Ring-Expanded N-Heterocyclic Carbene (reNHC) Complexes: Applications in Transition Metal Catalysis

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Abstract: In the past two decades, NHCs (NHC = N-heterocyclic carbenes) have emerged as one of the most important classes of ligands in transition metal catalysis. Although historically 5-membered carbenes, such as imidazol-2-ylidenes, have been the dominant class of NHC ligands in transition metal catalysis, recently, ring expanded carbenes on 6-, 7-, 8-, 9- and 10-membered ring systems have been shown to provide significant advantages in numerous catalytic reactions embracing various metals, transformations and mechanisms. In this comprehensive review, we provide a survey of the applications of ring-expanded N-heterocyclic carbenes (reNHCs) in transition metal catalysis. Spanning from the initial reports on ring-expanded NHCs through June 2023, the review centers on the types of ring-expanded NHCs, their organometallic complexes and applications in catalytic processes. By delving into the impact of ring-expanded NHC ligands, the review aims to provide the reader with an understanding of the significance of this ligand class and its pivotal role in transition metal catalysis and organometallic chemistry.

Table of Contents

1. Introduction

Transition metal catalysis represents the most powerful approach for the synthesis of molecules in both academic and industrial settings with a myriad of practical applications in the fields of pharmaceutical, agrochemical, materials and fine chemicals industries [1-4]. Transition-metal-catalyzed reactions are highly dependent on ancillary ligands tuning the properties of the metal centers with N-heterocyclic carbenes (NHCs) as one of the most important classes of ligands for transition metal catalysis [5-11]. After the initial studies in catalysis in 1990s, at present, NHC ligand are widely employed as ligands for transition metal catalysis [12-19] as well as for the stabilization of main group elements [20, 21], organocatalysis [22, 23] and materials chemistry [24, 25].

Although at present 5-membered NHCs, such as imidazol-2-ylidenes and imidazolin-2-ylidenes, are the most common class of N-heterocyclic carbenes utilized in organometallic chemistry [12-19], since the beginning of this field, researchers have recognized the importance of other classes of NHC ligands [26, 27]. In particular, ring expanded carbenes on 6-, 7-, 8-, 9- and 10-membered ring systems have gained major interest because of their unique electronic and steric properties [28-30]. These ring-expanded carbenes have been shown to provide significant advantages in numerous catalytic reactions embracing various metals, transformations and mechanisms. From the standpoint of catalysis, ring expansion significantly affects the properties and reactivity of coordinated metals in various chemical transformations. Compared to saturated and unsaturated imidazole-type N-heterocyclic carbenes, ring-expanded NHCs exhibit higher basicity [31] and significantly enhanced σ-donating capabilities (e.g., TEP values using the correlation method: IMes, 2051 cm^{-1}; 6-Mes, 2043 cm^{-1}; 7-Mes, 2043 cm^{-1}). The widened N-C-N angle in ring-expanded NHCs results in the location of the electron lone pair in an orbital with increased p-character. For example, a typical N-C-N angle for five-membered free carbene (IMes) is 101.4° while for a six-membered analog (6-Mes) it is 114.6°. Furthermore, the higher energy of the HOMO orbital occupied by a lone pair causes stronger electron-donating ability of the ligand. Moreover, the presence of additional methylene groups in the backbone contributes to the positive inductive effect of the scaffold. Crucially, ring-expanded NHC are also sterically distinct from their 5-membered counterparts. Steric properties are the key factor in the design of NHC-metal catalysts for various transformations. Ring-expanded NHCs typically show greater steric demand than their 5-membered congeners with identical N-wingtips as a result of the widened N-C-N angle and more flexible backbone. For example, the percent buried volume (%V_{bur}) of five-, six-, and seven-membered NHCs containing 2,6-diisopropylphenyl wingtips are 47.0%, 50.9% and 52.7%, respectively. Furthermore, a larger ring size directs the N-substituents towards the metal center leading to a more effective interaction with the catalytic pocket and an enhanced metal stabilization by blocking two faces of the metal coordination sphere [30,32-34]. Thus, it is not surprising that ring-expanded N-heterocyclic carbene complexes have found wide applications in transition-metal-catalyzed reactions owing to their unique electronic and steric properties. The structures of the most commonly used ring-expanded NHC ligands are shown in **Figure 1A.** The comparative representation of steric (%V_{bur}) and electronic properties (TEP) of the most common NHCs are shown in **Figure 1B**.

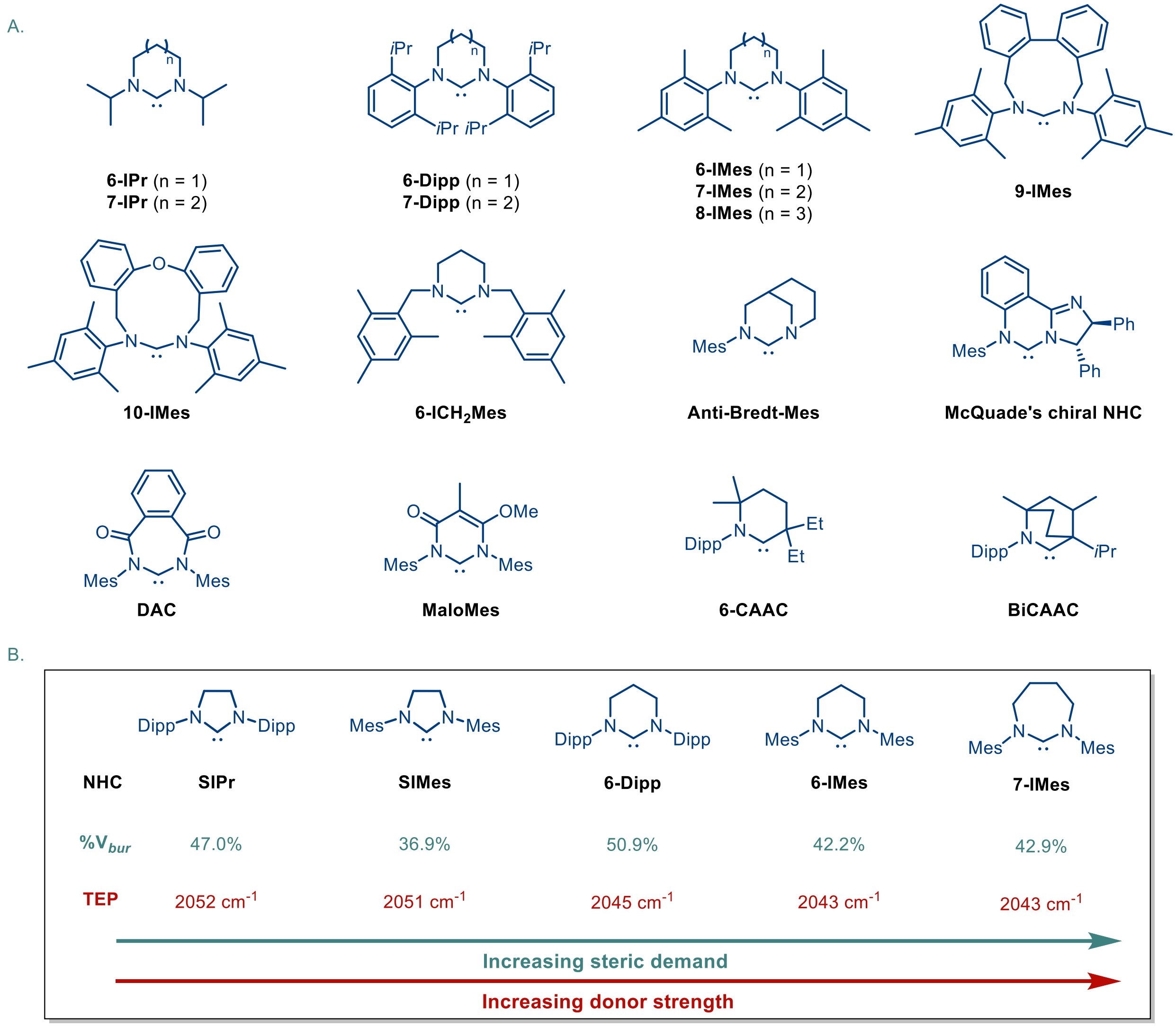


Fig. 1. (a) Structures of the most commonly used ring-expanded NHC ligands. (b) Graphical representation of steric (%V_{bur}) and electronic properties (TEP) of the most common NHCs.

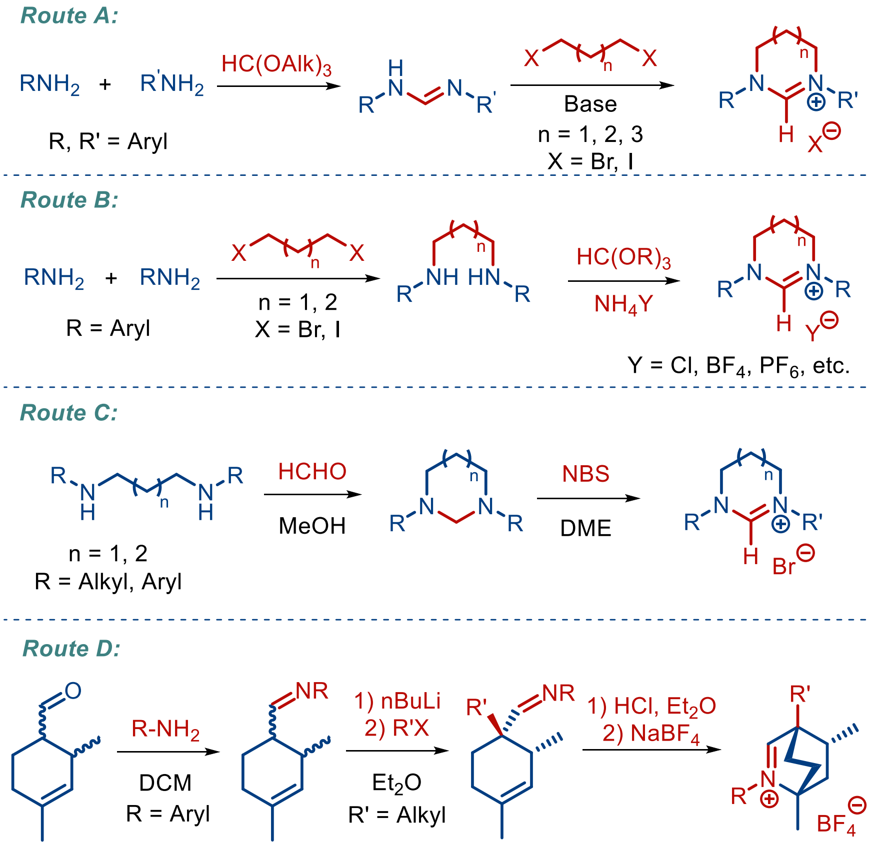
In this comprehensive review, we provide a survey of the applications of ring-expanded N-heterocyclic carbenes (reNHCs) in transition metal catalysis and their corresponding metal complexes. The scope of the review covers the literature from the initial reports on ring-expanded NHCs [35] through June 2023, with a particular emphasis on both organometallic complexes and their applications in catalytic processes. Through a discussion of the role of ring-expanded NHC ligands, the review aims to provide the reader with an understanding of the significance of this ligand class and its pivotal role in transition metal catalysis and organometallic chemistry.

The review is organized based the metal and subsequently categorized by the type of reactions involved. The first section covers the most common methods of the synthesis of ring-expanded NHC ligands and their metal complexes. The catalysis section starts with the reactions catalyzed by group 8 metal-NHC complexes. The review also briefly discusses organometallic complexes of ring-expanded NHCs that at present have not been applied in catalysis. We hope that by discussing ring-expanded metal-NHC complexes with a focus on their structure and reactivity will enable a better understanding of their properties and stimulate an increased use of this powerful class of ligands by the broad research community.

2. Synthesis of Ring-Expanded NHCs

2.1. Synthesis of NHCs Salts

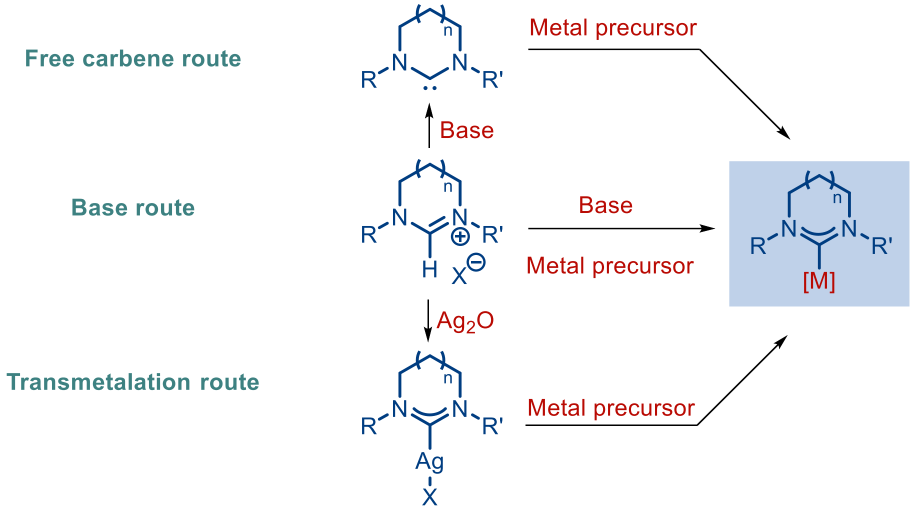
Depending on the type of N-heterocyclic carbenes, there are four most commonly used methods for the synthesis of their precursors as shown in **Scheme 1** [36]. For N-aryl substituted ring-expanded NHC salts, routes A [37-39] and B [35,40-43] can be applied for ring construction. In route A, the first step involves formamidine synthesis from the corresponding anilines and formyl units [37-39]. In particular, this process could be well-controlled, which means that both symmetrical and unsymmetrical formamidines could be obtained depending on the conditions used [44]. Subsequently, dihaloalkanes are used for ring closure under basic conditions. Unlike route A, the key intermediates in route B are diamines prepared from anilines by cross-coupling or through substitution under basic conditions [40-43]. Next, the ring is closed in the presence of a formyl unit and a source of counterion. Route C represents a new method developed by Perillo [45], where hexahydropyrimidines are first prepared from diamines, followed by dehydrogenation using N-halosuccinimides to the corresponding NHC salts [46]. Importantly, the cyclization step in this process could proceed under neutral conditions, in contrast to the other routes. Consequently, this approach is suitable for sensitive substrates [47]. The general method for the synthesis of bicyclic (alkyl)(amino)carbene (BICAAC) precursors is shown as Route D. The synthesis includes the following steps: condensation of aldehyde with the corresponding aniline, deprotonation, and alkylation to afford imines, which after protonation and anion exchange furnish iminium salts. The method can also be applied for the synthesis of cyclic (alkyl)(amino)carbenes (CAACs) [48]. Notably, at present, there is no universal method available for the synthesis of ring-expanded NHC precursors. Various methods are necessary for different NHC salts, depending on the ring size, backbone and N-substitution.



Scheme 1. General methods for the synthesis of ring-expanded NHC precursors.

2.2. Synthesis of NHC Metal Complexes

Various approaches have been used for the preparation of the ring-expanded NHC metal complexes from the corresponding precursors with the three most commonly used methods shown in **Scheme 2** [49]. The free carbene route involves deprotonation of the NHC salts using strong bases to form carbenes that are added to metal precursors or trapped with metal precursors in situ [47b, 50]. It is also worth emphasizing the importance of the counterion present in the starting salt. For example, the exchange of the anion from Br^- to BF_4^- results in a weakening of the hydrogen bonding interactions of the NCHN proton with the anion, where an upfield shift is observed (e.g., for 7-Dipp·HI 7.40 ppm vs. 7.29 ppm for 7-Dipp·HBF_4). This has a direct impact on the carbene generation and the choice of base used. Another approach is the two-step silver transmetalation process, where the corresponding silver complexes are formed in the facile reaction of NHC salts with silver(I) oxide [38, 39]. The second step involves transfer of the ring-expanded Ag-NHC to the desired transition metal. Furthermore, the weak base approach [51a] can be successfully used for the synthesis of ring-expanded NHC-metal complexes. Cazin and co-workers reported the synthesis of ring-expanded NHC-copper complexes with a mild inorganic base under microwave irradiation [51b]. An alternative weak base route has been reported by Jazzar and Bertrand for the in situ metalation of BiCAACs with copper [52]. However, this protocol has not yet been applied for the synthesis of other ring-expanded NHC-metal complexes.



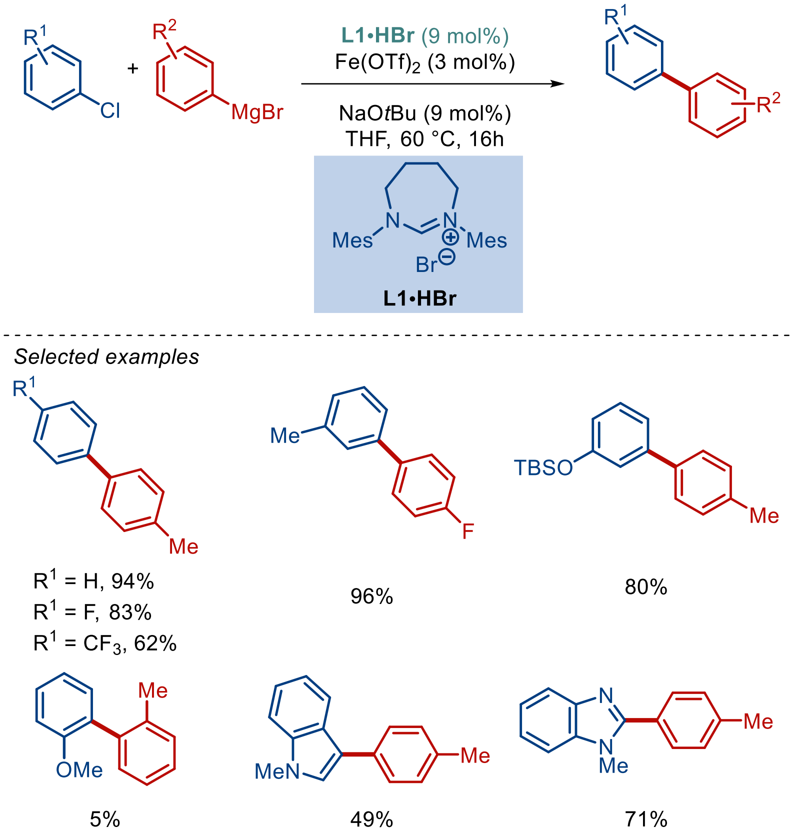
Scheme 2. Synthesis of ring-expanded NHC-metal complexes.

3. Ring-Expanded Iron-NHC Complexes

Several examples of ring-expanded N-heterocyclic carbene iron complexes have been described in the literature. These compounds have found application in various reactions catalyzed by iron, including cross-coupling [44], homocoupling [53], hydrosilylation [54] and polymerization [55].

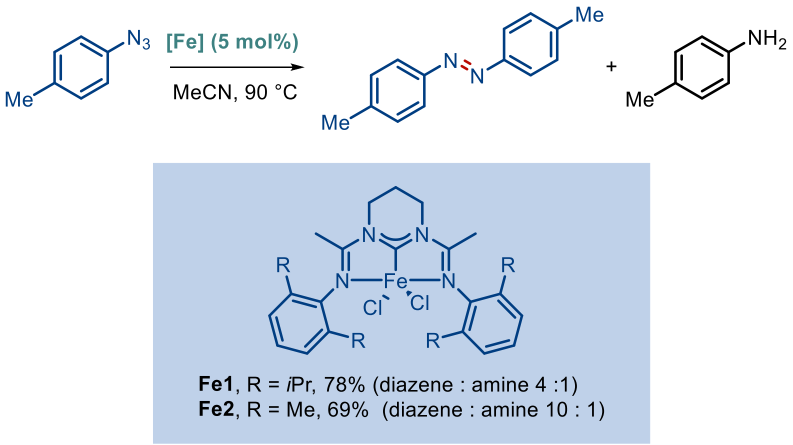
3.1 Fe-NHC Catalyzed Coupling Reactions

In 2018, Huynh and co-workers reported an interesting iron-catalyzed Kumda-Tamao-Corriu aryl-aryl coupling of aryl chlorides using $Fe(OTf)_2$ and 7-membered **Mes L1** as a ligand (**Scheme 3**) [44]. The authors comprehensively screened various ring-expanded NHCs with systems spanning from 6- to 8-membered rings in conjunction with the steric effect of N-wingtips (Dipp, Mes, Ph), including N-symmetrical and N-unsymmetrical ligands. Importantly, they found that steric hindrance of both the ring and the N-substituent had a significant effect on the reaction outcome, whereas 7-Mes was optimal in terms of the steric impact. For catalytic performance, the steric hindrance of N-substituent should decrease with increasing ring size. Furthermore, they found that the counteranion of the NHC salt had a considerable effect on the yield, where halides gave better results than tetrafluoroborate salts.



Scheme 3. Ring-expanded NHC-Fe catalyzed Kumada-Tamao-Corriu coupling reported by Huynh in 2018.

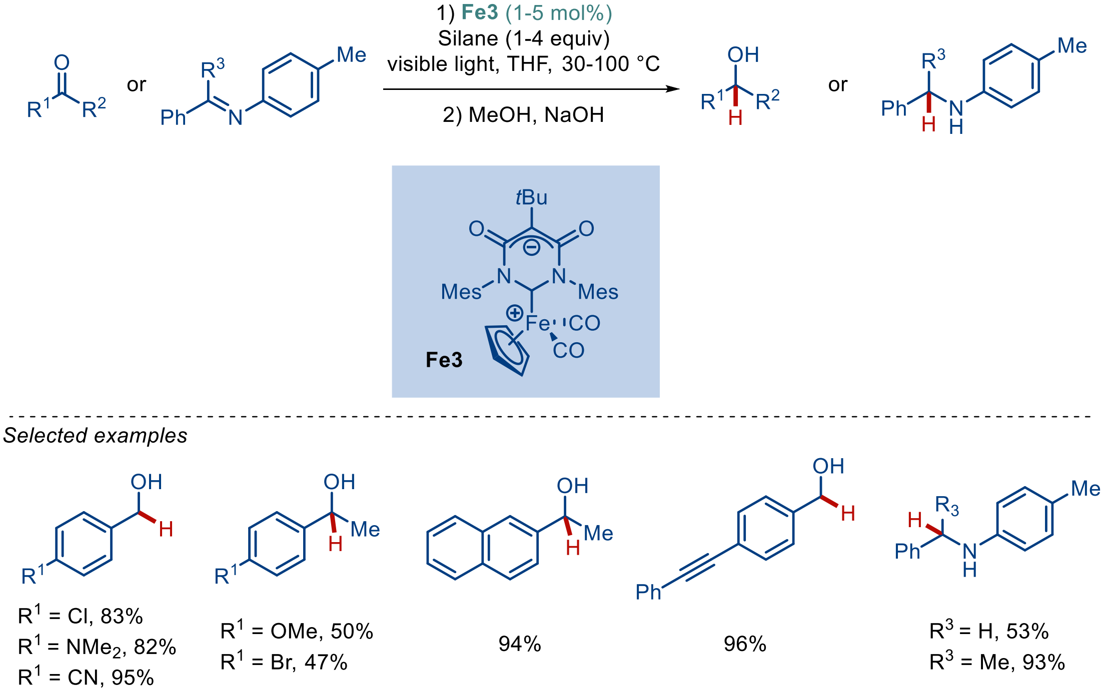
The homocoupling of aryl azides catalyzed by bis(amidinato)-NHC iron(II) complexes **Fe1** and **Fe2** was reported by Byers and co-workers in 2015 (**Scheme 4**) [53]. Complex **Fe1** was first synthesized and characterized in 2012 as an analogue of the iron bis(imino)pyridine complex [56]. The diazene product was formed as a result of the reaction between a high formal oxidative state iron-nitrene intermediate and azide. The authors proposed that a decrease of steric hindrance results in an improvement of catalytic efficiency, which was proved by kinetic measurements with k_{obs} for **Fe2** five times higher than that for **Fe1**. High selectivity for the formation of the diazene product was observed using **Fe2** due to a steric effect.



Scheme 4. Ring-expanded NHC-Fe catalyzed homocoupling of aryl azides reported by Byers in 2015.

3.2 Fe-NHC Catalyzed Hydrosilylation Reactions

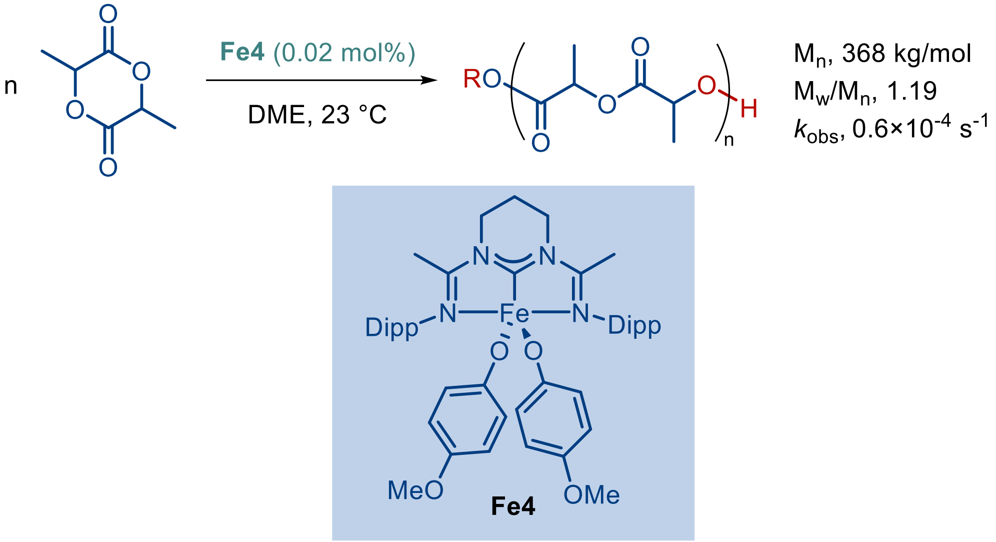
In 2013, Lugan and co-workers reported the zwitterionic Fe-NHC complex **Fe3** for the catalytic hydrosilylation of aldehydes, ketones and imines (**Scheme 5**) [54]. Mechanistically, complex **Fe3** is a saturated 18e complex that is activated by CO loss under visible light irradiation. The catalytic reactivity of this precatalyst was found to be sensitive to acid since protonation of the backbone was possible in the presence of traces of acid. Importantly, this catalyst is compatible with unsaturated groups such as nitriles and alkynes and good chemoselectivity in these cases was observed. The hydrosilylation of ketones required higher temperatures (70 °C) than aldehydes, affording the products in moderate to good yields. Ketimines and aldimines could also be hydrosilylated, although a higher catalyst loading (5 mol%) was required.



Scheme 5. Hydrosilylation reactions catalyzed by ring-expanded NHC-Fe reported by Lugan in 2013.

3.3 Fe-NHC Catalyzed Polymerization Reactions

In 2014, Byers et al. reported the controlled polymerization of (*rac*)-lactide using a bis(amidinato)-NHC iron(II) bis(alkoxide) complex **Fe4** (**Scheme 6**) [55]. Higher molecular weight polymers (M_n > 360 kg/mol, M_w/M_n = 1.19) were observed at low catalyst loading (0.02 mol%) and in a shorter period of time than when using the analogous bis(amino)pyridine iron complex due to the stronger σ-donating ability of NHC ancillary ligands compared to pyridines. Their mechanistic investigations revealed that a decrease in initiation rates and an increase in propagation rates contributed to the above results.



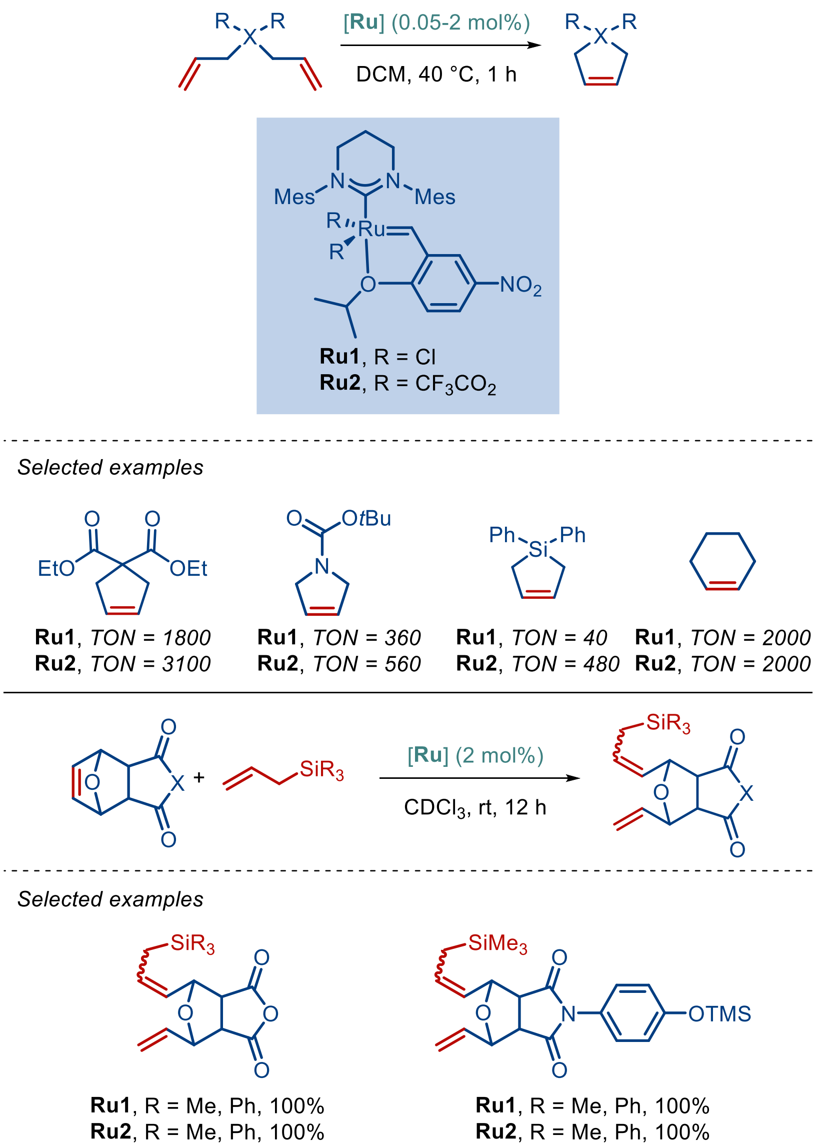
Scheme 6. Ring-expanded NHC-Fe catalyzed polymerization reactions reported by Byers in 2014.

4. Ring-Expanded Ruthenium NHC Complexes

Ring-expanded ruthenium NHC complexes have distinct properties and have been widely used for olefin metathesis [57-65], C-H arylation [66, 67], hydrogenation [68], allylic substitution [69], polymerization [70-73] and acylation reactions [74]. In select reactions, the use of ring-expanded NHC afforded better results than in the case of their five-membered counterparts.

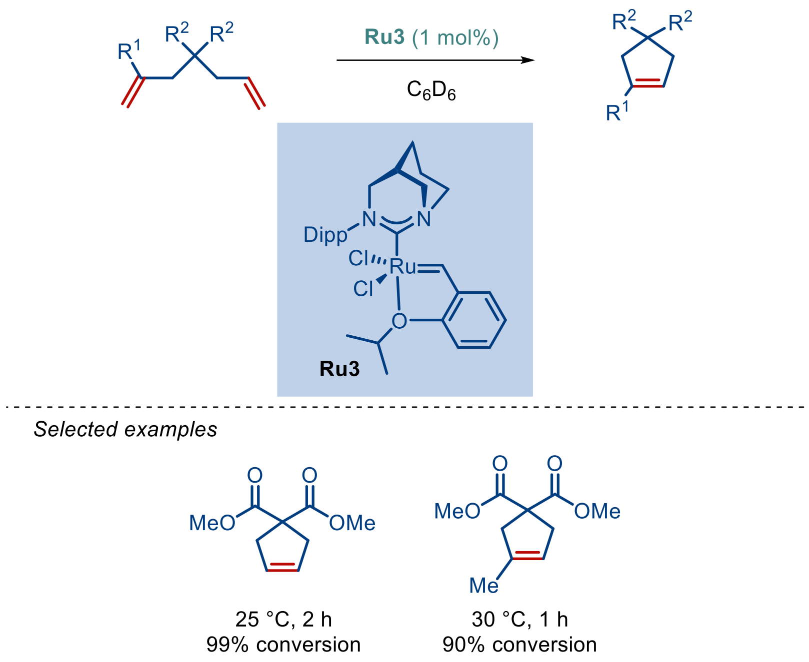
4.1 Ru-NHC Catalyzed Olefin Metathesis Reactions

In 2004, Buchmeiser and co-workers reported two highly active ruthenium catalysts **Ru1** and **Ru2** on the six-membered NHC 6-Mes ligand for olefin ring-closing metathesis (RCM) and ring-opening cross-metathesis (ROCM) (**Scheme 7**) [57]. Turnover numbers (TONs) of up to 1,800 and 3,100 were determined for the catalysts **Ru1** and **Ru2**, respectively. In most cases, complex **Ru2** showed higher catalytic activity than **Ru1** during ring-closing metathesis of diethyl diallylmalonate. Furthermore, these complexes showed remarkable efficiency in ring-opening cross-metathesis. Quantitative yields were observed for both **Ru1** and **Ru2** complexes in the ROCM of 7-oxanorborn-5-ene derivatives at room temperature at 2 mol% catalyst loading.



