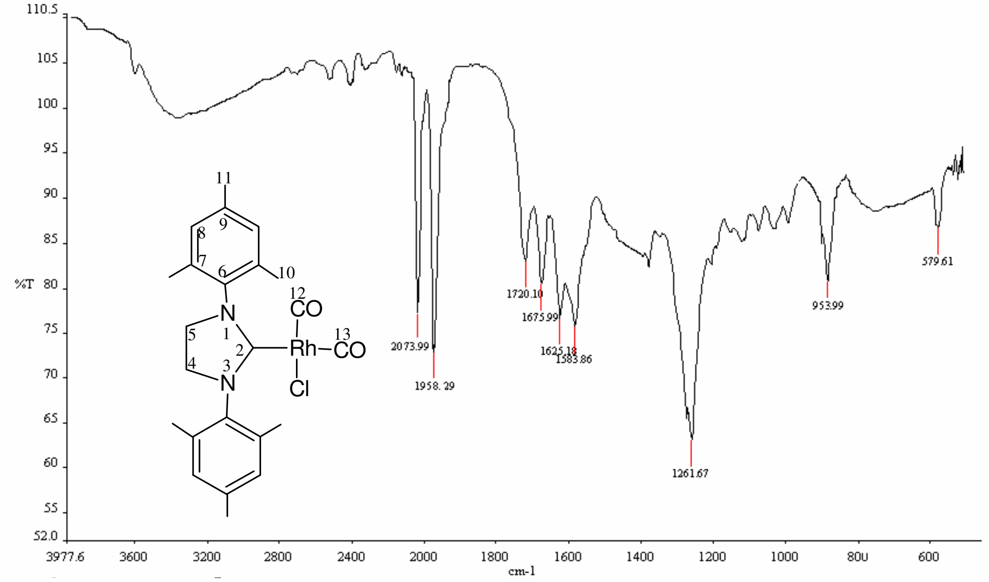


Figure 3.22. IR spectra of 9b

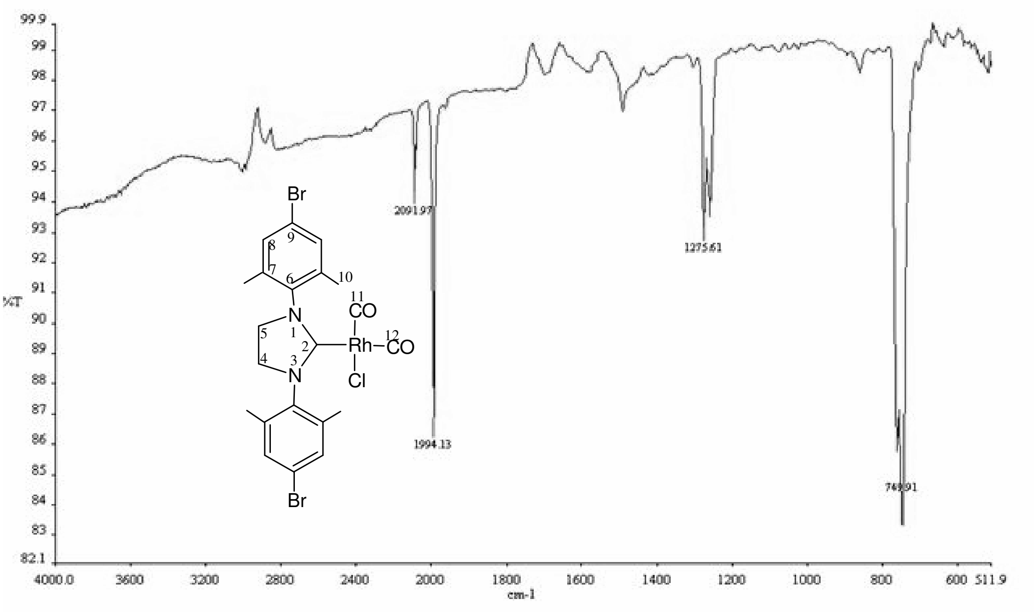


Figure 3.23. IR spectra of 9c

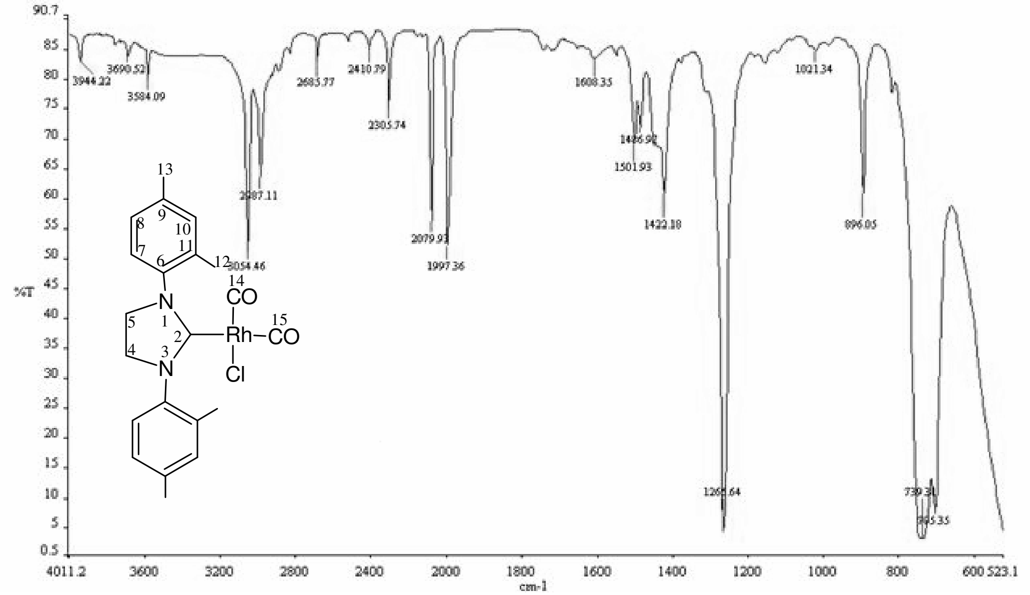


Figure 3.24. IR spectra of 9d

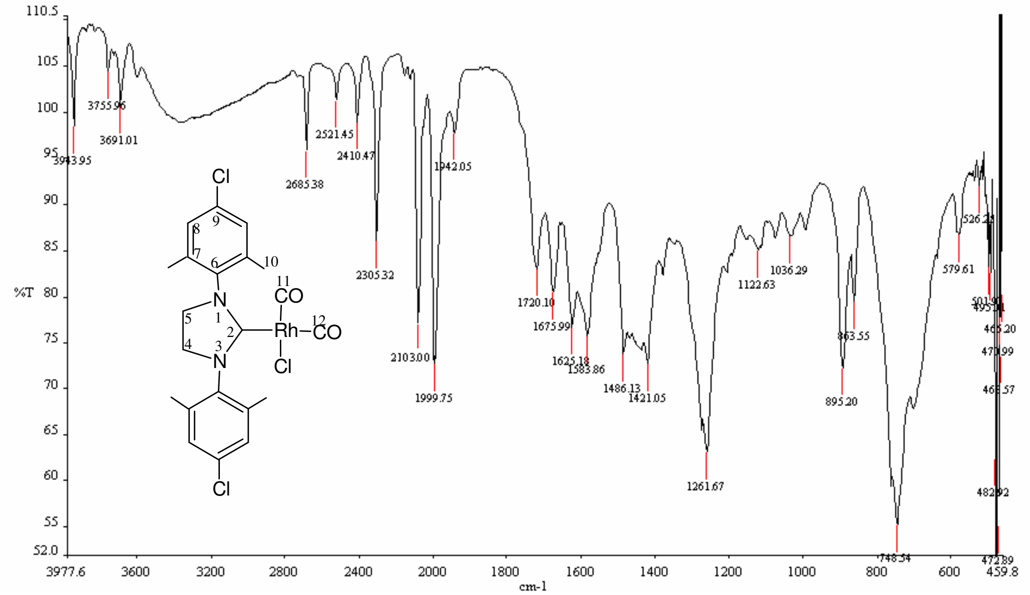


Figure 3.25. IR spectra of 9e

3. RESULTS AND DISCUSSION

As can be seen in section 1, NHC ligands are the most widely used ligands in organometallic chemistry. Such ligands have proven to be excellent supporting ligands in numerious transition-metal-mediated reactions. Their ability to strongly coordinate to metal centers allows for the formation of stable metal species facilitating catalyst design efforts. A leading motive is the advantage of NHCs as ligands in organometallic catalysis, where they extend the scope of application reached by phosphines (functionalized, chiral, water-soluble and immobilized derivatives).

