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Review

# Redox processes involving hydrocarbylmetal (*N*-heterocyclic carbene) complexes and associated imidazolium salts: ramifications for catalysis

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## Contents

## Abstract

The comparison of nucleophilic heterocyclic carbenes with phosphines and the premise that they are phosphine analogues is a useful but limited concept. Electronically and sterically NHC's are different. These differences lead to unique chemical behavior where the NHC can act as a spectator ligand or as a participative ligand—finishing up in the products in altered form. Here, we review the redox processes undergone by the NHC/imidazolium salt couple in conjunction with Group 10 metals. The often facile reductive elimination reaction of hydrocarbylM-carbene complexes, yielding 2-substituted imidazolium salt and M(0) is examined, with factors influencing the reaction reviewed in some detail. Conversely, the related imidazolium salts (the important imidazolium based ionic liquids (IL's)) may generate carbene complexes by oxidative addition to low valent metal centres. The significance of these reactions for the application of carbene complexes in catalysis, and for the use of imidazolium based ionic liquids as solvents is manifest.

*Keywords:* Nucleophilic heterocyclic carbenes; Metal-complexes; Redox processes; Experimental studies; Theoretical studies

## 1. Introduction

Nucleophilic-heterocyclic carbenes (NHC's) have been known for many years. The pioneering work of Wanzlick et al. in the 1960s and 1970s generated much interest in the field (a general method based on electron rich enetetramines (carbene dimers) was developed by Lappert and co-workers in the early 1970s [1–3]). Lappert and co-workers [4] and Hill and Nile [5] provided early examples of the application of transition metal-carbene complexes in catalysis. However, the need to generate the free carbene ligand in situ via electron rich tetra-amino alkenes or by in situ

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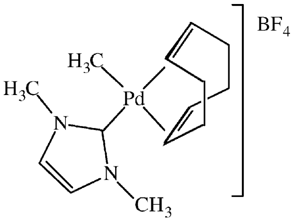
deprotonation of the precursor imidazolium salt curbed the application of NHC's as ligands and impeded further development. In 1991, interest in the field was reactivated by the reported synthesis of free imidazol-2-ylidene carbenes by Arduengo et al. [6]. Following this breakthrough many groups have studied the application of NHC's as ligands. Herrmann looked at the synthesis of a broad range of metal-complexes—complexes of p-, d- and f-block metals have been reported. Herrmann also investigated the application of metal-carbene complexes in a range of catalytic processes. The background to the development of stable carbenes and their application as ligands has been comprehensively reviewed by Regitz [7], by Herrmann and Köcher [8], and in an excellent review by Bertrand and co-workers [9]. Very recently, Herrmann has also reviewed aspects of the application of NHC-complexes in catalysis [10].

From early studies comparison's were made between these singlet carbenes and the ubiquitous phosphines [11]. This accepted similarity has been a driving force for much of the recently published research. However, while such a comparison has some justification it also has its limitations. *N*-Heterocyclic carbenes have unique structural and electronic properties that lead to a distinctive chemistry, and an understanding of this issue is essential if carbene chemistry is to develop. In particular, the pure donor nature of NHC's can lead to chemical reactivity more closely related to that observed with anionic sp$^3$ and sp$^2$ alkyl/aryl ligands. In this review, we wish to explore aspects of the chemistry in which reaction occurs at the 2-position of the heterocyclic ring, and look selectively at the non-innocent behavior of NHC's and their associated imidazolium salts. The imidazole ring often finishes up in the products and, consequently, this reactivity has significant implications for the application of carbene complexes in catalysis and for the use of imidazolium based ionic liquids as solvents.

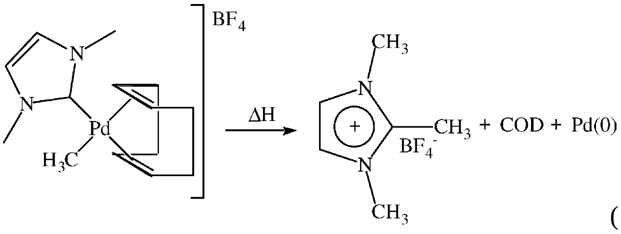
## 2. Reductive elimination from hydrocarbylM-carbene complexes of Group 10 metals

### 2.1. Reductive elimination from hydrocarbylPd-carbene complexes

In the latter part of the 1990s we synthesized the first examples of simple alkylpalladium *N*-heterocyclic carbene complexes [12,13], and the first alkylpalladium complexes with donor-functionalized carbenes [14]. During these studies we prepared the unstable complex (**1**) [13]. The complex has several interesting features—it contains only Pd-carbon bonds; it has three different types of Pd-carbon bonds; and it contains a *cis* alkyl/alkene arrangement. On investigating the controlled decomposition of the complex it was found the reaction followed an unexpected pathway, yielding 1,2,3-trimethylimidazolium salt, free COD and Pd(0) as the only detectable products (Eq. (1)).



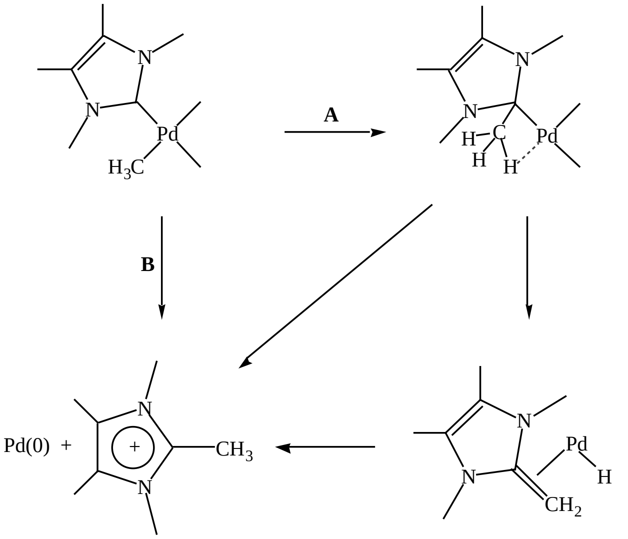
(**1**)