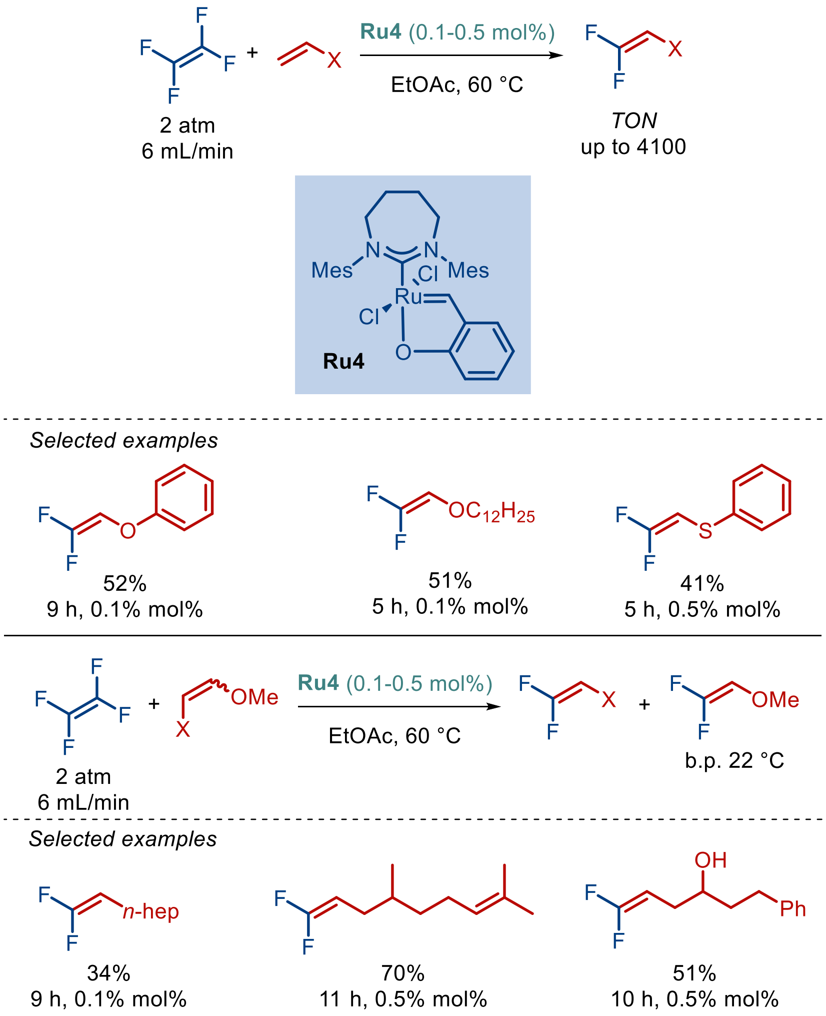
Scheme 7. Ring-expanded NHC-Ru catalyzed olefin metathesis reactions reported by Buchmeiser in 2004.

Subsequently, Bertrand et al. reported ring-closing metathesis catalyzed by ruthenium complex **Ru3** supported by an anti-Bredt-type ring-expanded NHC in 2016 (**Scheme 8**) [58]. Complex **Ru3** was found to show higher reactivity in diethyl dialkylmalonate RCM than its congeners, including 6-membered NHC, CAAC and DAC-based catalysts. Furthermore, the complex **Ru3** was capable of catalyzing the formation of a trisubstituted olefin. However, **Ru3** did not show catalytic reactivity in the synthesis of tetrasubstituted olefins, which is considered a challenging transformation that is achieved only by a limited number of catalysts.



Scheme 8. Ring-expanded anti-Bredt-NHC-Ru catalyzed olefin metathesis reported by Bertrand in 2016.

In 2021, Nozaki and co-workers reported the cross-metathesis of tetrafluoroethylene (TFE) and vinyl ethers catalyzed by complex **Ru4** (**Scheme 9**) [59]. Valuable difluoroalkenes were produced with high efficiency (TON up to 4,100) using a continuous-flow system and a 7-membered NHC as ligand. TFE was readily engaged in reactions with a diverse array of terminal and internal olefins, yielding the olefin metathesis products in good to high yields.



Scheme 9. Ring-expanded NHC-Ru catalyzed cross-metathesis of tetrafluoroethylene reported by Nozaki in 2021.

The proposed mechanism of the cross-metathesis of tetrafluoroethylene catalyzed by the ring-expanded NHC-Ru complex **Ru4** is shown in **Figure 2** [59]. First, the alkylideneruthenium complex **A** coordinates to TFE, leading to an intermediate **B**. Subsequently, this intermediate undergoes a cycloaddition to ruthenacycle **C**, followed by elimination of the difluoroalkene. This elimination reaction results in the formation of difluoromethylideneruthenium complex **E**, which exists in equilibrium with the chloro-bridged diruthenium complex **E'**. Next, the olefin coordinates with either complex **E** or **E'**, resulting in the formation of intermediate **F** and ruthenacycle **G**. Subsequently, complex **A** is regenerated by releasing 1,1-difluoroethene. It has been found that ring expanded NHC was able to destabilize the difluorocarbene intermediate, resulting in a lower energy barrier from intermediate **G** to intermediate **H**.

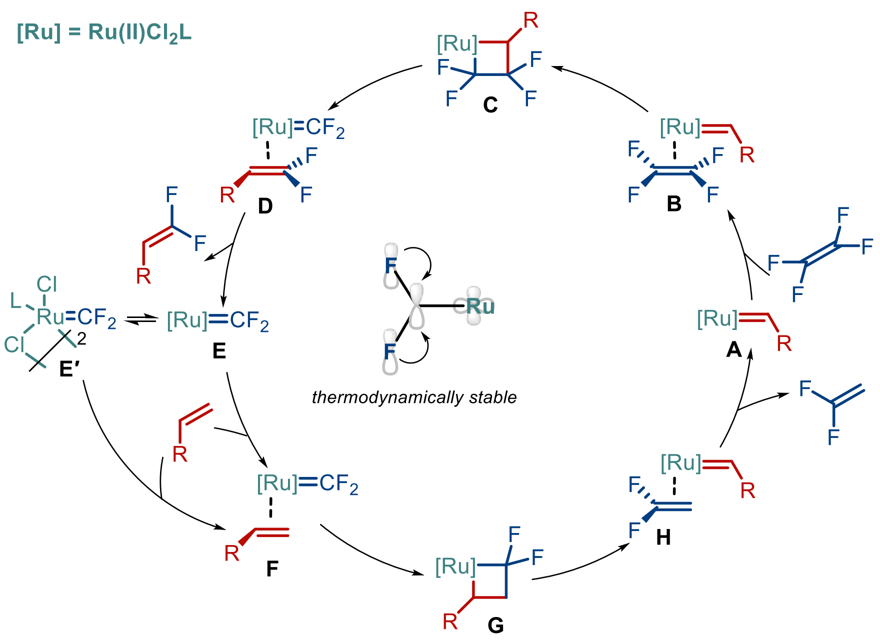
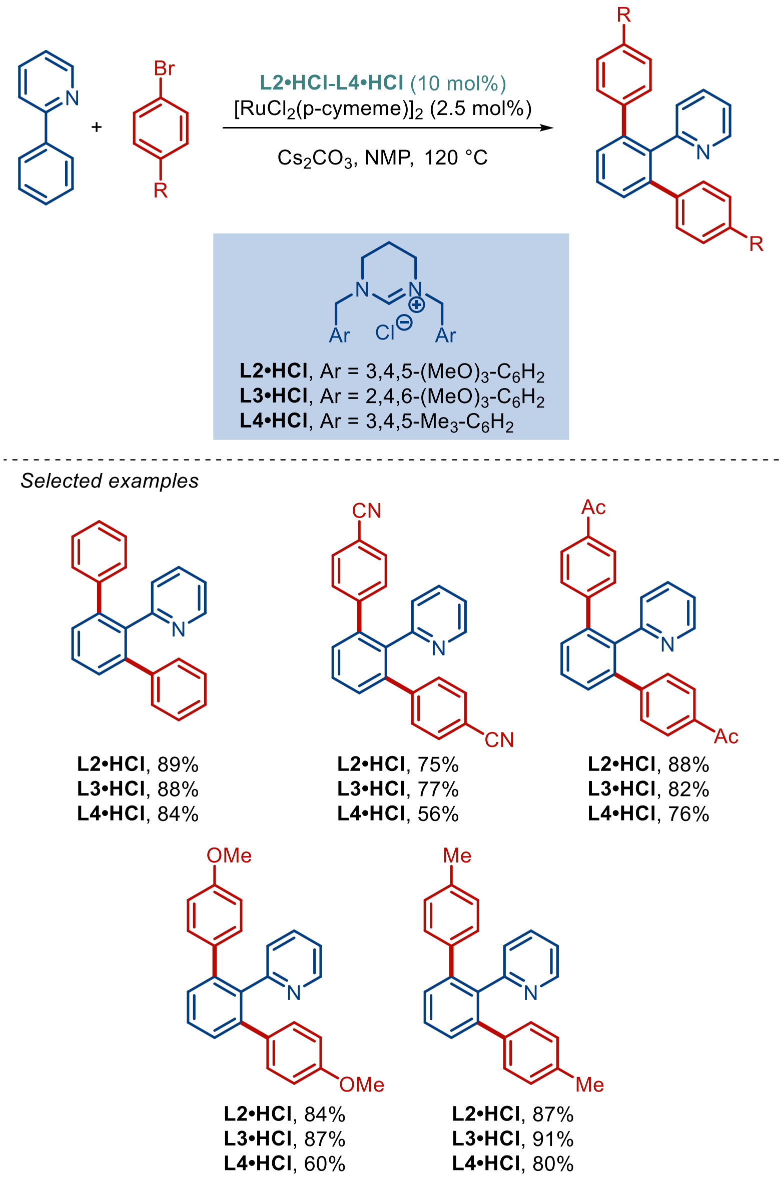


Fig. 2. Mechanism of tetrafluoroethylene cross-metathesis catalyzed by **Ru4**.

Additional examples of olefin metathesis catalyzed by ring-expanded NHC-Ru complexes are included in polymerization reactions (part 4.5) as reported by Grubbs [60, 61], Buchmeiser [62], Bielawski [63], Togni [64], and Wilhelm [65].

4.2 Ru-NHC Catalyzed C-H Activation/Arylation Reactions

In 2008, Dixneuf and co-workers reported 6-membered ring NHCs for the double arylation of 2-pyridylbenzene in the presence of $[RuCl_2(p\text{-cymene})]_2$ and carbonate salts (**Scheme 10**) [66]. The catalytic species, Ru-NHC complexes, were formed in situ by the reaction of pyrimidinium salts, $[RuCl_2(p\text{-cymene})]_2$ and Cs_2CO_3. Various *ortho*-diarylated products were obtained in high yields despite differences in electronic properties of aryl bromide substrates, which excluded the electrophilic substitution pathway.



Scheme 10. C-H activation/arylation catalyzed by ring-expanded NHC-Ru reported by Dixneuf in 2008.

A possible mechanism for this C-H arylation is shown in **Figure 3** [66]. This reaction proceeds by the orthometalation of 2-phenylpyridine *via* base assisted deprotonation, as proposed on the basis of DFT calculations. Next, a reversible oxidative addition of aryl bromide gives the Ru(IV) intermediate. Subsequently, reductive elimination releases the arylated product and regenerates the catalyst.

Burke and co-workers reported a related study on Ru-catalyzed asymmetric arylation of *N*-tosylarylaldimines using a chiral seven-membered NHC as a ligand. The authors used $(PhBO)_3$ as the phenyl transfer reagent, commercial ruthenium dimer as the precatalyst, silver salt (AgOTf) as an additive, and the NHC precursor to form the active carbene complex. In the case of electron-rich substrates high enantioselectivities (72 and 80 % *ee*) were observed [67].

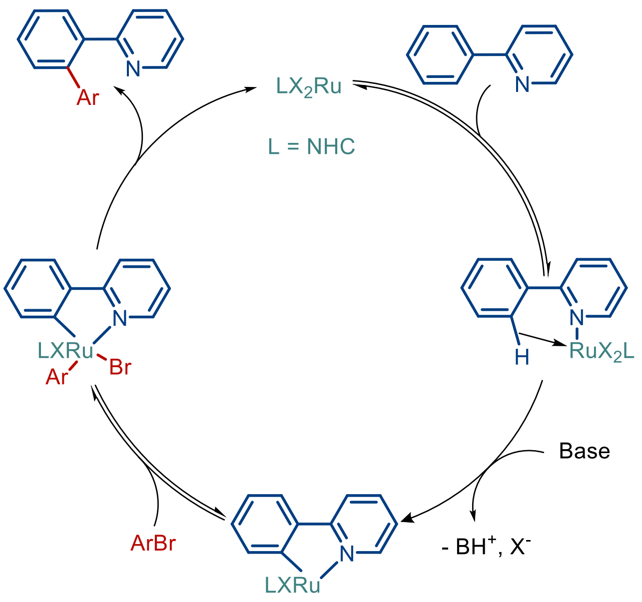
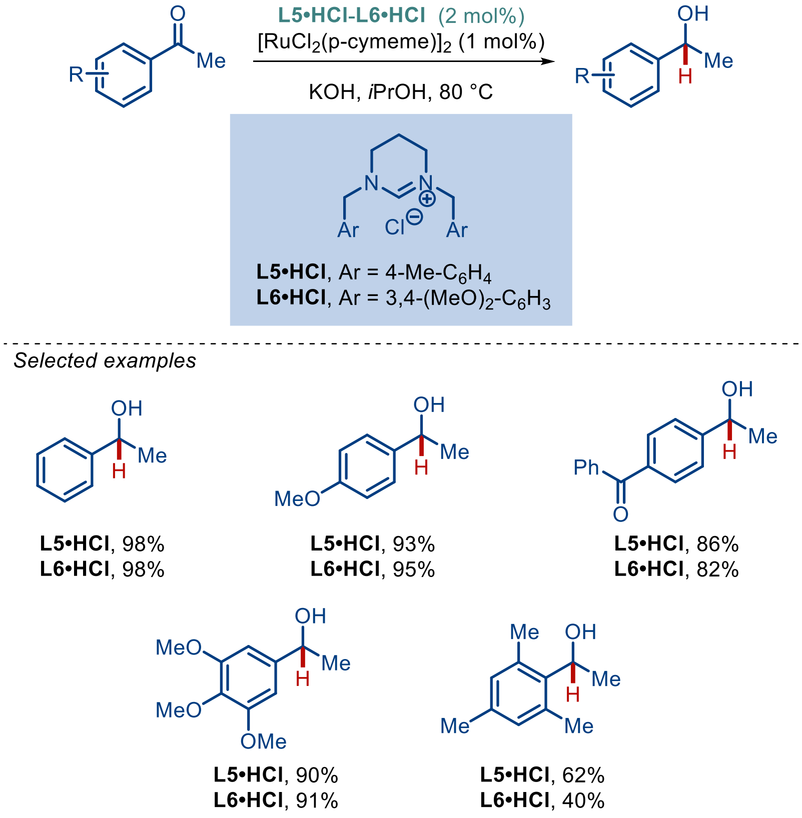


Fig. 3. Mechanism for ring-expanded NHC-Ru catalyzed C-H activation/arylation reactions.

4.3 Ru-NHC Catalyzed Hydrogenation Reactions

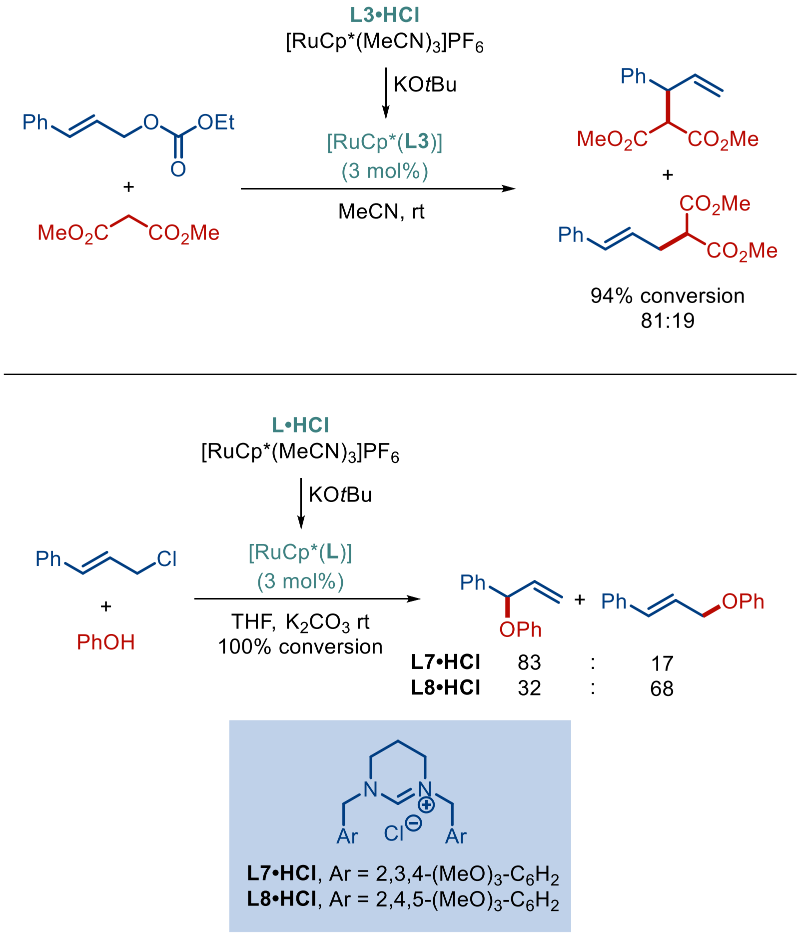
In 2015, Özdemir et al. reported Ru-NHC catalyzed hydrogenation of ketones using ring-expanded NHCs in the presence of *i*PrOH as a hydrogen source (**Scheme 11**) [68]. Under optimized reaction conditions with [RuCl$_2$(*p*-cymene)]$_2$ and tetrahydropyrimidinium salts **L5·HCl** and **L6·HCl**, acetophenone derivatives were reduced to the corresponding alcohols in good to excellent yields. The NHC salt **L5·HCl** was found to be the most reactive precursor for hydrogen transfer to ketones, while **L6·HCl** gave similar yields for most substrates tested. The yields decreased when substrates with bulky substituents at the *ortho* positions of the aromatic ring were used.



Scheme 11. Hydrogenation of ketones to secondary alcohols in the presence of *i*PrOH as a hydrogen source catalyzed by ring-expanded NHC-Ru reported by Özdemir in 2015.

4.4 Ru-NHC Catalyzed Allylic Substitution Reactions

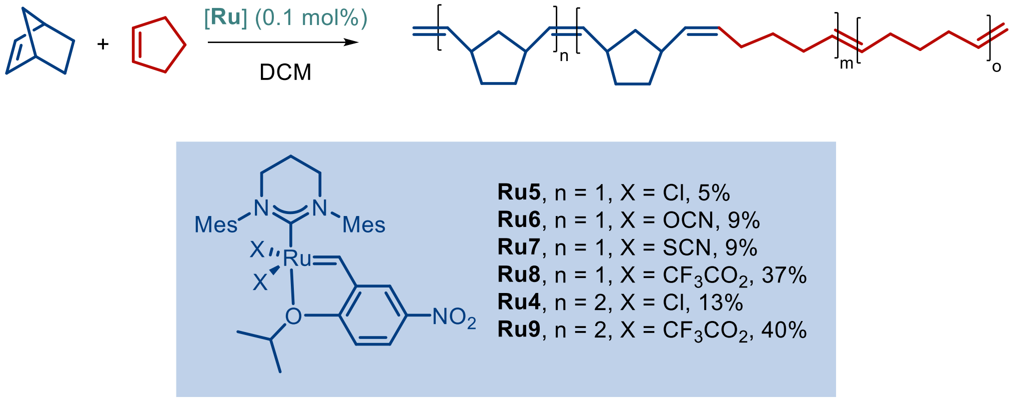
In 2008 Bruneau and co-workers reported allylic substitution catalyzed by air-sensitive [RuCp*(NHC)] complexes obtained from ring-expanded N-benzylic-3,4,5,6-tetrahydropyrimidinium salts **L3·HCl**, **L7·HCl**, and **L8·HCl**, $[RuCp^*(MeCN)_3]PF_6$, and KO*t*Bu (**Scheme 12**) [69]. It should be noted that the above complexes were not fully characterized and in situ generation was used. The catalyst formed from **L3·HCl** was the most effective system in allylic alkylation of cinnamyl carbonate and 94% conversion was observed at room temperature conditions at 3 mol% catalyst loading. The branched isomer was favored with a branched/linear ratio of 89:11. Interestingly, catalyst systems derived from **L7·HCl**, and **L8·HCl** were more reactive in allylic etherification of cinnamyl chloride, where both catalysts led to full conversions after 16 h. The branched isomer was formed as the main product using **L7** as ligand, while an intriguing regioselectivity with the linear product favored with **L8** was observed.



Scheme 12. Allylic substitution catalyzed by ring-expanded NHC-Ru reported by Bruneau in 2008.

4.5 Ru-NHC Catalyzed Polymerization Reactions

In 2011, Buchmeiser and co-workers investigated a series of ruthenium complexes **Ru4-Ru9** supported by the ring-expanded NHC 6-Mes for the catalytic copolymerization of norbornene (NBE) with cyclopentene (CPE) and *cis*-cyclooctene (COE) (**Scheme 13**) [70]. Their studies determined that the pseudohalide ligands have a large effect on the ratio of the alternating diads, namely poly(NBE-alt-CPE)$_n$ and poly(NBE-alt-COE)$_n$, respectively. The authors observed that the ring size of the NHC had a comparatively lower effect on the reaction outcome. In the alternating copolymerization of NBE with CPE, the highest content of the alternating copolymer with ring-expanded NHC was achieved using complex **Ru9** with electron-withdrawing CF_3CO_2 ligand. Nonliving polymerization behavior was identified with the M_n values in the range of 3,000-4,000.



Scheme 13. Ring-expanded NHC-Ru catalyzed polymerization reported by Buchmeiser in 2011.

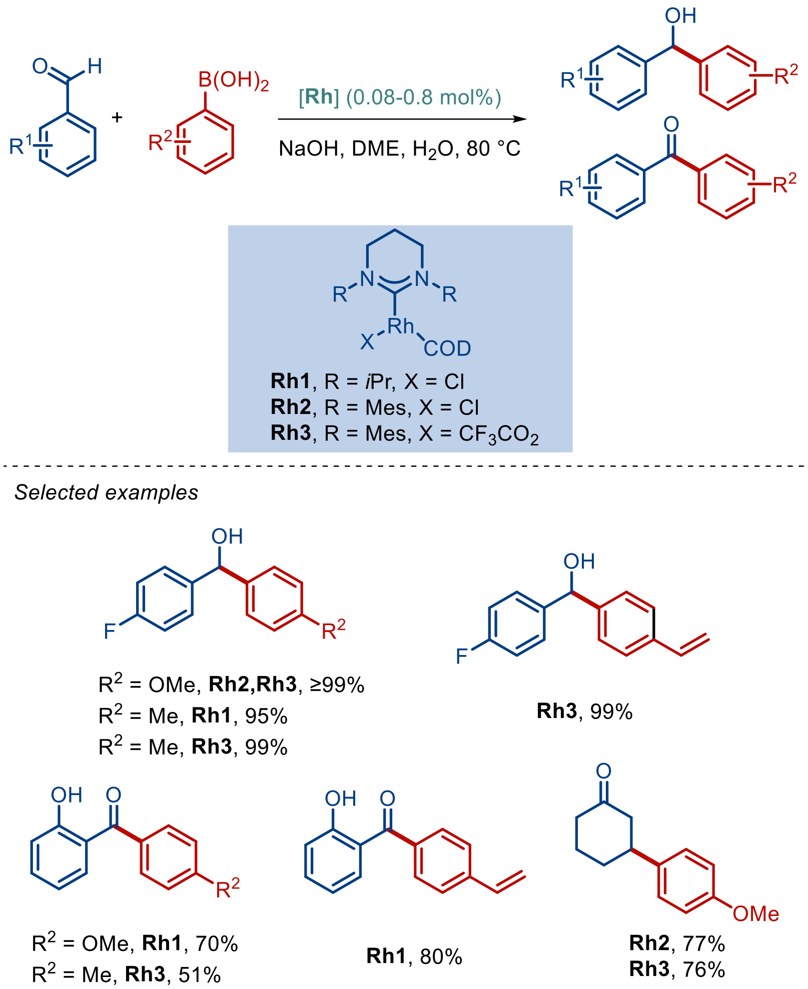
Buchmeiser also investigated ring-expanded NHC-Ru complexes as suitable catalysts for the polymerization of phenylacetylene [71], norbornene derivatives [72], and *N*,*N*-dipropargyl-3,4-dialkoxyanilines [73].

5. Ring-Expanded Rhodium-NHC Complexes

Ring-expanded NHC-Rh complexes have been successfully applied in arylation [75-79], hydrogenation [80-82], hydrosilylation [77], hydroformylation [83], formylation [84], methylation [84], hydrodefluorination [85] and polymerization reactions [71, 86, 87].

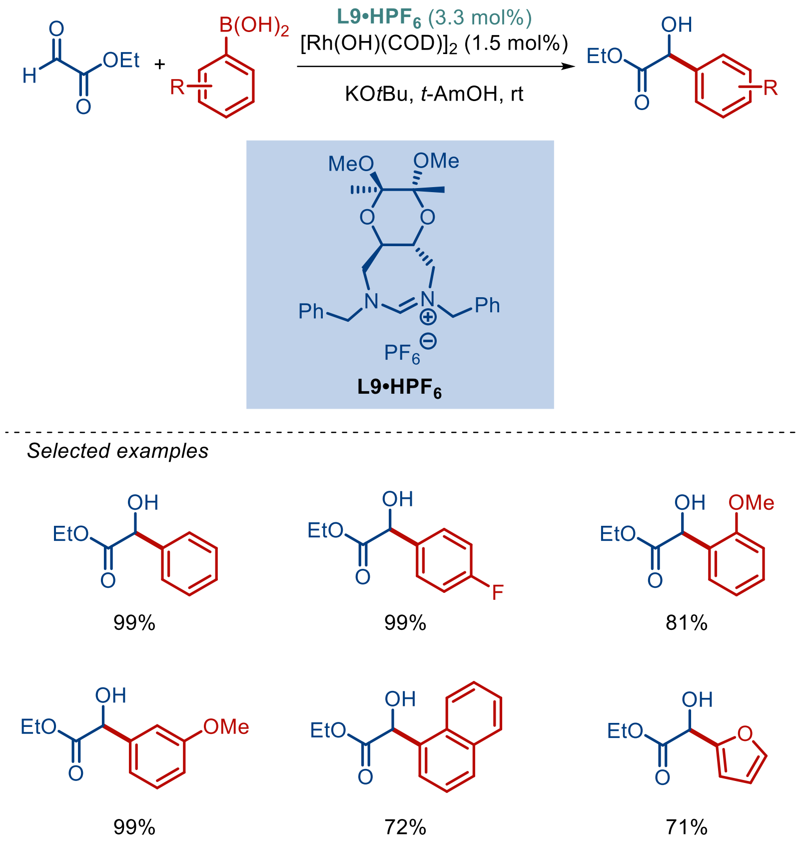
5.1 Rh-NHC Catalyzed Arylation

In 2004, Buchmeiser and co-workers reported arylation of aldehydes using boronic acids as the aryl source catalyzed by ring-expanded NHC-Rh complexes **Rh1-Rh3** (**Scheme 14**) [75]. Both alcohol and ketone products were observed, depending on the structure of the substrates. Furthermore, 1,4-addition products were obtained when cyclohex-2-enone was used. A significant impact of the N-wingtip substitution on the reactivity was observed with **Rh1** affording higher yields than **Rh2** in most cases. Moreover, an pseudohalide X ligand with stronger electron-withdrawing capacity as in **Rh3** was more favorable than chloride as in **Rh2** due to more facile reductive elimination and carbon-carbon formation.



Scheme 14. Aldehyde arylation catalyzed by ring-expanded NHC-Rh reported by Buchmeiser in 2004.

Subsequently, Burke et al. disclosed a related catalytic system for the arylation of ethyl glyoxalate with aryl boronic acids for the synthesis of α-hydroxyesters catalyzed by ring-expanded NHC-Rh (**Scheme 15**) [76]. The chiral eight-membered NHC salt **L9·HPF₆** was synthesized in a two-step procedure from a known chiral diamine. However, no enantioselectivity was observed, although a chiral ligand was used. They also found that the steric hindrance of the ligand has a deleterious effect on the reactivity, with the less bulky **L9** as the most efficient ligand. This observation was explained by the fact that steric hindrance could block the coordination sites on the metal. Lower yields were obtained when the boronic acids were decorated with OH, NH_2 and electron-rich substituents.

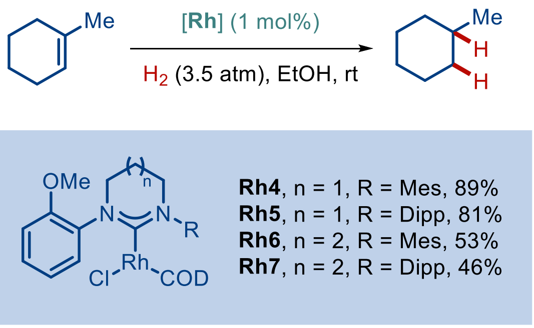


Scheme 15. Aldehyde arylation catalyzed by ring-expanded NHC-Rh reported by Burke in 2012.

Additional examples of ring-expanded NHC-Rh complexes in aldehyde arylation reactions were reported by Buchmeiser [77], Özdemir [78], and Burke [79].

5.2 Rh-NHC Catalyzed Hydrogenation Reactions

In 2009, Cavell reported hydrogenation of alkenes with molecular hydrogen using rhodium complexes **Rh4**-**Rh7** bearing non-symmetrically substituted six- and seven-membered NHC precursors (**Scheme 16**) [80]. Hydrogenation of 1-methylcyclohexene was achieved with all complexes tested. It should be noted that six-membered ligands **Rh4** and **Rh5** were more effective than seven-membered ligands **Rh6** and **Rh7**. Thus, in this case, the ligand bulk had a negative effect the reactivity with the least hindered **Rh4** as the most reactive complex.

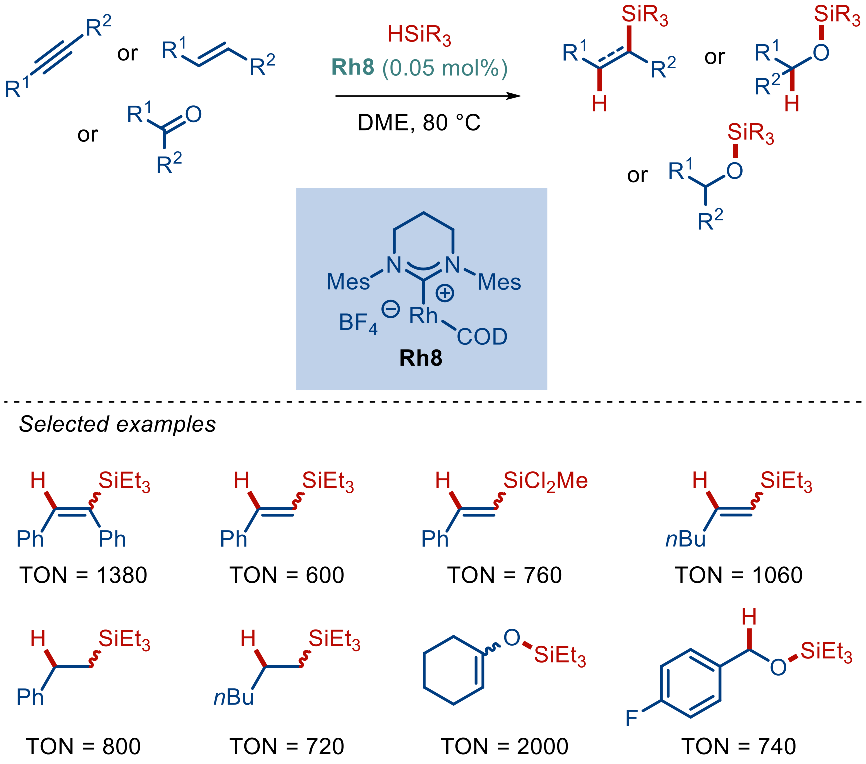


Scheme 16. Hydrogenation of alkenes catalyzed by ring-expanded NHC-Rh reported by Cavell in 2009.