NHCs have been shown to be highly effective as supporting ligands in a range of catalytic processes, such as palladium-catalyzed Suzuki or Heck-type coupling, CO-C_2H_4 copolymerizations, ruthenium-catalyzed olefin metathesis, cyclopropanations, furan synthesis and rhodium-catalyzedhydrogenation, hydroformylation and hydrosilylations. These useful catalytic reactions have attracted interest in the search for new catalysts with high activity. Thus, in the thesis NHCs and metal complexes were synthesized in order to obtain efficient and stable catalysts.

The nature and electronic effects imported by the substituents on the carbene carbon have a profound effect. The most commonly, currently used NHCs are those that employ alkyl or aryl substituents at the nitrogens of the imidazole ring. The steric and electronic environment, which is imposed by these ligands, can also be modified.

The strong σ-donor properties of NHCs combined with a poor π-acceptor ability result in metal complexes with high chemical and thermal stability together with good catalytic activity. Successful application of these complexes in asymmetric catalysis is evolving but electronic and steric variations of NHCs will be neccessary for further progress in this field.

In this thesis, it was aimed to synthesize NHC complexes bearing different substituents at the phenyl ring of 1,3-disubstituted imidazolines and containing hydrogen, methyl, acenaphthyl at the C_4-C_5 position of imidazolidine ring. The structurally and sterically similar 1,3-bis(2,6-dimethylphenyl) imidazolinium salts with H, CH_3, Br and Cl substituents at the *p*-position of the aryl ring were used to prepare two series of palladium complexes $PdCl_2(NHC)_2$, **6**, $PdCl_2(NHC)(PPh_3)$, **7**, rhodium complexes [RhCl(NHC)(COD)], **8**, $[RhCl(NHC)(CO)_2]$, **9** and silver complex AgCl(NHC), **5**. In this way *o*-substituents of NHC's were held constant and only the nature of the *p*-substituent was varied. In both cases the efficiency increased with the electron donating nature of the p-substituent (Cl < Br < H< Me).

The 4,5-positions of the imidazolidine ring seems to be ideally suited for substitution, since they are quite far from the catalytically active metal site. Therefore, we focused on the design of an acenaphthylene-anellated NHC ligand to modify the environment of the metal center.

In Part III, synthesis and characterisation of thione (**4**), silver (**5**) and rhodium complexes (**8**), (**9**) of these salts will be explained. Synthesis and characterisation of imidazolium salts and their palladium complexes (**6**), (**7**) obtained have been described (Türkmen and Çetinkaya, 2006).

Carbenes are known to react with sulfur to give thioureas. Therefore, α-elimination of $CHCl_3$ from **2d** to give NHC was investigated. When toluene solution of **2d** was heated with an electrophilic reagent such as S_8 under reflux conditions the corresponding NHC derivative (**4d**) were obtained. With this viable protocol in hand, the scope of the reaction was further probed using a variety of platinum metal substrates in the same context. NHC.$CHCl_3$ underwent smooth $CHCl_3$ elimination to give **7d** and **8d**.

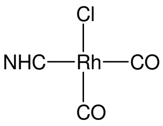
On the other hand, the treatment of $Pd(OAc)_2$ with the imidazolinium salts, **3,** did not give the expected compound.It was observed that, Pd(II) was reduced Pd(0). So, we attempted to synthesize silver N-heterocyclic carbene complexes ,**5**, from **3** and Ag_2O. Ag-NHC complexes represent an attractive class of NHC-transfer reagents, with potential for the desired transmetallation of NHC ligands to be accompanied by the thermodynamically favorable precipitation of AgX.

