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Review

Stability and reactivity of *N*-heterocyclic carbene complexes

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Abstract

The use of *N*-heterocyclic carbenes as ligands for transition metals has increased dramatically in the last few years, spurred on by their remarkable successes in the areas of metathesis chemistry and coupling reactions. 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. However, to quote Danopoulos, "recent reports are questioning the belief that the NHC–metal bond is inert" [Chem. Commun. (2003) 756]. This review describes some of the reactions that *N*-heterocyclic carbenes undergo in the metal co-ordination sphere that lead to decomposition of the NHC–metal complex. Implications for catalysis using these species are described.

Keywords: *N*-heterocyclic carbenes; Catalysis; Late transition metal complexes; Suzuki coupling reactions

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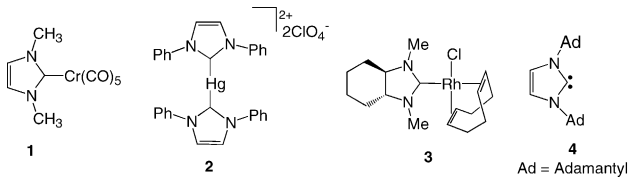


Plate 1. Early examples of NHC–complexes and Arduengo's isolated free carbene.

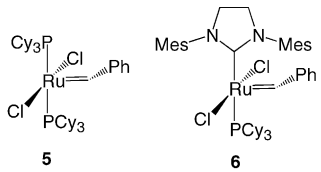


Plate 2. Grubbs first and second generation metathesis catalysts.

1. Introduction

The use of *N*-heterocyclic carbenes (NHC's) as ligands for transition metal complexes was described 36 years ago by Öfele and Wanzlick who prepared compounds **1** and **2** [2,3]. With the notable exception of Lappert's extensive studies into the chemistry of late transition metal carbene complexes such as **3** [4], little attention was paid to these species until the 1991 report of Arduengo et al. describing the isolation and crystallization of a free carbene (**4**) [5] (Plate 1).

When bound to metals, *N*-heterocyclic carbenes are significantly less reactive than the two major classes of carbene ligands, Schrock carbenes and Fischer carbenes. In fact, relative to these two types of ligands, NHC's can be considered to be spectator ligands. They do not undergo metathesis reactions, cyclopropanations, or many of the other reactions typically attributed to metal carbenes [6]. It is possibly because of this that NHC's were not as prominent in organometallic chemistry as their more reactive cousins. However, pioneering studies by Grubbs [7], Herrmann [8], Nolan [9], Fürstner [10], Hoveyda [11] and others in addition to the comprehensive and seminal studies of Lappert [4] have clearly demonstrated the utility and uniqueness of these species as ancillary ligands on a variety of transition metals.

Although there is no doubt that NHC's are less reactive than alkylidenes and Fischer carbenes, recent reports indicate that they are certainly not inert. NHC ligands have been shown to undergo reductive elimination reactions (Section 3), displacements by other ligands (Section 4), and C–H and C–C insertions (Section 5). At the same time, some NHC–ligated complexes are stable in boiling solvent in air [8e,12a] and can be purified by silica gel chromatography [12b]. The purpose of this review is to examine the behaviour of NHC's in the immediate coordination sphere of various transition metals, specifically those reactions that lead to decomposition of the metal *N*-heterocyclic carbene complex.

2. Key reactions catalyzed by *N*-heterocyclic carbene complexes

The application of *N*-heterocyclic carbenes as ligands for transition metals has led to significant advances in several important catalytic reactions, most notably the metathesis of olefins [7] and Pd-catalyzed coupling reactions [8,13].

In the area of metathesis chemistry, the key discovery was that the replacement of a phosphine with an NHC ligand in well-characterized Ru alkylidene complexes (Plate 2) leads to a dramatic improvement in activity for the metathesis of a wide range of olefins [7b], even permitting the formation of tetrasubstituted olefins [8d]. With catalyst **6**, the ring closing metathesis of highly functionalized olefins can be carried out permitting the synthesis of complex natural products [10f–i]. Through elegant studies of the exchange phenomena of these complexes, Grubbs has demonstrated that the increased activity of complex **6** relative to **5**, can be attributed, at least in part, to the increased preference for binding to olefins rather than phosphines, despite the fact that **6** initiates significantly more slowly than **5** [7e].

Carbene complexes are also superior to their phosphine analogs in many Pd-catalyzed coupling reactions, and special attention has been given to the Mizoroki–Heck and Suzuki–Miyaura reactions [8,13]. The ability of NHC's to stabilize low valent Pd species is likely responsible for the enhanced activity observed in these cases [14]. The first report of the use of an NHC-ligated complex in a coupling reaction was the application of complexes **7** and **8** in the Mizoroki–Heck reaction by Herrmann in 1995 [8e]. It is believed that the carbene ligands enhance oxidative addition of the aryl halide because their strong sigma-donating abilities make the metal more electron rich, although Whittlesey and co-workers have recently shown that oxidative addition of non-polar bonds (C–H, H–H) is not accelerated with NHC-modified Ru complexes [15]. NHC ligands should also promote reductive elimination in the more highly substituted complexes formed at the end of the catalytic cycles because of their greater steric hindrance. A large variety of carbene complexes have subsequently been employed in the Heck reaction. Some of these complexes will be described in Section 3 of this review (Plate 3).

N-Heterocyclic carbenes have been employed in a wide variety of reactions [16] including polymerization [16e], hydrogenation [16f–l], hydrosilylation [16m–s] hydroboration [16t], hydroformylation [16u,v], allylic substitution [16w],

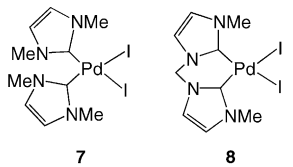


Plate 3. Initial application of NHC complexes in the Mizoroki–Heck reaction.

and methenylation [16t]. Recent reports have begun to document the preparation of *N*-heterocyclic carbene complexes anchored to solid or reusable supports by virtue of the NHC ligand [17].

Despite the fact that NHC's generally confer greater thermal and oxidative stability on their metal complexes than the corresponding phosphines, presumably because of decreased ligand lability, it is still important to be aware of the potential decomposition pathways available to NHC ligands. This is especially crucial in cases where the kinetic stability of the metal–ligand bond is important, for example chiral NHC's for asymmetric catalysis [7f,11a,b,18], or supported versions of NHC complexes [10b,17].

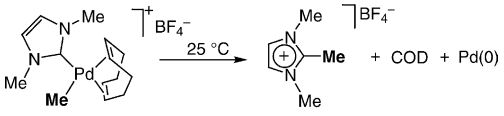
3. Reductive elimination of carbenes and cis ligands

3.1. Monodentate Pd–NHC complexes

Since the metal–NHC bond bears significant resemblance to a simple metal–carbon bond in terms of bond length and polarization [19], it is perhaps not surprising that it suffers some of the same decomposition reactions that alkyl complexes undergo, namely reductive eliminations. The steric bulk of the most common carbenes such as IMes and SIMes[1] facilitate reductive elimination by increasing the steric bulk around the metal.

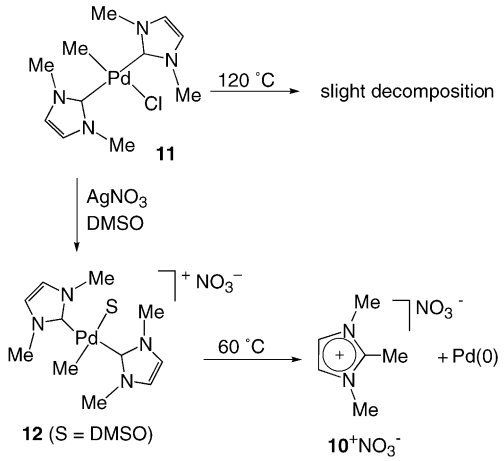
3.1.1. Alkyl Pd–NHC complexes

Cavell has reported a number of cases in which reductive elimination occurs quite readily between *N*-heterocyclic carbenes and *cis*-disposed ligands. The first of these reports was published in 1998 [20]. The synthesis and behaviour of complex **9** was examined, since pre-catalysts which have a Pd–Me bond in place of the more common Pd–halide display increased catalytic activity.[2] Surprisingly, complex **9** underwent immediate reductive elimination at room temperature generating 1,2,3-trimethyl-imdazolium tetrafluoroborate (**10**$^{+}$BF$_4^{-}$) (Eq. (1)). Free COD and precipitated Pd(0) were also observed.



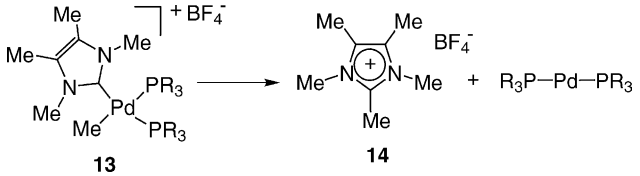
9 **10**$^{+}$BF$_4^{-}$ (1)

Neutral Pd complex **11** also decomposes via reductive elimination, although significantly more slowly and at higher temperature (120 °C) than cationic complex **9**, which shows signs of decomposition even at −20 °C [20]. When **11** is treated with $AgNO_3$ in DMSO, cationic species **12** is generated, which reductively eliminates rapidly at 60 °C generating **10**$^{+}$NO$_3^{-}$ (Scheme 1). As expected, the presence of a positive charge on Pd facilitates reductive elimination, but the ancillary ligands play a relatively large role in the absolute rates of reaction (compare cationic complexes **12** and **9**).



Scheme 1. Stability and reactivity of Pd complex **11**.

Several mechanisms can be envisioned for the reductive elimination. Considering that the NHC ligand has a bond length similar to that of a regular organic ligand [19], simple reductive elimination of the NHC and associated ligands is possible. On the other hand, the free carbene is isoelectronic with carbon monoxide and isonitriles and so a migratory insertion/decomplexation mechanism is also possible. In order to gain some insight into the mechanism, the rate of decomposition of a series of Pd–NHC complexes was studied [21]. The thermal decomposition of (TMIY)PdMe(PR$_3$)$_2$ (**13**), where (PR$_3$)$_2$ = (PPh$_3$)$_2$, (PMePh$_2$)$_2$, (P(OPh)$_3$)$_2$ and DPPP, was shown to give Pd(0) and pentamethylimidazolium (**14**) cleanly (Eq. (2)).



13 **14** (2)

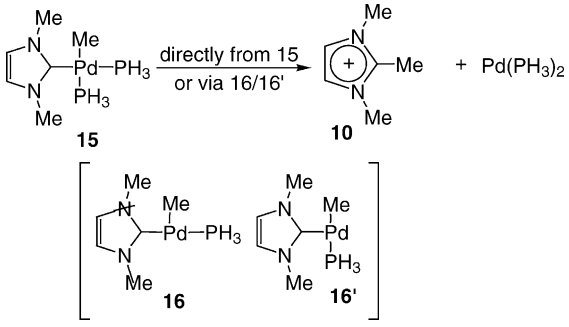
The rates of the reductive eliminations were monitored by NMR, and it was found that sterically bulky ligands accelerated the reaction. For example, the PCy$_3$ complex could not be made, and only the reductive elimination product **14** was observed. Electron rich ligands decreased the rate of elimination, which correlates with the decreased rate of elimination observed for neutral versus cationic complexes. This is also consistent with the reductive elimination mechanism since it is known that charge builds up on the metal

[1] Imes: 1,3-dimesitylimidazol-2-ylidene; SIMes: 1,3-dimesitylimidazolin-2-ylidene; DMIY: 1,3-dimethylimidazol-2-ylidene; TMIY: 1,3,4,5-tetramethylimidazol-2-ylidene; Cy: cyclohexyl.

[2] This phenomenon that has been termed the "methyl effect". It is believed that insertion of the Pd–Me bond into the olefinic substrate followed by β-hydride elimination provides a facile route for the generation of the active Pd(0) catalyst.

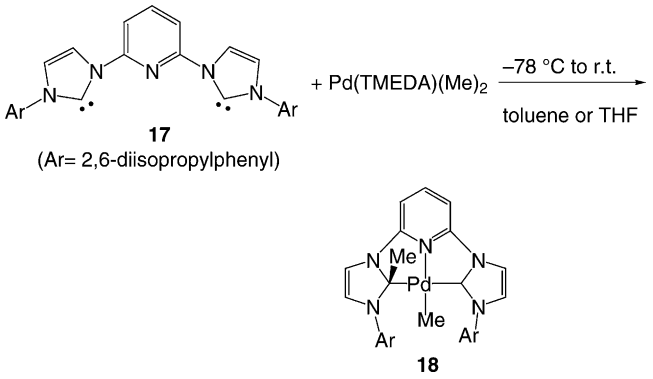
during this reaction. The bidentate ligands DPPP and COD greatly reduced the rate of production of **14** such that for the DPPP complex, no reaction was observed. Bidentate ligands are believed to decrease the rate of reductive elimination by restricting the bite angle [21a], so the experimental results are consistent with simple reductive elimination as the mechanism for the production of **14**. If a migratory insertion reaction were operative, strong donor ligands *trans* to the migrating ligand would facilitate the reaction. Thus the observed increase in stability upon changing the ligand from PPh_3 to $PMePh_2$ is not consistent with this pathway.

DFT calculations carried out on a model system suggest that the reductive elimination occurs from a four-coordinate Pd complex [21a]. Thus the reaction shown in Eq. (3) can proceed directly from compound **15**, or by prior dissociation of a phosphine to yield **16** or **16′**. Complex **16**, obtained by dissociation of a PH_3 ligand *trans* to the methyl group, was of approximately the same energy (20.8 kcal/mol) as the transition state for reductive elimination of Me and TMIY in compound **15** (22.3 kcal/mol). Loss of a phosphine *trans* to the carbene gave a higher energy intermediate **16′** (26.8 kcal/mol). Importantly, reductive elimination from both of these three-coordinate species occurred with an overall activation energy of 35.1 kcal/mol, which is significantly higher than the 22.3 kcal/mol activation energy for reductive elimination directly from the four coordinate complex **15**. Calculations were also performed on the $P(OPh)_3$ analog, and reductive elimination from the four coordinate complex was found to be even more facile, occurring with an activation energy of only 14.1 kcal/mol.[3] Although most $PdR_2(PR_3')_2$ systems undergo reductive elimination after dissociation of a phosphine, in specific cases, the reaction is known to occur through a four coordinate complex when R is sp^2 hybridized [21c] and theorectical calculations support the feasibility of this pathway in other systems [21b].