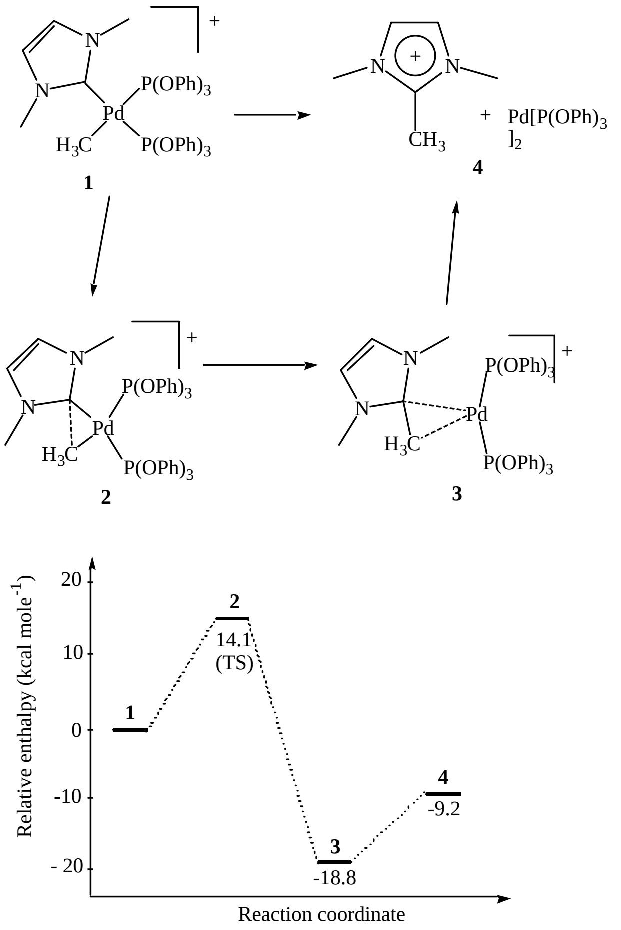
(1)

Subsequently, by exploring the decomposition of appropriate complexes, in which the Pd(0) is trapped as a stable complex [PdL$_2$, where L = PR$_3$] it was demonstrated that Pd(0) is the primary product from this reaction, and is not generated after a sequence of reaction steps (Eq. (2)) [15]. Accordingly, several mechanisms may be proposed for the decomposition process (Scheme 1). For example, the reaction may proceed via migratory insertion, followed by a heterolytic cleavage (or β-elimination) to give the product imidazolium salt and Pd(0), or the reaction may occur by concerted reductive elimination.

Kinetic studies (Eq. (2)) on these complexes provided important mechanistic information about the decomposition process and results were consistent with a reductive elimination process, although not conclusive [15]. To provide further mechanistic information detailed DFT calculations were undertaken. No pathway corresponding to a migratory insertion process could be found on the potential energy surface (PES). However, stationary points corresponding to

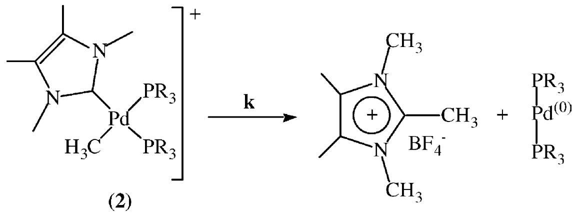


Scheme 1.



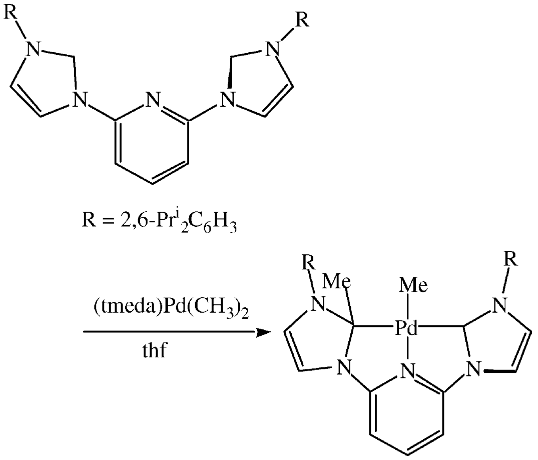
Scheme 2.

reductive elimination were observed [15]. Although there is a small activation barrier the reductive elimination is exothermic (Scheme 2). Notably, when a chelating di-phosphine spectator ligand is used instead of two monodentate phosphines (complex (**2**), Eq. (2)) there is a much higher barrier to reductive elimination and experimentally forcing conditions are required to induce reductive elimination. Computational studies (Scheme 2) show that as reductive elimination proceeds the "bite angle" between the spectator ligands opens up and the attendant angle between the *cis*-methyl group and carbene concurrently closes down, allowing effective orbital overlap for rapid reaction [15]. A chelating spectator ligand will block this process, until hemilability is induced. Similarly, a chelating ligand in which the carbene is one component will also impede this process—vide infra.