Moreover, Özdemir [81] and Gülcemal [82] reported transfer hydrogenation of ketones using ring-expanded NHC-Rh complexes.

5.3 Rh-NHC Catalyzed Hydrosilylation Reactions

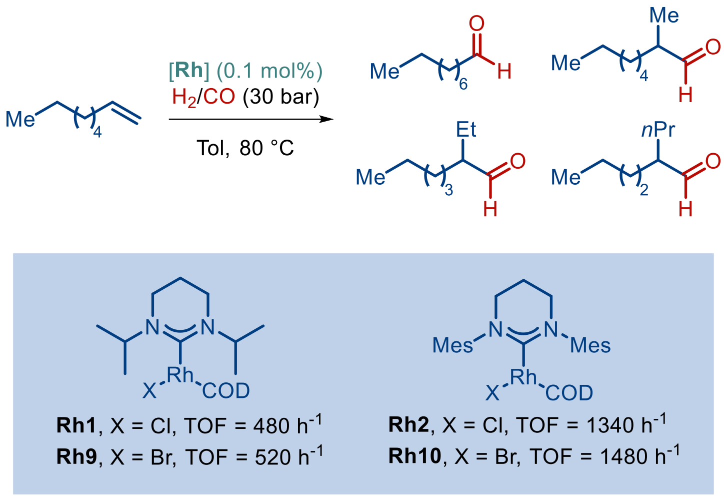
In 2005, Buchmeiser et al. reported a cationic complex **Rh8** for the catalytic hydrosilylation of unsaturated systems (**Scheme 17**) [77]. Hydrosilylation of alkynes, alkenes, and carbonyl compounds proceed smoothly at 80 °C at low 0.05 mol% catalyst loading in DME. The highest TON of 2,000 was determined for the 1,4-addition hydrosilylation of cyclohex-2-en-1-one. Interestingly, this cationic complex was found to be more reactive than the analogous CF_3CO_2-ligated complex **Rh3**.



Scheme 17. Hydrosilylation reactions catalyzed by ring-expanded NHC-Rh reported by Buchmeiser in 2005.

5.4 Rh-NHC Catalyzed Hydroformylation Reactions

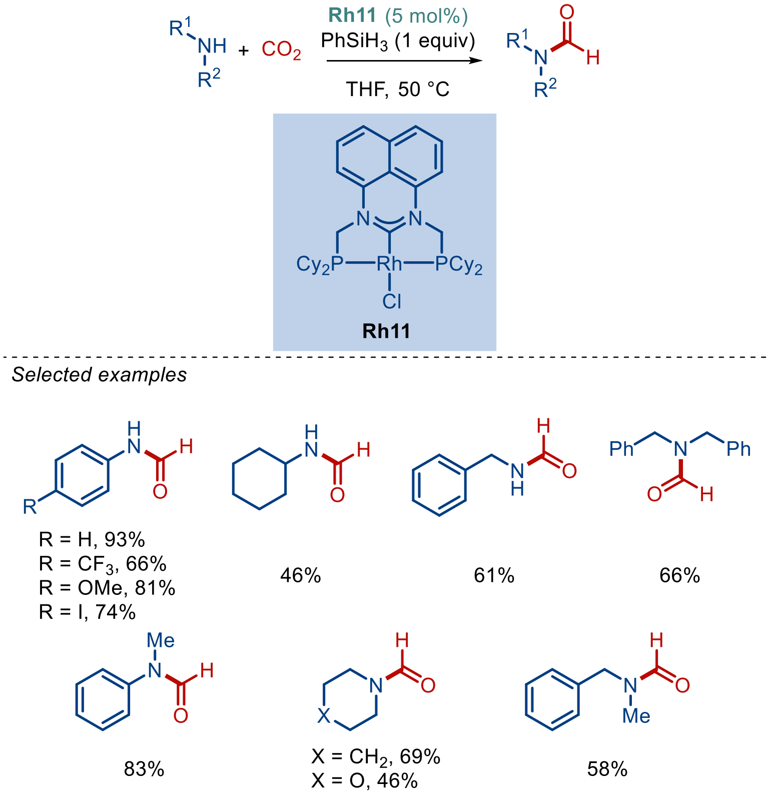
In 2005, high pressure hydroformylation of 1-octene catalyzed by ring-expanded NHC-Rh complexes using carbon monoxide and hydrogen gas as a formyl source was reported by Buchmeiser (**Scheme 18**) [83]. In contrast to hydrosilylation, no significant effect on the reactivity was observed using chloride and bromide ligated complexes. However, a remarkable improvement was achieved when the ligand was changed from N-*i*Pr (1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) to N-Mes (1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) with a three-fold increase of TOF from 520 h^{-1} to 1480 h^{-1}.



Scheme 18. Hydroformylation of alkenes catalyzed by ring-expanded NHC-Rh reported by Buchmeiser in 2005.

5.5 Rh-NHC Catalyzed Formylation Reactions

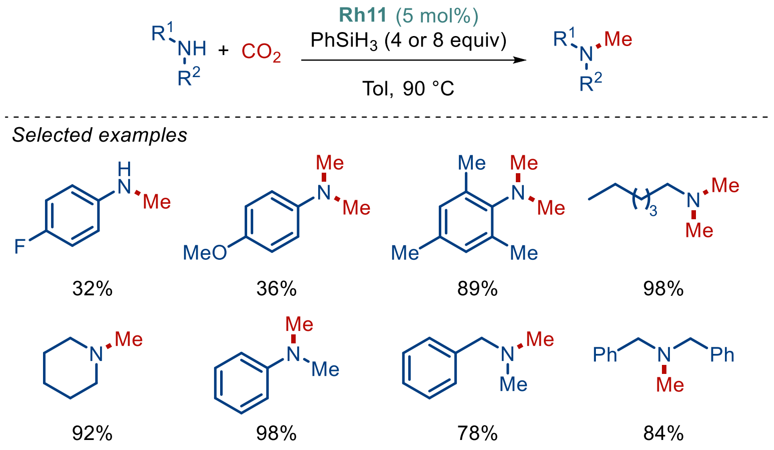
In 2019, Messerle and co-workers reported formylation of amines using carbon dioxide as a sustainable feedstock catalyzed by a Rh(I)-NHC/phosphine pincer complex **Rh11** (**Scheme 19**) [84]. The catalyst **Rh11** was prepared from N,N′-bis(phoshinomethyl)-dihydroperimidines and [RhCl(PPh_3)$_3$] *via* chelate-assisted double C–H activation. It is worthwhile to note that replacing PCy_2 arms with PPh_2 resulted in an inactive catalyst due to weaker σ-donating ability of PPh_2. The formylation of amines proceeded well in THF at 50 °C in the presence of 1 equivalent of phenylsilane. In terms of scope, aniline derivatives were formylated in good to excellent yields, while secondary and primary aliphatic amines were also tolerated under the reaction conditions.



Scheme 19. Formylation of amines catalyzed by ring-expanded NHC-Rh reported by Messerle in 2019.

5.6 Rh-NHC Catalyzed Methylation Reactions

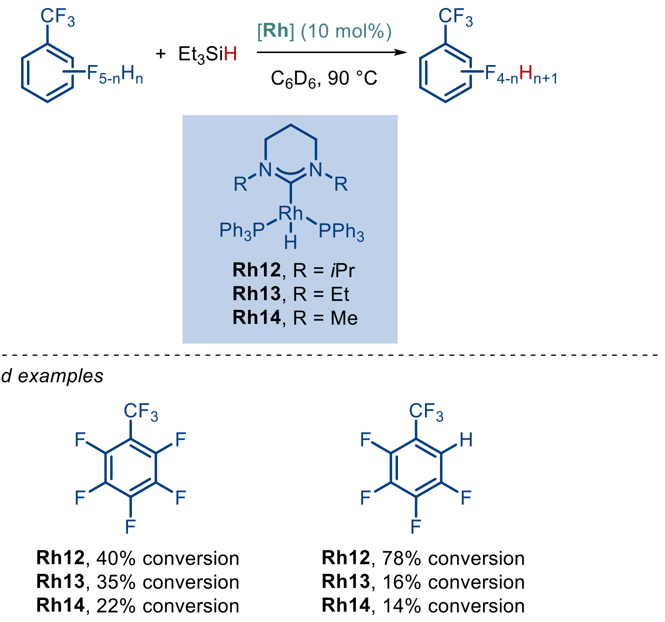
The Messerle group also reported methylation of amines using **Rh11** pincer complex under similar conditions (**Scheme 20**) [84]. A large excess of phenylsilane as a reducing reagent converted the formamide group into the methylamino group. Toluene was found to be the optimum solvent to maintain high conversion. In this process, primary anilines typically afforded mixtures of products, consisting of formamide, methylamine, and dimethylated derivatives, while secondary amines gave products in high yields.



Scheme 20. Methylation of amines catalyzed by ring-expanded NHC-Rh reported by Messerle in 2019.

5.7 Rh-NHC Catalyzed Hydrodefluorination Reactions

In 2014, Whittlesey and co-workers demonstrated that six-membered NHC complexes **Rh12-Rh14** are capable of catalyzing hydrodefluorination of polyfluorinated toluenes (**Scheme 21**) [85]. The stoichiometric study showed that **Rh12** could activate the C(sp^2)-F bond of perfluorotoluene ($C_6F_5CF_3$) selectively at the *para* position at room temperature. Under the catalytic conditions of 10 mol% catalysts at 90 °C, both mono- and multiple hydrodefluorination products of perfluorotoluene were observed with the C(sp^3)-F bond intact. It is worth noting that for both substrates tested, the reactivity of the catalysts decreased on the order of **Rh12**, **Rh13**, and **Rh14**, consistent with a decrease of steric hindrance of the N-wingtips.



Scheme 21. Hydrodefluorination catalyzed by ring-expanded NHC-Rh reported by Whittlesey in 2014.

A mechanism involving two steps has been proposed for this hydrodefluorination process (**Figure 4**) [85]. A direct displacement of the C-F bond of the substrate to the C-H bond occurs by a nucleophilic aromatic substitution pathway to generate the rhodium fluoride complex supported by the N-heterocyclic carbene ligand. Next, interconversion of the catalytic species is achieved by H-F exchange with silane.

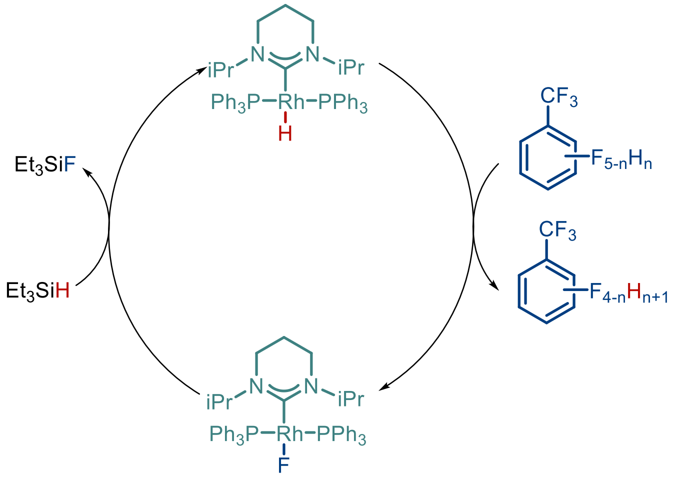
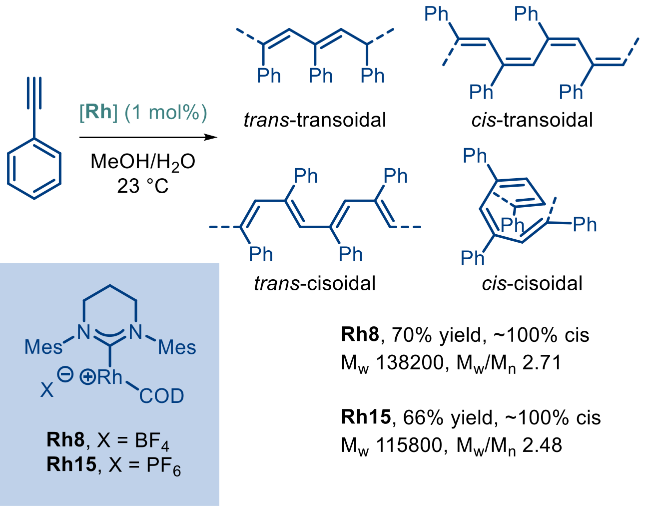


Fig. 4. Mechanism of hydrodefluorination catalyzed by ring-expanded NHC-Rh.

5.8 Rh-NHC Catalyzed Polymerization Reactions

In 2005, Buchmeiser and co-workers reported the reactivity of two ionic rhodium complexes **Rh8** and **Rh15** supported by a six-membered NHC in the catalytic polymerization of phenylacetylene (**Scheme 22**) [71]. Considering that four isomeric products could be formed, catalyst **Rh8** was able to selectively promote the polymerization to *cis*-poly(phenylacetylene) with a molecular weight up to 138,200 in a protic solvent at room temperature. The complex **Rh15** showed similar reactivity, indicating a limited effect of the counterion on this process.



Scheme 22. Polymerization of phenylacetylene catalyzed by ring-expanded NHC-Rh reported by Buchmeiser in 2005.

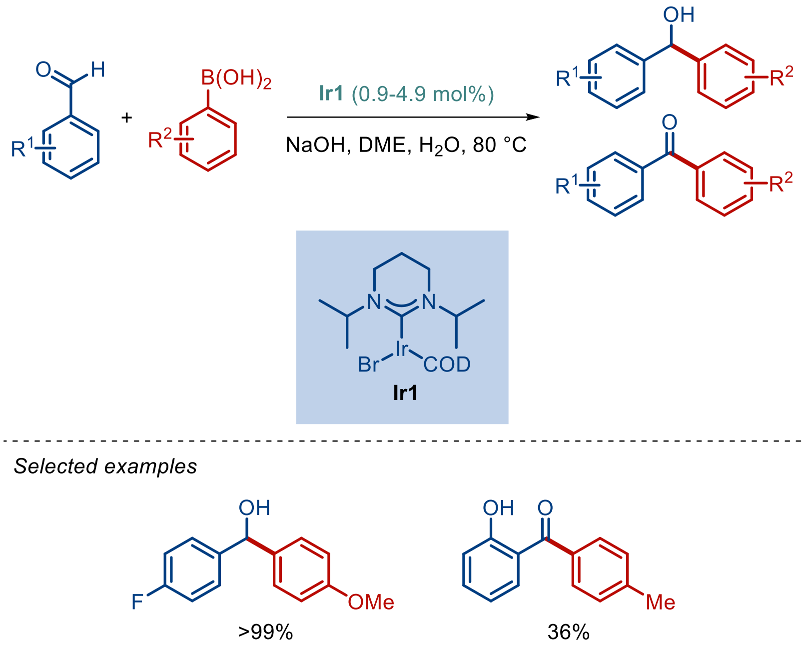
In addition, Buchmeiser reported resin-bound ring-expanded NHC-Rh [86], while Lavigne disclosed maloNHC-Rh for related polymerization of phenylacetylene [87].

6. Ring-Expanded Iridium-NHC Complexes

Ring-expanded NHC-iridium complexes were found to be a highly reactive in arylation [75], alkylation [88-90], hydrogenation [80, 86, 91-94], silylation [95], addition [96], isomerization [96] and polymerizaton [71] reactions.

6.1 Ir-NHC Catalyzed Arylation Reactions

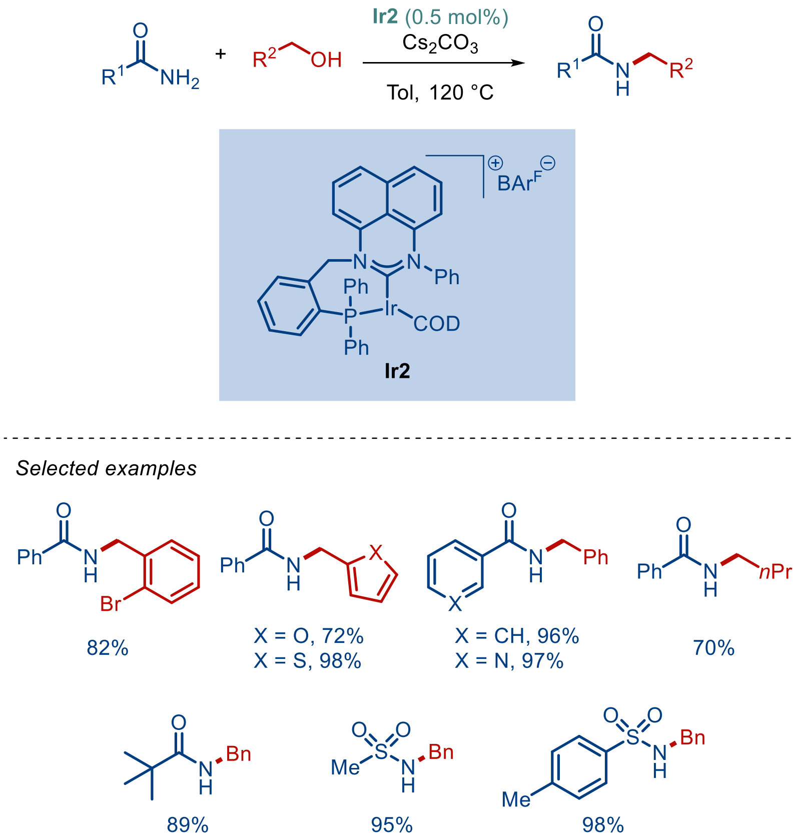
The Buchmeiser group reported the organoiridium complex **Ir1** supported by a six-membered NHC for the arylation of aldehydes with aryl boronic acids (**Scheme 23**) [75]. The outcome of this process was also dependent on the type of aryl aldehyde used. For example, 4-fluorobenzaldehyde was arylated to the corresponding secondary alcohol in a nearly quantitative yield, while a hydroxyl-containing aldehyde afforded the ketone product. Interestingly, the 'soft' Ir complex **Ir1** was less reactive than the corresponding 'hard' Rh complex **Rh1** (**Scheme 14**).



Scheme 23. Arylation of aldehydes catalyzed by ring-expanded NHC-Ir complexes reported by Buchmeiser in 2004.

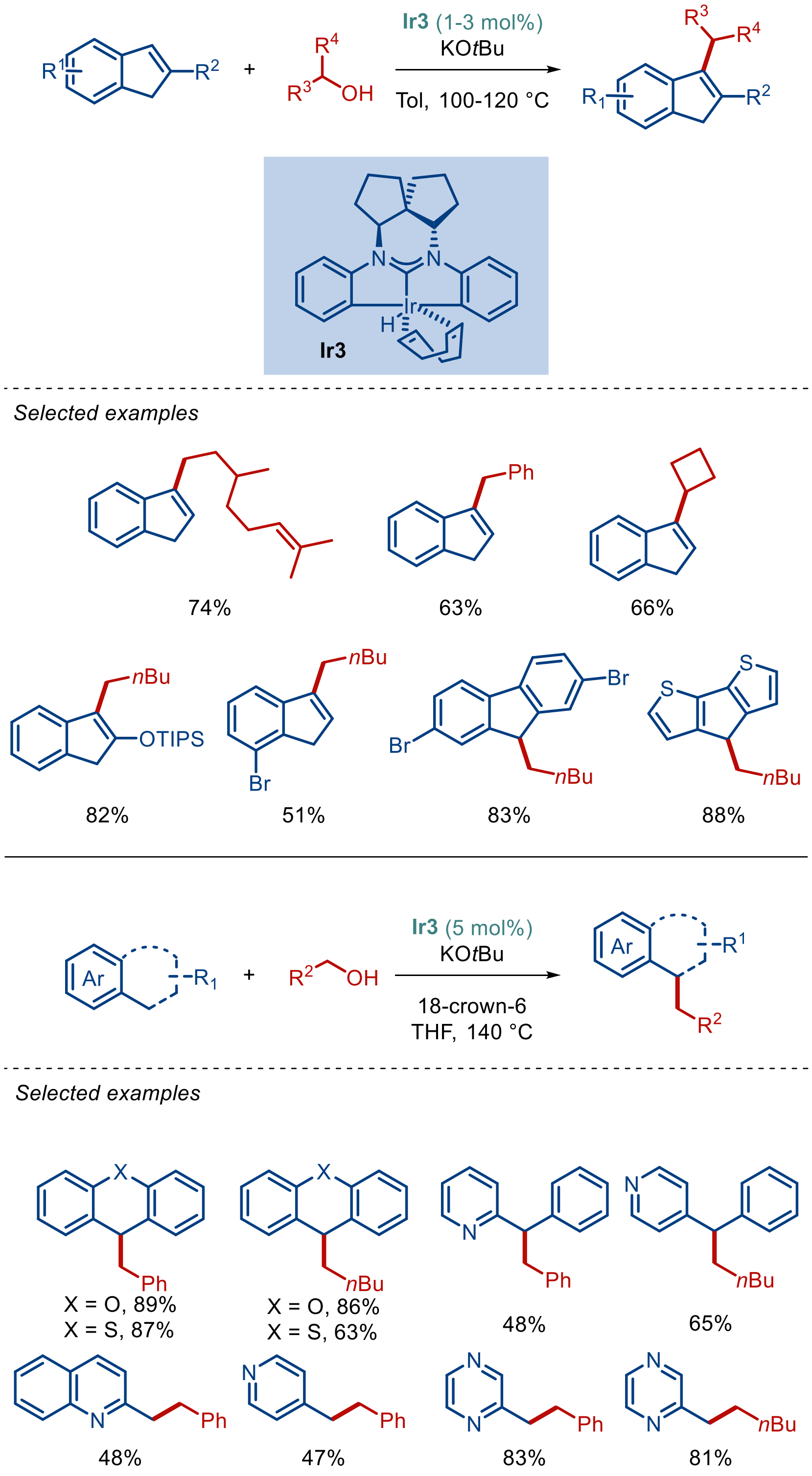
6.2 Ir-NHC Catalyzed Alkylation Reactions

In 2015, Andersson and co-workers found that a cationic Ir complex **Ir2** bearing NHC/phosphine mixed ligands was highly active in N-alkylation of primary amide at low catalyst loading by a borrowing hydrogen process (**Scheme 24**) [88]. Alcohols were used as alkylating reagents were first were oxidized to aldehydes. Subsequently, a condensation step with amides gave the intermediate imines, which were reduced to the N-alkylated amides. This reaction is characterized by a broad generality in that various benzamides, heterocyclic amides, aliphatic amides, and sulfonamides could be alkylated with benzylic alcohols, heterocyclic alcohols, and butanol.



Scheme 24. N-Alkylation of amides catalyzed by ring-expanded NHC-Ir reported by Andersson in 2015.

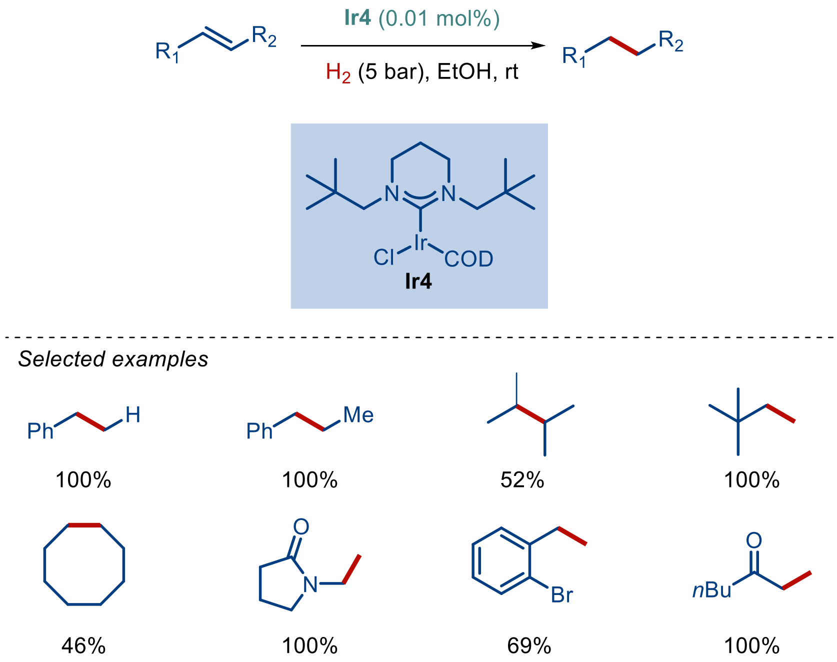
Subsequently. Tu *et al*. reported an impressive regioselective C3 alkylation of indenes using a ring-expanded CCC pincer Ir hydride complex **Ir3** (**Scheme 25**) [89]. A wide range of primary and secondary alcohols were successfully used as alkylating reagents *via* borrowing hydrogen strategy. The scope was also extended to the alkylation of inert C(sp^3)-H bonds. Xanthene and its analogs, acyclic diaryl methanes, and methyl heteroarenes were alkylated in good to high yields. Mechanistic studies indicated that the reactions proceed *via* a dehydrogenation, condensation, and hydrogenation sequence, where a hemilabile Ir(III)-dihydride is the key intermediate.



Scheme 25. Alkylation of indenes and activated C-H bonds catalyzed by ring-expanded NHC-Ir reported by Tu in 2022.

6.3 Ir-NHC Catalyzed Hydrogenation Reactions

In 2013, Cavell investigated the catalytic behavior of N-alkyl functionalized six-membered NHC-ligated iridium complex **Ir4** in alkene hydrogenation (**Scheme 26**) [91]. They found that non-hindered terminal alkenes were hydrogenated smoothly at low catalyst loading of 0.01 mol%, while lower yields were observed with hindered substrates. Unsaturated functionalities such as amides and ketones as well aryl halides such as bromides were well-tolerated in this process.

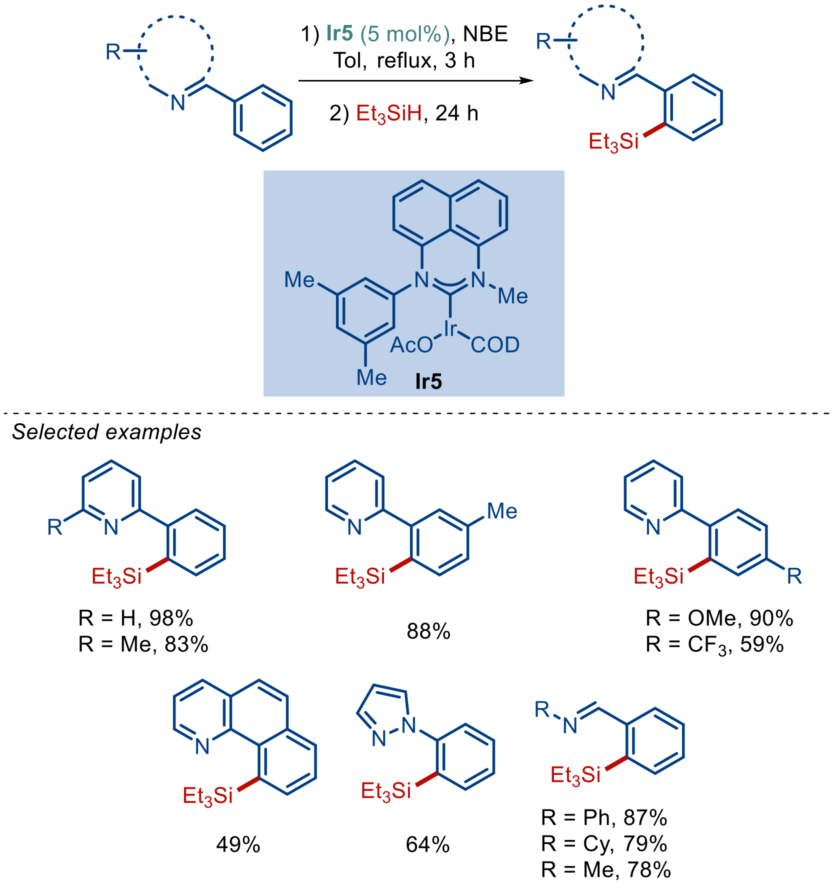


Scheme 26. Hydrogenation of alkenes catalyzed by ring-expanded NHC-Ir reported by Cavell in 2013.

Additional examples of hydrogenation reactions catalyzed by ring-expanded NHC-Ir complexes were reported by Cavell [80, 92, 93], Buchmeiser [86], and Andersson [94].

6.4 Ir-NHC Catalyzed C-H Activation/Silylation Reactions

In 2013, Mashima and co-workers reported the direct dehydrogenative C-H silylation of pyridyl and iminyl derivatives *via* C-H activation using a hemilabile N-arylperimidine iridium complex **Ir5** (**Scheme 27**) [95]. This silylation was performed using triethylsilane as the silylating reagent and norbornene (NBE) as the hydrogen acceptor. The authors found that the acetate anion on Ir was crucial for this reaction as the Cl congeners did not show reactivity under the reaction conditions. Interestingly, the imine moiety was compatible under the reductive conditions. In terms of scope, substituents on the phenyl ring affected the yields due to steric hindrance.



Scheme 27. C-H Activation/silylation catalyzed by ring-expanded NHC-Ir reported by Mashima in 2013.

A mechanism involving repeated metalation and demetallation was proposed for this C-H silylation process (**Figure 5**) [95]. Initially, the bis(cyclometalated)iridium complex **I**, proposed as one of the active intermediates, was prepared and isolated by refluxing the catalyst with 2-phenylpyridine. The iridium hydride complex **II** was then generated from **I** through metathesis, followed by demetallation of the *N*-3,5-xylyl ring in the presence of Et_3SiH to give complex **III**. Notably, complex **III** was unstable and easily deactivated by the formation of complex **X** *via* C-H activation. Next, 2-norbornene was inserted into the Ir-H bond of complex **III** to give norbornyliridium complex **IV**, which could undergo deactivation by metalation of the C-H bond of the methyl group. Norbornane was evolved along with the formation of complex **V**, wherein the C-H bond of *N*-3,5-xylyl was metalated again. Coordination of Et_3SiH to the Ir center of complex **V** led to **VI**, which gave the ortho-silylated Ir hydride complex **VIII** *via* σ-complex-assisted metathesis intermediate **VII**. The exchange of ligand with 2-phenylpyridine released the silylated product and intermediate **IX**, which regenerated catalytic species **II** after the loss of Et_3SiH.