(3)

However, Danopoulos et al. have isolated a palladium carbene complex in which the *N*-heterocyclic carbene has reacted with one of the methyl substituents on Pd in a manner suggestive of a migratory insertion reaction (Eq. (4)) [1]. Treatment of $Pd(TMEDA)Me_2$ with biscarbene/pyridyl ligand **17** in toluene at room temperature gives compound **18**, in which one of the methyl groups has migrated from Pd to the NHC.

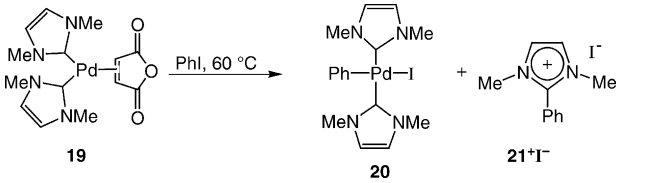


(4)

The structure of compound **18** was confirmed by spectroscopy and X-ray crystallography [1]. The Pd(II) complex corresponds to a reaction in which the methyl group has migrated to the carbene carbon in much the same way as alkyl or aryl substituents on transition metals undergo migratory insertion into bound carbon monoxide or isonitriles. DFT calculations were carried out on a simplified version (N–H instead of N–Ar) and indicated that the reaction is highly exothermic (32.2 kcal/mol) and proceeds with a small activation energy of 7.8 kcal/mol. A five coordinate Pd intermediate was found en route to the final product **18** [1]. These studies demonstrate that migratory insertion-type reactions do occur in Pd–NHC complexes, illustrating the complex behaviour of these species.

3.1.2. Aryl Pd–NHC complexes

Aryl groups also undergo reductive elimination with NHC's [22]. Pd(0) carbene complex **19** (Eq. (5)) was reacted stoichiometrically with several aryl iodides. With phenyl iodide, heating to 60 °C was necessary to affect oxidative addition generating **20**. At this temperature, the expected complex (**20**) was contaminated with **21**, resulting from reductive elimination of the phenyl and NHC ligands.

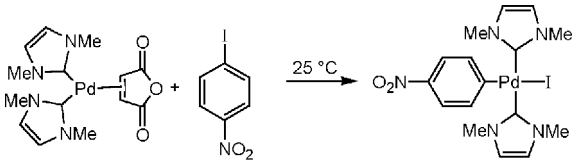


(5)

The addition of a nitro substituent to the aryl halide facilitated the oxidative addition such that at room temperature, the desired Pd(II) complex was obtained in 51% yield, with no formation of the corresponding arylated imidazolium species (Eq. (6)) [22]. However, with time, reductive elimination of the aryl and NHC ligands is also observed from this complex under relatively mild conditions ($t_{1/2} = 3$ days in CD_2Cl_2 at room temperature). Thus it is likely that the lower

[3] Note that the calculations were not performed on the three coordinate intermediates using $P(OPh)_3$, only PH_3.

temperatures required for the oxidative addition are responsible for the increased ease of isolation of compound **23**.



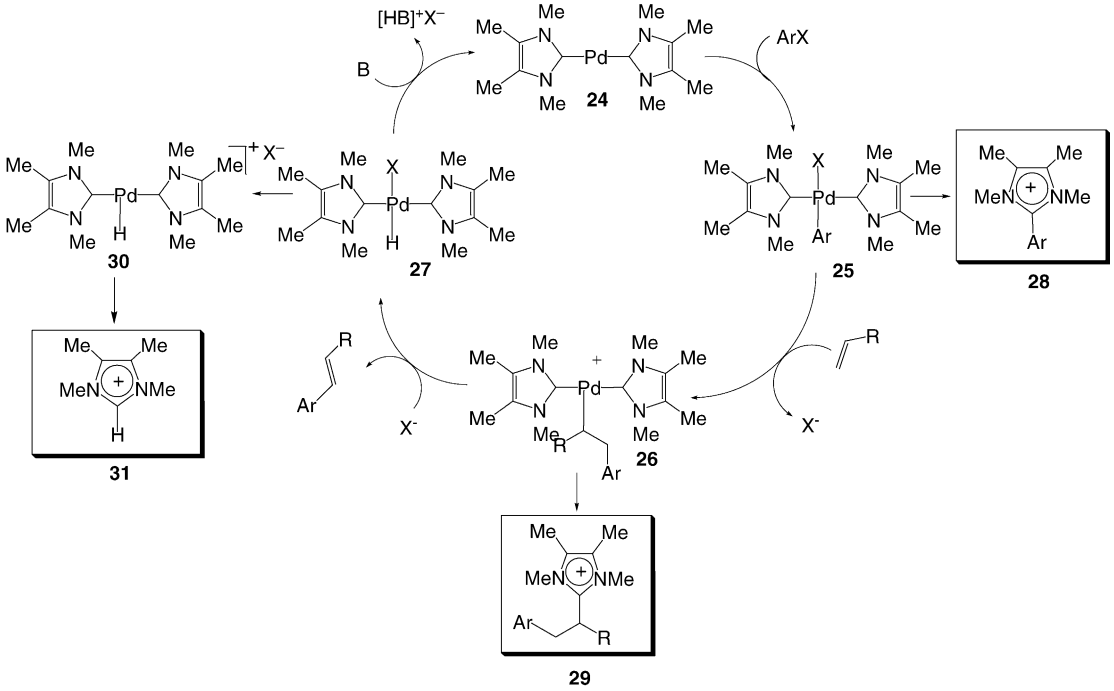
19 **22** **23** (6)

Despite the fact that nitrophenylate complex **23** does undergo reductive elimination under mild conditions, it is a highly efficient catalyst for the reaction between 4-iodonitrobenzene and butyl acrylate at 120 °C [22]. There is little evidence of catalyst decomposition during the catalytic cycle. The Mizoroki–Heck reaction between bromoacetophenone and butyl acrylate is catalyzed by both **23** and **20**, proceeding at a rate of 50,000 turnovers/h. The high temperature is believed to be required to promote halide dissociation [22].

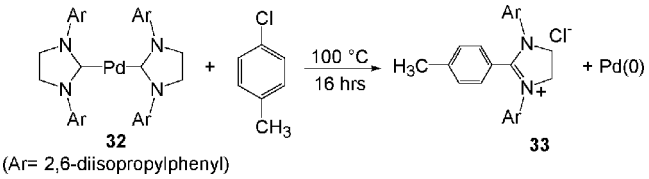
The stoichiometric reaction of **23** with $AgBF_4$ and butyl acrylate leads to several decomposition products resulting from reductive elimination of the NHC ligand with aryl, alkyl and hydride ligands on Pd [22]. In fact, decomposition products stemming from *all of the key intermediates in the catalytic cycle* for the Mizoroki–Heck reaction are observed. The proposed catalytic cycle is shown in Scheme 2. Oxidative addition of the aryl halide and $Pd(TMIY)_2$ (**24**) generates arylated complex **25**. Loss of halide permits coordination of the olefin and subsequent arylation yielding **26**. Finally, β-hydride elimination generates the coupling product and complex **27**. Removal of HX by the base regenerates the catalyst. Under stoichiometric conditions, compounds **28**, **29** and **31** are all observed, resulting from reductive eliminations from **25**, **26** and **30**, respectively [22]. Although **28** and **29** represent irreversible deactivation of the catalyst, it should be noted that the carbene Pd complex can be regenerated from the imidazolium salt **31**, either by deprotonation or oxidative addition (Section 5).

The stability of the Pd complexes under catalytic conditions is believed to stem from the increased rate of β-hydride elimination from the key Pd intermediate **26** at higher temperatures [22], where this reaction becomes competitive with reductive elimination of the NHC and the aryl or alkyl group. Thus the catalyst does not decompose as long as there is substrate present. However, it is also possible that the actual catalyst for the coupling reaction is a mono-ligated complex and that the decomposition pathways observed in the stoichiometric reaction merely serve to generate the active mono-ligated complex. Regardless, it is remarkable that high catalytic activity is attained despite the demonstrated susceptibility of several of the intermediates to decomposition.

As part of a study directed towards the application of Pd–NHC complexes as catalysts for the arylation of amines, Caddick et al. studied the synthesis and stoichiometric reactivities of several Pd–NHC complexes with aryl halides [23]. Well-characterized Pd(0)–bis NHC complexes were reacted with 4-chlorotoluene in an attempt to affect oxidative addition, the first step of the amination reaction. In the case of **32**, oxidative addition did not take place at ambient temperature, and so the reaction was performed at elevated temperatures (100 °C for 16 h). Instead of isolating the desired Pd(II) species, reductive elimination product **33** was obtained along with Pd metal (Eq. (7)) [23].

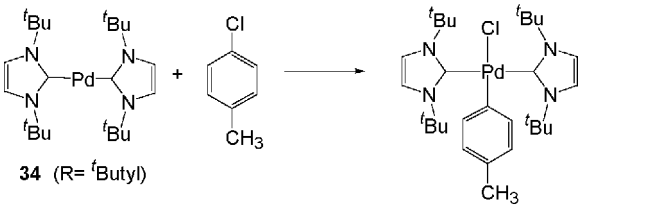


Scheme 2. Catalytic cycle of Mizoroki–Heck reaction catalyzed by **24**.



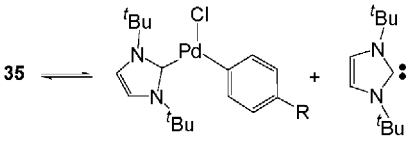
(7)

Complex **34** underwent oxidative addition more quickly (90 °C, 1 h), without generating reductive elimination product **33** (Eq. (8)) [23]. This species, when treated with morpholine, gave the arylated amine in >95% yield. The *trans* arrangement of the two carbene ligands in **35** suggested to Cloke and Caddick that either the initially formed (but undetected) *cis* complex underwent direct isomerization to the *trans* form, or that one of the carbene ligands in **35** dissociated after oxidative addition of 4-chlorotoluene [23]. Recent studies from the same lab indicate that dissociation of one of the carbene ligands from **35** takes place under relatively mild conditions [24].



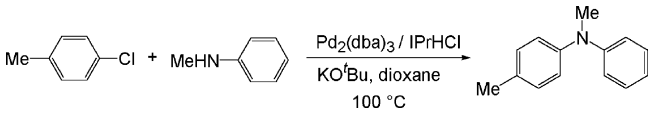
(8)

Heating **35** to 90 °C in C_6D_6 led to the observation of the free carbene in solution (Eq. (9)) [24]. The dissociation was reversible, since cooling to room temperature resulted in reformation of carbene complex **35**. Analysis of the equilibrium constants at different temperatures permitted the authors to determine the BDE for the Pd–carbene bond to be 25.57 kcal/mol. Interestingly, the extent of carbene dissociation seemed to depend on the electronics of the aryl chloride. The electron withdrawing CO_2Me substituent increased the propensity for dissociation, which occurred only above 60 °C, and the OMe substituted complex began to dissociate at 40 °C [24].



(9)

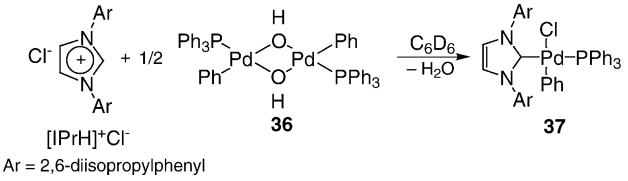
A detailed kinetic analysis of the amination of aromatic chlorides with $Pd(NHC)_2$ led Caddick and Cloke to conclude that the reaction occurs by prior dissociation of one of the carbene ligands from $Pd(NHC)_2$, followed by rate determining oxidative addition [24]. These results are in agreement with the in situ procedure developed by Nolan et al., in which the optimum ratio of imidazolium ligand to Pd was found to be 1:1 for the amination shown in Eq. (10) [25]. The addition of a second equivalent of imidazolium slowed the reaction.



(10)

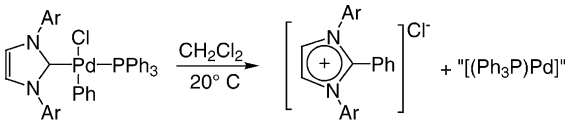
As is obvious from the examples given above, the study of aryl–Pd complexes is difficult because the temperatures required for their synthesis are often high enough to promote decomposition by reductive elimination. Recently, Marshall and Grushin have described a novel synthetic route to Pd–NHC–aryl species that involves a bridge splitting reaction on a complex with preformed Pd–Ph bonds (**36**) (Eq. (11)) [26]. This reaction occurs under mild conditions and provides a very useful alternative to the oxidative addition route.

The reaction formally takes place by substitution of the bridging OH^- ligands with the Cl^- counterion of the imidazolium salt. Deprotonation of the imidazolium cation with liberated hydroxide generates the carbene, which forms the carbene complex (Eq. (11)) [26]. The methylated Pd complex was prepared analogously starting with $[(PPh_3)_2Pd_2(Me)_2(\mu\text{-}OH)_2]$. In both cases the carbene precursor is the 2,6-diisopropyl-phenyl imidazolium ion, otherwise known as IPrHCl. This particular carbene was chosen since Pd complexes containing it are known to be highly active for coupling reactions involving unreactive aryl chlorides [26].



(11)

Employing $[IPrH]^+I^-$ instead of $[IPrH]^+Cl^-$, Grushin and Marshall found that reductive elimination was so facile that the iodo analog of **37** could not be isolated. Instead, IPr–Ph (**38** I^-) was obtained from reductive elimination [26]. Chloro–Pd species **37** also underwent rapid reductive elimination when dissolved in CH_2Cl_2 at room temperature, despite its stability in benzene at this temperature. The reductive elimination was virtually shut down by the addition of two equivalents of PPh_3, indicating that the reaction likely proceeds by initial dissociative loss of phosphine, unlike Cavell's system where the less bulky TMIY and DMIY[1] complexes undergo reductive eliminations from four coordinate Pd species.