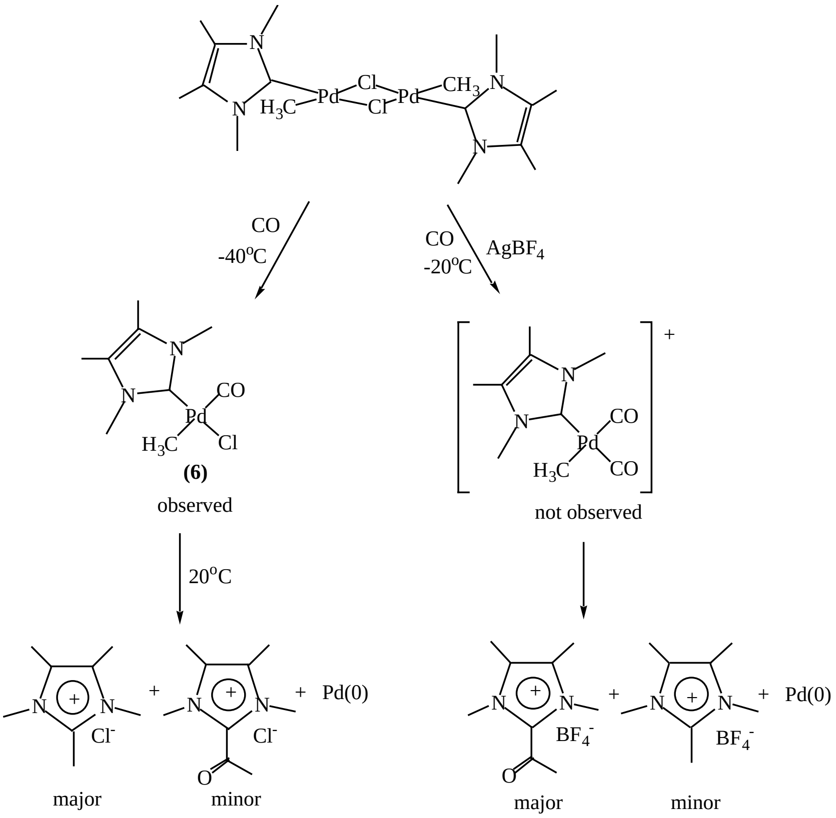
$PR_3 = PMePh_2, P(OPh)_3, PPh_3, P(Cy)_3$ (2)

Since we first reported the C–C reductive elimination reaction a number of examples of this remarkably facile reaction have been recorded. Interestingly, Danopoulos et al., have recently shown that under certain conditions, i.e. by reacting a (dimethyl)Pd complex with a bis-NHC pincer ligand, decomposition to give imidazolium salt does not occur (Eq. (3)), instead migratory insertion occurs in preference to reductive elimination [16]. That reaction between coordinated alkyl- and carbene ligands can occur by an alternative pathway is probably not surprising. It had previously been shown that the barrier to reductive elimination can vary quite markedly depending on the complex from which the reaction occurs [15], and in a theoretical study on methyl-palladium *N*-heterocyclic silylene and germylene complexes it was shown that for these systems there is a very low activation barrier for methyl migration [17]. During decomposition of NHC complexes it was found that in the "encounter" complex, formed between the product and the metal, if the interaction was weak, then the reaction is best described as reductive elimination [15]. Whereas, for silylenes and germylenes, during the decomposition process the geometry about E (E = Si, Ge) approaches tetrahedral and the Pd–E bond lengths are consistent with $sp^3$ hybridization, thus the reaction is better described as methyl migration. In summary, if an encounter complex involving a weak interaction between the metal fragment and the imidazolium cation is formed a reductive elimination pathway is followed, as this interaction becomes stronger, at some point the reaction is best described as a methyl-migration, in which the metal centre is not formally reduced [17].



(3)

In subsequent studies on the reaction behaviour of a range of hydrocarbylPd- and hydrocarbylNi-carbene complexes, it was found that the decomposition reaction is ubiquitous. It occurs with varying ease, for nearly all such carbene complexes that were investigated, including monocarbene, dicarbene and functionalized chelating carbene based complexes [13–15,18–22]. Just as P–C bond cleavage in phosphine based catalysts can lead to catalyst deactivation [23] reductive elimination represents a potential achilles heel for carbene based catalysts.



Scheme 3.

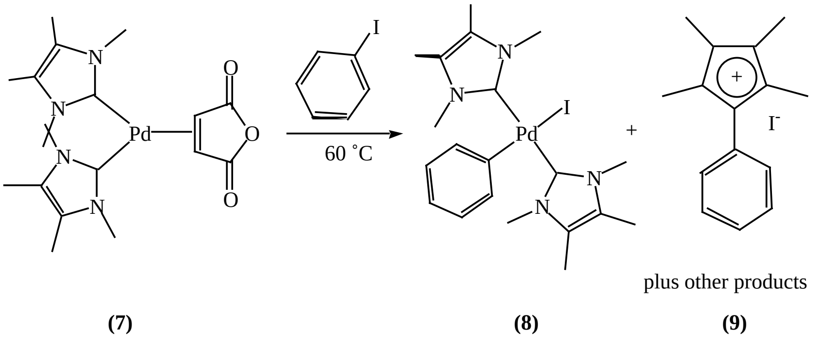
## 2.2. Reactions of Pd-carbene complexes with CO

Reactions of a methylpalladium-carbene complex with CO have been investigated, facile reductive elimination is observed (Scheme 3) [20]. The relative amounts of imidazolium salts formed in this reaction was found to be dependent on reaction conditions. Bubbling CO through a solution of the methylpalladium-carbene chloro-bridged dimer at −40 °C resulted in the formation of an intermediate carbonyl complex, which decomposed on warming to room temperature to give 2-methylimidazolium salt as the major product with small amounts of 2-acylimidazolium salt and Pd(0) also formed (Scheme 3). However, when the reaction was repeated in the presence of $Ag^+$ no intermediate complex was observed and the distribution of products was reversed, 2-acylimidazolium salt was the major product with the methylimidazolium salt as the minor product. Which product predominates appears to depend on the structure of the intermediate palladium complex. A *trans*-methyl/CO arrangement as in complex (**6**) disfavours carbonylation, whereas a cis arrangement allows carbonylation to occur. These results indicate that carbonylation does occur, and may even be the faster reaction, however the resulting acyl complex rapidly decomposes by reductive elimination. These observations may explain the lack of success to date in using Pd-carbene complexes in CO/ethylene copolymerization reactions. Only the example of Herrmann and coworkers, using a chelating di-carbene ligand, has demonstrated any success in this reaction [24].

## 2.3. Reductive coupling to give 2-arylimidazolium salts

Further evidence of the universality of the reductive C–C coupling reaction was provided in a comprehensive study of the reaction behaviour of hydrocarbylPd and -Ni NHC complexes [18]. Oxidative addition of phenyliodide to bis(tmiy)$Pd^{(0)}$MAH (**7**), (tmiy = 1,3,4,5-tetramethylimidazol-2-ylidene; MAH = maleic anhydride) at 60 °C yielded a mixture, which included, the expected Pd(II) complex, $Pd(carbene)_2(Ph)I$ (**8**) (Scheme 4), and the reductive elimination product, 2-phenyl-1,3,4,5-tetramethylimidazolium iodide salt (**9**), which were indentified by MS and NMR [18].