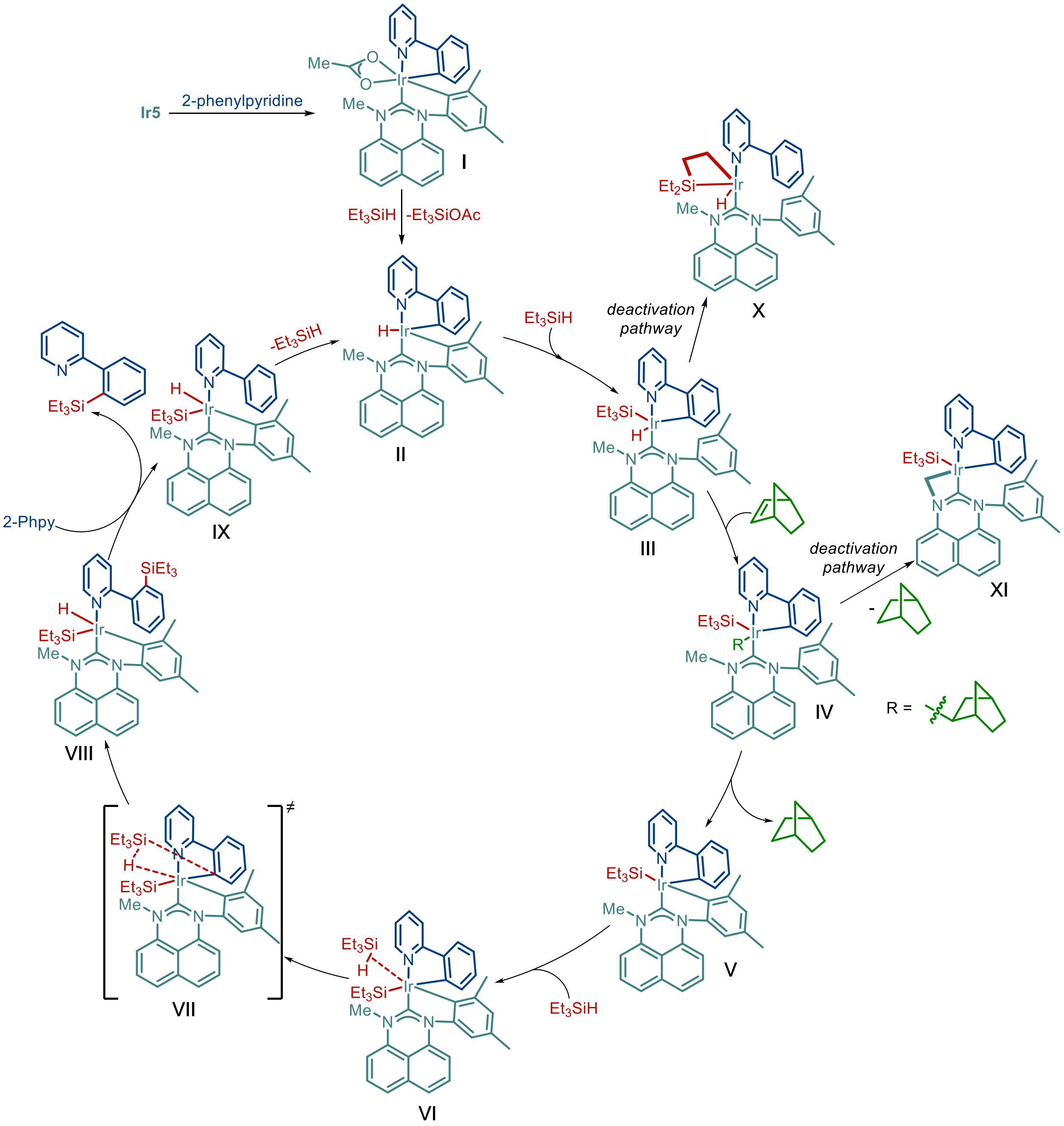
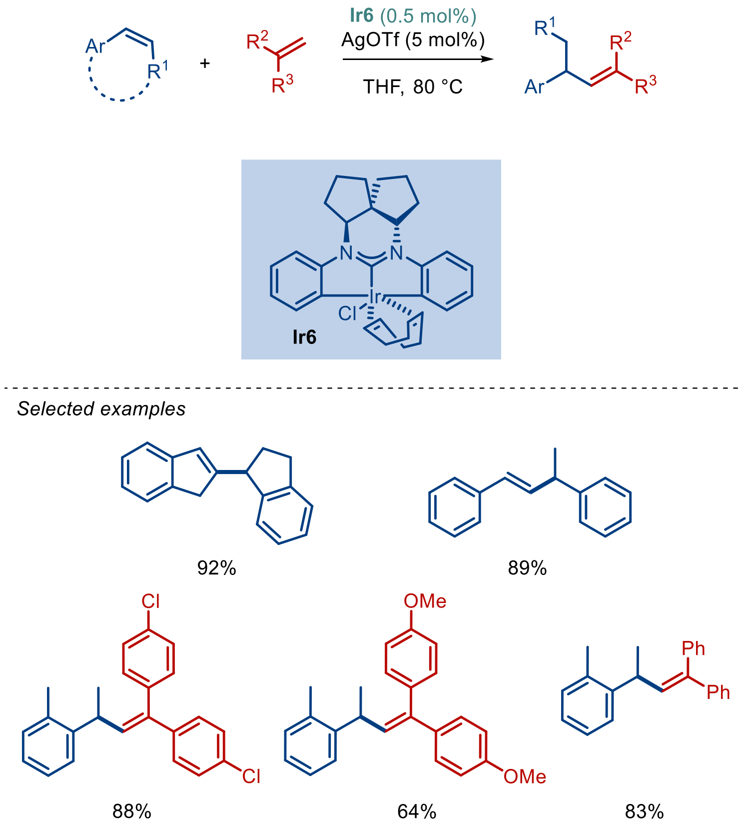


Fig. 5. Mechanism for C-H activation/silylation catalyzed by ring-expanded NHC-Ir.

6.5 Ir-NHC Catalyzed Addition Reactions

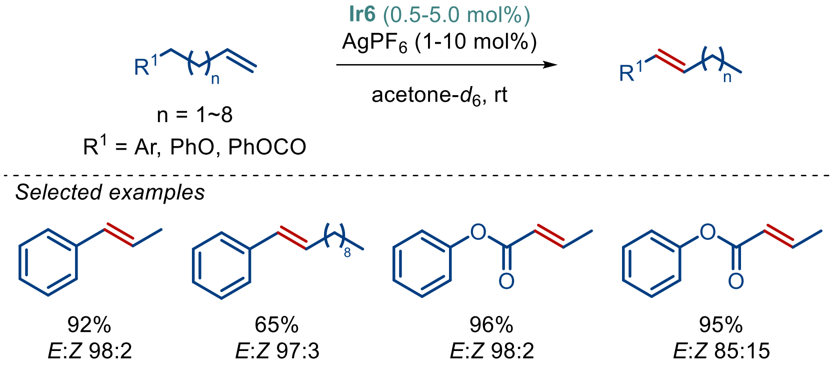
In 2020, Tu reported the synthesis of the six-membered carbene-coordinated Ir-hydride complex **Ir3** and its conversion to the corresponding Ir-chloride complex **Ir6** (**Scheme 28**) [96]. Complex **Ir6** was found to efficiently catalyze the regioselective homo- or hetero-addition of styrenes in high to excellent yields at low 0.5-1 mol% catalyst loading. Both electron-rich and electron-deficient substrates were tolerated in this reaction.



Scheme 28. Head-to-tail addition of styrenes catalyzed by ring-expanded NHC-Ir reported by Tu in 2020.

6.6 Ir-NHC Catalyzed Isomerization Reactions

The Tu group also found that the iridium-chloride complex **Ir6** could be used for isomerization of terminal olefins to internal alkenes with excellent regio- and *E*/*Z*-selectivity at room temperature (**Scheme 29**) [96]. The substrate scope has been determined to encompass a wide range of compounds, including olefins with a distal phenyl group, phenyl allylcarbonate esters and phenyl allyl ethers. Ir(III)/Ir(V) mechanism was proposed for both the addition and isomerization process.

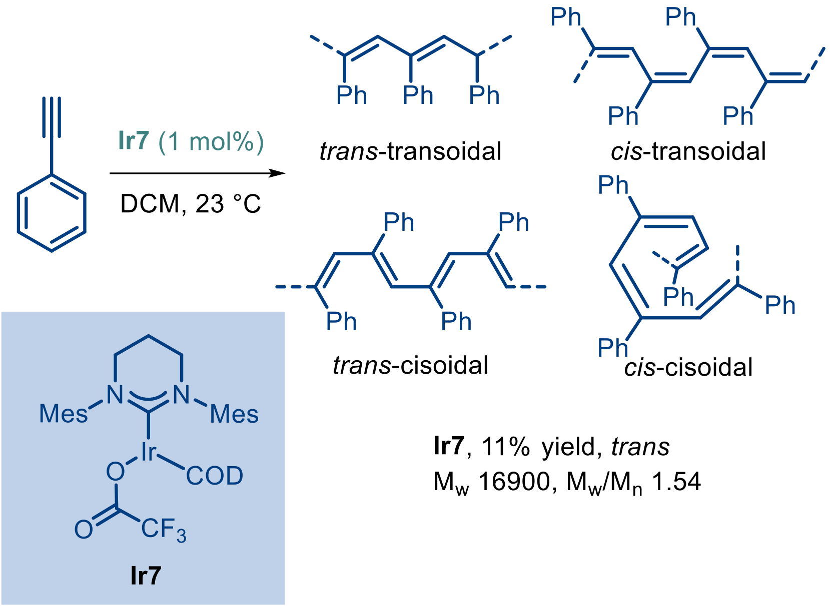


Scheme 29. Olefin isomerization catalyzed by ring-expanded NHC-Ir reported by Tu in 2020.

6.7 Ir-NHC Catalyzed Polymerizaton Reactions

Following their research on ring-expanded NHC-Rh complexes in alkyne polymerization (**Scheme 22**), the Buchmeiser group showed that the ring-expanded NHC iridium complex **Ir7** was also reactive in the same reaction (**Scheme**

30) [71]. They found that the iridium-based catalyst **Ir7** supported by the six-membered 6-Mes catalyzed the formation of *trans*-poly(phenylacetylene) in modest yield (11%) and molecular weight up to 16,900.



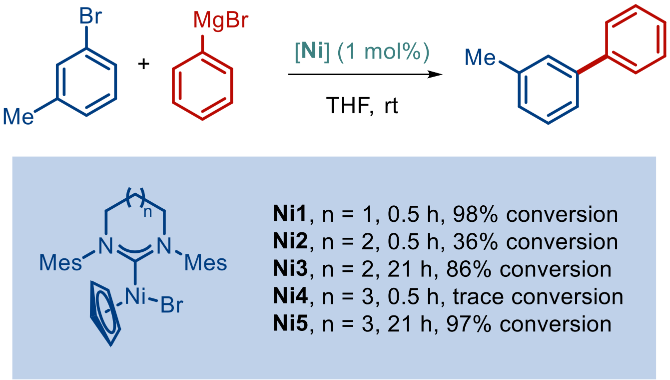
Scheme 30. Polymerization of phenylacetylene catalyzed by ring-expanded NHC-Ir reported by Buchmeiser in 2005.

7. Ring-Expanded Nickel-NHC Complexes

Ring-expanded NHC-Ni complexes show high reactivity in Kumada cross-coupling [97, 98], Suzuki-Miyaura cross-coupling [99], hydrogenation [100], hydrosilylation [99], hydrodehalogenation [101], cross-hydroalkenylation [102], cross-dimerization [103], and [5 + 1] benzannulation [104] reactions.

7.1 Ni-NHC Catalyzed Kumada-Tamao-Corriu Coupling Reactions

In 2016, Buchowicz and co-workers investigated the effect of ring size of cyclopentadienyl [(NHC)NiCpBr] complexes on the catalytic efficiency in the Kumda-Tamao-Corriu coupling reactions of aryl halides (**Scheme 31**) [97]. These ring-expanded [(NHC)NiCpBr] complexes were prepared by the reaction of Ni(DME)Br$_2$ and CpLi with free carbenes. The six-membered 6-Mes complex **Ni1** was found to be more efficient than the five-membered IMes. A decrease in reactivity was observed as the carbene ring size increased from six-membered to eight-membered.

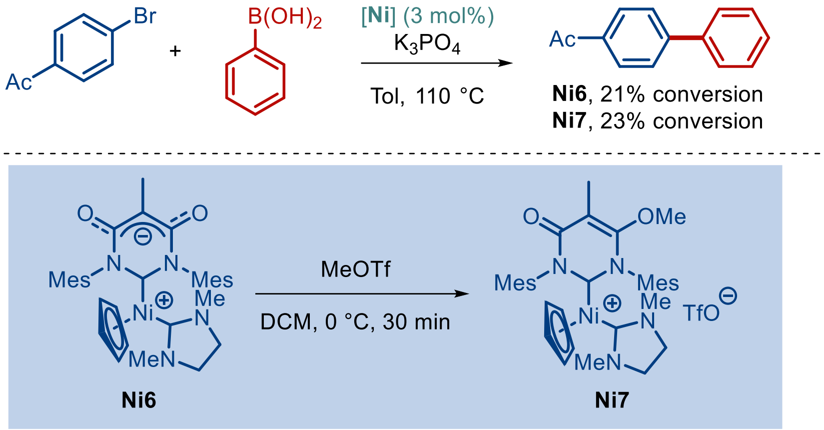


Scheme 31. Kumda-Tamao-Corriu coupling catalyzed by ring-expanded NHC-Ni reported by Buchowicz in 2016.

In addition, Whittlesey reported ring-expanded [(NHC)Ni(PPh$_3$)X] (X = Cl, Br) complexes for Kumda-Tamao-Corriu cross-coupling of aryl chlorides and fluorides [98].

7.2 Ni-NHC Catalyzed Suzuki-Miyaura Coupling Reactions

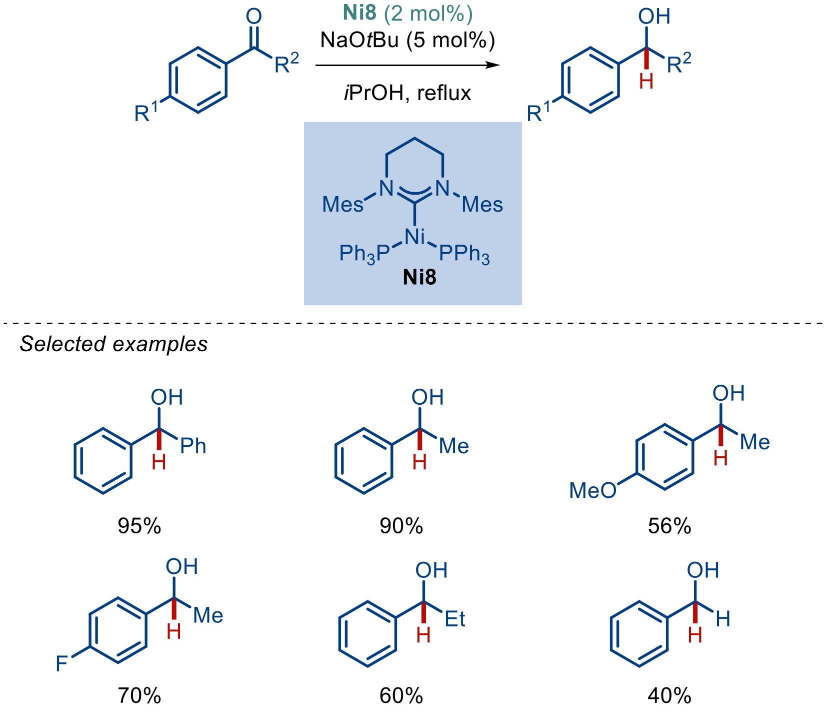
In 2017, Ritleng et al. reported the catalytic activity of zwitterionic heteroleptic biscarbene complex **Ni6** and the cationic complex **Ni7** prepared by *O*-methylation from **Ni6** in the Suzuki-Miyaura cross-coupling of aryl bromides (**Scheme 32**) [99]. The authors found that both **Ni6** and **Ni7** are less effective catalysts for this transformation in the presence of K_3PO_4 at 110 °C in toluene. The low efficiency was proposed to originate from the encumbered steric environment and the labialization of Cp ring, which was confirmed by displacement experiments.



Scheme 32. Suzuki-Miyaura coupling catalyzed by ring-expanded NHC-Ni reported by Ritleng in 2017.

7.3 Ni-NHC Catalyzed Hydrogenation Reactions

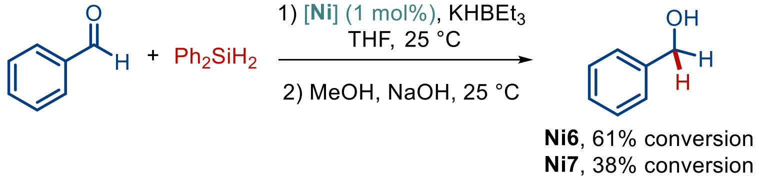
In 2017, Whittlesey and co-workers investigated hydrogenation of ketones with the three-coordinate nickel(0) complex **Ni8** (**Scheme 33**) [100]. The air-sensitive **Ni8** was obtained by either reduction of [Ni(6-Mes)(PPh_3)Br] with KO*t*Bu or by the reaction of 6-Mes and PPh_3 with Ni(cod)$_2$. The hydrogenation reactions were carried out in *i*PrOH at reflux in the presence of catalytic NaO*t*Bu. It should be noted that bromoacetophenone and chloroacetophenone could not be reduced under these conditions, while fluoroacetophenone was a suitable substrate.



Scheme 33. Hydrogenation of ketones catalyzed by ring-expanded NHC-Ni reported by Whittlesey in 2017.

7.4 Ni-NHC Catalyzed Hydrosilylation Reactions

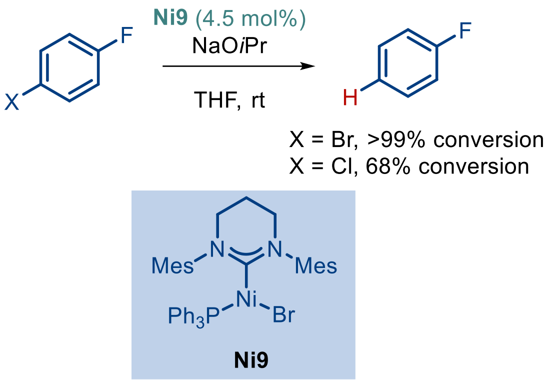
Following their work on the Suzuki-Miyaura cross-coupling (**Scheme 32**), Ritleng and co-workers also investigated the reactivity of complexes **Ni6** and **Ni7** in hydrosilylation of aldehydes (**Scheme 34**) [99]. Both **Ni6** and **Ni7** showed moderate reactivity in hydrosilylation of benzaldehyde. Interestingly, the authors observed that **Ni6** is twice as reactive as **Ni7** due to the stronger donating capacity of the anionic *malo*NHC ligand.



Scheme 34. Hydrosilylation of aldehydes catalyzed by ring-expanded NHC-Ni reported by Ritleng in 2017.

7.5 Ni-NHC Catalyzed Hydrodehalogenation Reactions

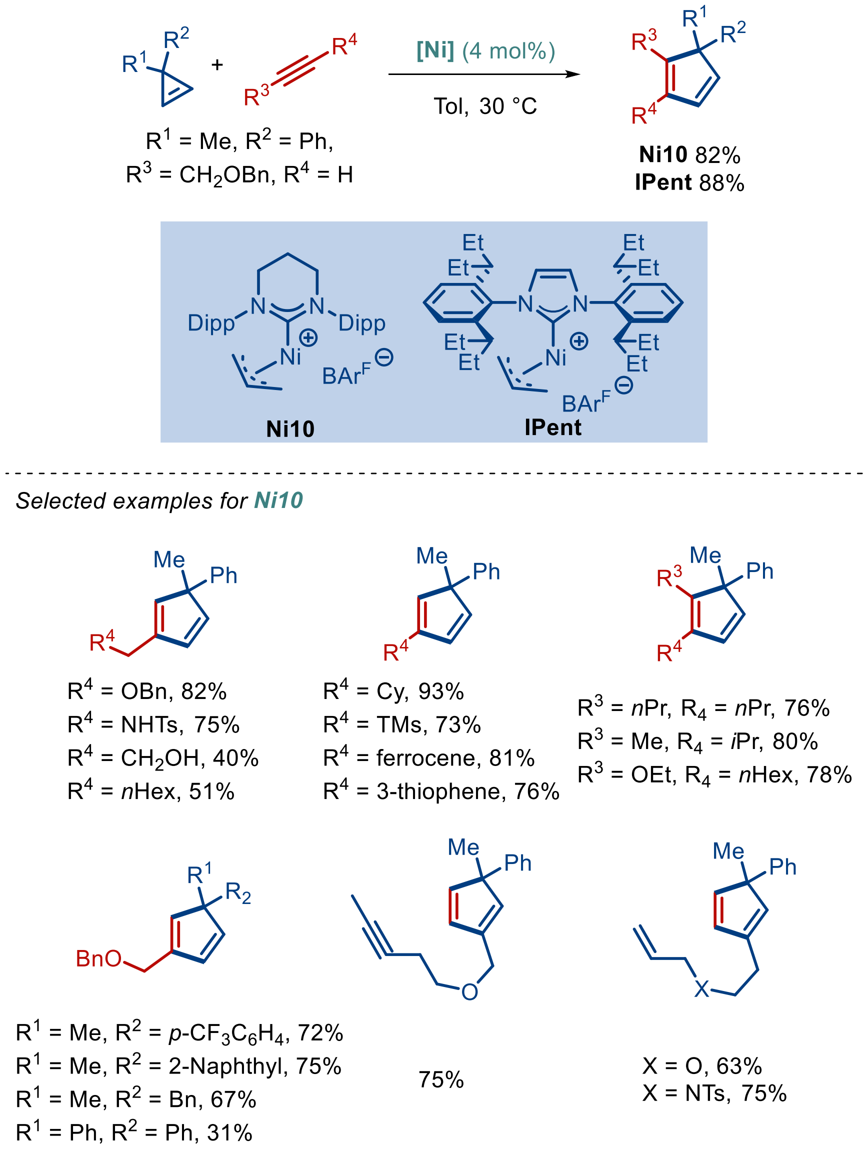
In 2010, Whittlesey et al. reported the three-coordinate Ni(I) complex **Ni9** for the hydrodehalogenation of disubstituted aryl halides (**Scheme 35**) [101]. The complex was synthesized by adding the free carbene 6-Mes to a mixture of Ni(cod)$_2$ and Ni(PPh$_3$)Br$_2$. Complex **Ni9** showed high reactivity in hydrodehalogenation in the presence of NaO*i*Pr at room temperature, while the aryl fluoride moiety remained intact. Interestingly, catalyst **Ni9** also showed promising reactivity in hydrodefluorination of fluorobenzene at 70 °C.



Scheme 35. Hydrodehalogenation of arenes catalyzed by ring-expanded NHC-Ni reported by Whittlesey in 2010.

7.6 Ni-NHC Catalyzed Cross-Hydroalkenylation Reactions

In 2017, Ho and co-workers reported the synthesis of multi-substituted cyclopentadienes through a cross-hydroalkenylation/rearrangement cascade of cyclopropenes with alkynes catalyzed by an ionic Ni(II) complex **Ni10** (**Scheme 36**) [102]. Among the ligands screened, the sterically-bulky ring-expanded 6-Dipp and imidazol-2-ylidene IPent gave the best results, leading to the desired product in 82% and 88% yields, respectively. The use of IMes as a ligand provided the worst results (23% yield), which highlighted the importance of steric impact in this transformation. [(NHC)Ni(II)-cyclopropanyl] complex, generated by chemoselective insertion of cyclopropene to the nickel center, and [(NHC)Ni(II)-vinylcyclopropenyl], formed by the second regioselective insertion of the alkyne, were proposed to be the key intermediates. This methodology is highlighted by a broad scope of highly functionalized cyclopentadienes obtained in high yields in one step at room temperature, demonstrating the generality of this cascade process. Subsequently, the same group demonstrated that ring-expanded NHC-Ni complexes also show promising reactivity in cross-dimerization of olefins [103] and cyclopropane/isocyanide [5 + 1] benzannulation [104].



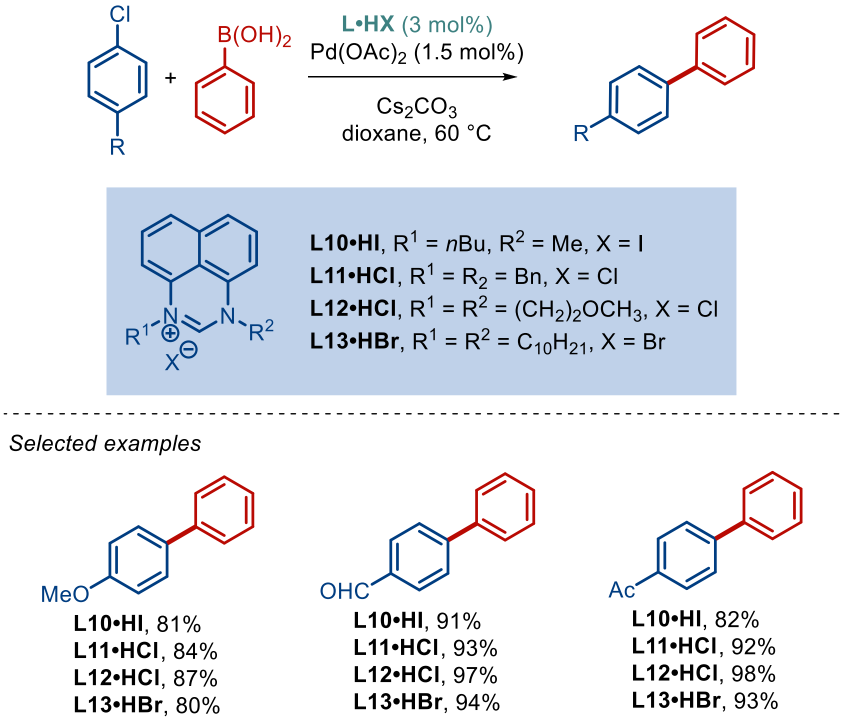
Scheme 36. Ni-NHC catalyzed cross-hydroalkenylation/rearrangement cascade reaction reported by Ho in 2017.

8. Ring-Expanded Palladium-NHC Complexes

Applications of ring-expanded NHC-palladium complexes have been centered on cross-coupling reactions, such as Suzuki-Miyaura cross-coupling [105-122], Mizoroki-Heck coupling [46, 47, 86, 108, 112, 113, 115, 123-128] and Buchwald-Hartwig cross-coupling [129-134]. Furthermore, ring-expanded NHC-palladium complexes were found as efficient catalysts for arylation [135-139], hydrogenation [140], cyclization [141, 142], polymerization [143-146] and isoprene telomerization [147] reactions.

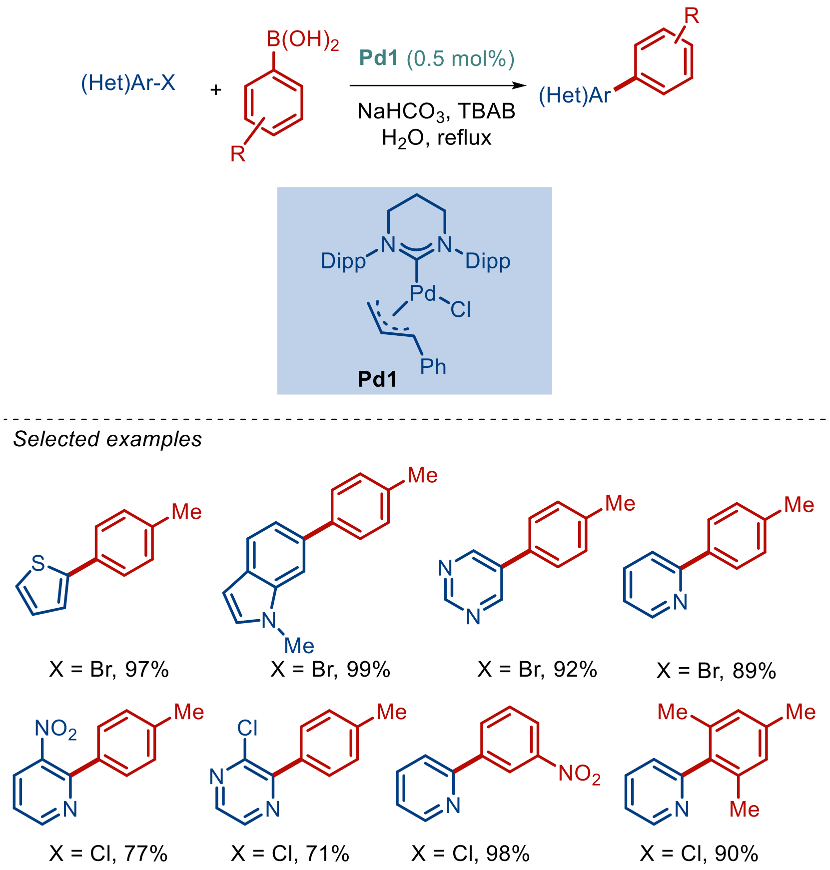
8.1 Pd-NHC Catalyzed Suzuki-Miyaura Cross-Coupling Reactions

In 2004, Özdemir and co-workers described the Suzuki-Miyaura cross-coupling of aryl chlorides catalyzed by ring-expanded N-alkyl NHC/Pd(OAc)$_2$/Cs$_2$CO$_3$ system (**Scheme 37**) [105]. Four new 1,3-dialkylperimidinium salts **L10-L13** were prepared and tested, and all of them afforded the coupled products in high yields. The authors proposed that the ligand bearing N-methoxyethyl wingtip gave slightly better reactivity than the other ligands due to the coordinating properties of the methoxyethyl group.



Scheme 37. Suzuki-Miyaura cross-coupling catalyzed by ring-expanded NHC-Pd reported by Özdemir in 2004.

In 2013, Nechaev and co-workers comprehensively investigated the effect of ring size and steric hinderance on the catalytic efficiency of well-defined Pd(II)–NHC complexes, [(NHC)Pd(cin)Cl], in Suzuki-Miyaura cross-coupling of heteroaromatic halides (**Scheme 38**) [106]. These reactions were performed under aqueous conditions in the presence of tetra-*n*-butylammonium bromide as a phase transfer agent. They found that the 6-Dipp-ligated complex **Pd1** showed the highest reactivity. Precatalysts bearing the less bulky 6-Mes and the more hindered 7-Dipp showed lower reactivity under the same reaction conditions. This cross-coupling is characterized by a wide scope of heteroaryl bromides and chlorides in the coupling with aryl boronic acids in excellent yields under air at 0.5 mol% catalyst loading.

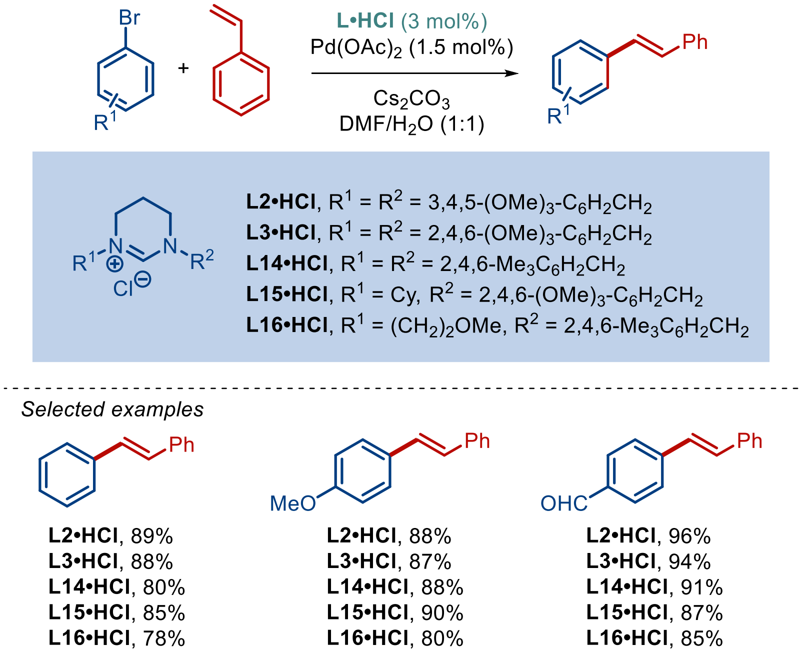


Scheme 38. Suzuki-Miyaura cross-coupling catalyzed by ring-expanded NHC-Pd reported by Nechaev in 2013.

Additional examples of the Suzuki-Miyaura cross-coupling using ring-expanded NHC-Pd complexes have been reported by Özdemir [107-110], Herrmann [111], Dötz [112], Çetinkaya [113], Newman [114], Siemeling [115], Nechaev [116, 117], Cavell [118], Hashmi [119], Karatas [120], Wilhelm [121], and Yasar [122].

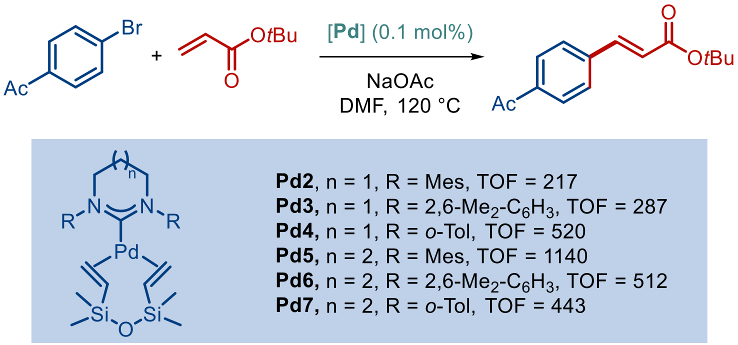
8.2 Pd-NHC Catalyzed Mizoroki-Heck Reactions

In 2005, Özdemir and co-workers reported the catalytic behavior of a series of sterically demanding N-alkyl symmetrical and N-alkyl/alkyl unsymmetrical ring-expanded tetrahydropyrimidinium salts in combination with $Pd(OAc)_2/Cs_2CO_3$ system in the alkenylation of aryl bromides (**Scheme 39**) [108]. They found that the methoxy group at the 4-position of the N-benzyl substituent was crucial to improve the reactivity. This reaction worked well with aryl bromides, while aryl chlorides were unreactive under the same reaction conditions.