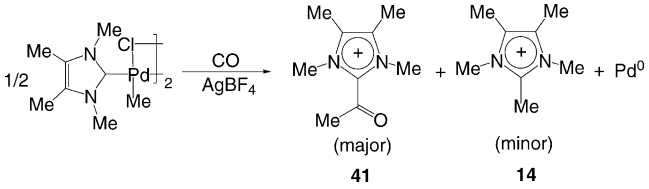
(12)

3.1.3. Acyl Pd–NHC complexes

N-Heterocyclic carbene complexes of Pd such as **39** are known to catalyze the co-polymerization of ethylene and carbon monoxide [16e]. However, the amount of the catalyst that appears to be participating in the reaction is believed to be only a fraction of the catalyst that is added to the reaction [16e]. McGuinness and Cavell have shown that this may in fact be due to decomposition of the catalyst by either reductive elimination or migratory insertion resulting in the ultimate decomposition of the Pd–NHC complex [27].

To study the decomposition of alkyl carbonyl complexes, the TMIY carbonyl complex **40** was prepared by reaction of $[PdMe(TMIY)Cl]_2$ with carbon monoxide at −40 °C [27]. Upon warming to room temperature, decomposition of **40** was observed leading to pentamethylimidazolium chloride (**14**) along with Pd(0) (Plate 4). Analysis of the mixture by mass spectroscopy indicated the presence of small amounts of 2-acetyl imidazolium (**41**) resulting from carbonylation followed by reductive elimination (Eq. (13)).

Since the original catalyst employed for the carbonylation of ethylene was a dicationic Pd(II) species, Cavell et al. treated $[PdMe(TMIY)Cl]_2$ with carbon monoxide in the presence of silver tetrafluoroborate (Eq. (13)) [27]. Under these conditions, the acetylated imidazolium ion **41** was the major product. Cavell suggests that silver is necessary to promote this reaction because in complex **40**, the methyl and CO ligands are *trans* to one another preventing the formation of the acyl complex[4] that would presumably precede reductive elimination [27]. This implies that the reaction of the NHC ligand with CO itself does not occur to a significant extent, as it is disposed *cis* to CO in **40**. On the other hand, reaction between the NHC ligand and the in situ generated acyl substituent is facile and may lead to catalyst decomposition during ethylene/CO polymerization reactions. However, as demonstrated for the Mizoroki–Heck reaction, the results obtained in stoichiometric studies are not necessarily applicable under catalytic conditions [22].

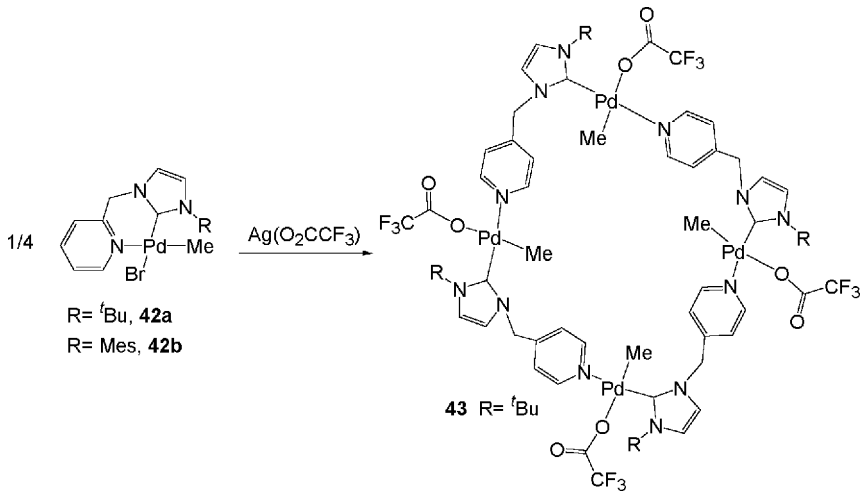


(13)

3.2. Chelating Pd–NHC complexes

3.2.1. Bidentate complexes

Relative to monodentate carbenes, chelating carbenes are significantly less prone to reductive elimination. This may result from the conformational rigidity imposed by the chelate ring, which prevents the NHC from adopting the correct conformation for reductive elimination [28]. Hursthouse has recently reported the preparation of complex **42**, in which the carbene and methyl substituents are *cis* to one another [29]. When this complex is treated with $Ag(O_2CCF_3)$ to abstract the halogen, rather than reductively eliminating the methylimidazolium species as would be expected based on results from monodentate complexes, the formation of carbene-bridged tetramer **43** was observed.



(14)

Complex **42a** was shown to be a highly active catalyst for the Mizoroki–Heck reaction between iodobenzene and methyl acrylate, giving almost 3 million turnovers and a turnover rate of >75,000 h^{-1} under optimized conditions (140 °C, dimethylacetamide as solvent, see Table 1) [29].

[4] Note that the acyl complex could not be observed in their study.

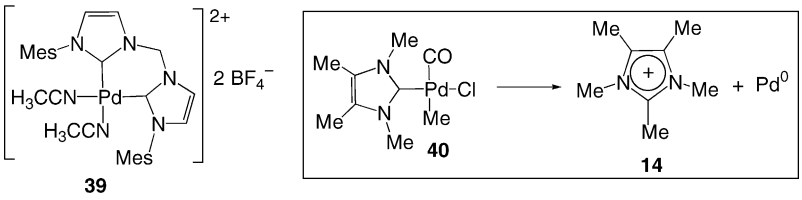
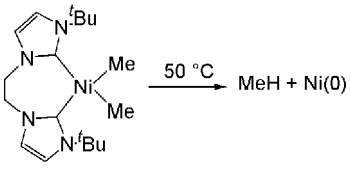


Plate 4. Decomposition palladium carbonyl NHC complexes.

It was also an effective catalyst for the amination of bromobenzene with PhNHMe.

The first report of an *N*-heterocyclic carbene complex used in the Heck reaction is bidentate Pd complex **8** (Plate 3) [8e]. This species was prepared by Herrmann and exhibits remarkable stability, surviving refluxing in THF for several days under an oxygen atmosphere and melting at close to 300 °C with little decomposition. Note that the two ancillary ligands are halogens, which adds significant stability to metal carbene complexes compared to their alkyl congeners.[5] Complex **8** and its bis DMIY relative **7** are both active in the Mizoroki–Heck reaction of bromoaromatics with butyl acrylate, after an induction period during which Pd(II) was reduced to Pd(0) [8e]. In order to circumvent this induction period, Herrmann prepared a Pd(0) complex by reaction of $Pd(dba)_2$ with two equivalents of the carbene 1,3-dimethyl-dihydroimidazole-2-ylidene. The resulting complex was highly active. Turnover frequencies of 15,000 turnovers/h and turnover numbers of up to 250,000 were observed for the reaction of 4-bromoacetophenone with butyl acrylate at 125 °C in dimethyl acetamide [8e].

Chelating bis carbenes have also been prepared by Douthwaite et al. Nickel complex **44** generates methane as the only observable product when it is heated to 50 °C (Eq. (15)) [30]. Despite the presence of two cis NHC/CH_3 interactions, no reductive elimination of the carbene ligand was observed. These results contrast with the results of the bisphosphine Ni complexes such as $[Ni(dppe)Me_2]$, in which a mixture of methane and ethane were observed upon thermal decomposition.



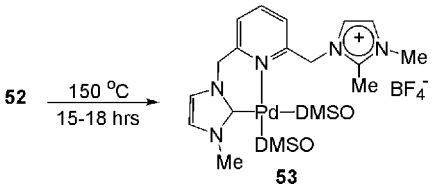
44 (15)

Pd complexes **45** and **46** also react by preferential loss of the two substituents rather than alkylation of the carbene (Scheme 3) [28]. When treated with pyridine, **45** and **46** lose methane, forming complexes **47** and **48** with both carbene–Pd bonds intact. Treatment with a chelating ligand (bipy) does result in displacement of the carbene ligand, which is subsequently trapped by the deuterated solvent (Scheme 3) [31].

Since these systems all have methyl and NHC ligands in *cis* orientations, they provide good evidence that the *alkyl–alkyl reaction is more favourable than alkyl–NHC reductive elimination*. In the absence of this alternative reaction pathway, reductive elimination of the carbene and aryl/alkyl ligands can occur, although more forcing conditions are required compared with those employed using monodentate carbenes (Eq. (1)). The results in the next section demonstrate that there are some instances in which reductive elimination of chelated carbenes does occur.

3.2.2. Tridentate ligands

Tridentate complexes **51** and **52** were prepared by reaction between 2,6-dibromomethyl pyridine and 1-methylimidazole (Scheme 4) [32]. Reaction with silver oxide followed by $AgBF_4$ yields the silver carbene cleanly.[6] Treatment with Pd complexes then generates the desired tridentate Pd–NHC complexes. Complex **52** is significantly more stable than monodentate carbene complexes, since heating to 150 °C for 15–18 h is required for complete loss of the Pd–Me signal.[7] Although conclusive identification of the structure of the decomposition product was not possible, it is believed to be the bidentate carbene DMSO complex **53** (Eq. (16)). Eventually, decomposition continues, giving Pd black by an as yet unknown mechanism [32].



(16)

Operating at 120 °C in DMAC, Cavell found complex **52** to be highly active and reasonably stable for the Mizoroki Heck reaction between aryl bromides and butyl acry-

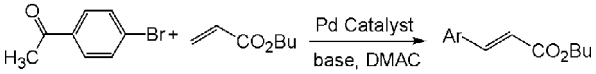
[5] Halogen ligands have been shown to be significantly less prone to reductive elimination than alkyl ligands (Ref. [34]).

[6] The addition of silver tetrafluoroborate gave the BF_4^- salt which was more easily purified. The carbene resulting from treatment with Ag_2O showed contamination by inorganic salts.

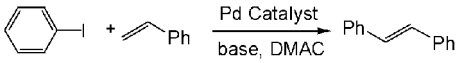
[7] Note that exact identification of the product of decomposition was not possible, but the initial product is proposed to be the monoligated bis DMSO complex with one methylated imidazolium species.

Table 1
Reactivity of Pd–NHC complexes in the Mizoroki–Heck reaction

Reaction A:



Reaction B:



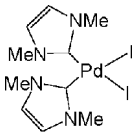
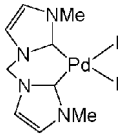
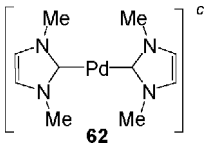
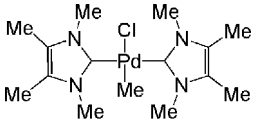
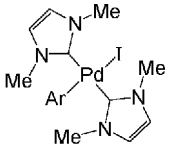
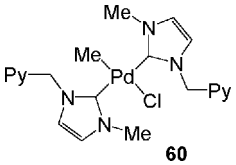
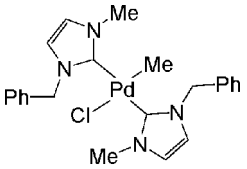
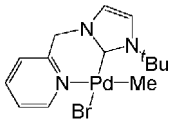
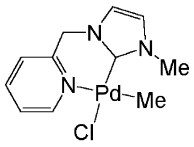
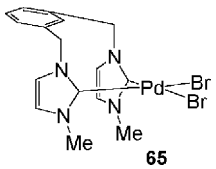
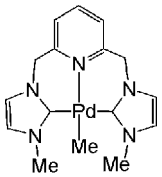
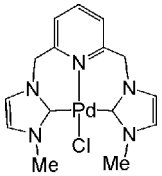
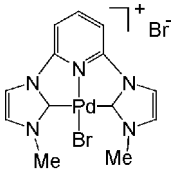
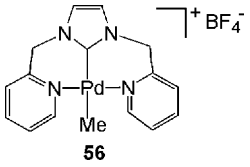
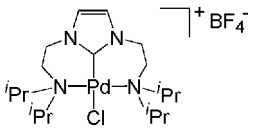
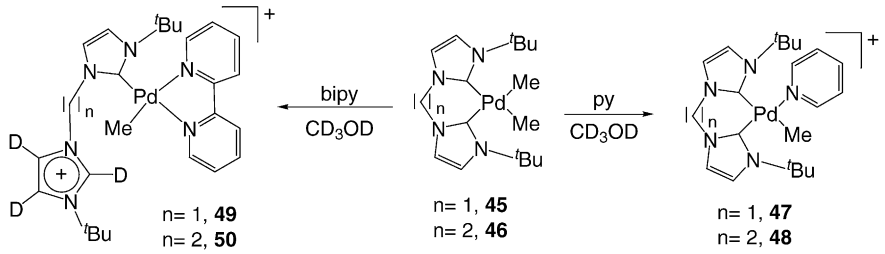
Entry	Catalyst	Reaction	Conditions/additives	TON[a] (TOF[b])
1	 **7**	**A**	100 °C	>200 [8e]
2	 **8**	**A**	100 °C	>200 [8e]
3	 **62**	**A**	125 °C	250,000 [8e] (15,000[c])
4	 **63**	**A**	120 °C	18,000 [34] (1,000)
5	 **19**, Ar = p-$NO_2C_6H_4$	**A**	120 °C	50,000 [22]
6	 **60**	**A**	120 °C/Pr_4NBr	1,700,000 [35] (14,166)
7	 **61**	**A**	120 °C/Pr_4NBr and $NH_2NH_2{\cdot}H_2O$	980,000 [34] (10,000)
8	 **42a**	**B**[d]	140 °C	2,858,000 [29] (75,000)

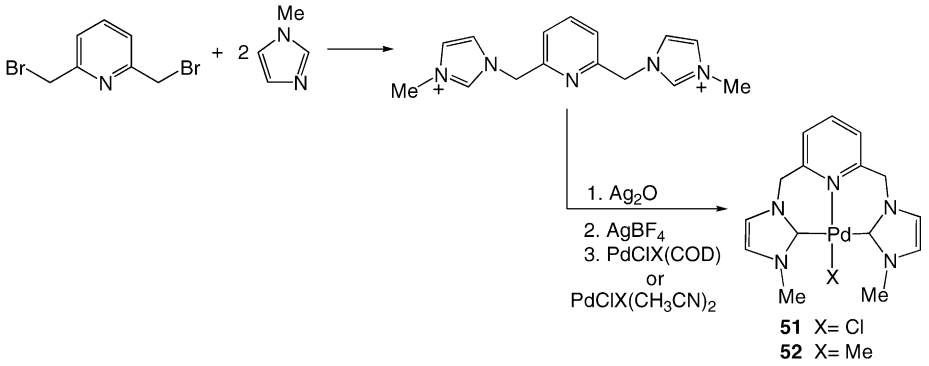
Table 1 (*Continued*)

Entry	Catalyst	Reaction	Conditions/additives	TON[a] (TOF[b])
9	 **64**	**A**	120 °C	610,000 [35] (5,080)
10	 **65**	**A**	120 °C/Pr_4NBr and $NH_2NH_2{\cdot}H_2O$	970,000 [34] (10,430)
11	 **52**	**A**	120 °C/Pr_4NBr	34,330 [32] (1,720)
12	 **51**	**A**	120 °C and $NH_2NH_2{\cdot}H_2O$	40,160 [32] (1,980)
13	 **66**	**A**	160 °C in air	330,000 [12a] (16,500) (85,000)[e]
14	 **56**	**A**	120 °C/Pr_4NBr	660,000 [34] (10,000)
15		**A**	120 °C and $NH_2NH_2{\cdot}H_2O$	44,000 [34] (1,000)

[a] TON: turnover number (moles product/moles catalyst).
[b] TOF: turnover frequency (TON/hr).
[c] Generated in situ from $Pd(dba)_2$ and free carbene.
[d] 4-Bromoanisole was used in the calculation of turnover frequency while 4-bromoacetophenone was cited for the turnover number.
[e] Methyl acrylate was employed as the olefin.
[f] Under argon.