NHC complexes of silver(I) are readily formed, in high yield by deprotonation of diazol(in)ium halides using silver oxide a variety of Ag-NHC complexes have been prepared. However, treatment of Ag_2O with 1,3-dimestylimidazolinium chloride derivatives in DCM at 25 ^{0}C produced Ag-NHC complexes (**5a, b, c, d, e**). The ^{1}H NMR spectra of complexes(**5**) give a single resonans at 3.80-4.00 for the saturated imidazole ring. The ^{13}C NMR spectra of Ag-NHC complex (**5b**) give a carbonic signal at 207.5 ppm as doublet of doublets with an observable coupling between carbon and silver of $J^1(^{13}C\text{-}^{109}Ag)$ = 256 Hz and $J^1(^{13}C\text{-}^{107}Ag)$ = 222 Hz. The similar values in chemical shift for (**5a, b', c, d, e**) indicate no significant difference in the electronic donor properties existing for the saturated carbenes in these silver systems.

Imidazolium salts (**3a, b, c, d, e**) readily reacted with $[Rh(OMe)(COD)]_2$ and S_8 in the presence of NaH to give **8a, b, c, d, e** and **4a, b, c, d, e** respectively (Fig). The thiones (**4**) are stable crystalline substances, the structures of which have been elucidated by NMR spectroscopy. The most important peak shown by ^{13}C NMR is the peak corresponding to C=S at δ 180.9- 181.9 ppm. ^{13}C chemical shifts, which provide a useful diagnostic tool for Rh-carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}C_{carb})$ are in the range 211.7- 215.2 ppm.

We found that the rhodium complexes show hindered rotation about the metal-NHC bond. As previous studies have indicated (Doyle and Lappert, 1974, Enders and Gielen, 2001) the barrier to rotation seems to be largely steric in nature, because the carbene M-C bond is essentially single. We decided to synthesize carbonyl derivatives to allow us to estimate the electron donor character of the NHCs.

The RhCl(NHC)(COD) complexes (**8**) were converted into *cis*-$[RhCl(NHC)(CO)_2]$ complexes (**9**) and the C-O stretching frequencies of carbonyl complexes(**9**), were recorded in CH_2Cl_2 solution. The C-O stretching frequencies of *cis*-$[RhCl(CO)_2(NHC)]$ are considered to be an excellent measure for the σ-donor/π-acceptor properties of the NHC ligands. The electron donating property and the *trans*-influence of substituents at the *p*-position of the aryl ring were compared with the electron donating nature of the *p*-substituent. The data indicate that the basicity increases in order: **e** < **d** < **c** < **a** < **b** ≈ **b'**. Comparison of IR data compiled for *cis*-$[RhCl(CO)_2(NHC)]$ complexes of NHCs in the table shows that acenaphthylene-anellated NHCs are a stronger donor than the corresponding non-anellated analogous bearing the imidazole skeleton. The ^{13}C NMR spectra of *cis*-$[RhCl(CO)_2(NHC)]$ complexes (**9**) give a carbonic signal at 205.7- 206.8 ppm as a doublet. Coupling constants $J(^{13}C-^{103}Rh)$ for **9** are in the range 41- 42 Hz.



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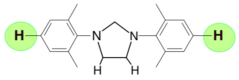
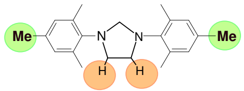
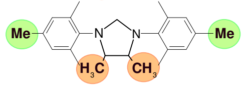
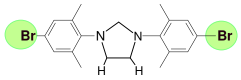
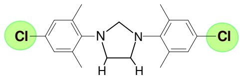
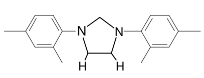
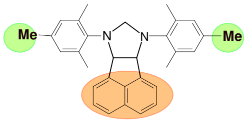
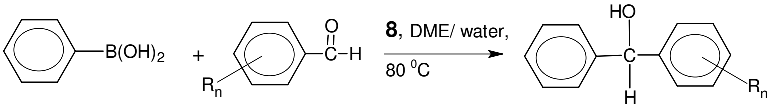
	2084	1996
	2081	1996
	2078	1994
	2092	1994
	2103	1999
	2080	1997
	2074	1988