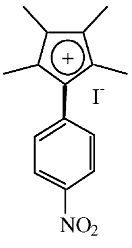
However, oxidative addition of 4-iodonitrobenzene to bis(tmiy)$Pd^{(0)}$MAH (**7**) at room temperature gave the oxidative addition product, $(tmiy)_2Pd(Ar)I$ in good yield. The arylPd-carbene complex was isolated and fully characterized, including microanalysis. On standing in solution the complex slowly decomposed via reductive C–C coupling to give the 2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium ion (**10**) as the major product [18]. Elegant studies on catalytic amination reactions by Caddick et al. established the oxidative addition of *p*-tolylchloride to $(carbene)_2Pd^{(0)}$ complexes, generating in one case the stable $(carbene)_2Pd(p\text{-tolyl})Cl$ (**11**) (carbene = 1,3-di-$^t$



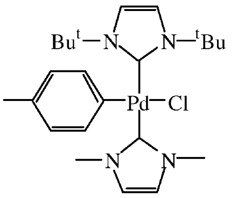
Scheme 4.

Bu-imidazol-2-ylidene) complex, for which an X-ray structure was obtained [25]. This complex was then reacted with morpholine to complete the catalytic cycle and give the arylated amine in nearly quantitative yield. Attempts to repeat the oxidative addition of arylchloride to a $L_2Pd^{(0)}$ complex (where L = the saturated carbene, 2,6-di($^i$Pr-$C_6H_3$)-imidazolidine-2-ylidene) gave only the reductive elimination product (**12**). It is evident that subtle electronic factors determine whether the desired catalytic process or decomposition via reductive elimination predominates.

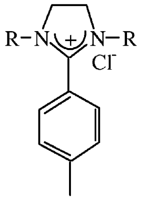
Following these earlier studies, Marshall and Grushin provided a further example of an isolated and fully characterized (σ-aryl)Pd(X)carbene complex (**13**) [26]. This complex also readily decomposed via reductive elimination to give the same type of 2-arylimidazolium salt (**14**) that had previously been observed [18,25]. Interestingly, attempts to prepare the analogous iodo-complex of (**13**) yielded only the the reductive coupling product (**14**), but with an iodide counter ion [26]. This result is noteworthy as it had previously been thought that using carbene ligands with large aromatic substituents on the nitrogens would provide protection from the reductive elimination process, this is clearly not the case.



**(10)**

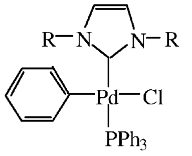


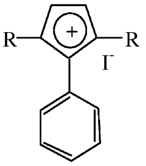
**(11)**



R = 2,6-($i$-Pr)$_2$$C_6H_3$

**(12)**



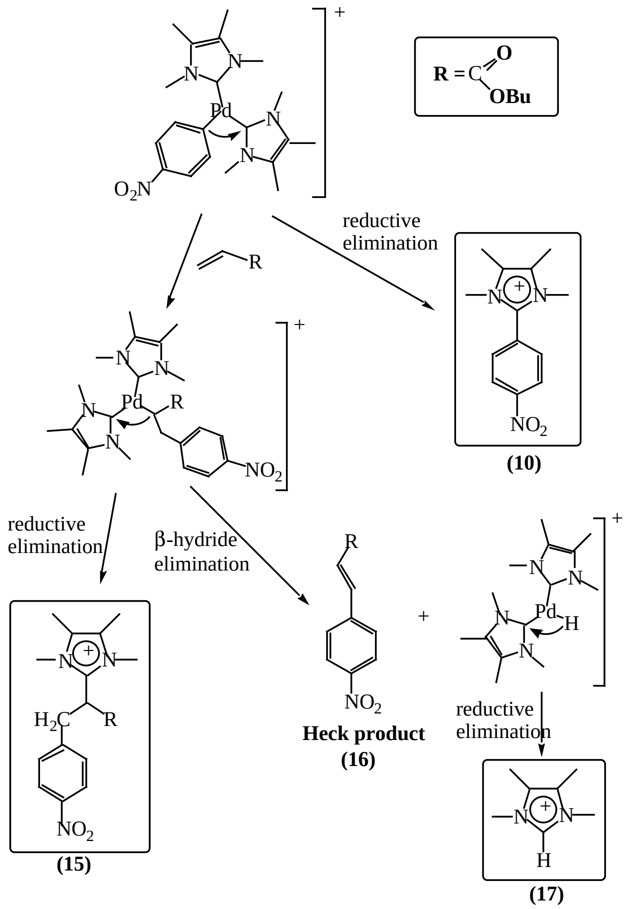


R = 2,6-($i$-Pr)$_2$$C_6H_3$

**(13)** **(14)**

### 2.4. *Reductive C–C coupling and the Heck reaction*

Mechanistic studies on the Heck coupling reaction catalyzed by palladium-carbene complexes also demonstrated the potential problems caused by C–C reductive coupling from hydrocarbylPd-carbene complexes [18]. Stoichiometric reaction of the $[(tmiy)_2Pd(Ar)]^+$ cation (where Ar = $p$-nitrophenyl) with butylacrylate gave a complex mixture of products (Scheme 5). The product distribution was dependent on temperature and other reaction conditions. At −30 °C only the reductive elimination products 2-(4-nitrophenyl)-1,3,4,5-tetramethylimidazolium ion, and



Scheme 5.