Scheme 39. Heck cross-coupling catalyzed by ring-expanded NHC-Pd reported by Özdemir in 2005.

In 2012, Cavell et al. comprehensively investigated the effect of ring size and steric hindrance on the catalytic performance of Pd(0)–NHC complexes, [(NHC)Pd(dvtms)], in the Mizoroki-Heck coupling (**Scheme 40**) [123]. The authors found that the seven-membered ligand 7-Mes showed better reactivity than the six-membered 6-Mes. Importantly, both complexes were still more reactive than the five-membered imidazol-2-ylidene IMes counterpart. These results were attributed to the σ-donating ability and steric hindrance increasing from five- to seven-membered ring. Furthermore, the steric effect of N-wingtip substitution was also important for catalytic performance. Catalyst **Pd5** displayed a TOF of 1,140 after 30 min, while **Pd6** and **Pd7** gave considerably lower TOFs.

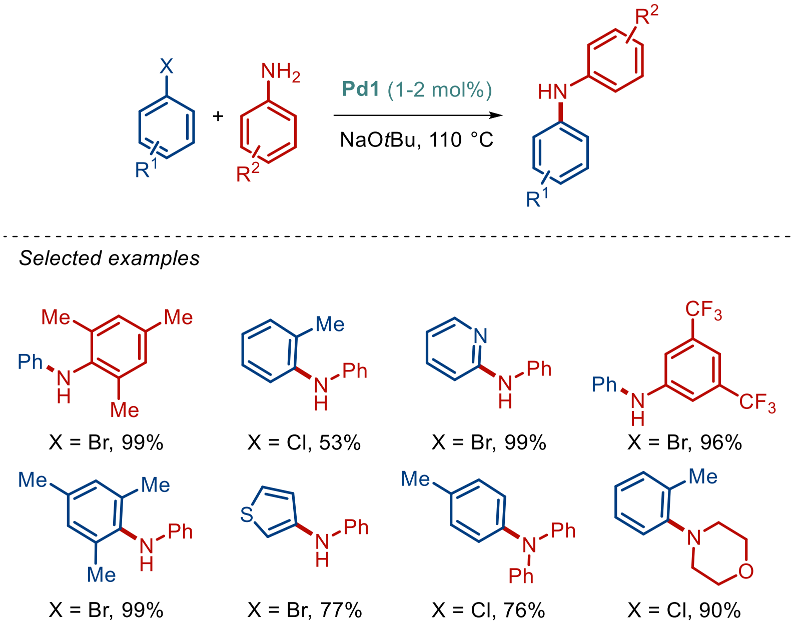


Scheme 40. Heck cross-coupling catalyzed by ring-expanded NHC-Pd reported by Cavell in 2012.

Additional examples of ring-expanded NHC-Pd complexes in Mizoroki-Heck coupling have been reported by Özdemir, Buchmeiser [46, 47, 86], Fürstner [124], Özdemir [125, 126] Dötz [112], Çetinkaya [113], Siemeling [115], Akkoc [127], and Mao [128].

8.3 Pd-NHC Complexes Catalyzed Buchwald-Hartwig Reactions

In 2016, Nechaev and co-workers reported Buchwald-Hartwig amination of aryl halides under solvent-free conditions using well-defined [(6-Dipp)Pd(cin)Cl] complex **Pd1** as precatalyst (**Scheme 41**) [129]. Aryl and heteroaryl bromides and chlorides featuring a range of electron-donating, electron-withdrawing, and bulky groups were coupled with primary and secondary amines in good to excellent yields.

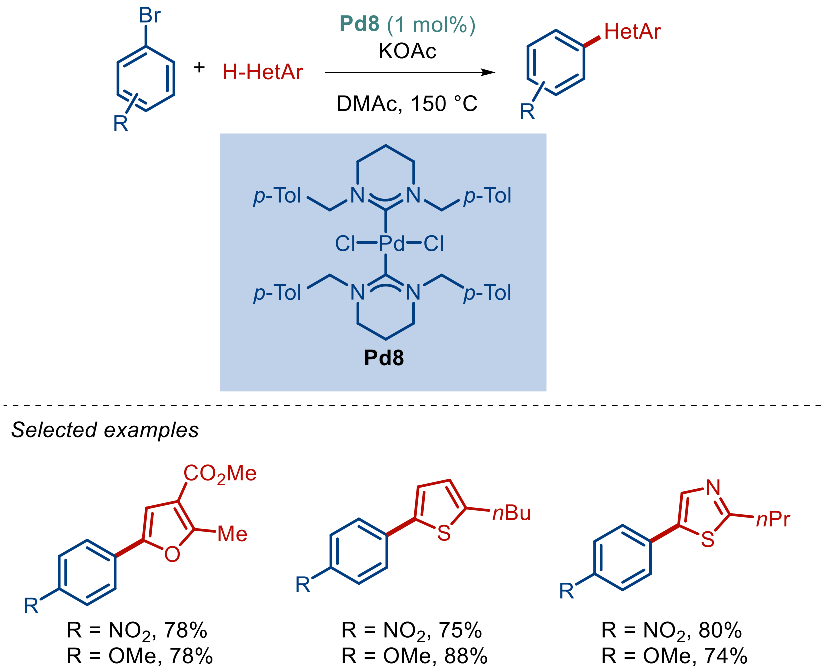


Scheme 41. Buchwald-Hartwig cross-coupling catalyzed by ring-expanded NHC-Pd reported by Nechaev in 2016.

Other examples of ring-expanded NHC-Pd complexes for Buchwald-Hartwig cross-coupling have been reported by Mao [130], Bermeshev [131, 132], Mani [133], and Gribanov [134].

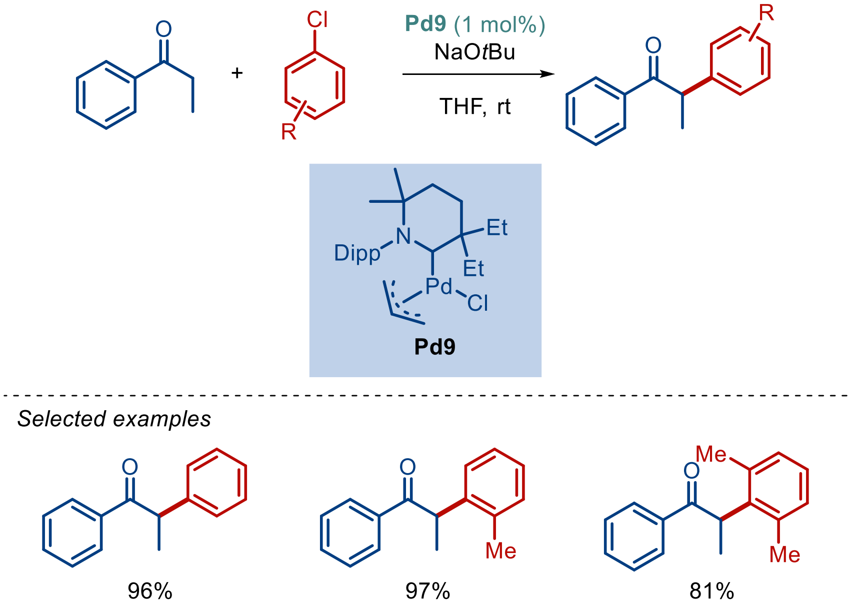
8.4 Pd-NHC Catalyzed C-H Activation/Arylation Reactions

In 2015, Çetinkaya and co-workers reported the synthesis and application of bis(NHC)-palladium complexes, $[(NHC)_2PdCl_2]$, in the direct C-H arylation of furans, thiophenes, and thiazoles (**Scheme 42**) [135]. Among the complexes tested, complex **Pd8** gave the arylated heterocycles in good to excellent yields with broad tolerance for the substitution of aryl bromides. This transformation was fully regioselective in that only C2/C5 arylated products were formed.



Scheme 42. C-H Arylation of heterocycles catalyzed by ring-expanded NHC-Pd reported by Çetinkaya in 2015.

In 2018, Bertrand and co-workers reported the synthesis of a new series of ring-expanded cyclic (alkyl)amino carbenes 6-CAAC and their reactivity in deprotonative cross-coupling (**Scheme 43**) [136]. These ligands are both more nucleophilic and more electrophilic than the five-membered analogues owing to the presence of the six-membered ring. The authors tested the reactivity of the palladium complex **Pd9** in the α-C-H arylation of ketones. The authors found that the six-membered CAAC ligand showed much higher reactivity (99% yield) than its five-membered analogue (11% yield). The enhanced reactivity was attributed to the stronger donating capability and more flexible backbone. The effect was particularly pronounced in the reactions of sterically hindered aryl chlorides.

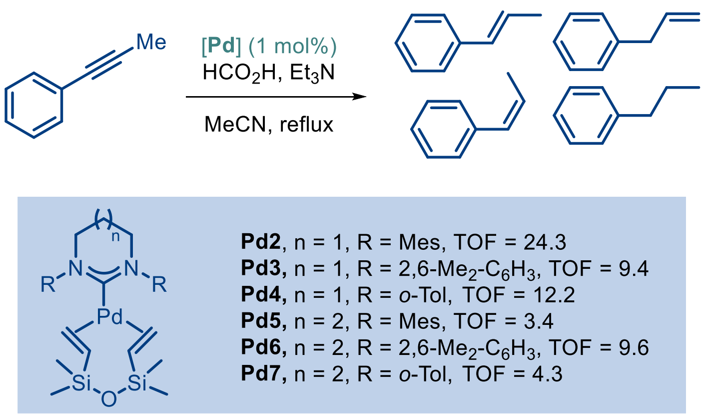


Scheme 43. α-C-H Arylation of ketones catalyzed by ring-expanded NHC-Pd reported by Bertrand in 2018.

In 2010, Kündig and co-workers reported asymmetric α-arylation of amides using chiral N-heterocycle carbene precursors. A chiral six-membered iminium salt was obtained by a four-step procedure in 70% overall yield. The use of a six-membered ligand resulted in a decrease in the yield and enantiomeric excess of the product compared to the five-membered analogue (60%, 68% *ee* vs. 98%, 88% *ee*) [137]. Additional examples of C-H arylation using ring-expanded NHC-palladium complexes have been reported by Trapp and co-workers (chiral Pd complexes for similar C-H arylations) [138], while Li and co-workers reported arylation of 4-benzylpyridines [139].

8.5 Pd-NHC Catalyzed Hydrogenation Reactions

In 2013, Elsevier and co-workers reported hydrogenation of alkynes to alkenes and alkanes using [(NHC)Pd(dvtms)] complexes **Pd2-Pd7** featuring ring-expanded NHC ligands (**Scheme 44**) [140]. The authors found that the catalytic performance decreased with an increase of steric hindrance in the series of six-membered NHCs in the reactions performed without maleic anhydride. Interestingly, an improved (*Z*)-alkene selectivity and decreased catalytic activity were obtained when maleic anhydride was added to the reaction.

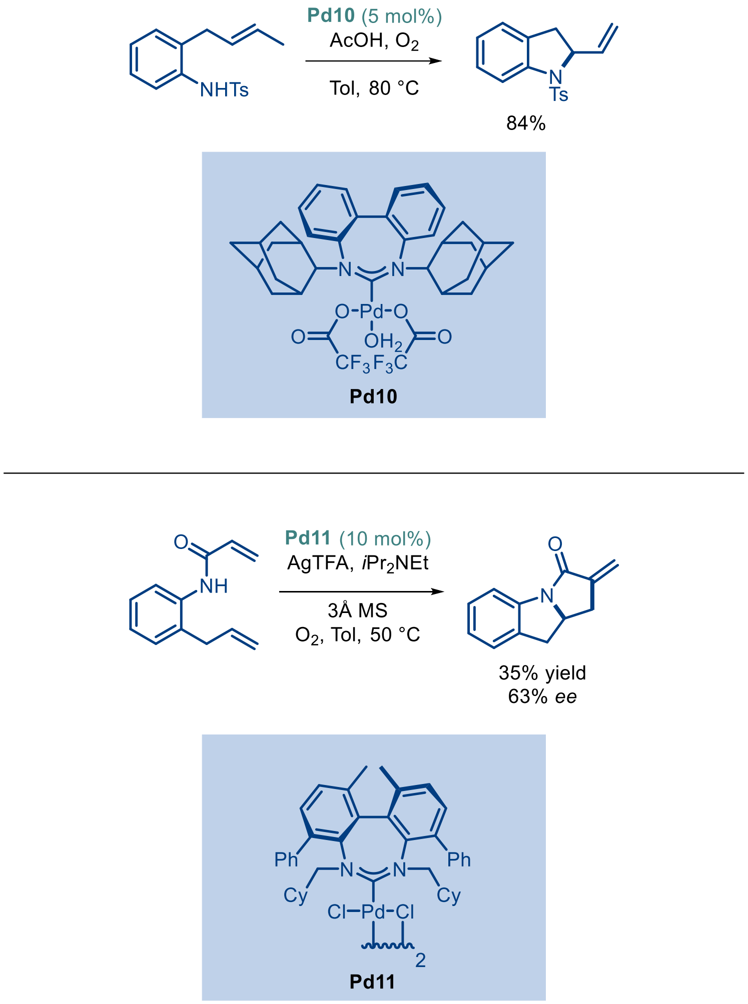


Pd2, n = 1, R = Mes, TOF = 24.3
Pd3, n = 1, R = 2,6-Me_2-C_6H_3, TOF = 9.4
Pd4, n = 1, R = *o*-Tol, TOF = 12.2
Pd5, n = 2, R = Mes, TOF = 3.4
Pd6, n = 2, R = 2,6-Me_2-C_6H_3, TOF = 9.6
Pd7, n = 2, R = *o*-Tol, TOF = 4.3

Scheme 44. Hydrogenation of alkynes catalyzed by ring-expanded NHC-Pd reported by Elsevier in 2013.

8.6 Pd-NHC Catalyzed Cyclization Reactions

In 2006, Stahl and co-workers reported a single example of the aerobic oxidative cyclization of alkenes using a seven-membered NHC-ligated palladium complex **Pd10** in the presence of acetic acid as a cocatalyst (**Scheme 45**) [141]. Subsequently, they reported an asymmetric version of the aerobic oxidative cyclization of alkenes using an enantiomerically resolved chloro dimer complex (*S*,*S*)**-Pd11** [142]. After extensive optimization, they achieved 63% ee with 35% yield of the cyclization product.



Scheme 45. Oxidative cyclization of alkenes catalyzed by ring-expanded NHC-Pd reported by Stahl in 2006-2009.

The proposed mechanism for this transformation is shown in **Figure 6** [141]. Intramolecular aminopalladation provides the alkyl-Pd(II) intermediate **II**, which furnishes the cyclized product after β-hydride elimination. Meanwhile, the palladium hydride complex **III** is produced and undergoes reversible reductive elimination to give the $L_2Pd(0)$ species **IV**. Next, complex **IV** is oxidized by molecular oxygen, yielding palladium dioxide intermediate **V**. The opening of the ring in the presence of carboxylic acid leads to the Pd(II)-hydroperoxide complex **VI**. Complex **VI** might also be generated *via* direct oxidation of complex **III** by oxygen. Finally, the reaction of **VI** with trifluoroacetic acid regenerates the active Pd(II) species **I**.

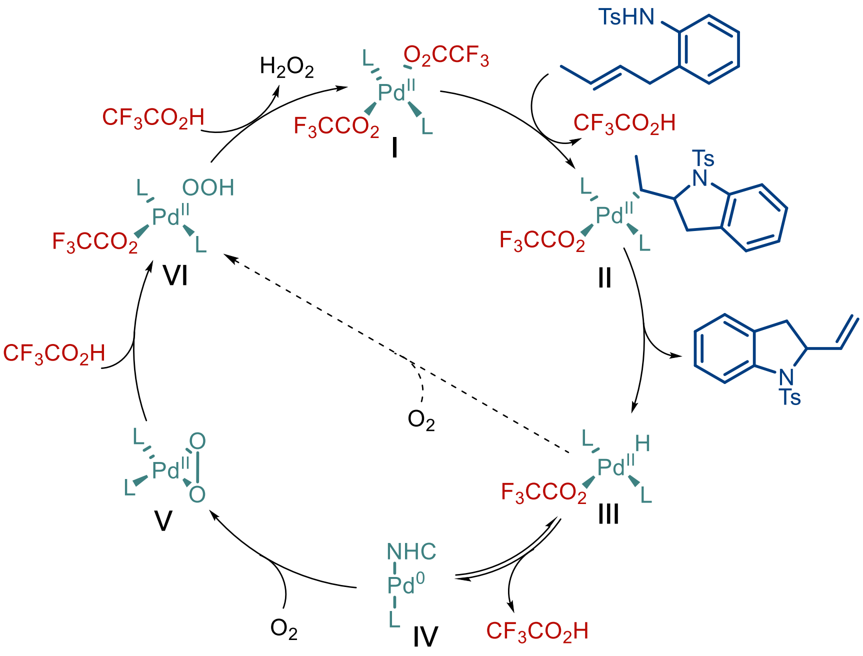
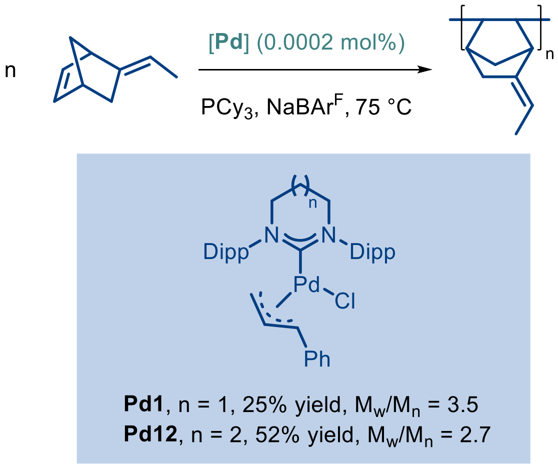


Fig. 6. Mechanism for aerobic oxidative cyclization of alkenes catalyzed by ring-expanded NHC-Pd.

8.7 Pd-NHC Catalyzed Polymerization Reactions

In 2018, Bermeshev and co-workers reported the catalytic polymerization of 5-ethylidene-2-norbornene (ENB) mediated by ring-expanded NHC-palladium complexes **Pd1** and **Pd12** at very low catalyst loading (0.0002 mol%) in the presence of tricyclohexylphosphine (**Scheme 46**) [143]. They found that the endocyclic double bond underwent selective polymerization, leaving the exocyclic double bond intact. Complex **Pd12** supported by 7-Dipp ligand outperformed the catalyst **Pd1** that featured a six-membered 6-Dipp.



Scheme 46. Polymerization of 5-ethylidene-2-norbornene catalyzed by ring-expanded NHC-Pd reported by Bermeshev in 2018.

The proposed mechanism for this intriguing polymerization is shown in **Figure 7** [144]. The Pd(II)–NHC precatalyst is activated to a cationic palladium species by chloride abstraction with NaBAr^F. Next, the reaction proceeds *via* repeated insertion of the monomers into the Pd-cin bond. The role of PCy$_3$ is to stabilize the formed Pd-poly(ENB) species by coordination. Considering that the insertion is slow, chain transfer is likely to occur by propagation. Opening of the restrained ENB ring followed by β-hydride elimination releases the corresponding poly(ENB), featuring a cin moiety as α-terminal. Additional examples of ring-expanded NHC-palladium complexes in polymerization have been reported by Bermeshev [145, 146].

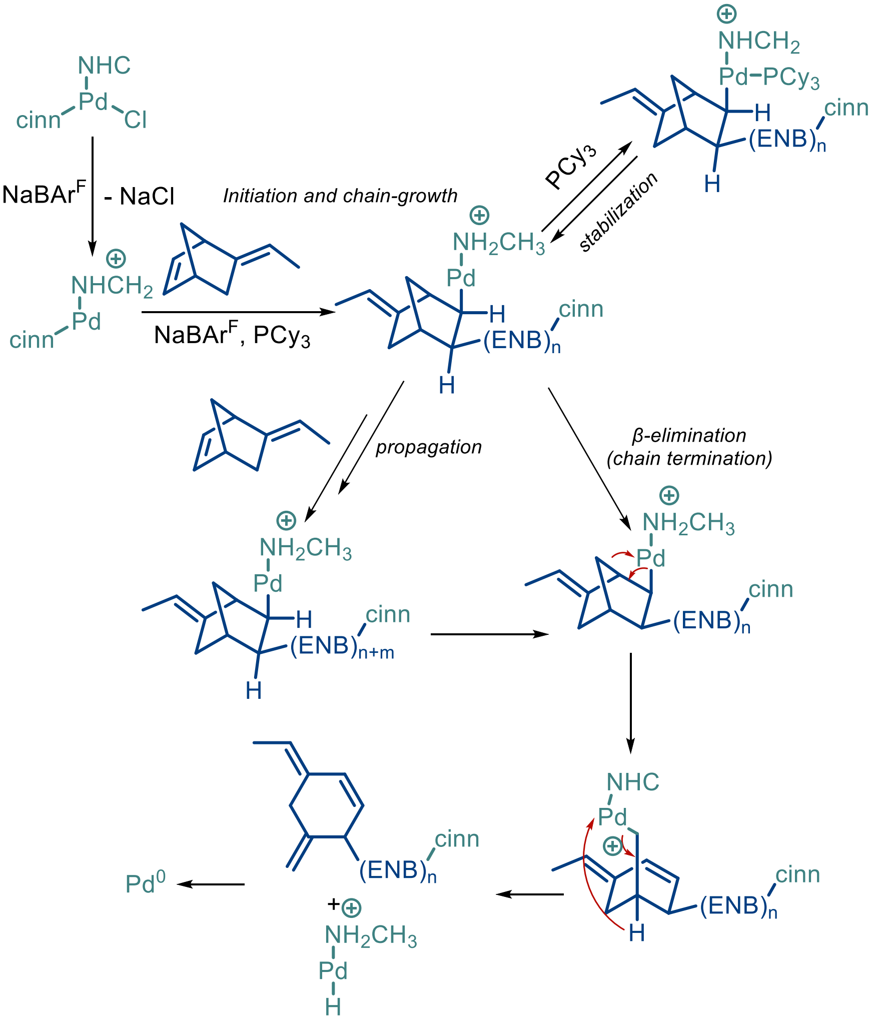


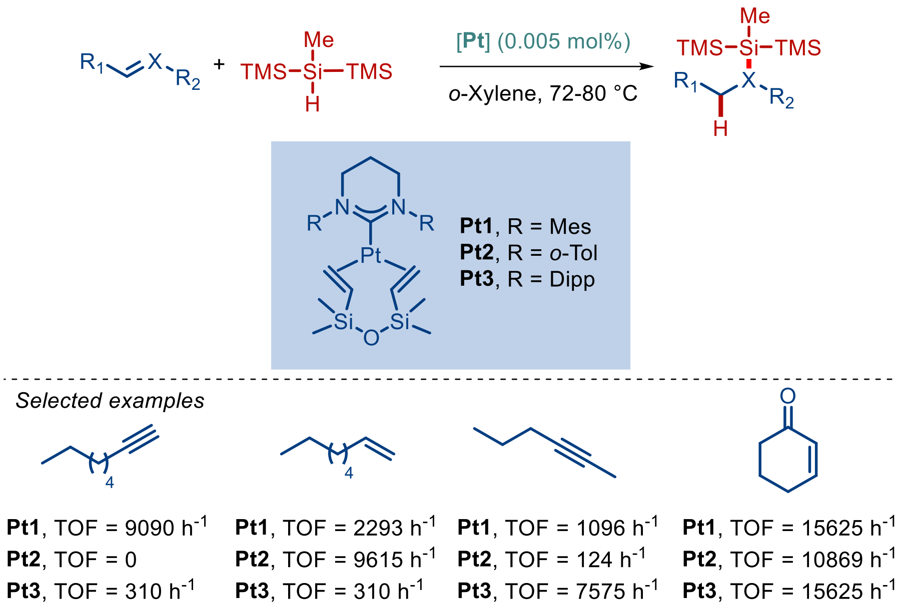
Fig. 7. Mechanism for polymerization of 5-ethylidene-2-norbornene catalyzed by ring-expanded NHC-Pd.

9. Ring-Expanded Platinum-NHC Complexes

Ring-expanded NHC-platinum complexes have been successfully applied in hydrosilylation [148], diboration [149], and borylation reactions [150].

9.1 Pt-NHC Catalyzed Hydrosilylation Reactions

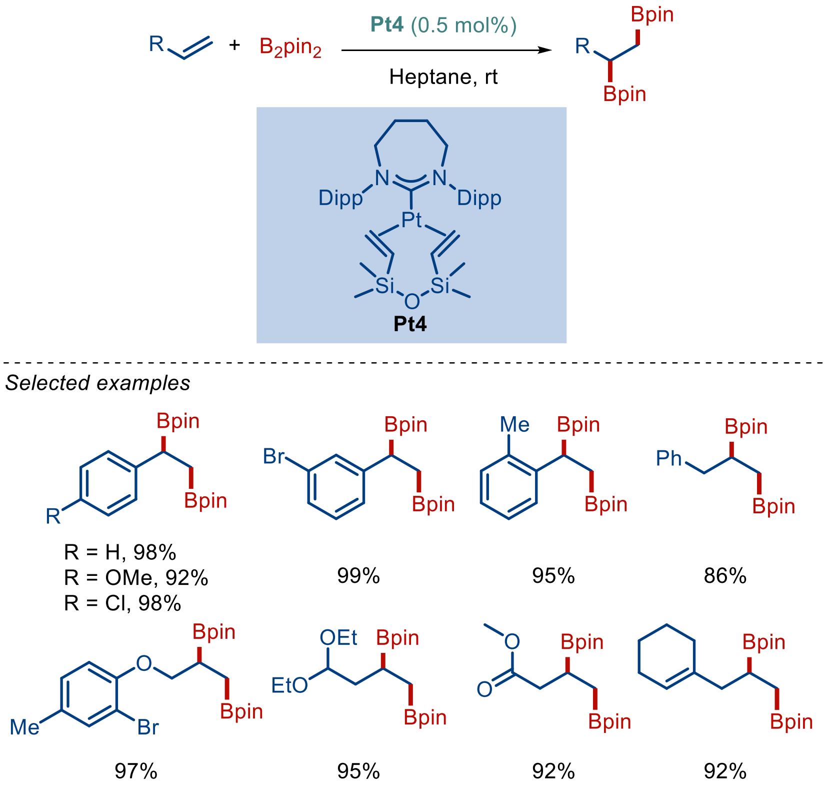
In 2011, Cavell and co-workers reported the hydrosilylation of alkynes, alkenes and ketones with a panel of ring-expanded (NHC)Pt(dvtms) complexes **Pt1-Pt3** (**Scheme 47**) [148]. Among the three ligands investigated, 6-Mes with moderate steric bulkiness demonstrated the highest reactivity in most cases. In contrast, **Pt2** bearing less hindered 6-*o*-Tol showed a low reactivity toward alkynes due to catalyst deactivation. In the case of 2-cyclohexene-1-one, a 1,4-addition product was obtained.



Scheme 47. Hydrosilylation reactions catalyzed by ring-expanded NHC-Pt reported by Cavell in 2011.

9.2 Pt-NHC Catalyzed Diboration Reactions

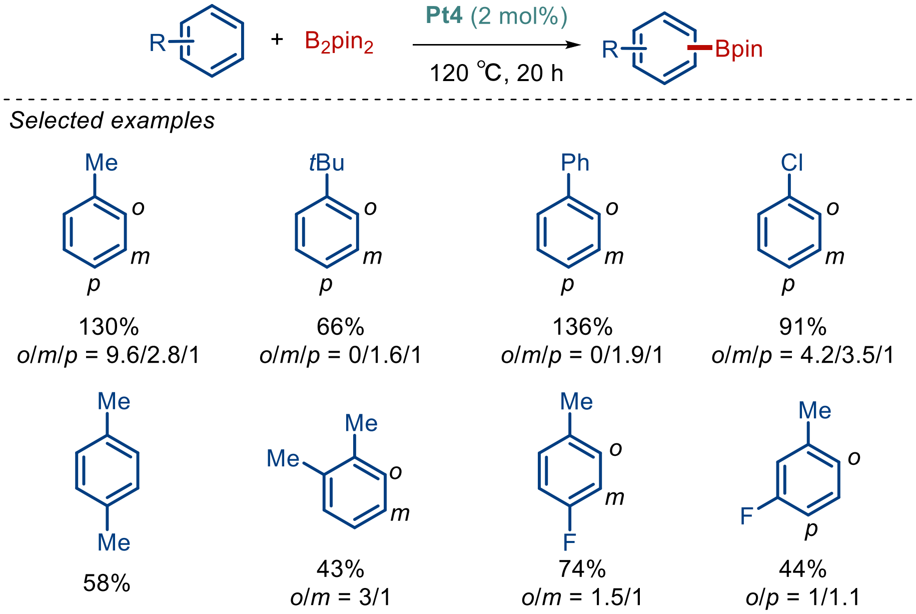
In 2020, Asachenko et al. reported a series of (NHC)Pt(dvtms) complexes and tested their reactivity in 1,2-diboration of terminal alkenes (**Scheme 48**) [149]. In the diboration of styrene, 7-Dipp complex **Pt4** outperformed other congeners that were supported by IMes, IPr, SIMes, SIPr, IPr^{Cl}, IPr*, IPr*^{OMe}, 6-Mes, 6-Dipp, and 7-IMes. A wide variety of functional groups were tolerated in this reaction. Alkenes bearing alkoxy, halides, ester, ketone, and acetal groups gave the corresponding 1,2-bis(boronates) in excellent yields.



Scheme 48. Diboration of alkenes catalyzed by ring-expanded NHC-Pt-NHC reported by Asachenko in 2020.

9.3 Pt-NHC Catalyzed Borylation Reactions

Asachenko and co-workers also reported an *ortho*-selective C-H borylation of arenes using (7-Dipp)Pt(dvtms) complex **Pt4** (**Scheme 49**) [150]. They found that 6- and 7-membered ring-expanded NHCs gave better regioselectivity than conventional 5-membered imidazol-2-ylidenes. Interestingly, reactions performed with bis(pinacolato)diboron generally resulted in higher *ortho* selectivity than the reactions conducted with pinacolborane. For monosubstituted benzenes, the *o*/*m*/*p*-selectivity as high as 10:3:1 was observed. Interestingly, the authors found that borylation also occurred with HBPin as the product of B_2Pin_2, leading to product yields exceeding 100% in some cases.



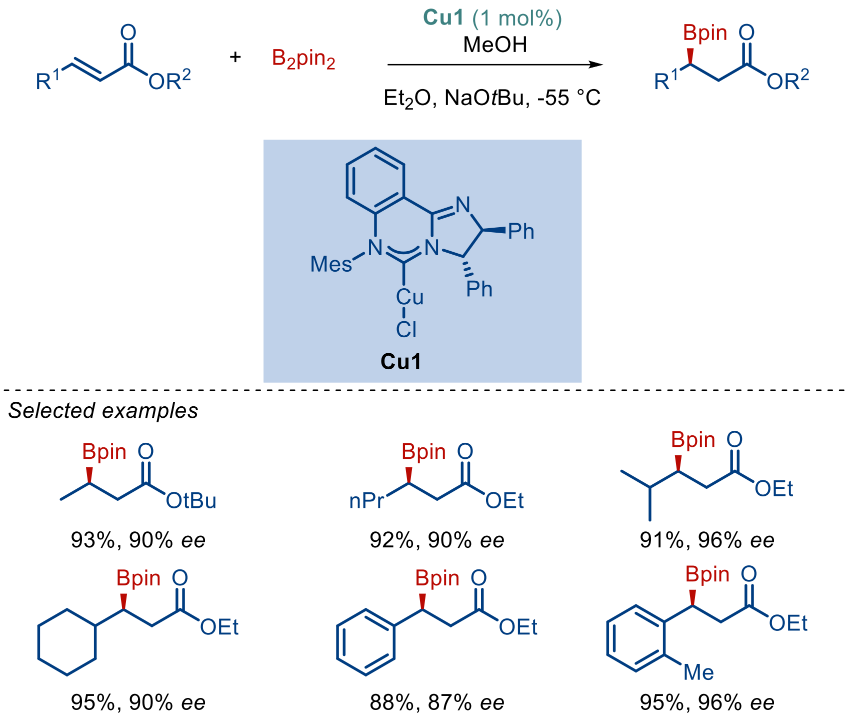
Scheme 49. Regioselective borylation of arenes catalyzed by ring-expanded NHC-Pt reported by Asachenko in 2020.