3.3. Catalytic Experiments

3.3.1. Rhodium-carbene catalyzed addition of phenylboronic acid to aldehydes

Miyaura and co-workers reported that rhodium catalyzes the addition of aryl and alkenylboronic acids to aldehydes giving secondary alcohols (Sakai *et al.,* 1998). The reactions were facilitated by the presence of an electron withdrawing group on the aldehyde and an electron donating group on the arylboronic acid, suggesting that the mechanism involves a nucleophilic attack of the aryl group on the aldehydes. The finding that these reactions were run with sterically hindered and strongly basic ligands attracted the attention of Fürstner who subsequently applied the reaction to *N*-heterocyclic carbene ligands. The *in situ* generated catalytic system for the addition of phenylboronic acid to aldehydes is prepared by combination of a rhodium salt, 1,3-bis(alkyl or aryl)imidazolium chloride and base (Fürstner and Krause, 2001). However, the influence on the catalytic activity of rhodium *N*-heterocyclic carbene complexes for the addition of phenylboronic acid to aldehydes was investigated by Özdemir (Özdemir *et al.*, 2004; 2005). In this respect, we have prepared new Rh *N*-heterocyclic carbene complexes (**8**) and measured their efficiencies as catalysts for the addition of phenylboronic acid to aldehydes were compared (Table 2).

Table 3.21. Rhodium-carbene catalyzed addition of phenylboronic acid to aldehydes



Entry	**8**	R	Yield (%)
1.	**a**	p-OCH$_3$	78
2.	**b**	p-OCH$_3$	87
3.	**b’**	p-OCH$_3$	90
4.	**c**	p-OCH$_3$	66
5.	**d**	p-OCH$_3$	65

6.	**e**	*p*-OCH_3	43
7.	**f**	*p*-OCH_3	92
8.	**a**	*p*-Cl	82
9.	**b**	*p*-Cl	89
10.	**b’**	*p*-Cl	90
11.	**c**	*p*-Cl	63
12.	**d**	*p*-Cl	60
13.	**e**	*p*-Cl	45
14.	**f**	*p*-Cl	92
15.	**a**	2, 4, 6-$(CH_3)_3$	80
16.	**b**	2, 4, 6-$(CH_3)_3$	93
17.	**b’**	2, 4, 6-$(CH_3)_3$	94
18.	**c**	2, 4, 6-$(CH_3)_3$	67
19.	**d**	2, 4, 6-$(CH_3)_3$	58
20.	**e**	2, 4, 6-$(CH_3)_3$	37
21.	**f**	2, 4, 6-$(CH_3)_3$	94
22.	**a**	3, 4, 5-$(OCH_3)_3$	79
23.	**b**	3, 4, 5-$(OCH_3)_3$	88
24.	**b’**	3, 4, 5-$(OCH_3)_3$	91
25.	**c**	3, 4, 5-$(OCH_3)_3$	64
26.	**d**	3, 4, 5-$(OCH_3)_3$	61
27.	**e**	3, 4, 5-$(OCH_3)_3$	33
28.	**f**	3, 4, 5-$(OCH_3)_3$	93

We have investigated the addition of phenylboronic acid to aldehydes and compared Rh(NHC)- complexes bearing strongly electron-donating and sterically more demanding ligands. The catalysts (**8a-f**) vary in both steric demand and in electron density around the rhodium-center. Both parameters are determined by the attached NHC-ligand only. The addition of phenylboronic acid to aldehydes proceeds in high yields and quite rapidly even with a low catalyst loading. Under those conditions, 4-methoxybenzaldehyde, 2,4,6-trimethylbenzaldehyde, 3,4,5-trimethoxybenzaldehyde and 4-chlorobenzaldehyde reacted very cleanly with phenylboronic acid in good yields (Table 2, entries 7, 16, 17, 21, 28). The activities of the different catalysts (Table 2) range from 33% for catalyst **8e** up to 94% for catalysts **8b'**and **8f**. We could show that electron-rich and bulky NHC-ligands lead to a higher activity with yields up to 94%. Applying bulky substituents to the NHC-ligand has an influence on the activity at **8f**.