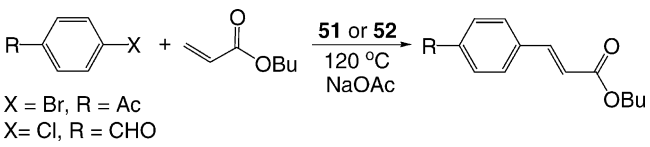


Scheme 3. Reaction of chelating carbene complexes **45** and **46**.



Scheme 4. Synthesis of NHC complexes **51** and **52**.

late (Eq. (17)) [32]. Interestingly, chloro complex **51** is consistently more active than the methylated derivative in terms maximum turnover rate (1980 h^{-1}), but the addition of Pr_4NBr to the methyl derivative brings the reactivity of **52** close to that of **51** (1720 turnovers/h). During the first 20 h of an extended run, methyl complex **52** performed at a rate of 827 turnovers/h, and during the next ca. 90 h, the rate was 638 turnovers/h indicating some loss of activity but not substantial. Interestingly, the chloride complex **51** actually lost more activity than the methyl species (50% of the initial activity was lost after 40 h) [32].



(17)

Complex **54**, with a less flexible chelate, was also prepared [32,33]. This cationic species underwent reductive elimination after 6 h at 140 °C as evidenced by the complete loss of the Pd–Me signal. Compared to the one carbon homologated species, **52**, which requires 18 h at 150 °C for complete decomposition, this compound is actually less stable [33]. The *N*-^{t}Bu analog of **54** could not be prepared. Instead treatment of [Pd(COD)ClMe] with the corresponding silver carbene NHC complex at room temperature gave the reductive elimination product **55** (Plate 5). Steric bulk likely plays a role in the ease of reductive elimination.

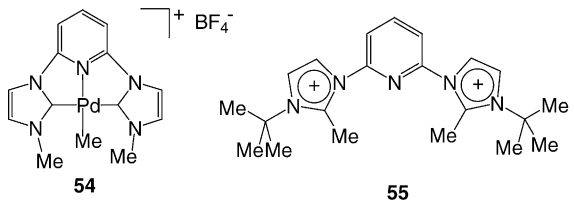
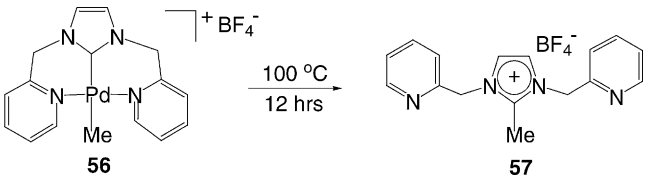


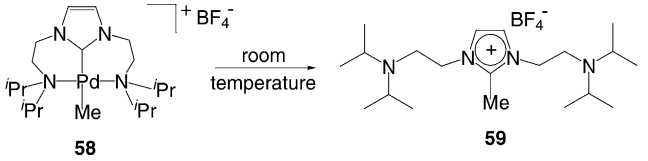
Plate 5. NHC complex **54** and decomposition product **55** from ^{t}Bu-substituted NHC.

The halogen derivative of complex **54** is significantly more stable than the methylated complex [12a]. Crabtree showed that this complex (**66**, entry 13, Table 1) could be refluxed for 24 h in air at 180 °C without decomposition [12a]. It is also a highly active catalyst for the Heck reaction between PhI and styrene. The catalyst can also be employed in air and give a TOF of 16,500 h^{-1} (85,000 h^{-1} under argon).

In complex **56**, the carbene ligand is *trans* to the methyl substituent, which should prevent decomposition by reductive elimination [34]. Remarkably, **56** did undergo reductive elimination yielding **57** after 12 h at 100 °C (Eq. (18)). In order for this to happen, the pyridyl ligand must first dissociate from the complex, which is probably assisted by the relatively polar solvent (DMSO) used in this study (note that the formation of tetramer **43** from complex **42** also requires initial pyridyl dissociation, Eq. (14)) [29]. It should be noted that the stability is certainly greater than that observed for regular cationic Pd species but interestingly, this complex is less stable than the closely related bis carbene **52**, which decomposes at 150 °C [32].



(18)



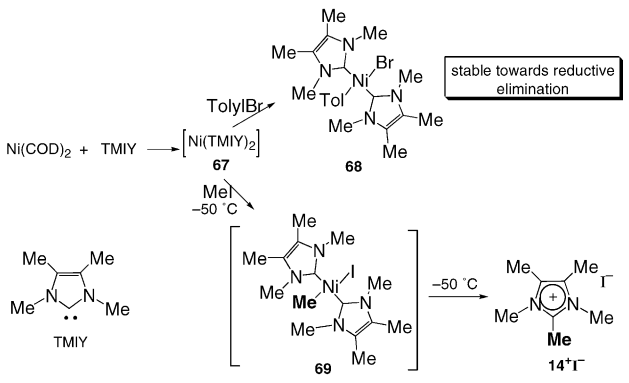
(19)

Complex **58**, which is more sterically hindered than **56**, undergoes more rapid reductive elimination at room temperature such that it cannot be prepared free of **59** (Eq. (19)) [34]. The chloro derivative of **58** could be prepared and was not susceptible to decomposition. These species were examined in the Mizoroki–Heck coupling reaction between bromoacetophenone and butyl acrylate [34]. The results are compiled in Table 1, along with selected examples of monodentate and bidentate carbene complexes for comparison.

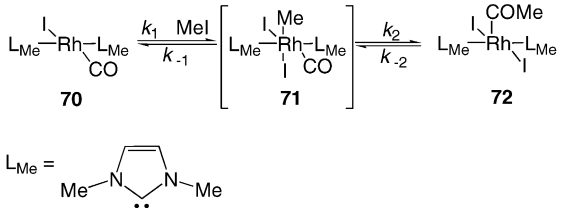
3.3. Nickel–NHC complexes

Reductive elimination of NHC ligands and aryl/alkyl ligands has also been observed in nickel complexes [22]. Reaction of free TMIY with $Ni(COD)_2$ is proposed to give $Ni(TMIY)_2$ (**67**), which reacts cleanly with tolylbromide to give the oxidative addition product **68** in high yield (71%, Scheme 5). Decomposition by reductive elimination was not observed, and the complex was shown to be an active catalyst for the Suzuki–Miyaura reaction, albeit less active than the Pd counterpart [22].

Oxidative addition also occurs rapidly with MeI, but in this case the reductive elimination occurs so quickly that the oxidative addition product could not be isolated, even when the synthesis and work up were performed at −50 °C. Instead, the presumed intermediate **69** reductively eliminates generating the pentamethyl imidazolium ion (**14**) as the major product [22].



Scheme 5. Reaction of Ni–NHC complexes after oxidative addition.



Scheme 6. Reactions of bis carbene **70** with MeI.

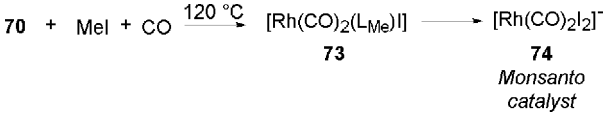
3.4. Rhodium NHC complexes

Haynes et al. have prepared phosphine-free Rh–NHC complexes such as **70** and examined their use in the industrially important carbonylation of iodomethane [36]. Carbene complexes such as **70** undergo oxidative addition with iodomethane significantly more slowly than phosphine complexes. This is surprising since IR analysis of the CO stretches in the key species indicate that the carbene complexes are more electron rich than the corresponding phosphines, which should facilitate oxidative addition [36] (Scheme 6). Also unlike phosphine complexes, the product of oxidative addition (in this case **71**) was not observed and instead underwent immediate conversion to acyl species **72**. Both of these facts are attributed to the greater steric bulk the NHC's impart to the Rh complexes. In the case of oxidative addition, the presence of the NMe substituents perpendicular to the plane of the Rh complex hinders approach of MeI to the Rh complex. The bulkier ligands would also destabilize the Rh(III) octahedral complex, promoting carbonylation to the less hindered 5-coordinate species **72**. These conclusions are in agreement with previous results from the Haynes lab with diimine ligated Rh complexes, where increased steric bulk decreases the facility for oxidative addition, and favours carbonylation [37].

Although acyl complex **72** could not be isolated in pure form, a sample enriched in this species was redissolved in dichloromethane, and was observed to revert into **70**. Despite the fact that the acyl ligand in **72** is *cis* to two carbenes, *reductive elimination of the carbene and acyl substituents was not observed* [36]. This is particularly remarkable since it is generally accepted that acyl substituents are among the most reactive towards reductive elimination [38]. Furthermore, complex **71**, although not observed, could presumably generate the methylated carbene (**10**) by reductive elimination as described for Pd complexes above. However, it appears that in this case, reductive elimination of the Me and I substitutents and regeneration of **70** or carbonylation to **72** is more favourable.

With the stoichiometric reactivity of complex **70** documented, Haynes and co-workers investigated its catalytic ac-

tivity for the carbonylation of iodomethane by high pressure IR spectroscopy [36]. Heating complex **70** to 120 °C in the presence of MeI and MeOH under 10 atm of CO leads to the production of two new signals in the IR spectrum. These signals are assigned to the monocarbene complex **73**, which was previously characterized by the Haynes group. After an additional 1–2 h, this species disappears to be replaced by $[Rh(CO)_2I_2]^-$ (**74**), which is the Monsanto catalyst [39] (Eq. (20)).



(20)

When Rh–phosphine complexes are employed as catalyst precursors for the carbonylation of methyl iodide, the Monsanto catalyst is the ultimate product since dissociation of the phosphine results in the formation of methylphosphonium species, and the various Rh species present in solution are carbonylated to yield $[Rh(CO)_2I_2]^-$ [39]. The fact that this species is generated from the reaction of Rh–NHC complexes with iodomethane requires cleavage of the Rh–NHC bond at some stage of the reaction, either by dissociation or reductive elimination. The reaction of **70** with HCl was found to give the chloro analog of complex **73**, resulting from loss of one of the carbene ligands and redistribution of the CO ligands on Rh [36].

Although the mechanism of decomposition of the NHC complex in these reactions is unclear, there are several possibilities. In the case of HCl treatment, formation of a Rh–H followed by reductive elimination of the NHC ligand leading to the protonated ligand is possible. In the catalytic reaction, the authors note that the fate of the carbene is not ascertained, but that methylation, acetylation or protonation of the Rh–carbene to give imidazolium cations are all possibilities [36]. These reactions could occur at the metal center, or after decomplexation of the carbene from Rh at these elevated temperatures. Recent work from our lab and others indicate that decomplexation of the carbene is a reasonable possibility (Section 4).

4. Decomplexation or displacement by competing ligands

The displacement of carbenes by competing ligands is another means by which decomposition of metal–NHC complexes can occur. For the preparation of chiral catalysts and supported versions of carbene ligands, understanding this reaction is critical. Although it is generally true that the carbene metal bond is significantly stronger than the metal phosphine bond [8e,9d], recent reports have documented the lability of the metal–carbene bond under certain conditions. Displacement of the NHC ligand from the coordination sphere of the metal has been observed directly and indirectly.

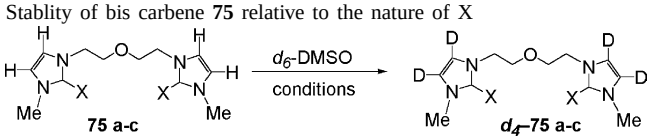
4.1. Non-transition metal complexes

In an attempt to generate free carbenes from BF_3 complexes by treatment with fluoride, free carbene was not observed, but the resulting BF_3 complex displayed extensive deuteration of the NHC by the solvent [40]. Denk and Rodezno [41] have reported that this reaction occurs with the free carbene, leading Cavell and co-workers to postulate that the deuteration observed at high temperature was caused by the small, unobservable equilibrium concentration of free carbene [40]. Indeed the free bis carbene derived from the deprotonation of **75b** was shown to undergo complete deuteration at the 4 and 5 positions upon room temperature treatment with d_6-DMSO. Complete deuteration was also observed when the silver carbene complexes **75c** were heated to 150 °C for 40 h in the absence of an additive. Deuteration of **75a** (X = BF_3) occurs quantitatively upon treatment of this species with CsF in DMSO [40]. Although the observation of deuteration is not conclusive evidence for carbene dissociation, it seems likely that the free carbene is being formed in these experiments, either as a result of fluoride treatment or thermally (Table 2).