10. Ring-Expanded Copper-NHC Complexes

Ring-expanded copper NHC complexes showed broad utility in hydroboration [151-157], allylic borylation [158-162], arylborylation [163-166], alkenylborylation [167], borylacylation [168], dehydrogenative borylation [169], hydrosilylation [170-176], allylic silylation [162, 177, 178], cyanosilylation [173], reduction [157, 179], allylation [180, 181], addition [182-184], cyclization [51, 185-191], and polymerization [173] reactions. In addition to these applications, ring-expanded copper-NHC complexes have also been used for the hydrophosphination [192], 1,6-conjugate allylation [193], and three-component borylfluoroallylation of alkenes [194].

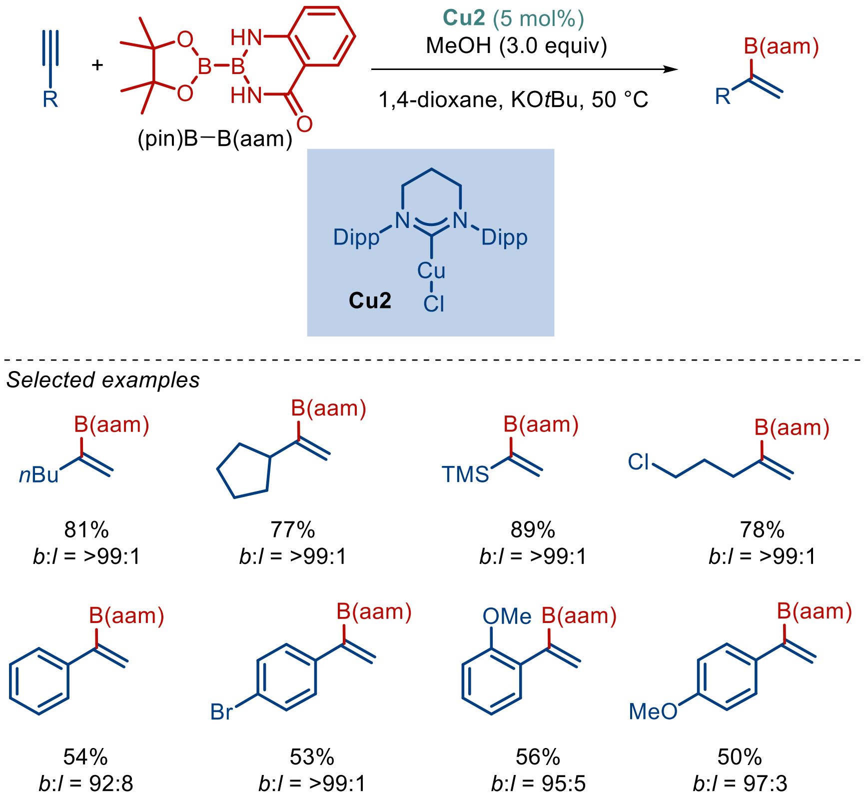
10.1 Cu-NHC Catalyzed Hydroboration Reactions

In 2010, McQuade and co-workers reported an inventive chiral six-membered NHC copper(I) complex **Cu1** for the enantioselective β-borylation of conjugated alkenes (**Scheme 50**) [151]. This McQuade's chiral NHC-Cu(I) complex **Cu1** catalyzed the borylation of α,β-unsaturated esters in high yields and with impressive enantioselectivity in the presence of methanol at -55 °C. Notably, **Cu1** showed a TON of 10,000 at 0.01 mol% catalyst loading with an 88% *ee* value.



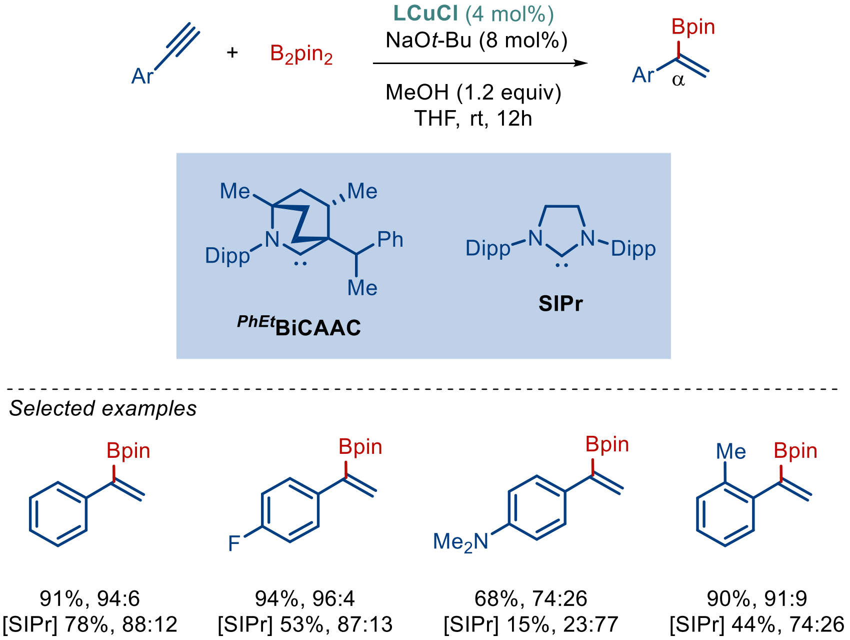
Scheme 50. β-Borylation of alkenes catalyzed by ring-expanded chiral NHC-Cu reported by McQuade in 2010.

In 2021, Yoshida explored the impact of Lewis acidity of boron reagents in conjunction with the steric hindrance of NHC ligands on the regioselectivity of Cu-NHC catalyzed borylation of alkynes (**Scheme 51**) [152]. When (pin)B–B(aam) was used as a boron source, they found that the branched:linear (*b*:*l*) selectivity increased dramatically when the buried volume of the NHC ligands increased. The complex **Cu2** supported by 6-Dipp with $\%V_{bur}$ of 53.4% gave >99:1 selectivity compared to 40:60 selectivity obtained with the analogous complex supported by IMes ($\%V_{bur}$ = 38.1%). The B(aam) moiety was successfully installed on the internal carbon of a wide range of terminal alkynes with good functional group tolerance.



Scheme 51. β-Borylation of terminal alkynes catalyzed by ring-expanded NHC-Cu reported by Yoshida in 2021.

In 2021, the catalytic activity of 6-CAAC and BiCAAC was investigated in protoboration (**Scheme 52**) and protosilylation reactions [153]. Selective copper-catalyzed Markovnikov hydrofunctionalization of terminal alkynes afforded alkenyl boronate and silane products. The method tolerates both electron-deficient and electron-rich terminal alkynes and provides desired products in higher yields and regioselectivity compared to five-membered SIPr.

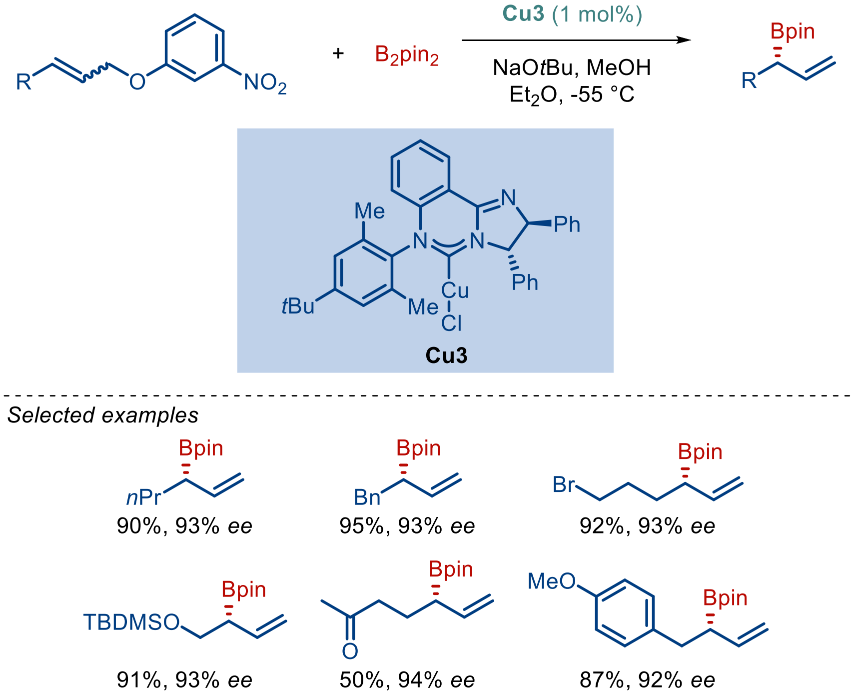


Scheme 52. α-Selective protoboration of terminal aryl-substituted alkynes reported by Bertrand, Jazzar and Engle in 2021.

In 2022, Bertrand, Jazzar, and Engle described an example of the Cu-catalyzed three-component carboboration of terminal alkynes using cyclic (alkyl)(amino)carbenes as ligands. A high level of selectivity to α-isomers was observed for various carbon electrophiles. The presented method opened up a new route for the synthesis polyfunctionalized alkenylboron derivatives [154]. Additional examples of using ring-expanded NHC-Cu complexes for hydroboration of π-systems have been reported. α-Selective hydroboration of propargylic ethers was reported by McQuade and co-workers [155]. Lin tested the McQuade ligand for enantioselective hydroboration of aldimines [156], however, the reaction led to racemic products. Sun and co-workers reported chiral six-membered NHCs based on 3,4-dhydroquinazoline framework for copper-catalyzed hydroboration of α,β-unsaturated esters, and up to 93% *ee* was achieved [157]. Wilhelm and co-workers disclosed a camphor-derived six-membered NHC for Cu-catalyzed hydroboration of α,β-unsaturated esters, and up to 82% *ee* was obtained [158]. Whittlesey and co-workers reported Cu-catalyzed hydroboration of alkynes with HBpin using well-defined [(6-Mes)Cu(O*t*Bu)] complex bearing *tert*-butoxide anion [159].

10.2 Cu-NHC Catalyzed Allylic Borylation Reactions

In 2011, McQuade and co-workers disclosed a chiral copper NHC complex **Cu3** for the stereoconvergent synthesis of chiral α-substituted allylboronates (**Scheme 53**) [160]. Compared with complex **Cu1** (**Scheme 50**), complex **Cu3** features a bulky *tert*-butyl group at the *para* position, which resulted in higher enantioselectivity. They found that the *Z*-allylic substrate gave the same configurational product as the *E* isomer. Moreover, the *E* isomer gave faster reaction rate than the corresponding *Z* isomer in this allylic substitution. The scope of this reaction is very broad. *E*/*Z* mixtures of alkenes containing bromide, TBDMS protected hydroxyl, and ketone functionalities were well tolerated, furnishing chiral allylboronates in high yields and with excellent *ee* values.

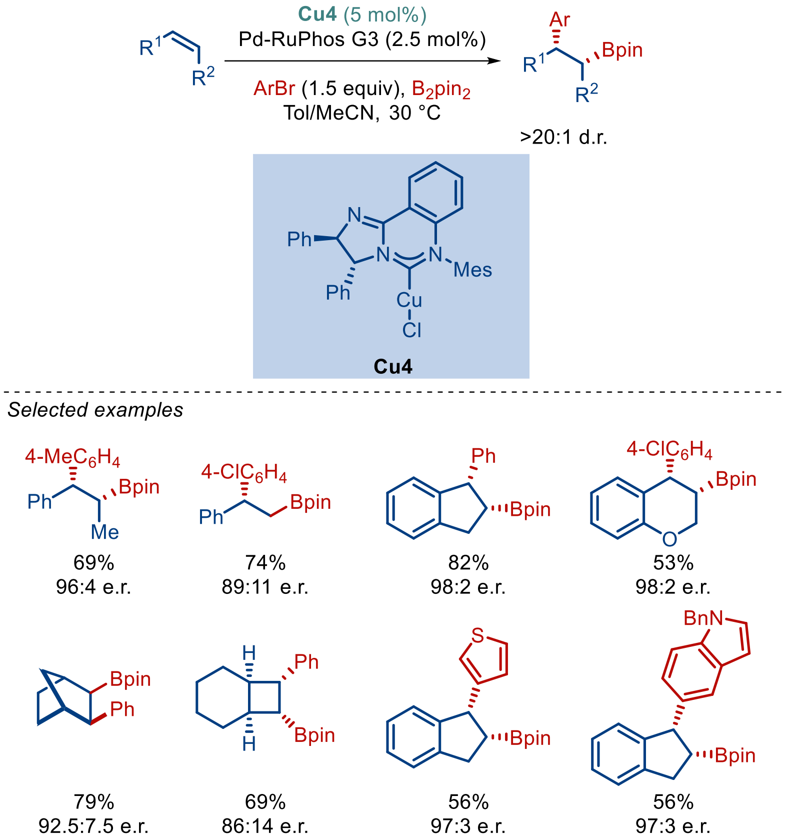


Scheme 53. Allylic borylation catalyzed by ring-expanded NHC-Cu reported by McQuade in 2011.

Additional examples of allylic borylation using McQuade's chiral ligand were reported by McQuade [161] and Oestreich [162].

10.3 Cu-NHC Catalyzed Arylboration Reactions

In 2017, Brown and co-workers reported enantioselective and diastereoselective arylboration of alkenylarenes using a combination of a copper complex **Cu4** and a Pd catalyst (**Scheme 54**) [163]. Both acyclic or cyclic alkenylarenes, and strained alkenes were borylated smoothly with electron-rich and electron-deficient (hetero)aryl bromides to give the corresponding 1,1-diarylalkanes with high e.r. values. It is worthwhile to note that a single diastereomer was obtained for all substrates (d.r. >20:1).



Scheme 54. Arylboration of alkenes catalyzed by ring-expanded NHC-Cu reported by Brown in 2017.

A mechanism involving dual Cu(I)/Pd(0) cycles has been proposed for this arylboration of alkenes (**Fig. 8**) [163]. Initially, Bpin is transferred to the copper center from B_2pin_2 in the presence of a base. The generated [(NHC)Cu(Bpin)] complex adds to the alkene double bond with the formation of two stereocenters under the control of the chiral ring-expanded NHC ligand. The palladium catalyzed cross-coupling completes the cycle with the key Cu to Pd transmetalation.

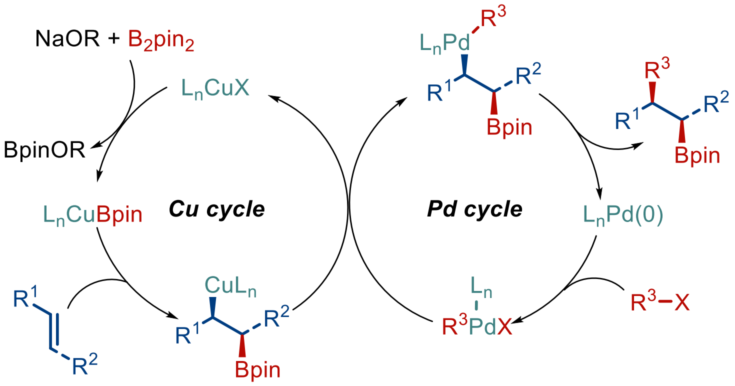
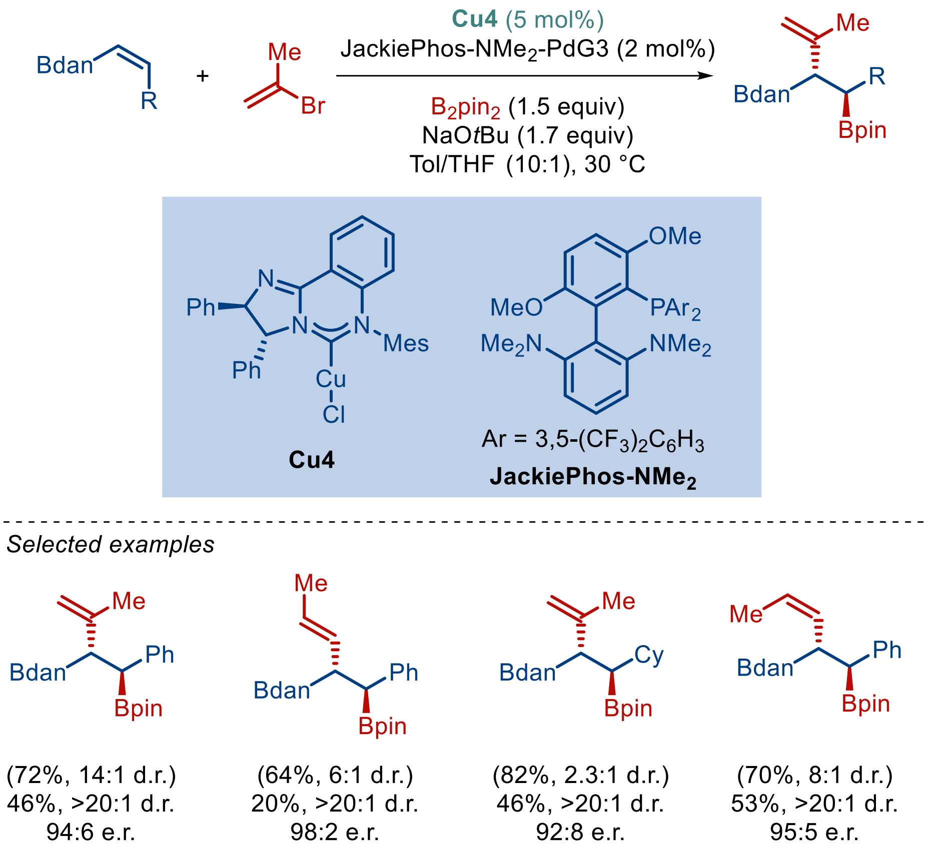


Fig. 8. Mechanism for arylboration of alkenes by Pd/Cu dual catalysis.

Brown and co-workers also reported enantioselective arylboration of cyclic dienes using similar conditions, where only the 1,2-addition product was generated with high enantioselectivity and diastereoselectivity [164]. The same group extended this strategy to heteroarylboration using six-membered pyrid-2-ylidene-copper complexes [165]. Later, the Brown group successfully achieved arylborylation of *N*-Boc-2-azetine using a similar catalytic system [166].

10.4 Cu-NHC Catalyzed Alkenylborylation Reactions

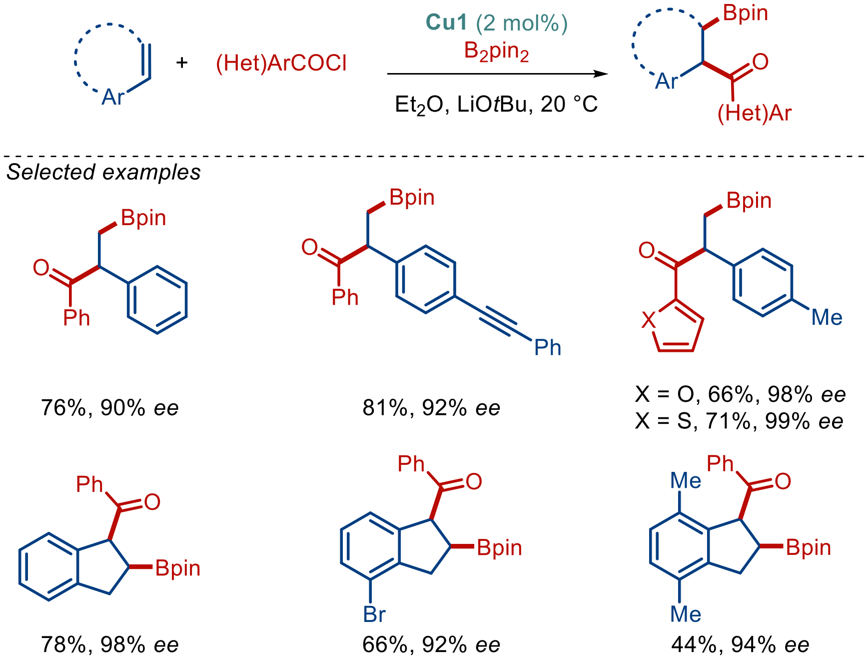
In 2021, Brown and co-workers reported enantioselective alkenylborylation of alkenes using their dual catalytic **Cu4**/**Pd** system (**Scheme 55**) [167]. They found that the use of JackiePhos-NMe_2 as the palladium ligand improved diastereoselectivity of this reaction. Notably, both *E*- and *Z*-vinylbromides demonstrated good reactivity in this alkenylborylation reaction. The allylated products are important intermediates in the synthesis of complex diols. Mechanistically, they proposed than the bulky Bdan moiety is positioned away from the N-Mes wingtip on the opposite side of the phenyl ring. Following borylcupration, the alkyl-Cu complex has the potential to undergo stereoretentive or stereoinvertive transmetallation.



Scheme 55. Alkenylboration of alkenes catalyzed by NHC-Cu reported by Brown in 2021. Yield/dr of crude reaction mixtures is shown in parentheses.

10.5 Cu-NHC Catalyzed Borylacylation Reactions

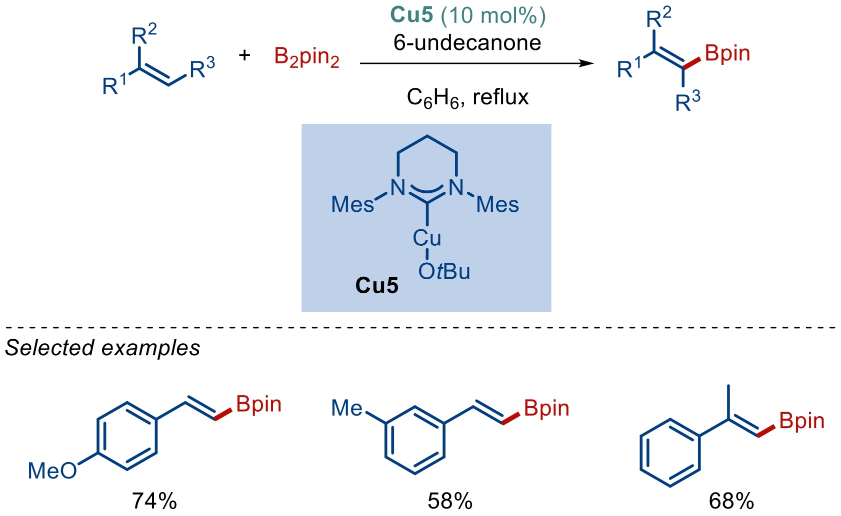
In 2021, Li reported asymmetric borylacylation of alkenes with acid chlorides and B_2pin_2 using McQuade's chiral Cu(I) complex **Cu1** (**Scheme 56**) [168]. This protocol tolerates a wide range of styrenes and indenes, and provides an efficient way to synthesize β-borylated ketones.



Scheme 56. Borylacylation of alkenes catalyzed by ring-expanded NHC-Cu reported by Li in 2021.

10.6 Cu-NHC Catalyzed Dehydrogenative Borylation Reactions

In 2017, Mankad and co-workers reported dehydrogenative borylation of styrenes catalyzed by well-defined complex [(6-Mes)Cu(O*t*Bu)] **Cu5** in the presence of a ketone additive (**Scheme 57**) [169a]. This reaction affords selectively *trans*-vinylboronates. The ketone additive served as an oxidant to trap the copper-hydride species, driving the catalytic cycle towards the formation of dehydrogenative products. The robustness of this method was tested using the Glorius robustness screen.[169b] The results showed that unsaturated functional groups, such as esters, nitriles, and internal alkynes were all compatible, while terminal alkynes, aldehydes, and amines had a deleterious effect due to competitive hydroboration. The method is also compatible with sterically-hindered trisubstituted alkenes.



Scheme 57. Dehydrogenative borylation of alkenes catalyzed by ring-expanded NHC-Cu reported by Mankad in 2017.

Mechanistically, in analogy to copper-catalyzed arylboration, the β-boroalkylcopper complex is initially formed by insertion (**Fig. 9**). The resulting complex undergoes β-hydride elimination to afford the *trans*-vinylboronate product and copper hydride intermediate [169a]. In this mechanism, an exogenous ketone is necessary to trap the copper hydride species and prevent the reinsertion that would lead to hydroboration.

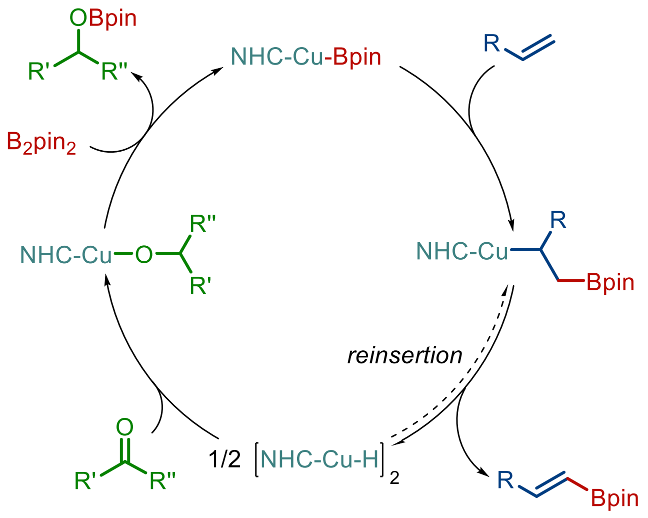
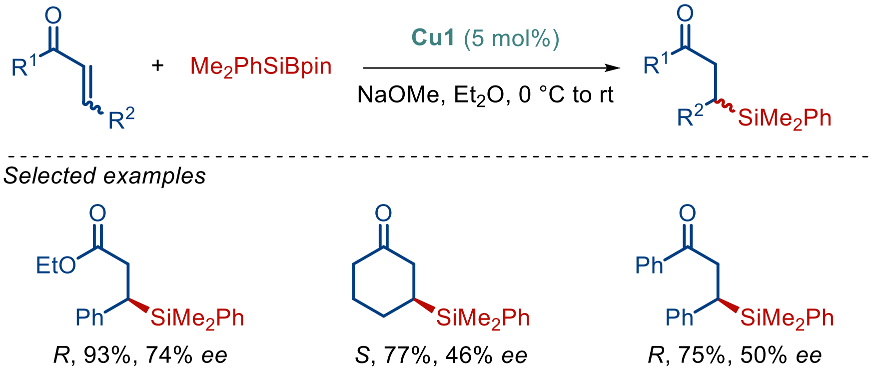


Fig. 9. Mechanism for dehydrogenative borylation catalyzed by ring-expanded NHC-Cu.

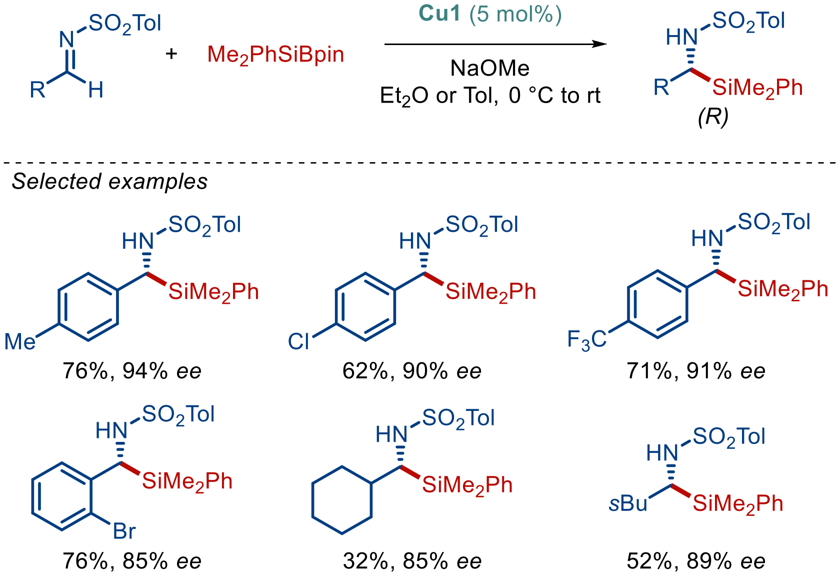
10.7 Cu-NHC Catalyzed Hydrosilylation Reactions

In 2014, Oestreich and co-workers reported the hydrosilylation of α,β-unsaturated compounds with Me_2PhSi-Bpin using McQuade's chiral complexes **Cu1** and **Cu3** as catalysts (**Scheme 58**) [170]. Interestingly, the results showed that the performance of catalysts depended on the solvent used. Typically, **Cu3** provided higher enantioselectivity in dichloromethane, while complex **Cu1** gave better results in diethyl ether. In particular, hydrosilylation of acyclic and cyclic α,β-unsaturated substrates was accomplished in high yields and with promising enantioselectivities.



Scheme 58. Hydrosilylation of alkenes catalyzed by ring-expanded NHC-Cu reported by Oestreich in 2014.

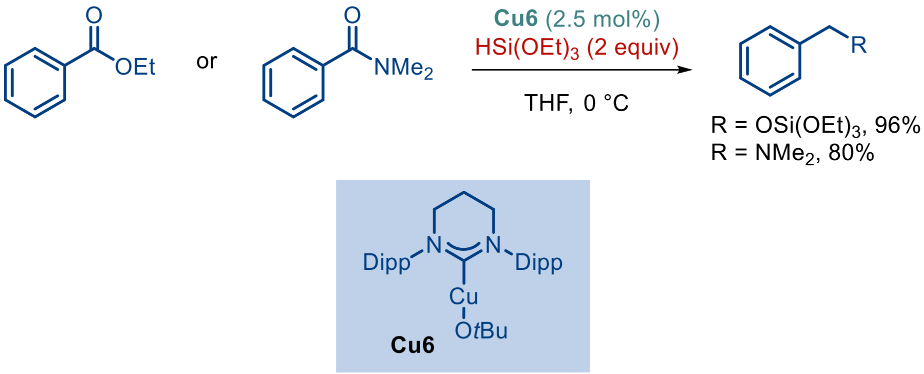
Oestreich and co-workers also reported the McQuade's chiral complex **Cu1** for the enantioselective hydrosilylation of aldimines (**Scheme 59**) [171]. This reaction affords valuable α-silylated imines by 1,2-addition. The highest *ee* values were obtained using sulfonyl-activated imines. Under the optimized conditions, aryl aldimines featuring electron-rich and electron-deficient substituents as well as aliphatic aldimines gave hydosilylated products in good yields and with excellent enantioselectivity. In addition to Me_2PhSi-Bpin, bulky silicon nucleophiles, such as $MePh_2Si$-Bpin, could also be used, albeit resulted in lower yield and enantioselectivity.



Scheme 59. Hydrosilylation of aldimines catalyzed by ring-expanded NHC-Cu reported by Oestreich in 2014.

In 2020, Bullock and co-workers disclosed a seminal report on the hydrosilylation of esters and amides using well-defined six-membered NHC complex [(6-Dipp)Cu(O*t*Bu)] **Cu6** (**Scheme 60**) [172]. Hydrosilylation of $PhCO_2Et$ and

$PhCONMe_2$ using 2.5 mol% of **Cu6** furnished $PhCH_2OSi(OEt)_3$ and $PhCH_2NMe_2$ in 96% and 80% yields, respectively. Importantly, IPr and SIPr ligated analogues were completely ineffective in this transformation due to rapid decomposition of the copper hydride species during the catalysis. Interestingly, even extremely bulky imidazol-2-ylidene, [(IPr*)Cu(O*t*Bu)], was less effective than the ring-expanded complex **Cu6**.