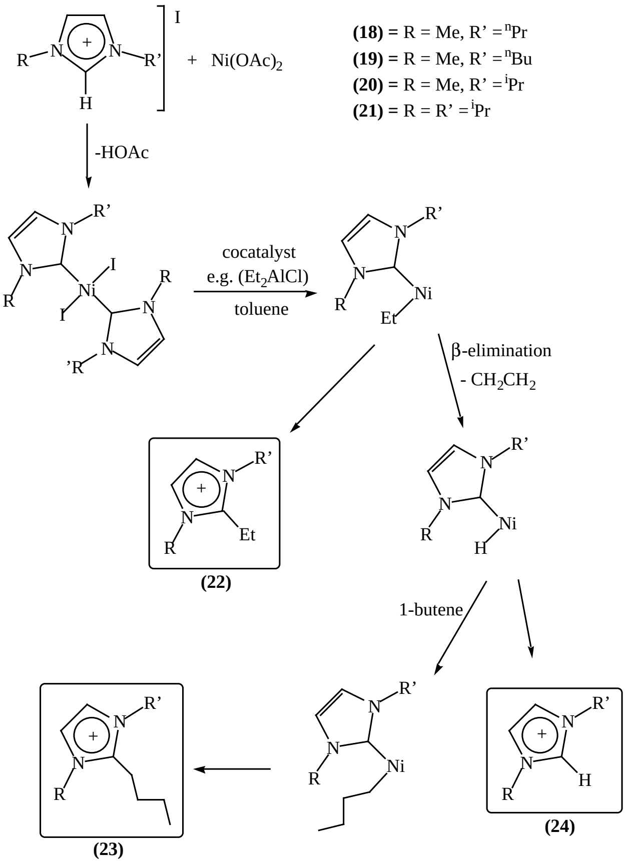
traces of the 2-substituted-imidazolium ion (**15**) were observed. On warming to −20 °C the Heck coupling product, *n*-butyl(*E*)-4-nitrocinnamate, (**16**) and a further product, 1,3,4,5-tetramethylimidazolium salt (**17**), were also observed. At room temperature the main products are the Heck product (**16**), and the 1,3,4,5-tetramethylimidazolium salt. It would appear that as the temperature is raised the steps leading to the Heck coupling product proceed more rapidly, i.e. the rates of migratory insertion plus β-elimination, as required for Heck catalysis, become more competitive with reductive elimination. When the process is run under catalytic conditions, i.e. base plus excess *p*-nitrophenyliodide and butylacrylate at around 120 °C only the Heck product is observed with high turnover frequencies and turnover numbers—no products generated from the reductive elimination reaction are observed. Clearly, thermodynamic parameters such as activation barriers and relative exothermicities play a crucial role.

### *2.5. Reductive elimination from hydrocarbylNi-carbene complexes and relevance to catalysis*

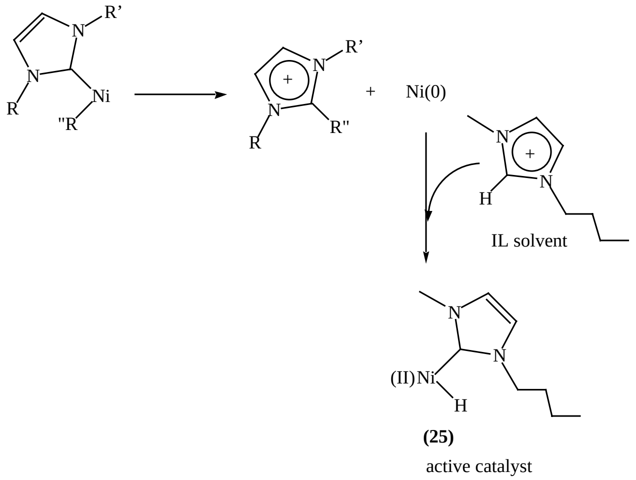
Hydrocarbylnickel-carbene complexes have also been shown to be very reactive towards reductive C–C coupling to give 2-substituted imidazolium salt [18,21]. Oxidative addition of *o*-tolylbromide to $Ni^{(0)}(tmiy)_2$, generated in situ, gives the expected $Ni(tmiy)_2$(*o*-tolyl)Br in good yield—a crystal structure of the complex has been obtained [18]. However, oxidative addition of MeI to the same $Ni(tmiy)_2$ complex, attempted at temperatures as low as −50 °C, gave the 1,2,3,4,5-pentamethylimidazolium salt as the major product with only small amounts of the $Ni(tmiy)_2(Me)I$ observed, thus demonstrating the susceptibility of hydrocarbylNi(II)-carbene complexes to the reductive elimination reaction.

Investigations on the use of “typical” $L_2Ni^{(II)}X_2$ type complexes (where L = 1,3,4,5-tetramethylimidazol-2-ylidene and $X = I^-$) as catalyst precursors for chain growth reactions—dimerization/oligomerization—illustrate the serious problems that the reductive elimination reaction may cause in some catalytic processes [21]. A range of bis-carbene-nickel complexes were synthesised (complexes (**18**)–(**21**), Scheme 6) and typical procedures for catalytic dimerization were followed— complexes were activated with appropriate alkylaluminium cocatalysts in toluene solvent under a variety of conditions. Propene and 1-butene were used as substrate. Apart from the catalyst generated from complex (**21**) where R $= {}^{i}$Pr, which gave small amounts of C8 alkenes, no alkene dimers or oligomers were detected. A variety of imidazolium salts, (**22**)–(**24**), and Ni(0) were in general the only products obtained (Scheme 6). These products could be readily accounted for by the reaction sequence described in Scheme 6.

Significantly, the same reaction conducted in ionic liquid solvent provided an entirely different outcome. In such a solvent, highly active and long-lived catalysts for alkene dimerization were generated. The dimer isomer distribution was essentially the same (within experimental error) for all catalysts tested. No products resulting from reductive elimination were observed. To explain this behaviour, a reaction sequence was proposed in which reductive elimination does occur initially, however this is rapidly followed by oxidative addition of the imidazolium based ionic liquid solvent to generate an active (carbene)-$Ni^{(II)}$-H intermediate, (**25**), from which the dimerization then proceeds (Scheme 7)



Scheme 6.

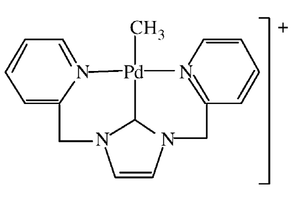


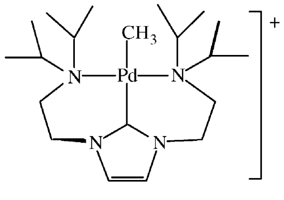
Scheme 7.