4.2. Palladium NHC complexes

As part of a study of the reactivity of Pd–NHC complexes directed towards understanding their behaviour in coupling reactions, Caddick and Cloke prepared a series of divalent

Table 2
Stablity of bis carbene **75** relative to the nature of X



Substrate	Conditions	Additives	Results
75a X = BF_3	95 °C, 100 h	CsF	Complete deuteration
75a X = BF_3	Room temperature	CsF	No deuteration
75b X = H	150 °C, 20 h	None	25% Deuteration
75c X = Ag (dimmer)	150 °C, 40 h	None	Complete deuteration
Free carbene	Room temperature	None	Complete deuteration

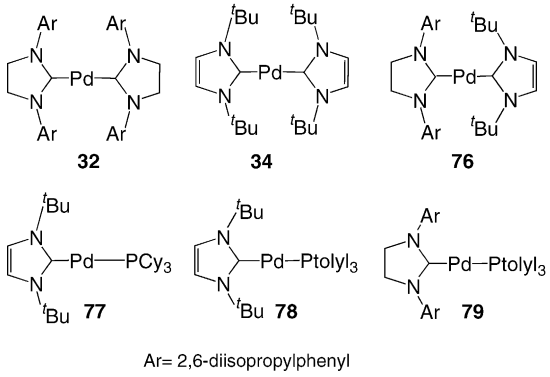
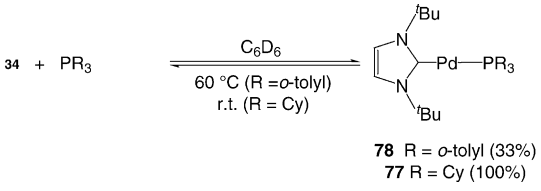


Plate 6. Mixed and homoleptic Pd–NHC complexes.

Pd(0) complexes **32**, **34** and **76**–**79**, shown below [42]. The catalytic activity of these complexes was examined for the amination of 4-chlorotoluene with morpholine. Surprisingly, the mixed carbene/phosphine complex **78** was less active than bis carbene complex **34** (56% yield compared to 95% under identical conditions). Considering that the proposed mechanism for amination requires a Pd complex modified by only one bulky electron rich ligand, this result was particularly surprising. The saturated bis carbene (**32**) and mixed carbene/phosphine complex (**79**) were also prepared, and showed similar catalytic activity despite their significantly different structure [42].

In order to examine the ligand substitution behaviour of these complexes, bis carbene complex **34** was treated with P(*o*-tolyl)$_3$ and remarkably produced the monophosphine complex **78** [42]. After heating at 60 °C for 16 h, 33% of complex **78** was observed. Since this amount did not increase with further heating, equilibrium was presumably achieved. Astonishingly, treatment of complex **34** with PCy_3 resulted in complete formation of the monophosphine complex **77** within 15 min at 25 °C (Eq. (21)) [42].

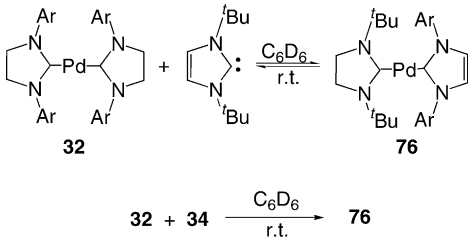


(21)

The saturated carbene complex **32** also reacts with P(*o*-tolyl)$_3$ to give the mixed species **79** (Plate 6). In this case the equilibrium appears to favour the bis carbene since only 30% of the mixed species was observed. Mixed carbene/phosphine complexes were also obtained by mixing **32** and **34** with [Pd(PR$_3$)$_2$] [42].

Finally, free carbenes can displace bound carbenes as shown in Scheme 7 [42]. Treatment of complex **32** with free carbene led to the mixed saturated/unsaturated carbene complex **76**. This same species could be obtained by ligand redistribution between complexes **32** and **34**.

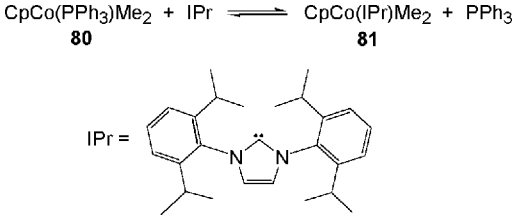
In subsequent studies, it was conclusively documented that Pd(II)–NHC complexes dissociate when heated to generate coordinatively unsaturated Pd species and free carbene, which was observed by ^{1}H NMR (see Eq. (9)) [24]. Thus it is likely that similar dissociation is responsible for the exchange observed the Pd(0) complexes described above.



Scheme 7. Reactions of Pd–NHC complexes: displacement and disproportionation.

4.3. Cobalt NHC complexes

Phosphine/carbene exchange has also been observed in cobalt complexes [43]. During an attempted synthesis of CpCo(IPr)Me$_2$ by displacement of phosphine from CpCo(PPh$_3$)Me$_2$, the formation of **81** was detected, but NMR studies indicated that **80** and **81** were equilibrating (Eq. (22)). The desired complex **81** could be isolated in pure form, albeit in low yield (9%) by chromatography of the mixture on alumina followed by recrystallization. Treatment of the isolated NHC complex with two equivalents of PMe$_3$ led to complete displacement of the carbene ligand. The small size and strong donor strength of PMe$_3$ makes it highly nucleophilic and decreases the lability of the phosphine in the resulting complex [44]. Baird and co-workers attribute the ease of dissociation of IPr to the considerable steric hindrance this large carbene imparts to complex **81** [43]. The large entropy of activation associated with the formation of complex **81**, as calculated from NMR studies of the exchange, suggests that there is considerable restricted rotation in this complex compared to free IPr and the Co–PPh$_3$ complex **80** [43].



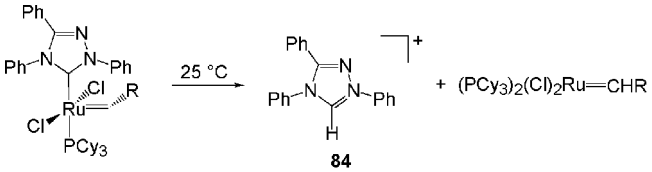
(22)

4.4. Ruthenium NHC complexes

Ru alkylidene complexes modified by *N*-heterocyclic carbenes are extremely important catalysts for the ring closing metathesis of a variety olefins in addition to ring opening metathesis reactions [7–10,45]. Fogg and co-workers have recently shown that tandem ring opening metathesis/hydrogenation reactions can be affected using carefully designed catalysts [45c,d]. The stoichiometric reaction of a

variety of IMes and SIMes complexes has been documented by Grubbs and co-workers during their study of the phosphine exchange behaviour of these complexes [7c]. As the exchange behaviour was commonly studied at temperatures of up to 80 °C, the thermal stability of complexes such as **6** is well documented.

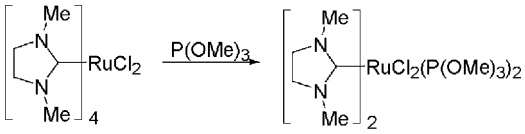
However, during a recent report of new synthetic methods for the synthesis of Ru–NHC complexes, Grubbs and co-workers prepared triazolium-substituted Ru complexes **82** and **83** [7d]. Unlike the IMes and SIMes derivatives, these complexes underwent rapid decomposition to generate the bis phosphine complexes along with protonated triazole **84**, even at room temperature (Eq. (23)). This increased lability precluded their use as catalysts for polymerization or metathesis reactions.



82 R= Ph
83 R= CH=CMe$_2$
84

(23)

Lappert also reported in 1978 that *N*-heterocyclic carbene complex **85** could be displaced by added trimethyl phosphite as shown in Eq. (24) [46]. It may be that the electron accepting properties of trimethyl phosphite increase the stability of complex **86** relative to the more electron rich tetracarbene **85**. Relief of steric strain is also likely a driving force for this reaction.



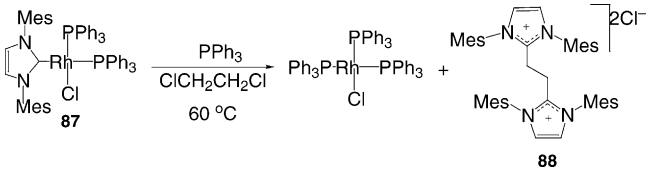
85 **86**

(24)

4.5. Rhodium NHC complexes

During an attempted synthesis of rhodium hydride complexes of NHC's, our group prepared the IMes-substituted rhodium complex **87**. This compound had very different properties compared with Wilkinson's catalyst ($ClRh(PPh_3)_3$), including significantly decreased rates of phosphine exchange. We estimate that the rate of exchange is 10–15 times slower in **87** than in Wilkinson's catalyst [47].

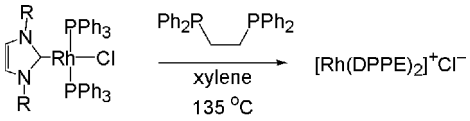
During our NMR studies, we noticed that the samples prepared in $ClCH_2CH_2Cl$ displayed additional signals in the ^{31}P NMR upon cooling, which were attributable to Wilkinson's catalyst (Eq. (25)). The facile exchange of Wilkinson's catalyst with added phosphine at elevated temperatures made its presence undetectable at high temperature.[8] The conversion of **87** to $ClRh(PAr_3)_3$ began even at room temperature, but was significantly faster at 60 °C. The carbene reacts with dichloroethane by a double S_N2 reaction forming **88** and removing the carbene from equilibrium.



87 **88**

(25)

Lappert has also reported the displacement of an *N*-heterocyclic carbene from the coordination sphere of Rh, but using bidentate phosphines [4e]. He showed that the reaction of complexes **89a–c** with bisdiphenylphosphinoethane can be affected at elevated temperatures (refluxing xylene) (Eq. (26)) [4e].



89a, R = Ph
89b,R = *p*-tolyl
89c, R = *p*-anisyl

(26)

5. C–H/C–C activations

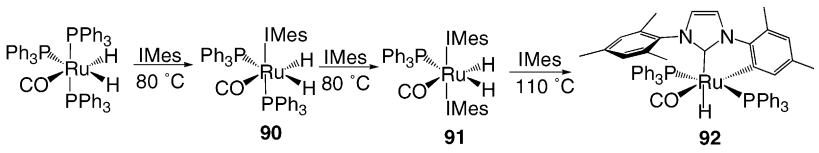
Second to reductive eliminations, the most common mechanism for decomposition of *N*-heterocyclic carbenes reported to date is C–H activation of the substituents on nitrogen. The facility of this reaction can be explained by the increased electron density on the metal as a result of the strongly electron donating carbene and the fact that C–H and C–C bonds are forced into close contact with the metal because of the steric bulk of the NHC. Selected examples of C–H and C–C activations of the NHC ligands follow.

5.1. Ru complexes

During an attempted synthesis of a Ru IMes hydride species, Whittlesey et al. reacted $[Ru(H)_2(PPh_3)_3(CO)]$ with free IMes at 80 °C for 14 days, which yielded the bis NHC-substituted complex **91** (Scheme 8) [48]. Continued heating at 110 °C for 2 days led to production of complex **92** in high yield (96%). In this species, one of the C–C bonds of one of the mesitylene ligands been cleaved and perhaps more remarkably, one IMes ligand has been replaced in the coordination sphere with PPh_3.

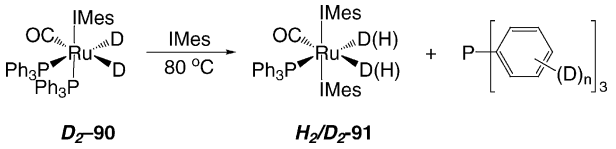
Despite the fact that complex **90** has all the ligands required for the preparation of **92**, its thermolysis in the absence of IMes gave only traces of **92**, implying that the presence of a second, possibly sacrificial IMes ligand is required [48]. Furthermore, although heating **90** at 80 °C in C_6D_6 produces **91** with no incorporation of deuterium, subsequent

[8] Some line broadening in the PPh_3 signals were the only indication of the presence of Wilkinson's.



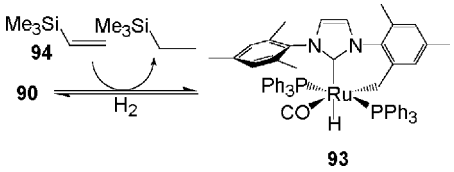
Scheme 8. Displacement and C–C activation promoted by IMes.

treatment at 100 °C gives extensive H–D exchange into all of the species present, including PPh_3. C–H activation of PPh_3 is also observed during the conversion of **90**-D_2 to **91** (Eq. (27)) [48].



(27)

In the presence of a hydrogen acceptor, C–H activation is the predominant pathway, and occurs under much milder conditions. Remarkably, compound **90** undergoes C–H activation at room temperature generating **93** when vinyltrimethylsilane (**94**) is added to the reaction mixture (Eq. (28)) [48].

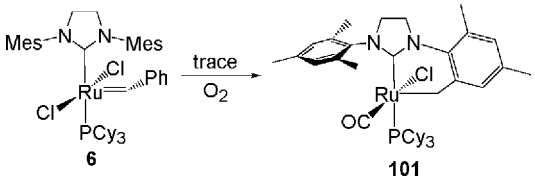


(28)

DFT calculations performed on C–C activation product **92** and C–H activation product **93** suggest that **92** is thermodynamically more stable, lying 7.5 kcal/mol lower in energy than **90** [48]. The CH activation product **93** is 11.3 kcal/mol higher in energy than **90**, explaining why it is only observed in the presence of a hydrogen acceptor.

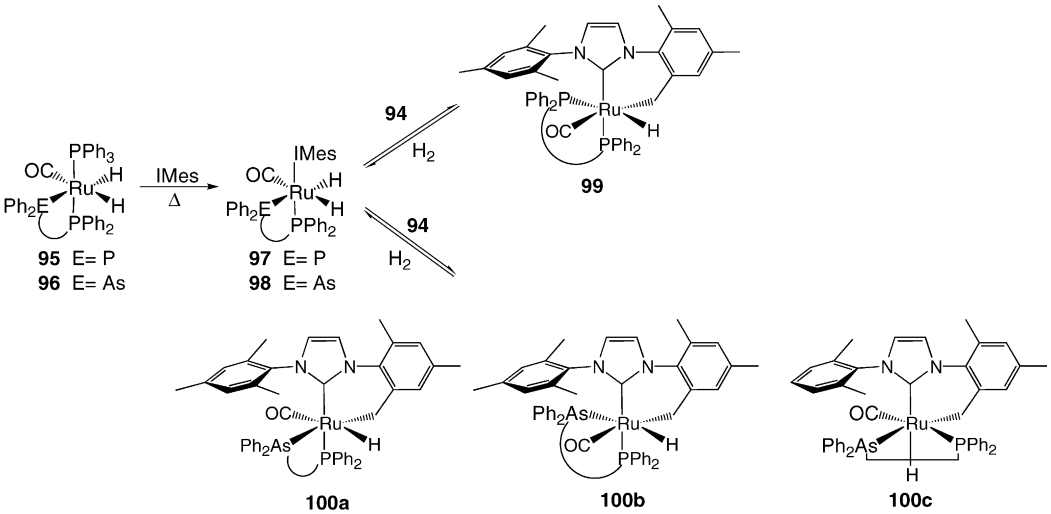
Bidentate phosphines and phosphine/arsine complexes **95** and **96** were also shown to undergo C–H activation when treated with vinyltrimethyl silane (Scheme 9) [49]. Complex **97** was prepared by treatment of **95** with IMes at 100 °C for 3 weeks. At room temperature, **97** does not react with vinyltrimethyl silane, but at 100 °C, the C–H activated complex (**99**) is obtained in quantitative yield along with Me_3SiEt. C–H activation also occurred in the As analog (**96**) giving a mixture of regioisomers as shown in Scheme 8 [49]. Treatment of **99** and **100** with hydrogen regenerates compounds **97** and **98**.