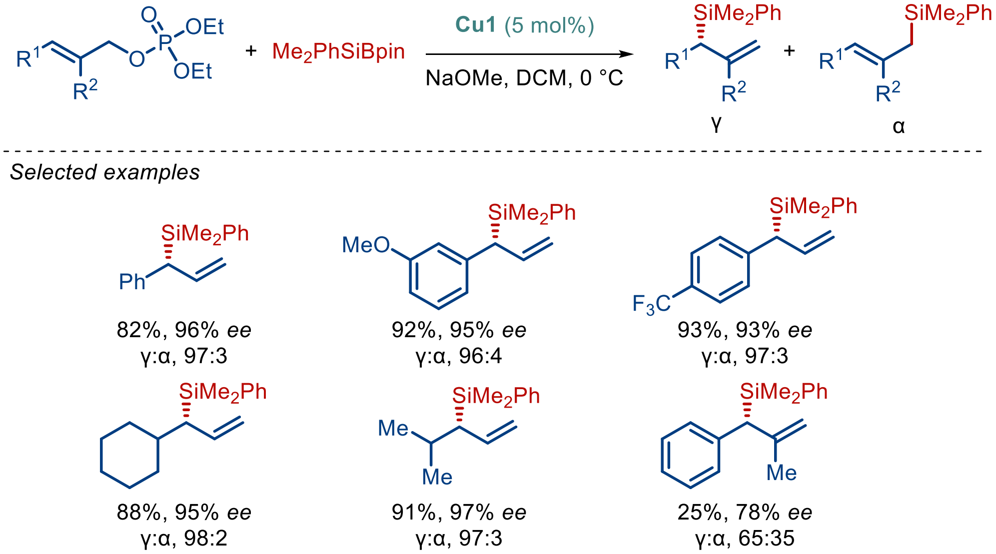


Scheme 60. Hydrosilylation of amides and esters catalyzed by ring-expanded NHC-Cu reported by Bullock in 2020.

Additional examples of hydrosilylation of unsaturated compounds using ring-expanded Cu-NHC complexes have been reported by Buchmeiser [173], Lavigne [174], Procter [175] and Whittlesey [176].

10.8 Cu-NHC Catalyzed Allylic Silylation Reactions

In 2013, Oestreich and co-workers reported enantioselective allylic substitution of allylic phosphates for the synthesis of α-chiral allylic silanes catalyzed by the chiral McQuade's complex **Cu1** (**Scheme 61**) [177]. This catalyst promoted the allylic substitution with Me_2PhSi-Bpin in a regio- and enantioconvergent manner, resulting in both *E* and *Z*-allylic substrates giving branched allylic silanes with the same stereoconfiguration. Aryl-, primary and secondary alkyl-substituted allylic phosphates were transferred to desired products in high yields and excellent enantiomeric excesses, while tertiary alkyl allylic phosphates gave predominantly linear products.

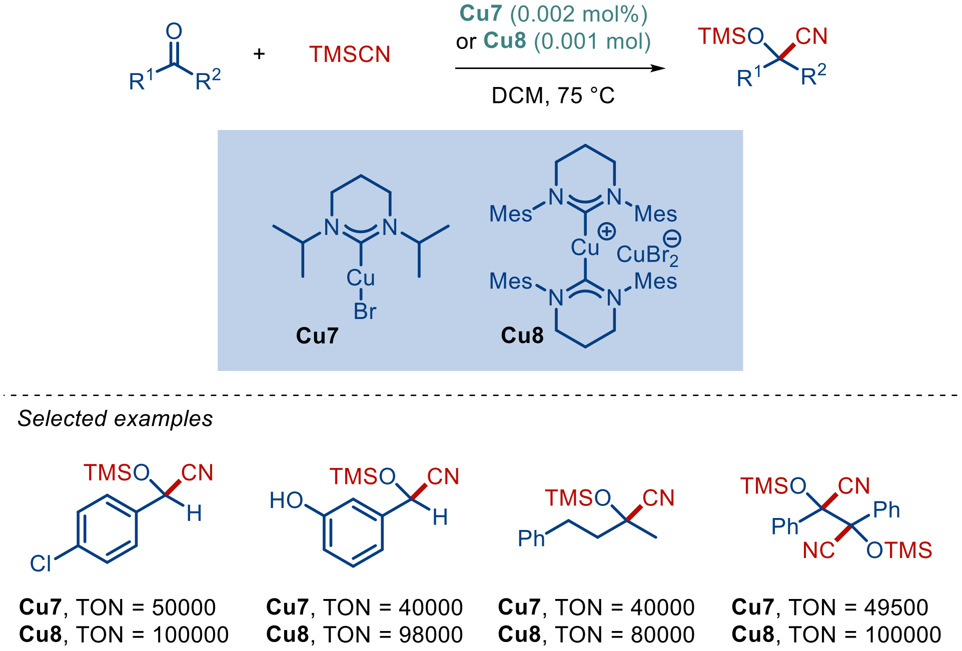


Scheme 61. Allylic silylation catalyzed by ring-expanded NHC-Cu reported by Oestreich in 2013.

In addition, the same group reported a similar method using $(Me_2PhSi)_2Zn\cdot 4LiCl$ as silicon nucleophile [162]. Moreover, enantioconvergent silylation of racemic allylic phosphates using **Cu1** as a catalyst was reported [178].

10.9 Cu-NHC Catalyzed Cyanosilylation Reactions

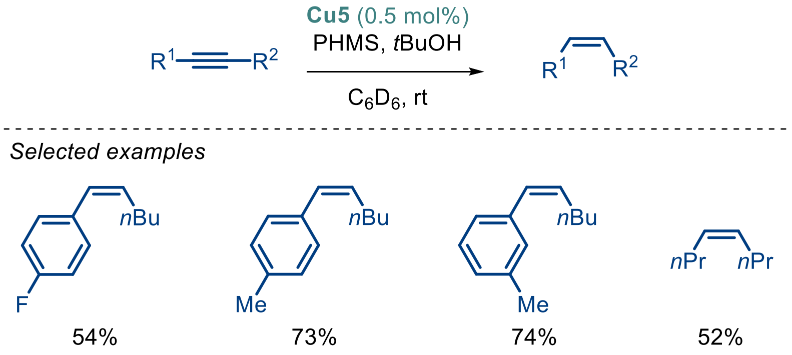
In 2005, Buchmeiser and co-workers reported six-membered copper-NHC complexes **Cu7** and **Cu8** for the cyanosilylation of ketones (**Scheme 62**) [173]. Both **Cu7** and **Cu8** showed excellent performance in this transformation at very low catalyst loading. TON for neutral complex **Cu7** was up to 50,000, while the cationic bis(NHC)-copper complex **Cu8** displayed enhanced reactivity with TON up to 100,000.



Scheme 62. Cyanosilylation of ketones catalyzed by ring-expanded NHC-Cu reported by Buchmeiser in 2005.

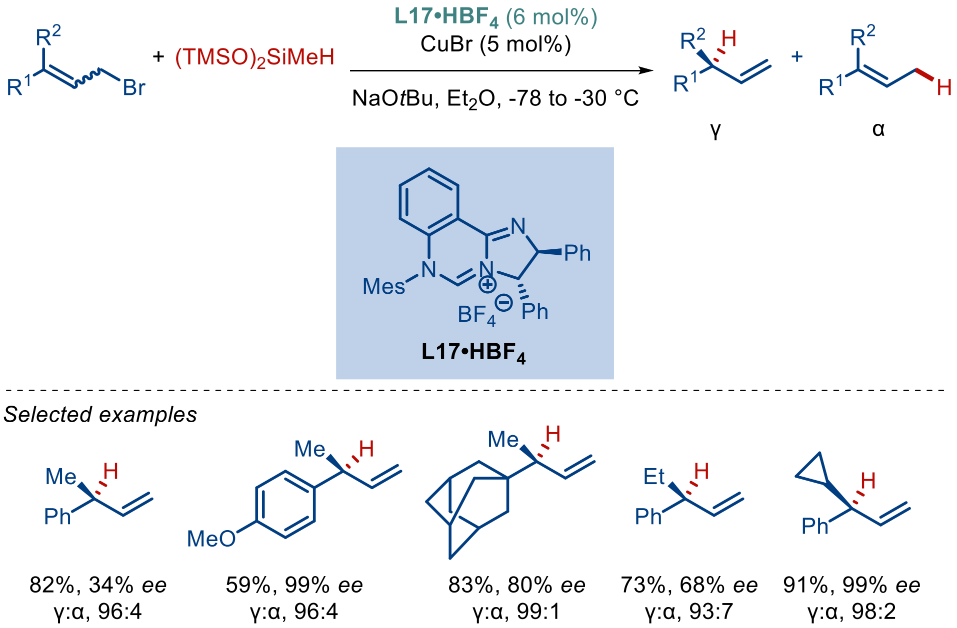
10.10 Cu-NHC Catalyzed Hydrogenation Reactions

In 2018, Whittlesey and co-workers reported semihydrogenation of alkynes to alkenes catalyzed by well-defined complex [(6-Mes)Cu(O*t*Bu)] **Cu5** and PHMS as a reductant (**Scheme 63**) [157]. The authors studied the effect of ligand on catalytic performance, and found that moderately bulky 6-Mes is the preferred ligand. In this method, internal alkynes were hydrogenated to (*Z*)-alkenes at 0.5 mol% **Cu5** at room temperature. Notably, overreduction side products were not formed during the process, demonstrating high selectivity for alkynes vs. alkenes of this protocol.



Scheme 63. Hydrogenation of alkynes catalyzed by ring-expanded NHC-Cu reported by Whittlesey in 2018.

In 2017, the Teichert group reported a regio- and stereoselective allylic reduction of allylic bromides catalyzed by CuBr/McQuade's chiral NHC salt **L17·HBF**$_4$ in the presence of $(TMSO)_2SiMeH$ (**Scheme 64**) [179]. This catalytic system permitted for the stereoconvergent reduction of *E*/*Z* mixtures of allylic bromides to same configurational products *via* hydride transfer in an S_N2' fashion. Impressively, trisubstituted alkenes were smoothly reduced to the corresponding terminal alkenes in high yields and with excellent *ee* values. Branched products were favored over linear ones in most cases examined.



Scheme 64. Allylic reduction catalyzed by ring-expanded NHC-Cu reported by Teichert in 2017.

Mechanistically, the reactive [(NHC)Cu(O*t*Bu)] complex is generated *in situ* and undergoes σ bond metathesis with silane to produce the copper hydride complex (**Fig. 10**) [179]. Subsequently, oxidative addition leads to the copper η^1-allyl complex, which exists in the equilibrium with the η^3-allyl complex. This was probed by the detection of a small amount of α-substituted alkenes from the reaction mixture. Next, reductive elimination affords the desired reduction product and [(NHC)CuBr], which regenerates [(NHC)Cu(O*t*Bu)] by ligand exchange.

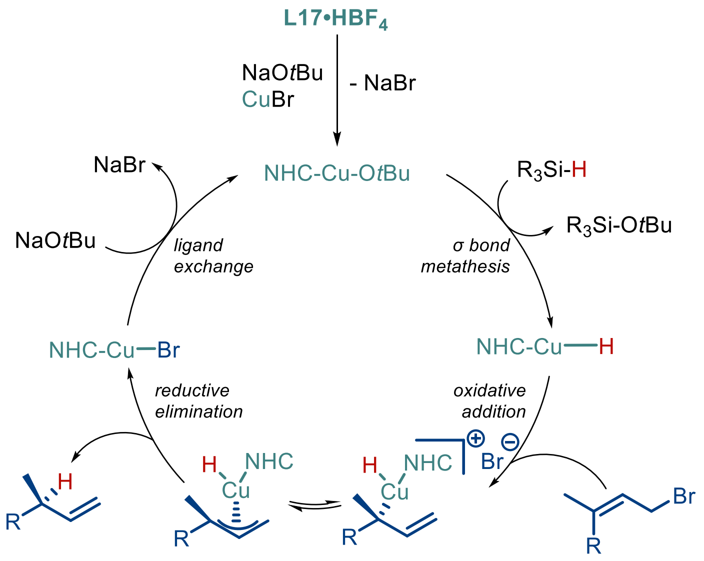
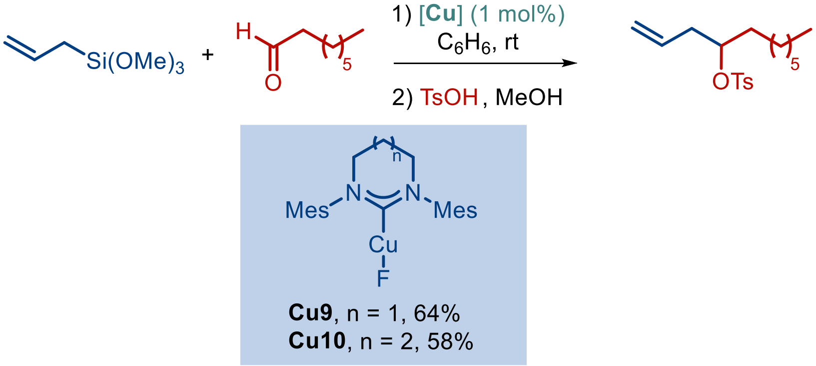


Fig. 10. Mechanism for allylic reduction catalyzed by ring-expanded NHC-Cu.

10.11 Cu-NHC Catalyzed Allylation Reactions

In 2020, Whittlesey and co-workers disclosed allylation of aldehydes with [(NHC)CuF] complexes as catalysts (**Scheme 65**) [180]. Using a catalyst loading of 1 mol%, these NHC-Cu-F complexes bearing a six- and seven-membered 6-Mes and 7-Mes gave isolated yields of 64% and 58% after trapping the product with *p*-toluenesulfonic acid.



Scheme 65. Allylation of aldehydes catalyzed by ring-expanded NHC-Cu reported by Whittlesey in 2020.

Proposed mechanism for the allylation of aldehydes catalyzed by [(NHC)CuF] complexes is shown in **Fig. 11** [180]. The Cu catalyst reacts with allylsilane to afford the copper allyl species and fluorosilane. Next, the copper allyl reacts with octanal to generate the copper alkoxide complex. Ligand exchange with fluorosilane gives the allylation product and regenerates the [(NHC)CuF] catalytic species.

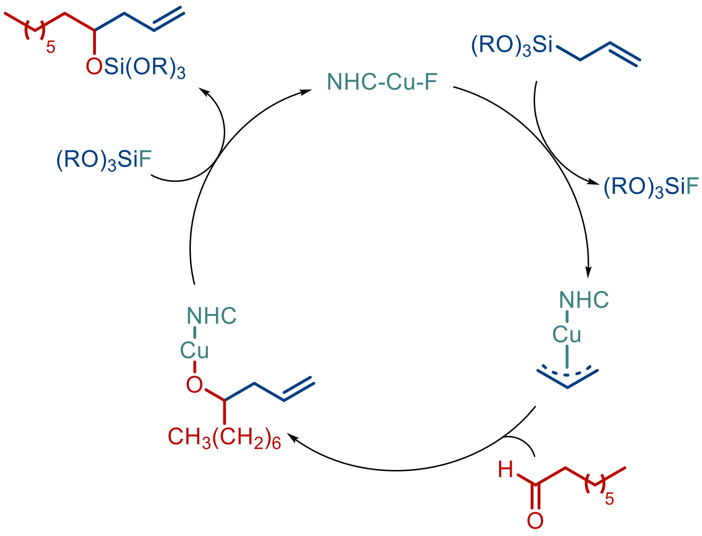
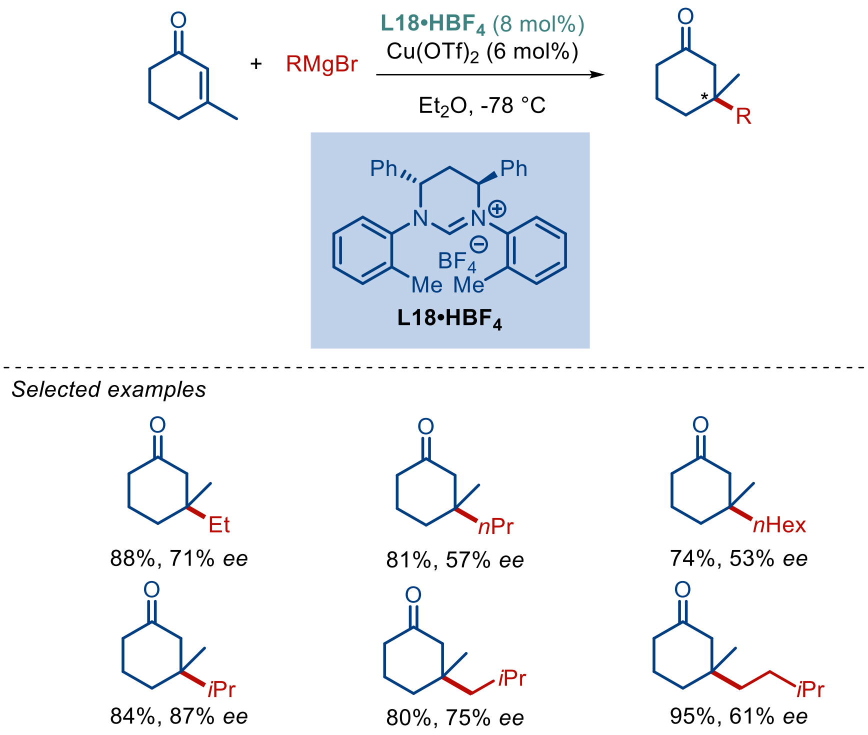


Fig. 11. Mechanism for allylation of aldehydes catalyzed by ring-expanded NHC-Cu.

In addition, Tran and co-workers studied allylation of carbonyls using a six-membered copper hydride complex [181].

10.12 Cu-NHC Catalyzed Addition Reactions

In 2015, Xu and co-workers reported chiral 3,4,5,6-tetrahydropyrimidinium salts as NHC precursors for the copper-catalyzed asymmetric 1,4-addition of alkylmagnesium bromides to 3-methylcyclohexenone (**Scheme 66**) [182]. **L18** featuring *o*-tolyl N-wingtips showed the highest reactivity and selectivity. This protocol allows for the conjugate alkylation in high yields and moderate to good enantioselectivity at -78 °C.

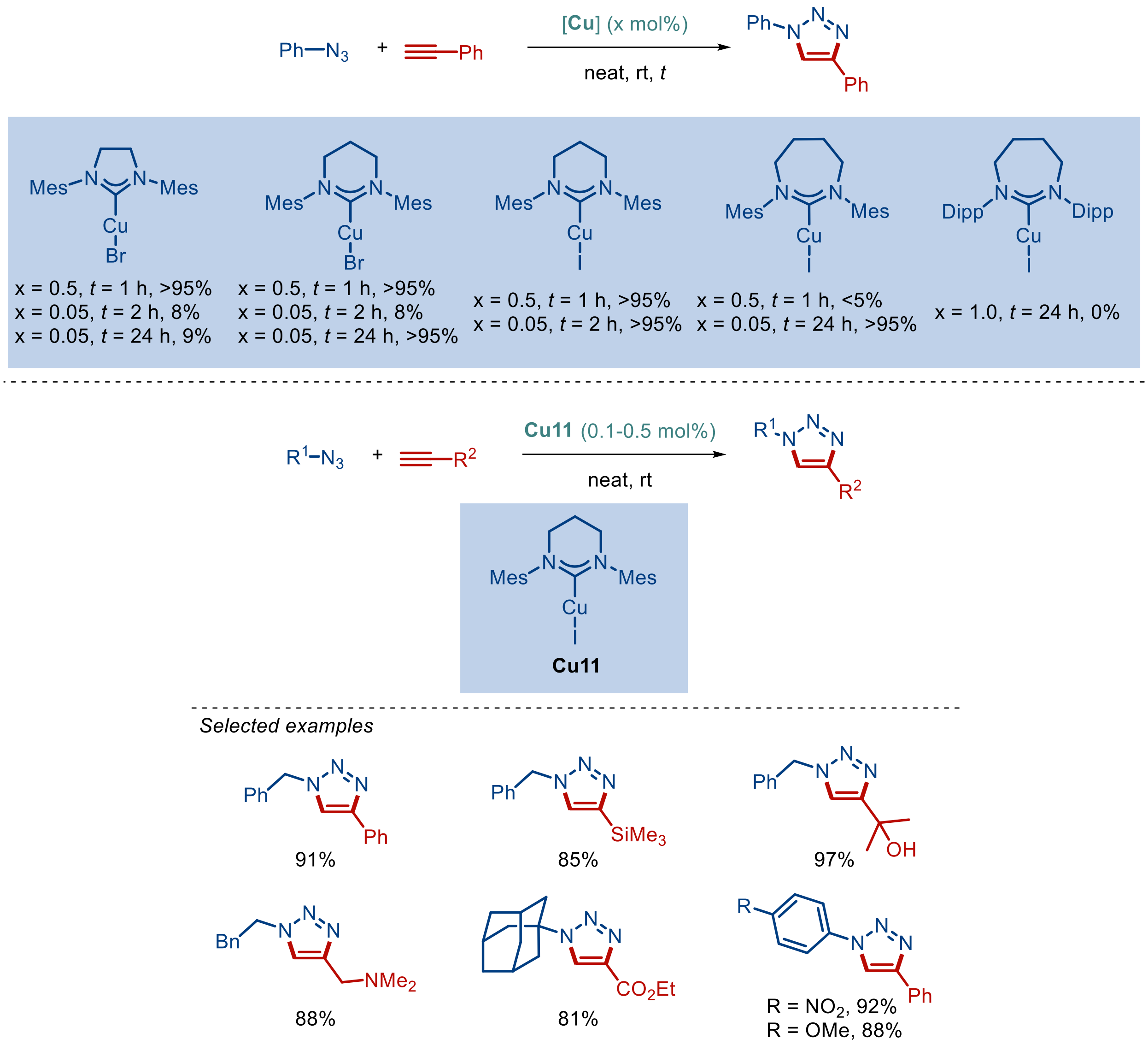


Scheme 66. Conjugate addition catalyzed by ring-expanded NHC-Cu reported by Xu in 2015.

In addition, Alexakis and co-workers reported copper-catalyzed conjugate addition of diethylzinc to cyclohexanone using chiral six-membered NHCs in 2001 [183] and 2005 [184]. However, low enantioselectivities were obtained.

10.13 Cu-NHC Catalyzed Cyclization Reactions

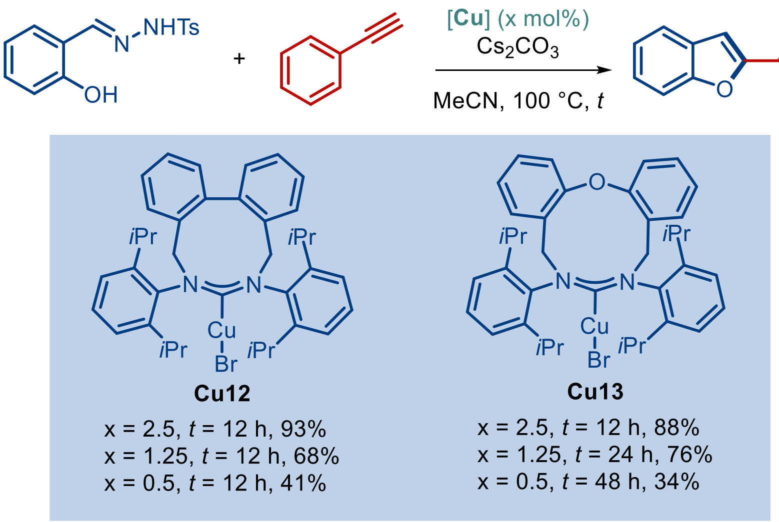
In 2018, Díez-González and co-workers reported a study on the catalytic performance of a series of [(NHC)CuX] (X = halide) complexes in the triazole click reaction (**Scheme 67**) [185]. Interestingly, they found that 6-Mes showed higher reactivity than SIMes, 7-Mes, and 7-Dipp. A reactivity order of 6-Mes > 5-Mes > 7-Mes was identified, underscoring the effect of ring size. Halide counterion also had a major effect on the catalytic outcome as [(6-Mes)CuI] outperformed its congener [(6-Mes)CuBr] at 0.05 mol% under identical conditions. A wide range of alkynes and azides featuring different electronic properties and functional groups, reacted successfully in this protocol to give the product triazoles in excellent yields at low 0.1-0.5 mol% catalyst loading. Notably, this catalyst system worked well at 100 ppm catalyst loading providing a TON of 10,000.



Scheme 67. Triazole click cycloaddition catalyzed by ring-expanded NHC-Cu reported by Díez-González in 2018.

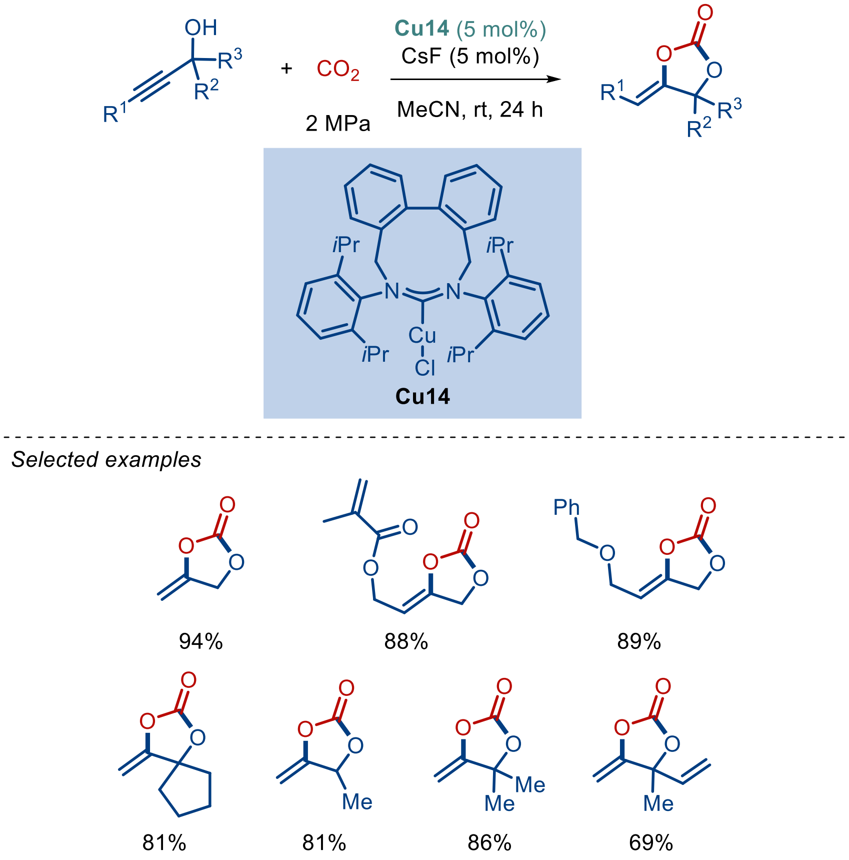
Additional examples of azide-alkyne cycloaddition using ring-expanded NHC-Cu complexes were reported by Whittlesey [186], Nechaev [187] and Asachenko [188]. Furthermore, Hua reported [(*malo*NHC)CuCl] as a catalyst for the synthesis of pyrazolo[5,1-*a*]isoquinolines [189]. Cazin conducted a comparative study on azide-alkyne cycloaddition using copper chloride complexes of 5- and 6-membered NHCs [51].

In 2020, the Hashmi group reported copper complexes **Cu12** and **Cu13** that feature intriguing 9- and 10-membered NHC ligands (**Scheme 68**) [190]. Compared with imidazol-2-ylidenes, **Cu12** is characterized by a much higher %V_{bur} (57.5%). The catalytic performance of **Cu12** and **Cu13** was investigated in the synthesis of benzofurans from *N*-tosylhydrazones and alkynes. These ring-expanded complexes promoted the reaction at 1.25 mol% catalyst loading, while **Cu13** was less effective than **Cu12** at lower catalyst loadings. This was ascribed to the existence of a flexible diphenyl ether moiety. Moreover, the authors demonstrated that the 9-membered **Cu12** could also catalyze the cycloisomerization of N-propargylamides, highlighting the generation of stable cationic ring-expanded Cu-NHCs after halide abstraction (not shown) [190].



Scheme 68. Synthesis of benzofurans catalyzed by ring-expanded NHC-Cu reported by Hashmi in 2020.

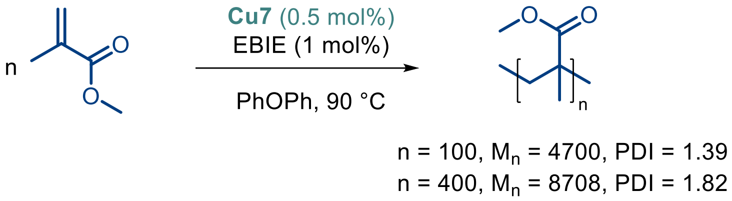
Later, the Hashmi group reported copper chloride complex **Cu14**, which was characterized by $\%V_{bur}$ of 57.9% [191]. The authors found that **Cu14** outperformed [(IPr)CuCl] in the carboxylative cyclization of propargylic alcohols (**Scheme 69**). The combination of IPrCuCl complex with CsF led to the desired product in 35% isolated yield, while the IMesCuCl/CsF system did not catalyze the reaction under the same conditions. In contrast, **Cu14**/CsF furnished the cyclic carbonate in 94% isolated yield. A wide range of primary, secondary, and tertiary propargylic alcohols were cyclized at atmospheric pressure of carbon dioxide. TON of 103 was determined after four successive additions, indicating reusability of the catalysts. This reaction affords valuable α-alkylidene cyclic carbonates with broad scope and excellent yields.



Scheme 69. Carboxylative cyclization of propargylic alcohols catalyzed by ring-expanded NHC-Cu reported by Hashmi in 2021.

10.14 Cu-NHC Catalyzed Polymerization Reactions

In 2005, Buchmeiser and co-workers reported atom transfer radical polymerization of methyl methacrylate catalyzed by the copper complex **Cu7** [(6-^{i}Pr)CuBr] (**Scheme 70**) [173]. During this process, a linear relationship between monomer consumption and time was observed. An initiation efficiency of 0.5 was obtained, indicating that controlled polymerization occurred.



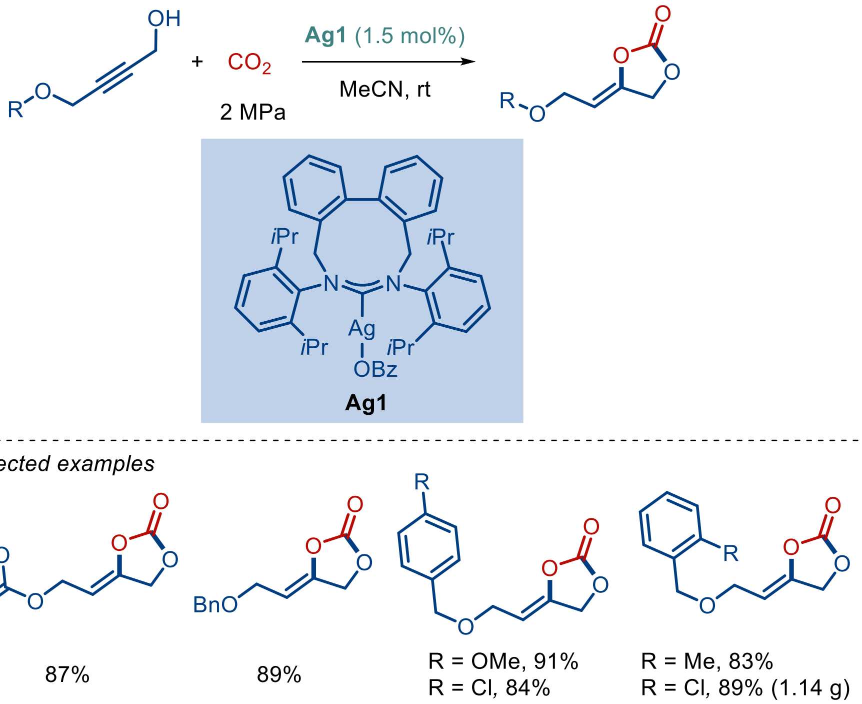
Scheme 70. Polymerization of acrylates catalyzed by ring-expanded NHC-Cu reported by Buchmeiser in 2005.

11. Ring-Expanded Silver-NHC Complexes

To date, only two carboxylative cyclization reactions involving ring-expanded silver-NHC complexes have been reported by Hashmi [195].