3.6.2. General procedure for rhodium- carbene catalyzed addion of phenylboronic acid to aldehydes.

Phenylboronic acid (1.20 g, 9.8 mmol), KOBu^t (4.9 mmol), diethyleneglycol di-*n*-butyl ether (0.6 mmol, internal standard), rhodium-carbene catalyst (1 mmol%) and dimethoxyethane (15 mL) were introduced into a Schlenk tube and then water (5 mL) was added. The resulting mixture was heated for 4 h at 80 ^{0}C under an argon atmosphere, cooled to ambient temperature and extracted with ethyl acetate(30 mL). After drying over $MgSO_4$ the organic phase was evaporated. The conversion was monitored by gas chromatography.

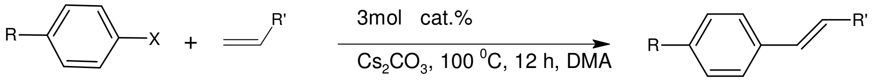
3.6.3. Palladium-carbene catalyzed arylation of alkenes

The palladium-catalyzed C-C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base is referred as the "Heck Reaction". Recent developments in the catalysts and reaction conditions have resulted in a much broader range of donors and acceptors being amenable to the Heck Reaction. The Heck reaction has shown to be very useful especially for the preparation of disubstituted olefins. In the palladium catalyzed reaction the carbon–carbon bond is formed from a vinyl functionality and an aryl and (or) alkyl halide. The reaction is well adapted for automation due to the fact that it does not require inert atmosphere conditions.

The intramolecular Heck reaction has been well-established as a powerful tool for the construction of complex polycyclic ring systems in the context of natural product synthesis. Palladium species have largely been used as catalysts for C-C bond forming reactions. The reactions are usually carried out homogenously in the presence of a base under inert atmosphere

We tested **6** and **7** for activity in the Heck reactions, using a set of standard substrates, under standard reaction conditions concerning solvent, temperature and base (Table 3). The electron donating property and the *trans*-influence of substituents at the *p*-position of the aryl ring were examined. The catalytic results indicate that among preformed complexes (**6**and **7**), **6b'**, **6f** and **7b'** could be the most effective catalyst precursors (Table 3, entries 16, 20, 24). This observation is consistent with previous reports (Türkmen and Çetinkaya, 2006). The results indicate that the effect of the *p*-substituent was significant. Also, palladium carbene complexes (**6b'**, **6f**, **7b'**) bearing methyl, acenaphthyl at the C_4-C_5 position of the imidazolidine ring have shown better catalytic activity than their hidrogen counterparts (**6b**,**7b**).

Table 3.22 The Heck reaction catalyzed by preformed **6** or **7**.



Entry	Cat	R	R'	X	Yield (%)
1	**6a**	Me(O)C	COOBu^n	Br	57
2	**6b**	″	″	″	59
3	**6b'**	″	″	″	60
5	**6c**	″	″	″	48
5	**6d**	″	″	″	30
6	**6e**	″	″	″	33
7	**6f**	″	″	″	68
8	**7a**	Me(O)C	COOBu^n	Br	67
9	**7b**	″	″	″	63
10	**7b'**	″	″	″	65
11	**7c**	″	″	″	57
12	**7d**	″	″	″	50

13	**7e**	″	″	″	39
14	**6a**	″	Ph	″	64
15	**6b**	″	″	″	66
16	**6b’**	″	″	″	69
17	**6c**	″	″	″	35
18	**6d**	″	″	″	47
19	**6e**	″	″	″	37
20	**6f**	″	″	″	70
21	**7a**	Me(O)C	″	Br	68
22	**7b**	″	″	″	67
23	**7b’**	″	″	″	71
24	**7c**	″	″	″	56
25	**7d**	″	″	″	53
26	**7e**	″	″	″	38
27	**7b’**	″	″	Cl	15
28	**7b’**	″	Ph	Cl	18
29	**6f**	″	″	″	22
30	**6f**	″	COOBu^n	″	25

3.1. General procedure for the Heck coupling reactions

A two-necked 25 mL flask fitted with a reflux condenser was charged with aryl halide (1.0 mmol), olefin (1.5 mmol), Cs_2CO_3 (1.5 mmol), *diethyleneglycol-di-n-butylether* (internal standard), 3 mL DMA, 3% preformed complex (**6** or **7**). The flask was placed in a preheated oil bath (100 °C) under argon atmosphere for 5 h. The conversion was monitored by gas chromatography.