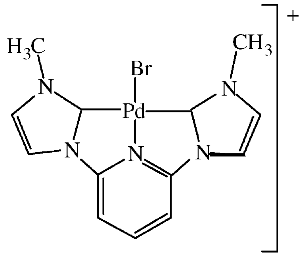
[21]. The uniformity of product distributions, irrespective of the starting nickel complex, is consistent with this proposal. The variation in catalyst turnover numbers observed for the 30 min tests was explained in terms of the variation in the induction periods necessary to generate the active hydride for each separate starting complex. Further study is required to provide more conclusive evidence for the proposed reaction sequence.

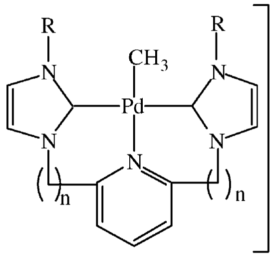
### 2.6. Effect of chelating ligands on reductive coupling

We had already noted, vide supra, that methylPd-carbene complexes containing a strongly bound chelating spectator ligand were more resistant to reductive elimination—the chelating ligand impedes the approach of the carbene and methyl groups and hence prevents effective orbital overlap between these species [15]. Similarly, complexes of chelating carbene-based ligands (both di-NHC's and mixed donor, NHC-donor ligands) also appear to show significantly enhanced resistance to reductive elimination [14,19,27–31]. In order for reductive elimination to occur, the carbene and alkyl group must occupy a *cis* arrangement, and *cis* donor functionality flanking the carbene can inhibit this reaction. To illustrate this point, while complex (**26**) which contains *cis*-pyridyl chelation is one of the most stable cationic MePd-carbene complexes we have prepared (limited decomposition below 100 °C), complex (**27**), with weaker amine donor groups, decomposes rapidly at room temperature [19]. An additional example is provided by the Pd complex of a pincer carbene-pyridine-carbene ligand (**28**), which was found to generate a thermally very robust catalyst for the Heck reaction—temperatures of 180 °C were used without decomposition [29]. In several specific examples decomposition of the carbene complex did not occur by reductive elimination at all, but rather by some other mechanism entirely [32,33]. However, such instances are rare and like the one case of alkyl to carbene migratory insertion, reported by Danopoulos et al. [16], it may reflect the uniqueness of the complex—all three examples in which reductive coupling does not occur are di-(methyl)M-carbene complexes with chelating ligands.


(**26**)


(**27**)


(**28**)


$n = 0,1$
$R = Me, {}^{n}Bu, {}^{t}Bu$

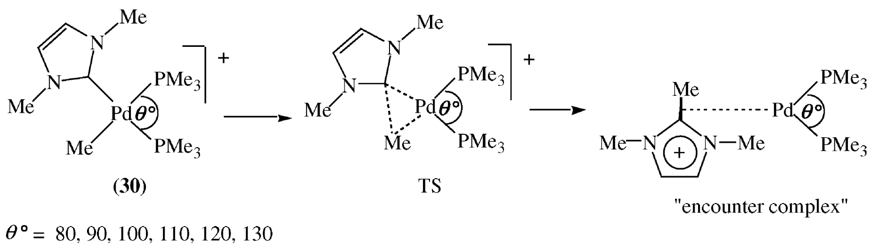
(**29**)

The thermal stabilities of a number of methyl-Pd complexes of pincer type ligands (**29**) have been investigated using experimental and theoretical methods [29]. The observed relative stabilities of the complexes (**29**) where (i) $n = 0$, $R = CH_3$; (ii) $n = 1$, $R = CH_3$; (iii) $n = 1$, $R = {}^{t}Bu$ correlate well with energy barriers to reductive elimination, calculated using DFT methods, (i) 185.1; (ii) 146.3; (iii) 125.7 kJ mol$^{-1}$, respectively. These energy barriers also appear to be related to out-of-plane carbene twist angles, calculated as (i) 1; (ii) 41; (iii) 50°. A simple explanation for these observations is that by forcing the plane of the carbene ring to approach coplanarity with the coordination plane it maintains the carbene-carbon "empty" $p_z$ orbital (which actually contains significant electron density due to donation of electron density fron the ring nitrogens) at approximately right angles to the coordination plane and directed away from the *cis*-hydrocarbyl group on the metal centre. As the carbene to coordination-plane twist angle increases the carbon $p_z$ orbital is twisted towards the *cis*-hydrocarbyl group and is increasingly able to interact with orbitals on this group. Furthermore, the reductive elimination process is assisted if the bond angle between the *cis* reacting species reduces, allowing more effective orbital overlap. Consequently, on two counts the presence of chelating ligands—either as a spectator ligand or as a chelate incorporating the carbene moiety—should help curtail the reductive elimination reaction.

### 2.7. Other factors that effect reductive coupling

#### 2.7.1. Spectator ligand bite-angle

Extensive theoretical studies on the influence of aspects of complex geometry on the stability of palladium-carbene complexes have been undertaken [34]. DFT calculations were used to investigate the influence of the spectator ligand bite-angle on reductive elimination of 1,2,3-trimethylimidazolium ion from palladium bisphosphine complexes of type (**30**) (Scheme 8). Spectator ligands were locked with bite angles of between 80 and 130°. These bite-angles subtend the range of commonly available



(**30**)

Scheme 8.

chelating ligands. It was found that changing the bite-angle had a profound effect on the reductive elimination reaction. Barriers to reductive elimination (activation energies) ranged from 12.7 kcal mol$^{-1}$ (bite angle = 130°) to 26.7 kcal mol$^{-1}$ (bite-angle = 80°) [34], thus resulting in superior kinetic stability with small bite angles. Below a bite-angle of around 85° there is little change in the activation energy, $E_{\text{act}}$ plateaus at approximately 27 kcal mol$^{-1}$. A further "benefit" of constraining the bite angle results from the decreasing thermodynamic stability of the $PdL_2$ product as the bite angle is reduced, thus providing a thermodynamic barrier to reductive elimination. A further consequence of these factors is that systems with a smaller bite angle prefer oxidative addition of imidazolium salt over reductive elimination—this will be discussed later.