Grubbs and co-workers have also reported the observation of C–H activation in their Grubbs II catalysts such as **6**. During the preparation of compound **6**, traces of air were found to promote C–H oxidative addition and loss of the alkylidene ligand yielding **101** (Eq. (29)) [7d].

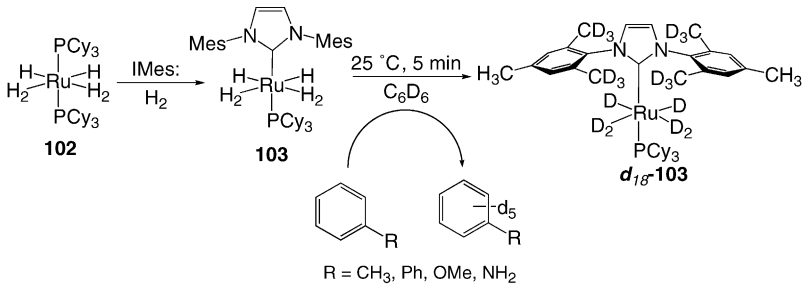


(29)

Lietner and co-workers have shown that compound **103**, which is an NHC analog of Chaudret's Ru complex $[(PCy_3)_2Ru(H)_2(H_2)_2]$ (**102**) [50,51] undergoes reversible C–H activation at the ortho methyl substitutents as evidenced by exchange with d_8-toluene (Scheme 10) [52]. This complex was prepared by reaction of **102** with the free carbene. When **103** was dissolved in d_8-toluene, the signals due



Scheme 9. C–H activation in Ru–NHC complexes.

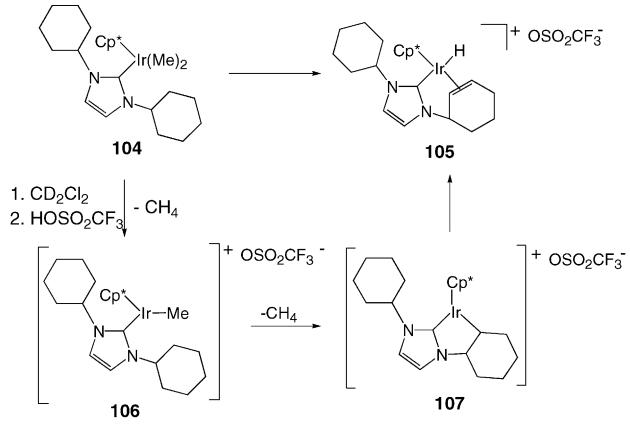


Scheme 10. C–H activation of ortho C–H's in Ru IMes complex.

to the ortho methyl protons were absent after 5 h. Exchange also occurred into the hydrides on Ru. After extended time, exchange was observed into the cyclohexyl ring of the PCy_3 substituent. This is in stark contrast to the behaviour of Chaudret's complex, which is completely stable under the same conditions [52]. Remarkably, in d_6-benzene complex **103** underwent a more rapid exchange such that complete scrambling was observed in less than 5 min, and it even catalyzed the C–H exchange into sp^2 C–H bonds of other aromatic species [52]. Thus when complex **103**, another aromatic species and d_6-benzene were mixed together in a ratio of 1:10:100, deuteration of the aromatic substrate was achieved. Biphenyl, anisole, aniline and toluene all reacted at the aromatic C–H's. Anisole was also slowly deuterated at the CH_3 substituent. Electron deficient aromatics such as chlorobenzene and benzonitrile were not deuterated under these conditions [52].

5.2. Iridium complexes

Herrmann has reported that Ir–NHC complexes such as **104** oxidatively add into the C–H bonds of the nitrogen-substituents ultimately yielding **105** by dehydrogenation of the substituent as shown in Scheme 11 [53]. Compound **104**, obtained by reaction of $[Cp^*IrCl_2]_2$ with 1,3-dicyclohexylimidazolin-2-ylidene followed by treatment with MeMgBr, eliminated methane when treated with triflic acid. The product obtained (**105**) had an unexpectedly short interaction between Ir and the cyclohexyl substituent, and



Scheme 11. C–H activation in Ir–NHC complexes.

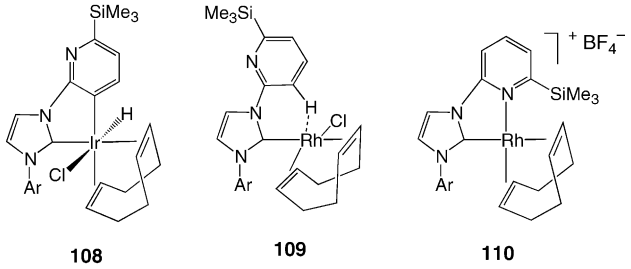
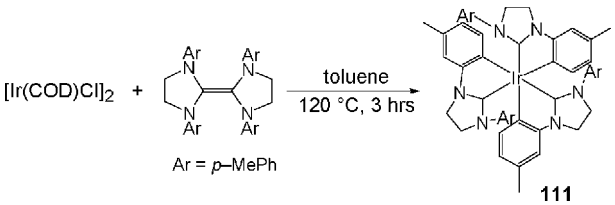


Plate 7. Alternative modes of bonding in Ir and Rh bidentate complexes.

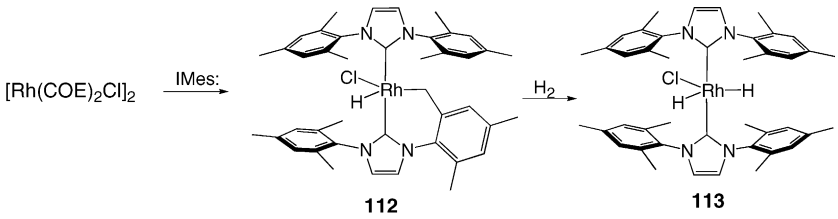
a short C–C bond indicating that it was in fact an olefin [53]. Herrmann proposed that the protolytic elimination of methane yields **106**. Subsequent C–H insertion into the cyclohexyl substituent and loss of methane yields **107**. Finally, β-hydride elimination generates **105**.

Danopoulos has described an example in which C–H activation of a pyridyl C–H in a bidentate ligand is observed [54]. Instead of yielding the expected pyridyl complex, the reaction of $[Ir(COD)Cl]_2$ with one equivalent of 1-[(2-(6-trimethylsilyl)pyridyl)]-3-[(2,6-di-*iso*-propyl)phenyl]imidazol-2-ylidene took place by C–H activation in the pyridine ring to yield compound **108** (Plate 7). In the Rh analog, an interaction between the same C–H and the Rh atom was observed by ^1H NMR spectroscopy and crystallography. Upon removal of the chloride ligand in the Rh complex with silver, the expected NHC/pyridyl complex (**110**) was formed [54].

Lappert has also reported an example of C–H activation in Ir–NHC complexes. Treatment of $[Ir(COD)Cl]_2$ with electron rich tetramine olefins produced NHC complexes in which one *N*-aryl substituent from each carbene has been metalated (Eq. (30)) [55]. Lappert proposes that excess enetetramine acts as a proton acceptor in the generation of **111**. Reaction of this compound with HCl results in protonation of one of the Ir–Ph bonds.



(30)



Scheme 12. C–H activation and reaction of Rh–IMes complex **112**.

5.3. Rhodium complexes

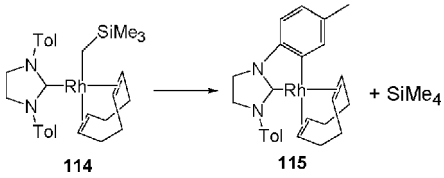
The C–H activation of one of the ortho methyl groups on IMes was reported by Nolan [56a]. Reaction of $[ClRh(COE)_2]_2$ with two equivalents of IMes at room temperature in THF resulted in displacement of the COE ligands, splitting of the dimer, and concomitant C–H activation of one of the methyl groups of IMes as shown in Scheme 12.

This reaction is quite remarkable because of the mild conditions under which it takes place. Hermann previously reported that $[Rh(COD)Cl]_2$ reacts with NHC's to give the simple substitution product with no C–H activation, although in Herrmann's case, the carbene employed did not have a bulk mesityl substituent [57]. Our group has also prepared $[ClRh(IMes)(PPh_3)_2]$ which seems to be stable towards C–H activation despite significant steric hindrance around the metal. The difference may be caused by the presence of two strongly electron donating IMes substituents in **112** which increase the electron density on Rh. The CO stretch of $[ClRh(IMes)_2(CO)]$, formed by treatment of **112** with CO is 1935 cm^{-1} [56a], indicating significant electron density at Rh. The NHC complex $[ClRh(IMes)(PPh_3)CO]$ has a CO stretch at 1944 [58], indicating a decrease in electron density at Rh upon substitution of one IMes with PPh_3.

Regeneration of the IMes ligand in its monodentate form can be affected by treatment of complex **112** with hydrogen, which generates Rh dihydride **113**. Note the relatively unusual trigonal bipyramidyl geometry of the Rh(III) complex, rather than the more common octahedral, which is likely caused by the extreme steric hindrance imposed by the IMes substituents.

Nolan has recently described the reaction of the bis t-butyl substituted carbene with $[Rh(COE)_2Cl]_2$. Depending on solvent, these two species react via simple displacement of an olefin, C–H activation into one of the *t*-butyl substituents, or C–H activation of two *t*-butyl substituents to give a highly unusual four co-ordinate, 14 electron Rh(III) species [56b].

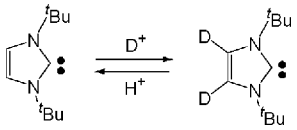
Lappert has also reported the C–H activation of a Rh–NHC complex. In this case, activation of an sp^2 C–H was observed from *p*-tolyl complex **114** [4e]. The C–H activation was followed by elimination of an alkyl group on Rh and the rhodium hydride generating **115** and $SiMe_4$ (Eq. (31)).



(31)

6. Miscellaneous reactions of the bound ligand

The π-bond of unsaturated *N*-heterocyclic carbenes is relatively inert, possibly because of the pseudo aromatic character of these species [59]. Also characteristic of aromatic species, many of the reactions that take place at the double bond ultimately regenerate it. For example, the free carbene is known to react with deuterated solvents in the presence of bases to yield the deuterated version (Eq. (32)) [31]. IMes will also react with halogenated solvents such as CCl_4 to substitute the olefinic hydrogens with chlorine (Eq. (33)) [60,61].



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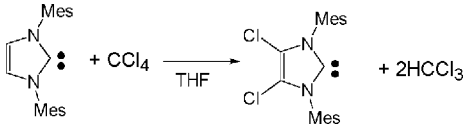
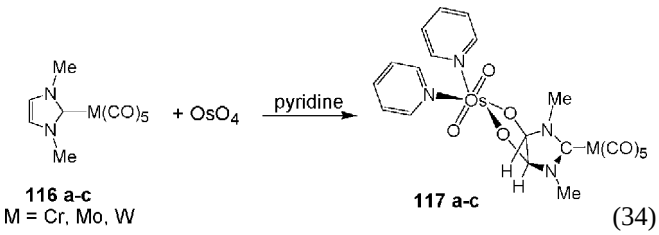


(33)

Transition metal complexes of unsaturated carbenes show similar resistance to reaction at the double bond. For example Ir–IMes species have been described as catalysts for the hydrogenation of olefins [16f–l]. However, without re-isolation of the catalyst at the end of the reaction, it is difficult to say categorically whether or not hydrogenation of the olefin had occurred. Nolan, however, did show that Rh complex **112** can be exposed to hydrogen without reduction of the IMes olefin [56]. During the synthesis of an Ir–NHC complex from an iridium pentahydride, Crabtree and Faller isolated an unusual species in which the imidazolium ring is partially hydrogenated. This species was spontaneously transformed into the fully unsaturated heterocycle (see Section 7.2, Eq. (46)) [62].

The NHC olefin in Cr, Mo and W complexes **116a–c** does undergo dihydroxylation in complexes as shown by Herrmann et al. (Eq. (34)) [63]. Interestingly, this reaction was

used as evidence for the non-aromaticity of the carbene ligands, since the aromaticity of these species has been debated in the literature [59].



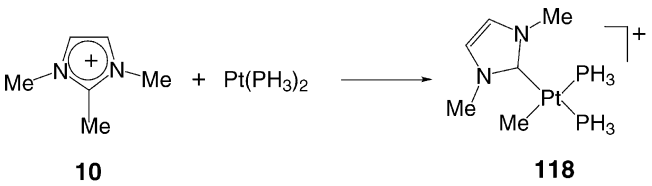
(34)

7. Generation of organometallic complexes by oxidative addition

The reactivity of the imidazolium ion precursor with transition metals can be used to synthesize NHC complexes without prior formation of the free carbene. Care must be taken, however, to ensure that C–H activation occurs in the desired location since several examples of activation in the "wrong" position have been described [62,64]. This reaction can also take place in certain types of ionic liquids leading to the in situ generation of the NHC complex [65].