3.2. X-ray studies

The structure of **6d** has been further confirmed by X-ray diffraction determination. The crystallographic data of the palladium complex is listed in Table 3.23. The molecular structure is shown in Figures 3.26.

Compound *trans*-**6d** crystallizes as a mononuclear complex with half a molecule in each asymmetric unit. The palladium center is coordinated by two carbene and two chloride ligands in a square-planar fashion. As found by ^{13}C NMR spectroscopy in solution, the two carbene ligands are arranged *trans* to each other with an ideal angle of 180° due to symmetry. Both a carbene ring planes are oriented almost perpendicular to the PdC_2Cl_2 plane with a torsion angle 93.60°. Both Pd-C distances are equivalent (2.007 and 2.024 Å) and are consistent with Pd-C single bonds. Here again, no distortion in the Pd-Cl distances is observed (2.303 and 2.317 Å).

Table 3.23. Crystallographic data for Pd complexes (**6d**).

	6d
Formula	$C_{38}H_{44}Cl_2N_4Pd$
Formula Weight.	734.09
Cryst. System	monoclinic
Space group	$P2_1/n$, No:14
a (Å)	13.8713(9)
b (Å)	12.1365(6)
c (Å)	21.5499(15)
α (°)	90
β (°)	93.187(5)
γ (°)	90
V (Å^3)	3622.3(4)
Z	4
P_{calc} (gcm^{-3})	1.346
μ (MoK$_\alpha$)	0.691 (mm^{-1})
T (K)	293(2)
Residuals (eÅ^{-3})	0.41, -0.43
wR_2 (all data)	0.0828
F(000)	1424

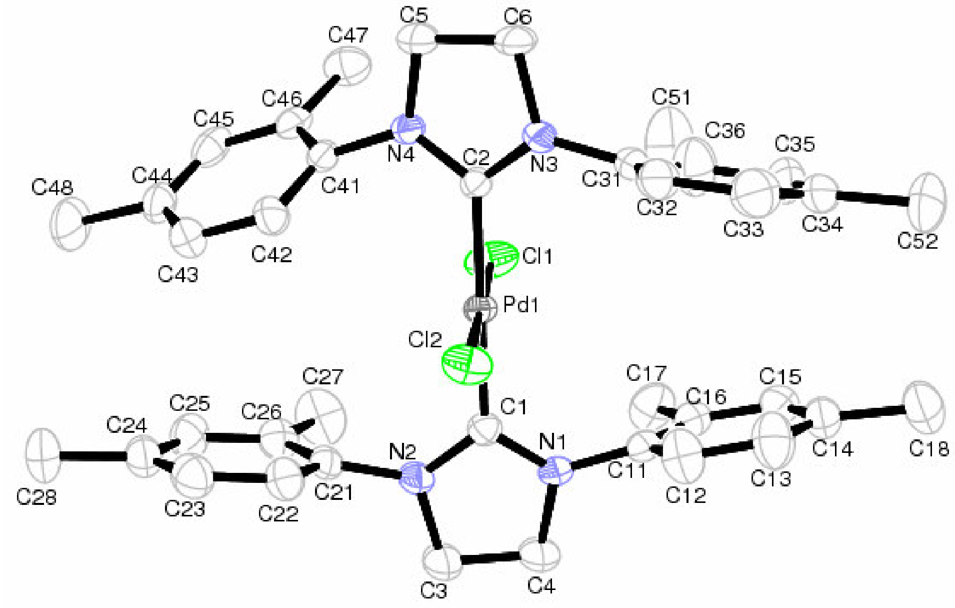


Figure 3.26. An ORTEP3 drawing of the **6d** shows the numbering scheme.