Consistent with previous studies [17], these investigations also demonstrate that energy differences between reductive elimination and migratory insertion reactions [16] in hydrocarbylM-carbene complexes, may be small—which reaction is actually observed may depend on the configuration of the starting complex. For the process in Scheme 8, as the auxiliary bite angle is decreased the $PdL_2$ fragment shows an increased interaction with the imidazolium salt, and for complexes with a bite angle <100° the carbon in the 2-position of the imidazolium salt in the "encounter complex" shows distortion toward $sp^3$ hybridisation. Thus for small bite angles the reaction more closely approaches migratory insertion, whereas for larger bite angles the reaction is reductive elimination.

### *2.7.2. Dihedral angle between the plane of the carbene and the coordination plane*

The dihedral angle between the carbene and coordination planes is another factor of importance in determining stability with respect to the reductive elimination reaction. DFT calculations show that as the carbene is twisted, increasing coplanarity with the coordination plane, any increase in the transition energy for reductive elimination (due to non-favourable orbital overlap between the methyl group and the carbene) is counterbalanced by the destabilisation of the complex caused by steric strain [34]. Consequently, releaving strain in complexes where the carbene is approximately coplanar with the $PdL_2$ is likely to result in systems that are very stable to reductive elimination. As discussed previously (vide supra) this may be achieved by linking the carbene into a chelate ligand.

### *2.7.3. R-substituent on the carbene N atoms*

DFT calculations addressing the effect of carbene N–R groups on resistance to reductive coupling have shown a well defined correlation between the R-group inductive effect and the barrier to reductive elimination [34]. N-substituents that possess appreciable σ-donating capability (e.g. branched alkyl groups) inductively confer a decreased positive charge on palladium thus providing a more stable system. The relative inductive effect of the substituents investigated in this study, and hence resistance to reductive elimination follow the trend H < Ph < Me < Cy < $^{i}$Pr < neopentyl ∼$^{t}$Bu. Steric bulk appears to play little role in these systems—the orientation of the carbene plane perpendicular to the coordination plane, and the fact that the N-substituent is a further atom removed from the coordination site helps limit the effect of steric bulk. A significant factor is the carbene $p_{\pi}$ orbital, which appears to be intimately involved in determining the barrier to reductive elimination, and hence a π-interaction between N and any coordinated substituent, for example a benzene ring, where the aromatic ring approaches coplanarity with the heterocyclic ring, reduces electron density in the carbene orbital and consequently leads to a more facile reductive elimination. However, the incorporation of steric bulk such as 2,6-methyl or di-isopropyl substituents on the aromatic ring makes the phenyl ring adopt an orientation perpendicular to the carbene plane, which eliminates any π-conjugation effects that may occur and hence any depletion of electron density brought about by π-interaction of the phenyl and imidazole rings.

## 3. Oxidative addition of imidazolium salts to low valent metal centres

Whilst exploring the C–C reductive elimination reaction and ways to eliminate or restrict the process we investigated the possibility of "reversing" the reaction, i.e. oxidatively adding an imidazolium salt to low valent metal centre. Previous reports had appeared in the literature in which M-carbene complexes were thought to be generated during catalytic reactions in ionic liquid solvents (IL's) [35–37]. In each case however, base was present in the reaction mixture, almost certainly leading to deprotonation of imidazolium ion, to give free carbene and a salt. It has been known for a long time that even a very weak base, such as a basic ligand on a transition metal compound, is enough to deprotonate an imidazolium salt under certain reaction conditions [1(d), 2(a), **27**]. This process should not be confused with C–H bond activation. Therefore, the important question was, would a low valent metal centre insert into the C–H bond of a imidazolium cation in the absence of base? That is, would an imidazolium salt oxidatively add to a low valent metal to form a carbene and metal-hydride intermediate?

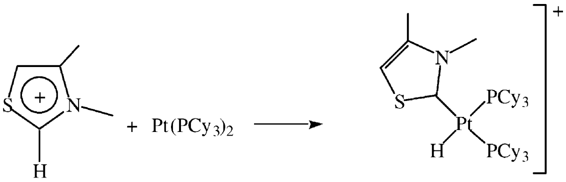
### 3.1. Theoretical studies on oxidative addition of imidazolium cations

Oxidative addition to Pt(0) is expected to be more favourable than to Pd(0) [38], and initial theoretical studies were carried out on the oxidative addition of the 1,2,3-trimethylimidazolium cation to $Pt(PH_3)_2$ [39a]. Although the activation barrier was rather high ($27.8\,kcal\,mol^{-1}$), the reaction was indeed predicted to be exothermic ($\Delta H = -13.5\,kcal\,mol^{-1}$). Subsequently, calculations on the Group 10 metals were undertaken to ascertain the factors which favour oxidative addition of various imidazolium cations [39b]. These studies showed that:

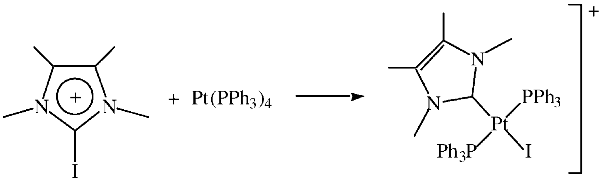
(i) Oxidative addition of imidazolium cations to Pt(0) and Ni(0) is more exothermic than to Pd(0), and Ni(0) reacts with a lower barrier.
(ii) A *cis*-chelating ligand on the M(0) complex both increases the exothermicity of the reaction and lowers the activation barrier relative to monodentate ligands.
(iii) Oxidative addition of 2-H imidazolium groups is easier and more exothermic than addition of the 2-alkylimidazolium moiety. A halo-imidazolium group should further lower the barrier and increase the exothermicity.
(iv) A compact, strongly basic spectator ligand lowers the activation barrier and increases the exothermicity of the reaction.