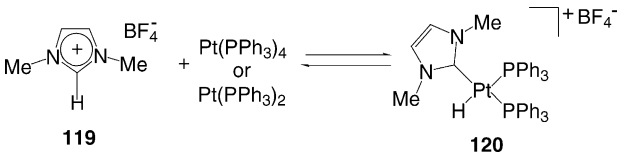
7.1. C–X oxidative addition

Imidazolium salts have been shown to undergo oxidative addition with electron rich d^{10} complexes such as $Pt(PPh_3)_4$ [66,67]. Pt was chosen because oxidative addition is more facile with this metal compared to Pd or Ni. Theoretical calculations indicate that the reaction of 1,2,3-trimethylimidazolium (**10**) with $Pt(PH_3)_2$ is exothermic by at least 13 kcal/mol, and has an activation enthalpy of 27.8 kcal/mol (Eq. (35)). The same process with Pd is slightly endothermic (+3.7 kcal/mol), while $Ni(PH_3)_2$ is exothermic (−11.5 kcal/mol) and takes place with a relatively low barrier (7.1 kcal/mol) [67].



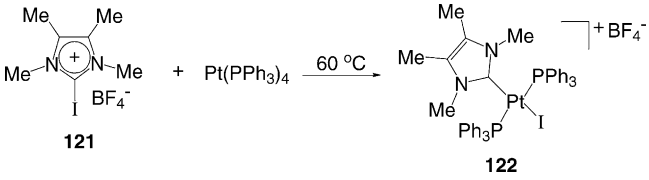
(35)

Although Cavell and co-workers were unable to observe oxidative addition into the C–C bond of **10** experimentally, oxidative addition of DMIY (**119**) and $Pt(PPh_3)_4$ does proceed to 15% conversion (Eq. (36)). At higher temperatures, the ratio of product to starting material did not increase, but the carbene complex **120** was observed to isomerize to the more stable *trans* species [67]. This suggests that the low extent of reaction is in fact due to the presence of an equilibrium between oxidative addition and reductive elimination products under these conditions. Using $Pt(PPh_3)_2$ as the starting material instead of $Pt(PPh_3)_4$, led to a significantly more successful synthesis, since the unfavourable dissociation of two phosphines did not need to be factored into the thermodymanics. Under these conditions, compound **120** was isolated in 63% yield. $Pt(PCy_3)_2$ was also shown to react with DMIY by oxidative addition into the C–H bond [67].



(36)

Calculations performed using $Pd(H_2PCH_2CH_2PH_2)$ analogs predicted that C–H activation would be more facile with chelating phosphines (exothermic by 27.5 kcal/mol and essentially barrierless) [67]. Oxidative addition into the C–Br bond of 2-bromo-1,3-dimethylimidazolium is also predicted to be a facile reaction since no transition structure could be detected, and the Pd(II) complex is 65.1 kcal/mol more stable than the starting material. In accord with this prediction, oxidative addition of 2-iodo tetramethyl-imidazolium tetrafluoroborate (**121**) took place quantitatively with both Pd and Pt complexes (Eqs. (37) and (38)) [67].



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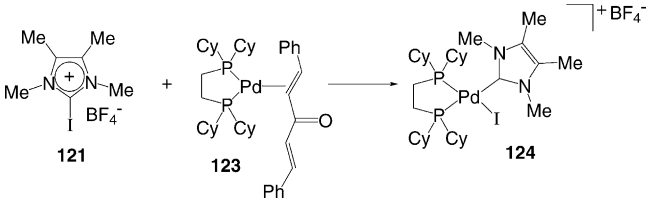
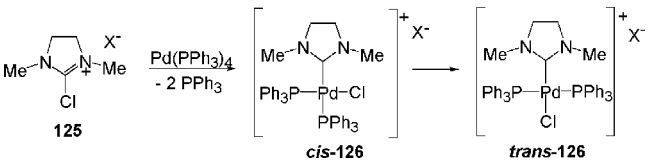


(38)

Fürstner has also shown that oxidative addition of imidazolium chlorides is a facile and convenient method for the preparation of NHC complexes of Pd (Eq. (39)) [68]. 2-Chloro-1,3-dimethylimidazolinium (**125**) [69] is even commercially available. For carbene precursors such as **129** that are not commercially available, Fürstner has described a convenient two-step synthesis (Scheme 13) [68]. The simplicity of this method will undoubtedly lead to its widespread application.



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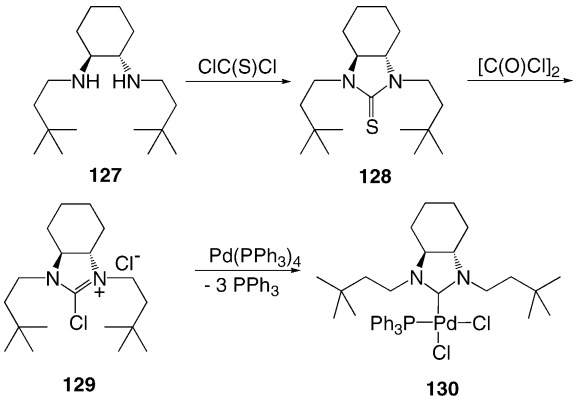
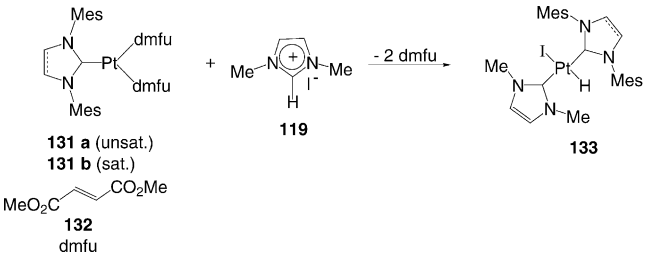


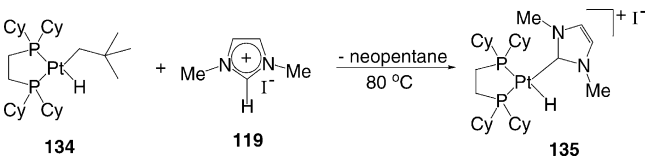
Scheme 13. Fürstner synthesis of Pd–carbene complex by oxidative addition into C–Cl bond.

C–H activation can be affected under quite mild conditions (room temperature 4–7 days) by using a second carbene as the ancillary ligand on Pt (Eq. (40)) [70]. Presumably, the strongly electron donating carbene increases the ability of the Pd complex to undergo oxidative addition. This reaction represents the first preparation of a thermally stable hydridoplatinum(II) bis carbene.



(40)

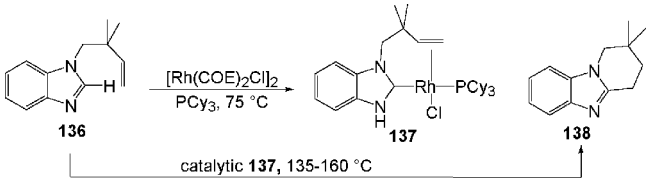
Phosphine ligated complexes can also react cleanly with imidazolium salts if the ligand is sufficiently electron rich to facilitate oxidative addition, and bulky enough to prevent decomposition of the catalyst [70]. The Pt–DCPE complex (**134**) was shown to react with DMIY at 80 °C overnight to give the Pt–carbene hydride **135** (Eq. (41)) [70]. The related Pd complex was previously shown to undergo oxidative addition of imidazolium iodides, but no reaction was observed at ambient temperature with DMIY.



(41)

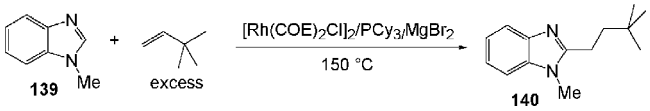
Andrus et al. have isolated Pd–NHC complexes from reaction of saturated carbene precursors with $Pd(OAc)_2$ at high temperature in the absence of base [71]. They propose that the reaction takes place not by a direct oxidative addition, but by complexation of the Pd to the imine, deprotonation by acetate and subsequent dimer formation.

Ellman and Bergman have also demonstrated that oxidative addition can actually be followed by reaction of the Rh–C bond with olefins, and have turned this process into a valuable process for the preparation of heterocycles [72]. During their study of the C–H activation of substrates such as **136** with Rh complexes, Ellman and Bergman isolated compound **137**, which is an unusual Rh–NHC complex in that it has an N–H bond on the heterocyclic ring (Eq. (42)). At elevated temperatures, **137** catalyzes the conversion of **136**–**138**.



(42)

Complex **137** was characterized by spectroscopic methods and X-ray crystallography. Under optimized conditions, the Rh–C bond can be added across olefins intermolecularly as well (Eq. (43)), and coupling reactions can be performed with aryl iodides. A proposed mechanism for the latter reaction is shown in Scheme 14.



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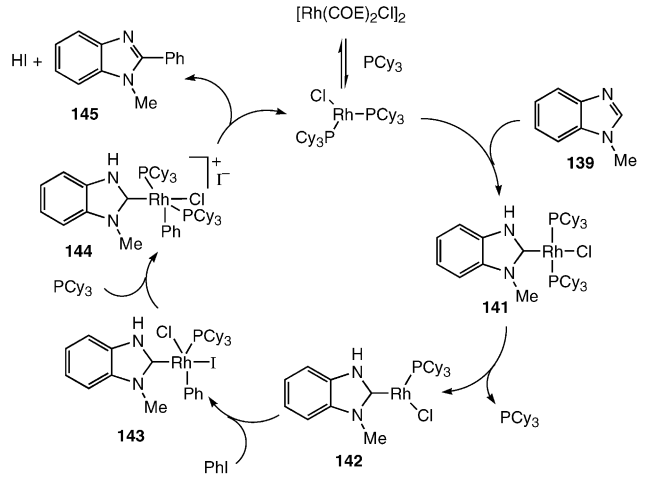
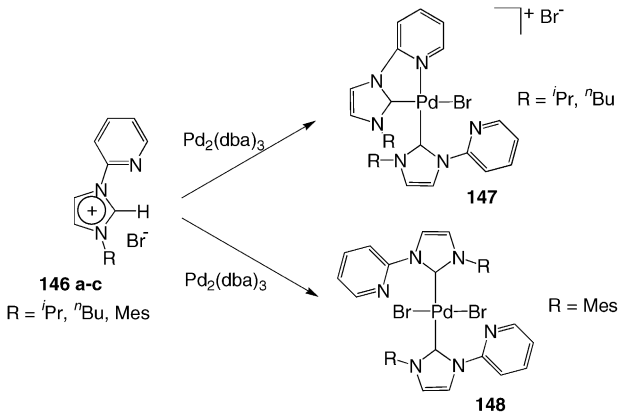


Scheme 14. Proposed mechanism for the C–H activation and functionalization of benzimidazole **139**.



Scheme 15. C–H activation of pyridyl substituted imidazolium salts.

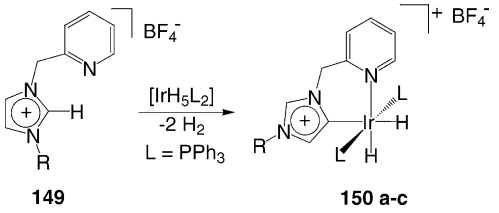
Oxidative addition into the C–H bond of benzimidazole **139** followed by hydride transfer to the imine yields **141**. After dissociation of PCy_3, oxidative addition of PhI takes place. Reductive elimination of HI and the product (**145**) regenerates the catalyst completing the catalytic cycle [72].

The reactivity displayed by the Rh–NHC bond is certainly remarkable considering that these should be inert spectator ligands. Although the proton on the nitrogen in intermediates **141**–**144** changes the situation relative to the other carbenes, the fact that the Rh–NHC bond would participate in additions to olefins and coupling reactions with aromatic iodides is a dramatic illustration of its potential reactivity.

7.2. Oxidative addition in chelated complexes

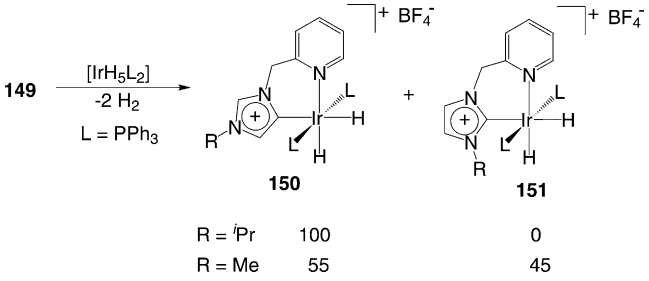
Bidentate ligands are known to be more susceptible to C–H activation than monodentate ligands since the first ligand brings the susceptible C–H bond into close contact with the metal [73]. Crabtree and Faller have described several bidentate systems in which oxidative addition of the C–H bond of imidazolium ions is observed [73]. Thus treatment of pyridyl substituted imidazolium ions **146a**–**c** with $Pd_2(dba)_3$ yields **147** or **148** depending on the bulkiness of the R group: *i*Pr or *n*Bu substituted imidazolium precursors gave cationic Pd complex **147**, while the mesitylene substituent gave the neutral complex **148**. Presumably the steric hindrance imposed by having the carbenes in a cis relationship is too severe when R = mesityl. Regardless of the stoichiometry of the reaction, bis carbene complexes were always isolated (Scheme 15). These complexes were remarkably stable. No decomposition was observed after treatment under an atmosphere of hydrogen for 30 min or treatment with HOAc or heating a $CHCl_3$ solution to 50 °C for 16 h [73a].

Interestingly, the reaction of closely related imidazolium salts with an iridium complex also lead to C–H activation, but in a different position [62a]. Treatment of compound **149** with $[IrH_5(PPh_3)_2]$ resulted in C–H activation not at the expected 2 position, but at carbon 5 to yield compound **150** (Eq. (44)). Despite the fact that calculations suggest the C-2 bound complex should be at least 20 kcal/mol more stable than the C-5 complex, compound **150** did not convert into this species even when heated to 100 °C for 1 h. Heating to 160 °C resulted in decomposition, but no rearrangement to the "normal" C-2 binding mode was observed [62a].



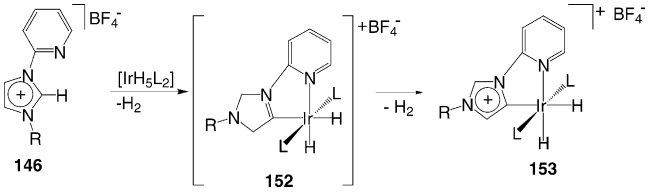
(44)

Crabtree and Faller have since shown that the position of C–H activation is controlled by several factors, including the size of the substituent R, with larger substituents favouring reaction at C-5 [62b]. Thus **149** reacted with Ir to give exclusively the C-5 activated complex when R = *i*Pr, but a 55:45 mixture of C-5 to C-2 is obtained for the less hindered Me case.