Table 3.24. Selected bond lengths (Å) and angles (^{o}) for **6d.**

Pd1-C1	2.007	N1-C1-Pd1	125.49
Pd1-C2	2.024	N2-C1-Pd1	126.73
Pd1-Cl1	2.303	N3-C2-Pd1	127.91
Pd1-Cl2	2.317	N4-C2-Pd1	124.03
C1-N2	1.351	C1-Pd1-Cl2	89.42
C1-N1	1.320	Cl2-Pd1-Cl2	179.50
C3-C4	1.516	C2-Pd1-Cl1	89.57
C2-N3	1.332	C2-Pd1-Cl2	90.79
C2-N4	1.330	N2-C1-N1	107.74
C5-C6	1.499	C3- N2- C1	101.91
C11-N1	1.426	C1- N1- C4	113.93
C21-N2	1.427	C2-N3-C6	112.36
C31-N3	1.424	N3-C2-N4	108.05
C41-N4	1.434	C2-N4-C5	113.49

3.3. Conclusions

In general, it appears that the catalytic reactions, which employ transition metal complexes of tertiary phosphines, may also be catalyzed via complexes of NHC and many of the precatalysts studied to date exhibit excellent thermal stability and the need for excess NHC ligand was not required. NHC ligands are stronger Lewis bases than the phosphine ligands. The IR data of CO ligands in corresponding carbene (carbonyl) complexes indicated that the CC-saturated dimesitlyimidazolidin-2-ylidene induced higher electron density at the metal atom than the CC-unsaturated imidazol-2-ylidens.

It has been observed that small changes in catalyst architecture had a large impact on the stability and activity of these complexes, and current studies are directed toward understanding the subtle steric and electronic factors that determine these properties.

Although a variety of saturated NHC precursors are available ranging from ero to imidazolinium salts IMs.HX, there is a continuing need to utilize new and improved reagents and improved reaction conditions to provide superior selectivity.

The synthetic studies can be subdivided into two parts; (i) Novel N-heterocycliccarbene ligands bearing different substituents at the *p*-position of the phenyl ring of the 1,3-disubstituted imidazolidin ring and their complexes (**5, 6, 7, 8, 9**) were obtained. (ii) Diazolinium salts containing hydrogen, methyl, acenaphthyl at the C_4-C_5 position of the imidazolidine ring were synthesized. These salts were reacted with Ag_2O. The transmetalation reactions with elemental sulfur, $PdCl_2(MeCN)_2$, $[RhCl(COD)]_2$ that use Ag-NHC as a transmetalation agent were successful, most likely owing to the steric demand of the carbene ligands. All compounds synthesized were characterized by elemental analyses, NMR spectroscopy. The molecular structures of the thione **4f** and the complexes **6d,7d**, **8f** were determined by X-ray crystallography.

The structurally and sterically similar 1,3-bis(2,6-dimethylphenyl) imidazolinium salts with H, CH_3, Br and Cl substituents at the *p*-position of the aryl ring were used to prepare two series of palladium–NHC complexes **5** and **6**. In both cases, the efficiency increased with the electron donating nature of the *p*-substituent (Cl < Br < H < Me). The preformed complexes allowed us to evaluate simultaneously subtle electronic influence of H, Me, Br and Cl without possible complications due to steric effects. The C–O stretching frequencies in $[RhCl(NHC)(CO)_2]$ complexes which derived from **8** are sensitive to the *p*-position of the phenyl ring of the 1,3-disubstituted imidazolidine ring and the C_4-C_5 position of the imidazolidine ring.

The variation of the *p*-substituents on the phenyl ring of the 1,3-diarylimidazolin-2-ylidenepalladium(II) complexes has a significant influence on the catalytic behavior of the Suzuki coupling of NHC-Pd complexes. The electron donating capability of the complexes via the C_4-C_5 position of the imidazolidine ring appears to play a role in the complex's catalytic activity. The rhodium–NHC catalyzed addition of phenyl boronic acid to aldehydes are summarized in Table 2. We also tested palladium carbene complexes in the Mizoroki- Heck reaction. Especially **6b'**, **6f**, **7b'** bearing methyl, acenaphthyl at the C_4-C_5 position of the imidazolidine ring have shown better catalytic activity. These studies allow us to compare the *p*-position of the phenyl ring of the 1,3-disubstituted imidazolidin ring and the C_4-C_5 position of imidazolidine ring.

Based on CO IR streching frequencies, the following complexes can be ranked from best electron rich to worst: f > b' > b > a > d > c > e

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