### 3.2. Experimental observation of oxidative addition to Group 10 metals

The theoretical calculations on Group 10 metals indicated that this is a very facile reaction and in certain systems occurs without an energy barrier [39b]. Experimental studies on the reaction of 1,3-dimethylimidazolium salt with $Pt^{(0)}L_n$ complexes ($L = PPh_3$, $PCy_3$ and $n = 4, 2$) yielded $(carbene)Pt(H)L_2$, thus demonstrating for the first time the feasibility of such a reaction [39], and also providing the first example of oxidative addition of a C–H bond to a Pt(0) complex not containing a chelating ligand. Crystal structures for several of the $(carbene)Pt(H)L_2$ complexes were obtained. A similar oxidative addition reaction was carried out between 3,4-dimethylthiazolium salt and $Pt^{(0)}(Cy_3)_2$ to give the (3,4-dimethylthiazolin-2-ylidene)$Pt(H)(PCy_3)_2$ complex (Eq. (4)). In one instance the oxidative addition product appeared to be in equilibrium with the reactants, indicating a $\Delta G_{react}$ value close to zero. If such a process were to occur in an imidazolium based ionic liquid, the large excess of the imidazolium cation would push the reaction towards the carbene–M–H complex. Attempts to repeat this reaction with a Pd(0) complex and imidazolium salt was unsuccessful, probably because of the instability of the Pd–H. However, at the same time as these studies were published Nolan and coworkers reported the observation of a Pd-hydride peak (at −16.3 ppm) (and the attendant loss of the imidazolium proton), in the $^1H$ NMR, whilst investigating the reaction of $Pd^{(0)}(dba)_2$ with imidazolium salt, indicating the probable oxidative addition of imidazolium salt to Pd(0) [40]. More recently Crabtree and coworkers were able to demonstrate the probable oxidative addition of imidazolium salt to Pd(0) [41]. By heating $Pd_2(dba)_3$ with *N*-(2-pyridyl)imidazolium salts bis-carbene complexes were formed, presumably through a sequential process of oxidative addition and reductive elimination.

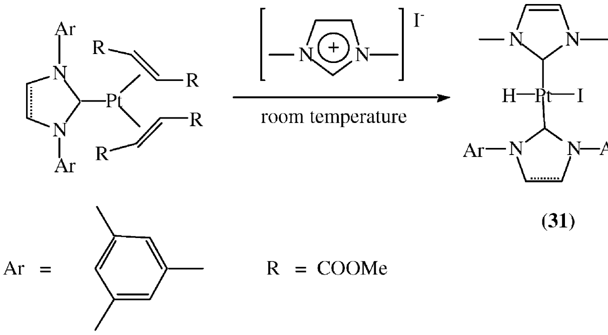


(4)



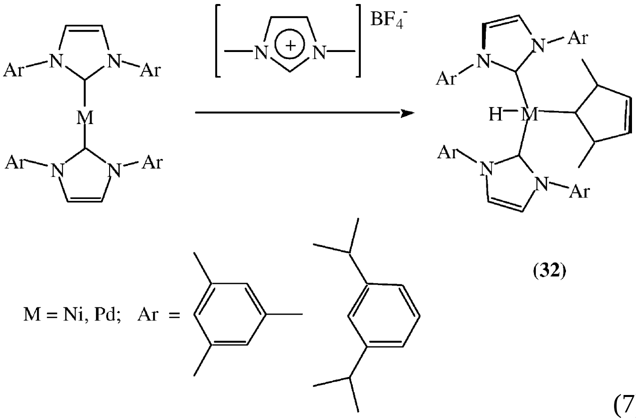
(5)

Oxidative addition of 2-haloimidazolium salts to low valent metal species, first investigated by Stone and co-workers [42], has become an established route for the synthesis of metal-carbene complexes [43,39b,44] and it provides a potentially valuable route to many unusual halo-M-(carbene) complexes (Eq. (5)). However, oxidative additon of simple imidazolium salts is of particular interest. It is an atom-efficient reaction for the generation of (carbene)-Mhydride complexes. Metal hydrides are of course thought to be intimately involved in many catalytic processes. Consequently, not only is such a reaction a way of generating metal-carbene complexes it is also a direct, in situ method for formation of an active catalytic species [21,40,45] and in some cases may explain the enhanced catalytic activity observed when catalysis is carried out in an imidazolium based ionic liquid. Very recently it has been shown that by using an electron-rich metal centre (Eqs. (6) and (7)) insertion of the metal into the C–H bond of an imidazolium salt can occur at or near room temperature [46,47]. Providing a very clear indication that IL's are not always "simple" solvents, they may become involved in catalyst generation/activation even in the absence of base. These reactions (Eqs. (6) and (7)) use strong donor carbenes as spectator ligands to increase electron density on the metal centre, and imidazolium salts as substrate to yield mixed carbene-M(hydride) complexes (**31**,**32**). By the use of sterically demanding carbenes as spectator ligands it is possible to generate surprisingly stable mixed carbene M-hydride complexes (M = Ni, Pd) (**32**) [47]. The M-hydrides may be isolated as crystalline solids and crystal structures have been obtained.



**(31)**

(6)



**(32)**

(7)

### 3.3. Implications for catalysis and future scope

It has been demonstrated, both theoretically and experimentally that oxidative addition of imidazolium salts to low valent Group 10 metals can be a facile process. These results confirm that a potentially important method of limiting decomposition of M-carbene catalysts could be to operate in imidazolium based ionic liquids. Significantly, it shows unambiguously the ‘non-innocent’ nature of ionic liquids in certain circumstances. Catalytic reactions in which redox active metals are employed in ionic liquids must thus be considered in this light. Examples of reactions that have been carried out in ILs include olefin dimerization (Ni) [48,49], Heck-type reactions (Pd) [50,51], and hydroformylation (Pt, Rh) [52,53]. While experimental observation of oxidative addition has thus far been limited to the Group 10 metals, in principle any transition metal fragment that is capable of oxidative addition could become involved in this reaction. For instance, the ability of Group 9 complexes to promote C–H activation is well known. Recent theoretical studies show that addition of azolium salts to Rh(I) complexes is quite feasible [54]. It seems likely that more examples of this reaction, possibly with a variety of metals, will be encountered as experimental studies on this chemistry continue.

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