(45)

In the one carbon truncated carbene precursor **146**, reaction occurs preferentially on the backside even when R = Me (Eq. (46)). The metal plays a significant effect as well, since the same species (**146**, R = Mes, *i*Pr and *n*Bu) reacted with Pd at C-2 (Scheme 15) [73a].



(46)

Remarkably, when the reaction was stopped at low conversions, an intermediate was observed in which the imidazolium ring was partially hydrogenated (**152**). Rapid loss of hydrogen at room temperature regenerated the aromatic ring. Only the mesityl version was stable enough to permit isolation and structure determination by crystallography. Complex **152** was only observed with the smaller bite-angle species **146**, not with **149** [62b].

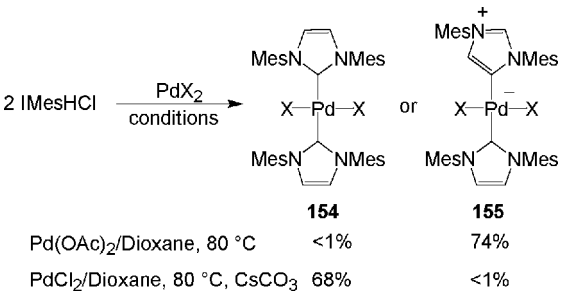
The counterion also affects the position of C–H activation [73b]. With the relatively unhindered methyl-substituted system, the use of Br^- as the counterion yields the expected C-2

activation as the major pathway (91:9). Changing the counterion to SbF_6^- results in a complete switch now favouring the "abnormal" C-4 activation (11:89).

Other multivalent carbenes have beeen reported to form "abnormal" bonds to transition metals including a Cu complex reported by Meyer and co-workers [74a] and an iron complex described by Danopolous et al. [74b].

Recent work by Faller and co-workers [73c] and Lebel et al. [64] indicates that "abnormal" activation may not be limited to multivalent ligands. Faller and co-workers showed that imidazolium salts which have one sterically encumbering group will react with IrH_5L_2 to give activation at C-5 selectively. Analysis of the position of the CO stretch in derived carbonyl complexes led to the conclusion that the C-5 bound ligand was significantly more electron donating than the regular C-2 ligand [73c].

In a related study, Lebel et al. reported that their attempt to prepare complexes of type $Pd(IMes)_2X_2$ gave none of the expected complex (**154**) [64]. What was isolated instead was a mixed complex in which oxidative addition occurred into the C-2 of one IMes and the C-5 position of the other (**155**). By adjusting the reaction conditions, the desired complex could be obtained exclusively. Remarkably, complex **154** in which the two carbene ligands are bound in the expected fashion, is completely inactive for the Suzuki–Miyaura and Mizoroki–Heck coupling reactions, while the zwitterionic compound **155** is highly active. These results are obviously of considerable importance for reactions carried out with in situ generated catalysts [64].



(47)

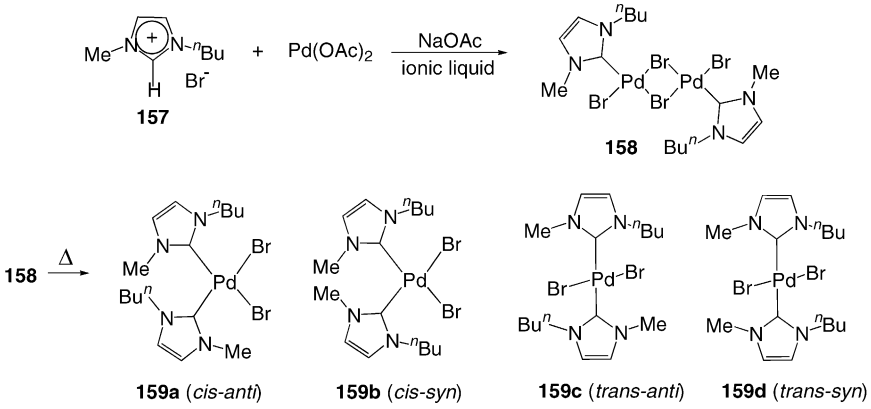
7.3. C–H activation of imidazolium ions in ionic liquids

In order to circumvent the difficulties associated with carbene reductive elimination and subsequent catalyst decomposition, reactions can be carried out in ionic liquids [75,76]. The large excess of the imidazolium ion inhibits reductive elimination, or at least permits catalyst regeneration by oxidative addition.

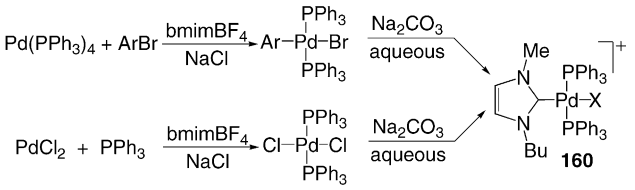
Earle, Seddon [65] and co-workers carried out the Mizoroki–Heck reaction between bromoarenes and butyl acrylate in several ionic liquids. In the case of 1-methyl, 3-butyl-imidazolium tetrafluoroborate ($bmim^+BF_4^-$), Pd black was found to precipitate at 100 °C, and *redissolve* at 140 °C. The authors postulated that the formation of a Pd–NHC complex was responsible for the behaviour of the Pd at higher temperatures.

Xiao was actually able to isolate a Pd–NHC complex from the reaction of $Pd(OAc)_2$ with an ionic liquid, although the counterion proved to be of critical importance [77a]. Xiao observed different reactivity and selectivity for the reaction of iodobenzene with styrene using $bmim^+Br^-$ (**157**) (100% conversion, 99% trans selectivity) and $bmim^+BF_4^-$ (21% conversion, 92% selectivity). To examine the stoichiometric reactivity of the ionic liquid, Xiao et al. reacted two equivalents of $bmim^+Br^-$ with $Pd(OAc)_2$ in THF at 45 °C for 1–2 h. Even under these mild conditions, the Pd–carbene dimer **158** could be isolated in 50% yield [77]. Heating this species converted it into a mixture of biscarbene complexes **159a–d**, which could also be obtained by initial reaction at higher temperature (Scheme 16). Both of these species were observed under catalytic conditions, along with another unidentified product. Although the mixture of **159a–d** catalyzed the Heck reaction in $bmim^+Br^-$, catalytic activity is weak in $bmim^+BF_4^-$, illustrating the importance of the counterion [77].

Welton and co-workers have also demonstrated that Pd complexes can be formed from the reaction of ionic liquids with Pd(II) species. *N*-heterocyclic carbene complexes of palladium were formed by reaction of $Pd(PPh_3)_4$ with



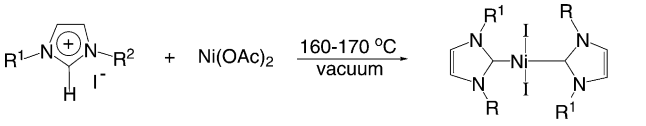
Scheme 16. Preparation of Pd–NHC complexes from reaction of $Pd(OAc)_2$ in ionic liquids.



Scheme 17. Preparation of Pd–NHC complexes from Pd(II) species in ionic liquids.

ArBr in the presence of bmim$^+$BF$_4^-$ and NaCl, or from reaction of $PdCl_2$ with triphenyl phosphine in the presence of $bmimBF_4$ (Scheme 17) [77b].

The use of ionic liquids as solvents for the Ni-catalyzed dimerization of olefins, an important part of the Shell Higher Olefin Process (SHOP) [78], has also been demonstrated [79]. Carbene complexes **161a–d** were shown to be significantly more stable in ionic liquids than in regular solvents (Eq. (48)).



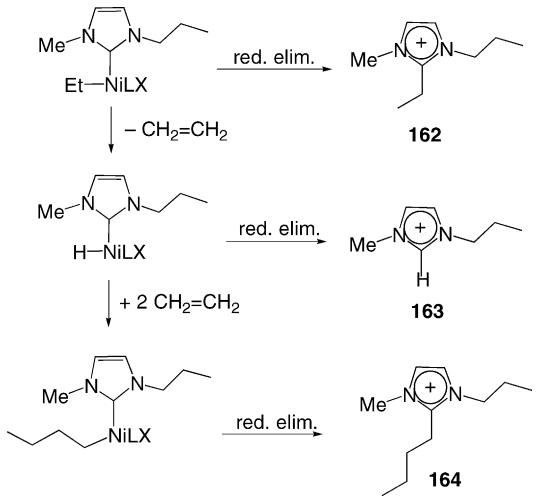
161a R^1 = Me, R^2= ^{n}Pr
161b R^1 = Me, R^2= ^{n}Bu
161c R^1 = Me, R^2= ^{i}Pr
161d R^1 = ^{i}Pr, R^2= ^{i}Pr

(48)

Complex **161a** was reacted with 1-butene (using $AlEt_2Cl$ as the co-catalyst). Upon addition of the diethylaluminum chloride, immediate decomposition of the catalyst to Ni(0) was observed. After reaction for 30 min, the mixture was analyzed and found to contain no butene dimers or oligomers, but imidazolium salts **162–164** were present. Cavell and co-workers proposed that these formed by reductive elimination of nickel hydrides and alkyl species as shown in Scheme 18 [79].

$AlCl_3$ and MAO were also examined as activators, but neither led to the desired butene dimers or oligomers. The only catalyst that was marginally successful was complex **161d**, in which the decomposition of the carbene is somewhat slowed by the increased bulk of the isopropyl substituents. In this case, using $AlEt_2Cl$ as the activator at $-15\,^\circ C$, some dimerization of butene was observed with a TON of $50\,h^{-1}$ [79].

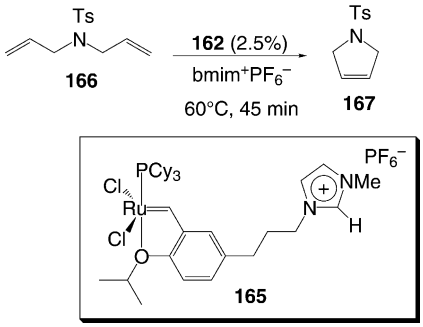
Significantly improved results were obtained when the reaction was performed in ionic liquids such as 1-butyl, 3-methyl imidazolium. Using this species as the solvent, turnover frequencies on the order of 5000–7000 h^{-1} were obtained. Unfortunately, the selectivity for the more desirable branched isomers was low and could not be improved by altering the steric bulk of the *N*-alkyl substituents. The negligible effect of the substituents on the reaction implies that the proposed reductive elimination/oxidative addition is



Scheme 18. Decomposition products of in situ generated Ni–NHC complex.

taking place, exchanging the ligands on the catalyst for the imidazolium ion present as solvent [79].

Mauduit and Guillemin have reported the synthesis of a ruthenium alkylidene (**165**) which is an active catalyst for the ring closing metathesis reaction of **166** in ionic liquids (Eq. (49)) [80]. After extraction of the product, the catalyst/IL mixture can be re-used multiple times without loss of activity. The possibility of carbene formation by intra- or intermolecular reaction of the Ru species with the imidazolium C–H was not discussed by the authors, although this reaction may be unlikely with the higher oxidation state Ru(II) species.



(49)

8. Conclusions

Despite the fact that *N*-heterocyclic carbenes are proving to be valuable alternatives to phosphines as stabilizing ligands for transition metals, these species are prone to certain types of decomposition reactions. For example, C–H activation of the methyl substituents of the commonly employed IMes ligand can occur at quite modest temperatures. As this reaction is often reversible, it may not be observed, but as it results in the transient generation of metal hydrides, it may affect the catalytic activity of the complex. In the presence of olefins, hydrogen transfer can occur making this reaction

irreversible. Activation of the sp^2 C–H bonds on aryl substituents has also been observed in a variety of NHC complexes. Carbon–carbon bond cleavage of adjacent methyl groups has also been observed, and in this case represents an irreversible decomposition pathway.

Simple dissociation of carbene ligands or displacement by incoming ligands has also been observed in Pd, Rh, Ru, Co and Ag complexes. In many (but not all) of these cases, the free ligand undergoes secondary reactions removing it from equilibrium. Dissociative equilibria in phosphine complexes does affect the stability of the complex, but when phosphines are released, they are usually stable towards other reactions such as protonation or reaction with solvent, while this may not be the case for carbenes. Interestingly, although the free carbene is more hydrolytically sensitive than phosphines, carbenes are reportedly more oxidatively stable than free phosphines [81]. Thus oxidation chemistry may be another area where NHC complexes will out-perform phosphine-ligated catalysts. Denk has demonstrated that isolated carbenes do not react with oxygen as one might expect [81], however, in the presence of Cu ureas were observed. It remains to be seen whether other metals can catalyze this reaction, but the application of carbene complexes to oxidation reactions has already begun to be investigated [82].

Perhaps most interestingly, NHC's have also been shown to undergo reactions with adjacent ligands in the coordination sphere of the metal. Migratory insertion and reductive elimination have both been observed, as well as addition of the M–NHC across alkenes. These reactions are intriguing because they illustrate the unique nature of the metal–carbene bond. Although this bond is quite strong, and in general unreactive, it is clear that correlations can be drawn between the reactivity of a metal carbene bond and a simple metal carbon bond. Indeed the bond length and polarity of a metal NHC bond resemble that of a simple metal–carbon bond. Still, there are a few key distinctions. For example, the presence of cis NHC and CO ligands does not lead to migratory insertion and the production of an acylated NHC ligand, at least in the cases examined thus far. The other important point to note is that under catalytic conditions, some of these pathways are not favourable and even complexes that decompose at relatively moderate temperatures can be highly active catalysts under more forcing conditions.

Finally we should also note that although decomposition pathways are available to certain types of carbene complexes, others have been discovered that are significantly more stable than their phosphine analogs. For example, we have found that Rh complexes of the type [Rh(NHC)(PR_3)(Cl)(CO)] can be isolated by silica gel chromatography in air while the all phosphine analog rapidly decomposes. Crabtree and Faller have isolated carbene complexes that can survive treatment with strong acid in air. Herrmann has also reported that the dibromo derivative of Pd–NHC complex **8** can be used for the conversion of methane to methanol under quite forcing conditions. The carbene catalyst survives treatment with concentrated trifluoroacetic acid and Oxone (peroxymonosulfuric acid potassium salt) [83]. This increased stability of these complexes is undoubtedly due to the lower lability of the metal–ligand bond.

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