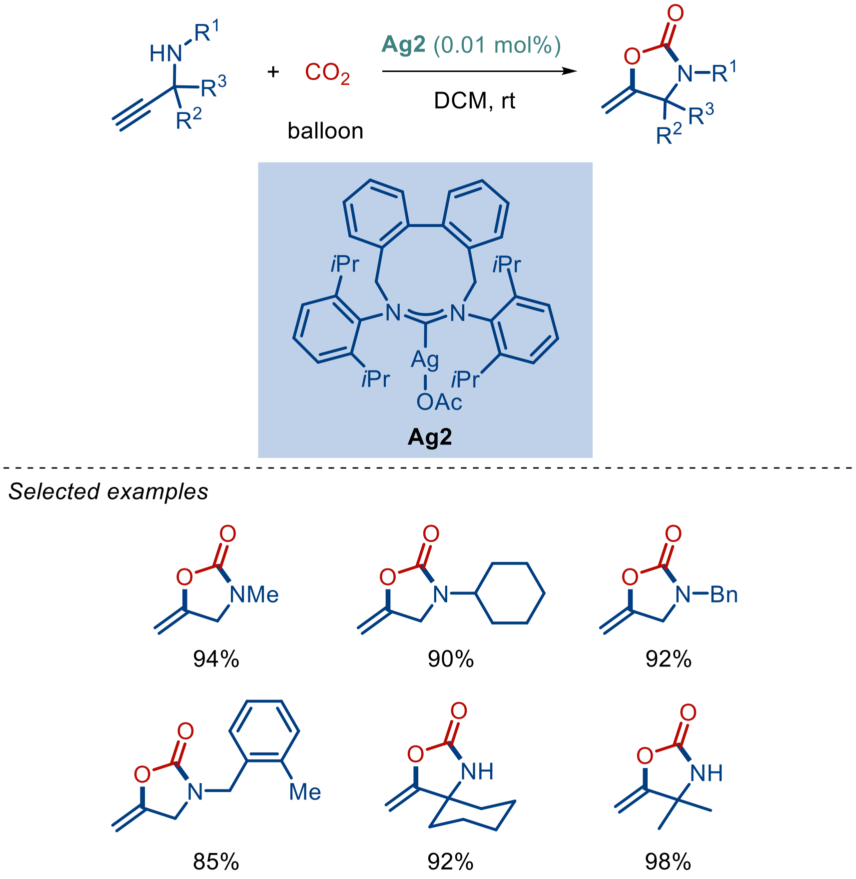
11.1 Ag-NHC Catalyzed Cyclization Reactions

In 2021, the Hashmi group disclosed 9-membered NHC-ligated silver carboxylate complexes for the carboxylative cyclization of primary propargylic alcohols (**Scheme 71**) [195]. Complex **Ag1** was characterized by a %V$_{bur}$ of 54.5% and was found to be highly reactive in promoting this reaction at room temperature. In the scale-up experiment, **Ag1** catalyzed the cyclization of 4-((2-chlorobenzyl)oxy)but-2-yn-1-ol in 89% yield at 2.3 MPa CO$_2$ pressure.



Scheme 71. Carboxylative cyclization of primary propargylic alcohols catalyzed by ring-expanded NHC-Ag reported by Hashmi in 2021.

In addition, the authors studied carboxylative cyclization of propargylamines in the presence of a 9-membered NHC silver complex **Ag2** (**Scheme 72**) [195]. Impressively, **Ag2** catalyzed the reaction at 0.01 mol% loading at atmospheric pressure CO_2 at room temperature. The reaction showed very broad scope for the terminal alkynes. Furthermore, a three-component reaction with 1-ethynyl-1-cyclohexanol, *n*-butylamine and carbon dioxide, proved to be successful. Moreover, **Ag2** was recyclable as it still exhibited a remarkable 90% yield in the seventh cycle.



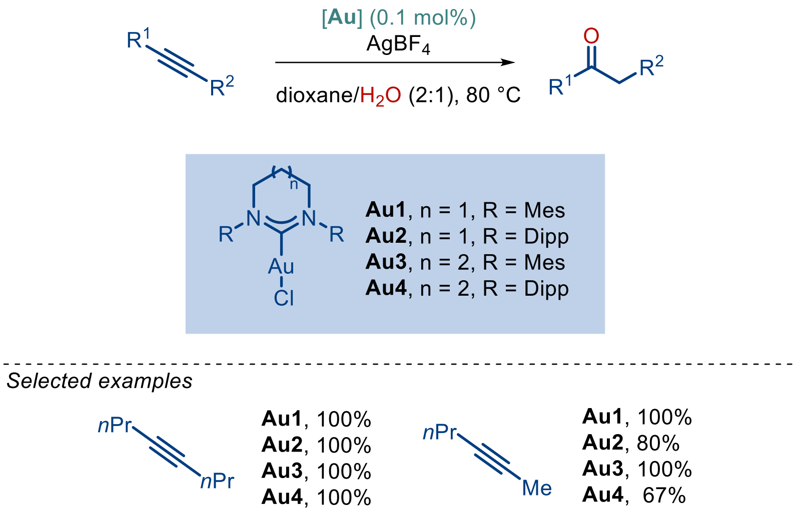
Scheme 72. Carboxylative cyclization of propargylic amines catalyzed by ring-expanded NHC-Ag reported by Hashmi in 2021.

12. Ring-Expanded Gold-NHC Complexes

Ring-expanded NHC-gold complexes have been used for hydration [196-198], hydroamination [199-203], hydroarylation [204, 205], and cyclization [206-214] reactions.

12.1 Au-NHC Catalyzed Hydration Reactions

In 2012, Cavell and co-workers reported the synthesis and application of ring-expanded NHC gold complexes **Au1-Au4** in alkyne hydration (**Scheme 73**) [196]. These complexes were readily prepared by reacting chloro(dimethyl sulfide)gold(I) with the corresponding free carbenes. Although all four complexes were inactive for the hydration of terminal alkynes, such as phenylacetylene, they showed remarkable reactivity in the hydration of internal alkynes. In particular, **Au1** and **Au3** featuring N-Mes wingtip showed high reactivity. It is worth noting that their five-membered imidazolin-2-ylidene congener, [(SIMes)AuCl], was inactive in a similar transformation.

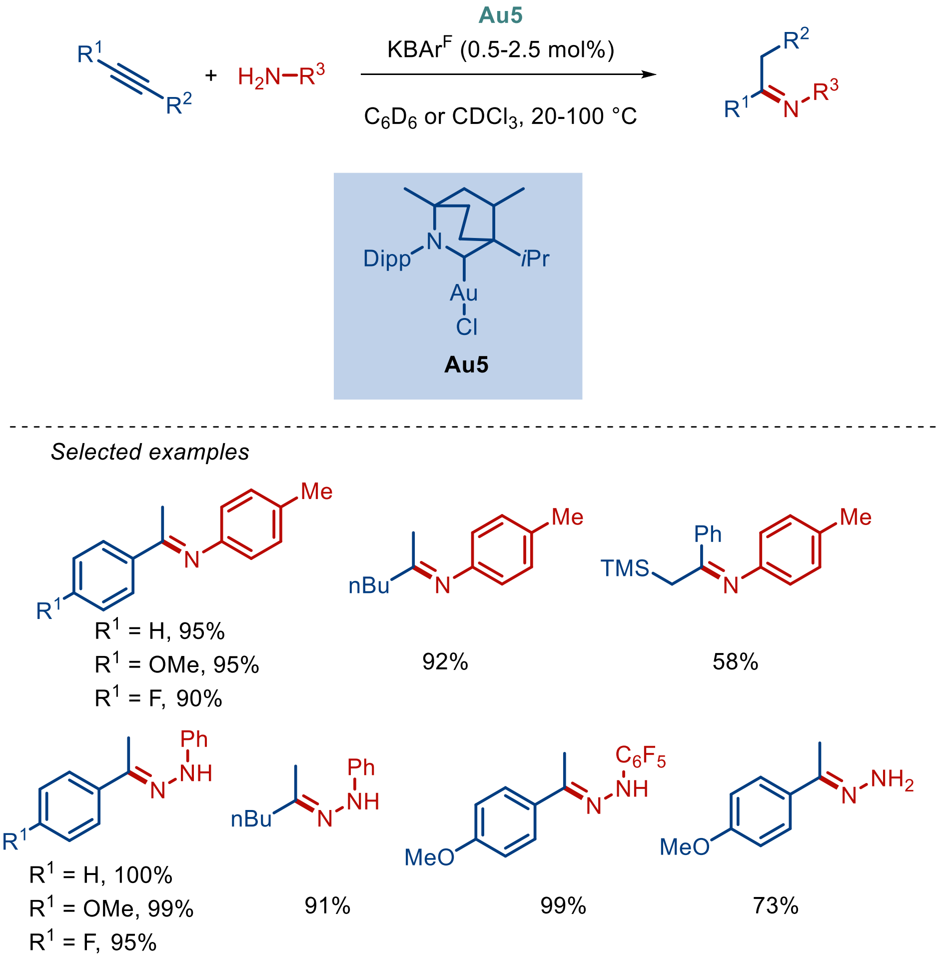


Scheme 73. Hydration of alkynes catalyzed by ring-expanded NHC-Au reported by Cavell in 2012.

In addition, Bielawski reported hydration of phenylacetylene catalyzed by a seven-membered N,N′-diamidocarbene gold complex [197]. Asachenko and co-workers investigated the effect of ring size on the regioselectivity of hydration of internal alkynes, showing that the regioselectivity can be controlled by changing the ligand [198].

12.2 Au-NHC Catalyzed Hydroamination Reactions

In 2020, Bertrand and co-workers reported the ring-expanded bicyclic (alkyl)(amino)carbene (BiCACC) gold chloride complex **Au5** for the hydroamination and hydrohydrazination of alkynes in the presence of $KBAr^F$ (**Scheme 74**) [199]. This process showed broad scope in that alkyl- and aryl-substituted alkynes featuring electron-donating and electron-withdrawing groups reacted with sterically hindered anilines, amines, and aryl hydrazines to furnish imines and hydrazones in high yields. Remarkably, TONs of up to 18,700 and 36,700 were obtained for hydroamination and hydrohydrazination using **Au5** at ppm catalyst loading.

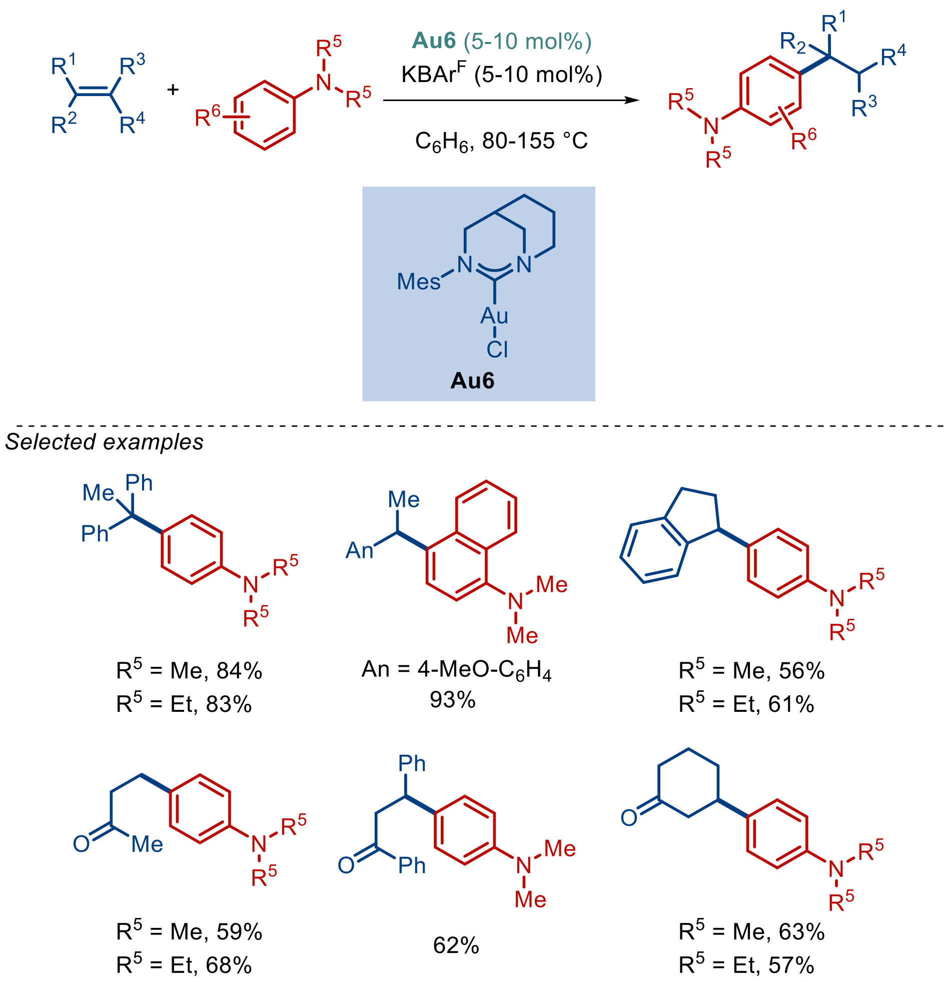


Scheme 74. Hydroamination and hydrohydrazination of alkynes catalyzed by ring-expanded NHC-Au reported by Bertrand in 2020.

Additional examples of hydroamination reactions catalyzed by ring-expanded NHC-Au were reported by Bertrand [200, 201], Nechaev [202] and Huynh [203].

12.3 Au-NHC Catalyzed Hydroarylation Reactions

In 2014, Bertrand and co-workers realized the gold-catalyzed hydroarylation of alkenes with dialkylanilines using a ring-expanded anti-Bredt type di(amino)carbene-ligated gold complex **Au6** (**Scheme 75**) [204]. This transformation proved to be challenging in the past using other methods owing to the high basicity and coordination of the nitrogen atom. The key was the use of complex **Au6** as catalyst in combination with KBAr^F as chloride scavenger This protocol allowed for the regioselective alkylation at the *para* position of dialkylanilines with styrenes, indene, norbornene, and even electron-poor enones in moderate to excellent yields.

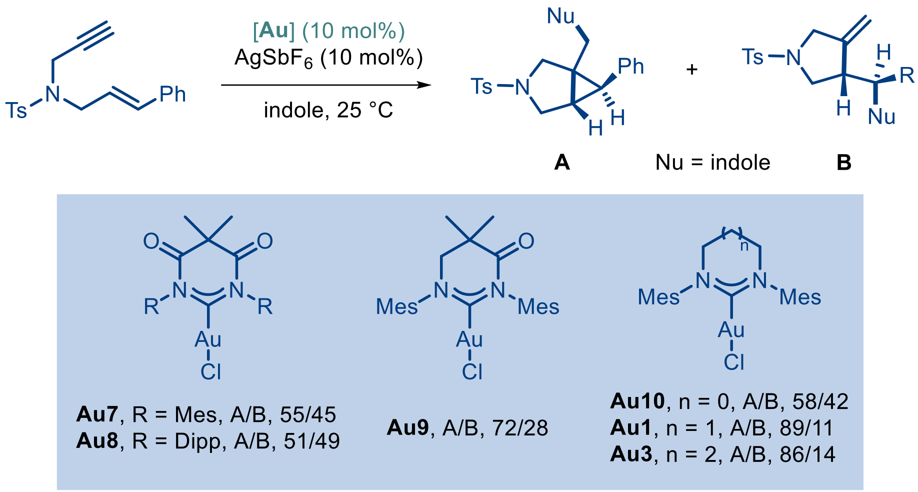


Scheme 75. Hydroarylation of alkenes catalyzed by ring-expanded NHC-Au reported by Bertrand in 2014.

In addition, Hu and co-workers reported complex **Au6** in the Friedel-Crafts alkylation of anilines with alkenes [205].

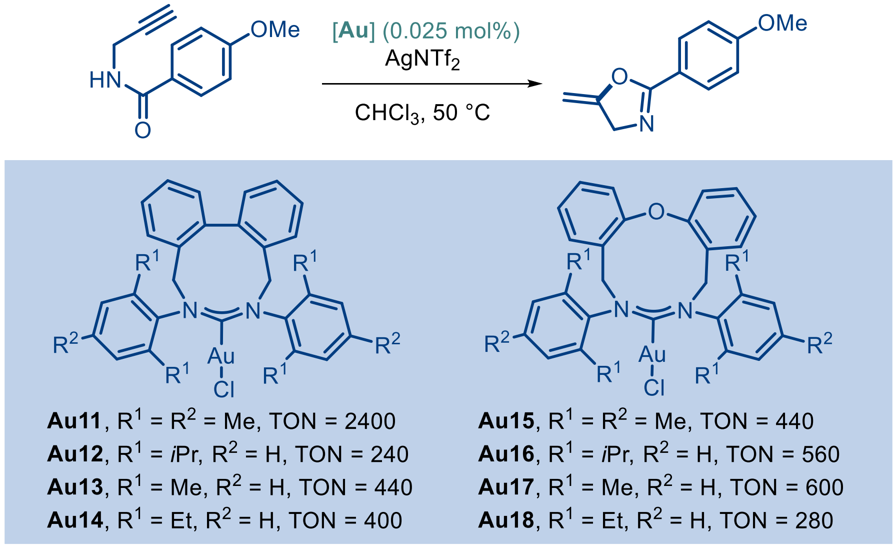
12.4 Au-NHC Catalyzed Cyclization Reactions

In 2014, Bielawski and colleagues reported the steric and electronic effect of ring-expanded NHCs on the gold-catalyzed 1,6-enyne cyclization (**Scheme 76**) [206]. Two possible products, namely the [5.1.0] bicycle **A** and olefin **B**, were formed in the presence of indole as nucleophile. By comparing the ratio of products **A** and **B** in the reactions catalyzed by **Au7** (55:45), **Au9** (72:28) and **Au1** (89:11), the authors concluded that electron-rich ligands favored the bicyclic product. Furthermore, the ring size of ligands had an effect on the reaction in that complexes supported by six- and seven-membered NHCs gave a larger ratio of the bicyclic product **A**, while their five-membered counterpart **Au10** showed little discrimination in product ratio. In contrast, the steric environment appeared not to have a significant impact on product distribution (**Au7**, 55:45 vs. **Au8**, 51:49).



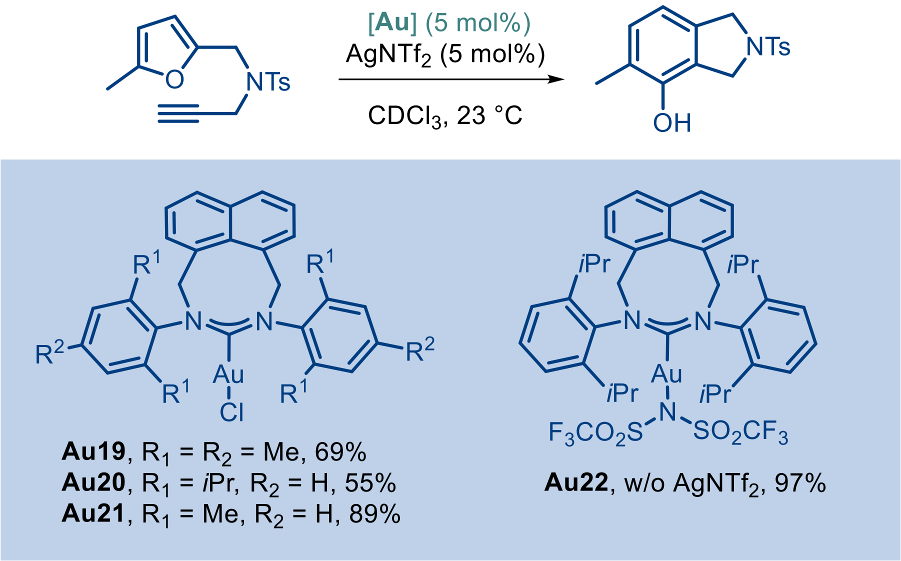
Scheme 76. 1,6-Enyne cyclization catalyzed by ring-expanded NHC-Au reported by Bielawski in 2014.

In 2019, Hashmi and co-workers reported the synthesis of nine- and ten-membered NHC-gold complexes **Au11-Au18** and their catalytic reactivity in cycloisomerization reactions (**Scheme 77**) [207]. Initially, nearly full conversions were achieved with all eight complexes at catalyst loadings greater than 0.1 mol% at room temperature. Then, the authors investigated catalytic behavior at low catalyst loading. At 250 ppm loading, most catalysts gave a yield less than 20%, while **Au11** showed a remarkable TON of up to 2,400.



Scheme 77. Cycloisomerization of amides catalyzed by ring-expanded NHC-Au reported by Hashmi in 2019.

In 2020, the Hashmi group reported eight-membered NHC-gold complexes and their catalytic activity in phenol synthesis (**Scheme 78**) [208]. Interestingly, the authors found that complex **Au20** (%V_{bur} = 54.0) with the bulkier ligand showed lower reactivity compared to the less bulky complexes **Au19** and **Au21** (%V_{bur} = 46.4). Furthermore, well-defined complex [(NHC)Au(NTf_2)] **Au22** afforded the product in nearly quantitative yield at room temperature.



Scheme 78. Phenol synthesis catalyzed by ring-expanded NHC-Au reported by Hashmi in 2020.

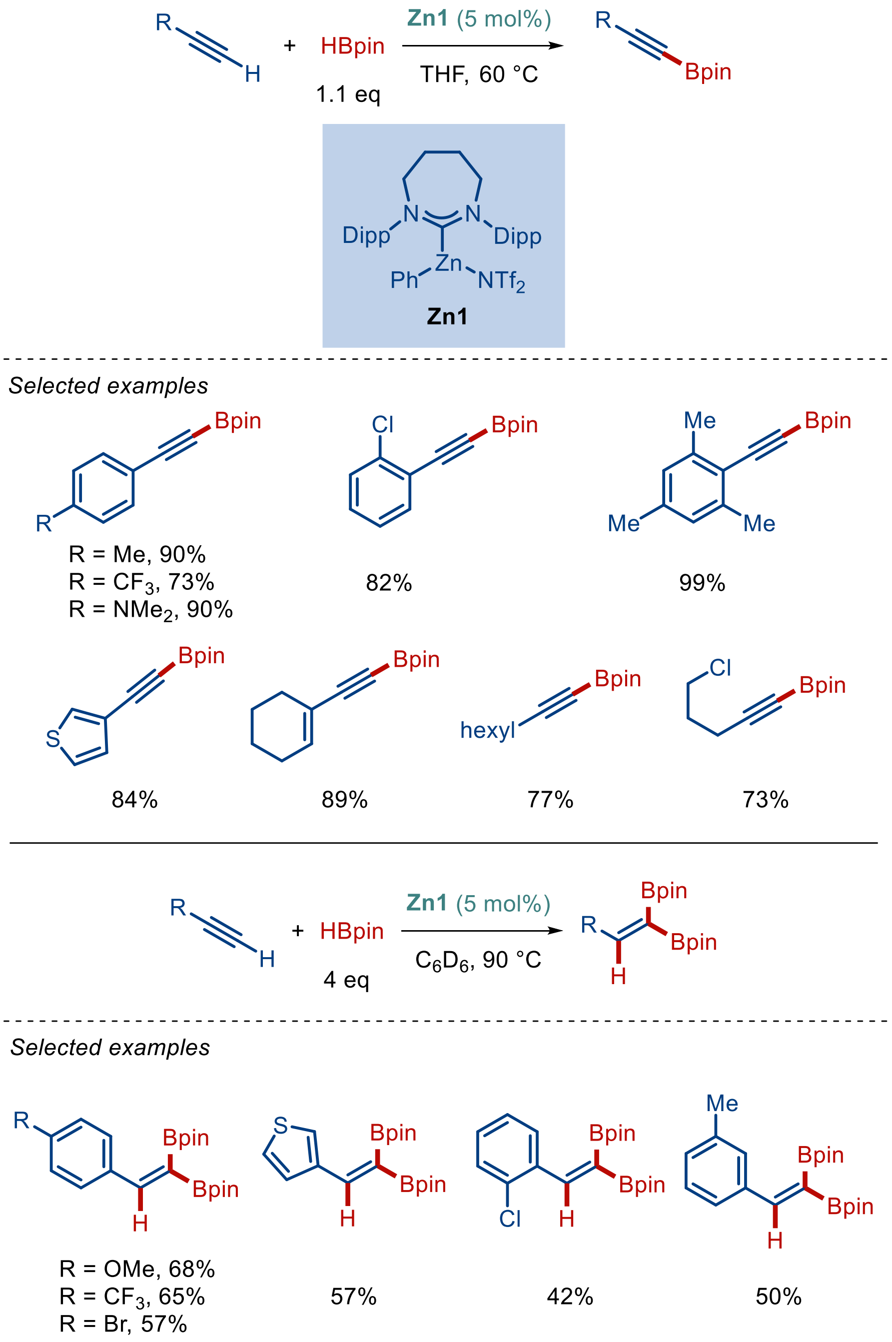
Additional examples of cyclization reactions catalyzed by ring-expanded NHC-Au complexes were reported by Nechaev [209], Ganter [210], Nenajdenko [211], Hashmi [212] and César [213]. Moreover, a DFT mechanism of the cyclization of propargylic amides was investigated by the Hussein group [214].

13. Ring-Expanded Zinc-NHC Complexes

Ring-expanded NHC-zinc complexes have been in borylation of alkynes [215, 216].

13.1 Zn-NHC Catalyzed Borylation Reactions

In 2019, Ingleson and co-workers reported 7-Dipp supported zinc(I) complex **Zn1** for dehydroboration and 1,1-diboration of terminal alkynes (**Scheme 79**) [215]. The dehydroboration reaction proceeded at 50 °C in the presence of 1.1 equiv of pinacolborane, while 1,1-diboration required a higher temperature and excess of pinacolborane (4 equiv). It is particularly worth noting that the analogous IPr complex gave low conversion under the same conditions due to the lower stability of the catalytic species. This dehydroboration method tolerated a wide range of substrates, such as aryl, heteroaryl, alkenyl, and alkyl alkynes with different electronic properties. Nitro and nitrile groups were incompatible due to facile reduction under the reaction conditions. The formed alkynyl boronate esters could be further hydroborated without isolation to give 1,1-diborated alkenes in one-pot synthesis. Aryl- and heteroaryl-substituted terminal alkynes were all suitable substrates for this reaction. Furthermore, the reaction was highly regioselective in that 1,2-diborated products were not observed.



Scheme 79. Dehydroboration and 1,1-diboration of alkynes catalyzed by ring-expanded NHC-Zn reported by Ingleson in 2019.

Mechanistically, the authors proposed that a zinc hydride complex is generated from complex **Zn1** *via* σ-bond metathesis with HBpin (**Fig. 12**) [215]. Next, the alkynyl zinc species is formed by protonolysis with terminal alkyne with a concomitant release of hydrogen. The alkynyl zinc complex undergoes metathesis with HBpin to afford the dehydrogenative borylation product and regenerate the zinc hydride complex. Under the forcing conditions, the zinc hydride complex reacts further with alkynyl boronate esters through hydrozincation to afford the alkenyl zinc complex. Finally, the 1,1-diborated product is formed after metathesis with excess HBpin.

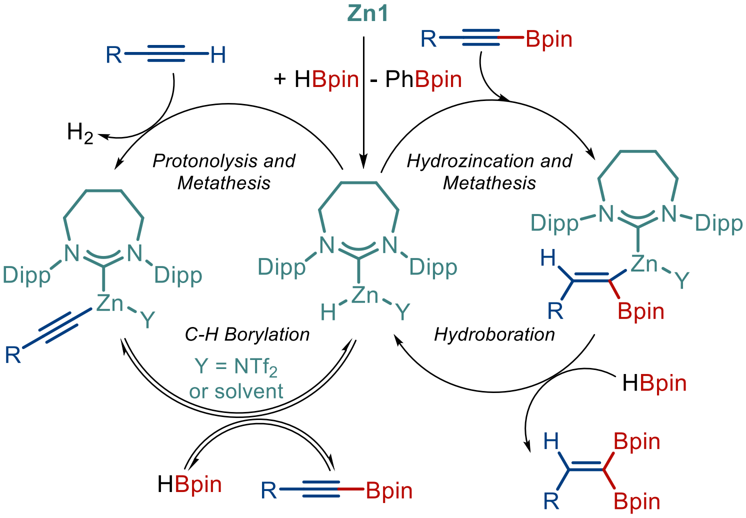


Fig. 12. Mechanism for dehydrogenative borylation and 1,1-diboration of alkynes.

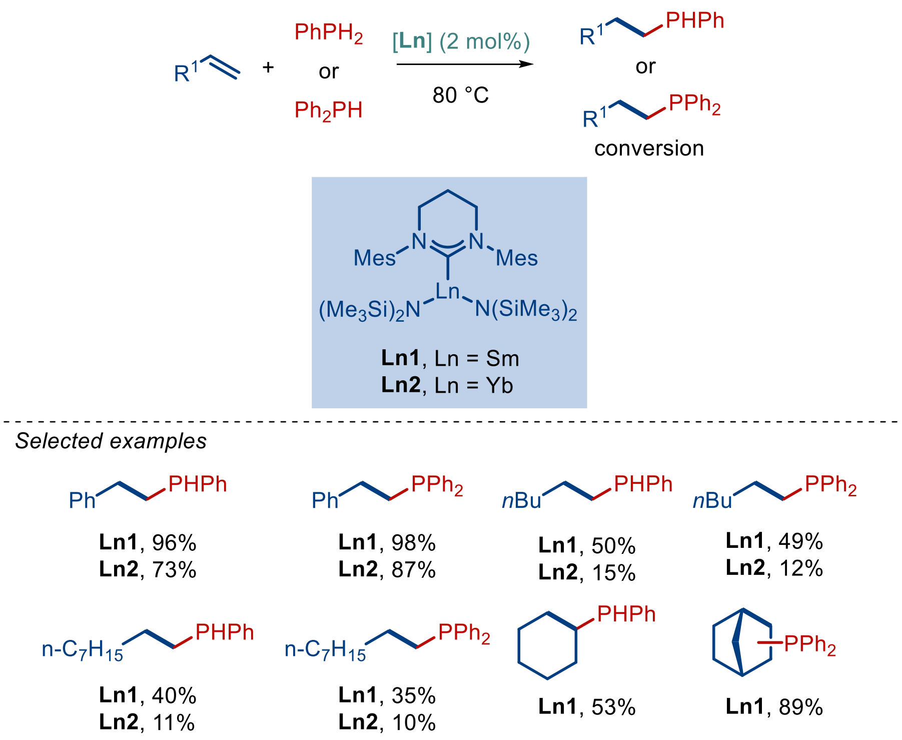
In addition, Ingleson and co-workers reported zinc hydride complex, [(7-Dipp)Zn(H)NTf_2], for di- and triboration of alkynes [216].

14. Other Ring-Expanded Metal-NHC Complexes

In addition to the examples described, ring-expanded NHC-Sm and Yb complexes have been used for hydrophosphination of alkenes [217], while ring expanded NHC-Nd and Y complexes exhibited reactivity in polymerization of isocyanates [218].

14.1 Sm, Yb-NHC Catalyzed Hydrophosphination Reactions

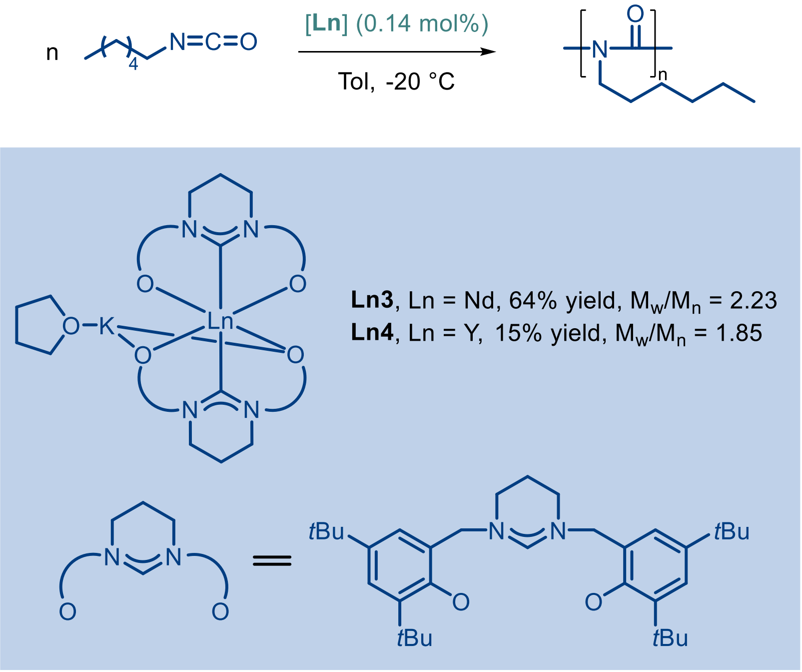
In 2020, Trifonov and co-workers reported the synthesis and evaluation of catalytic activity in hydrophosphination of olefins of bis(amido) complexes of Sm(II) and Yb(II) supported by 6-Mes (**Scheme 80**) [217]. Both complexes yielded anti-Markovnikov products. The Sm complex **Ln1** showed higher reactivity compared to the Yb complex **Ln2**. Moreover, the complex **Ln1** was reactive in hydrophosphination of typically less reactive cyclohexene and norbornene.



Scheme 80. Hydrophosphination of olefins catalyzed by ring-expanded NHC-Sm and NHC-Yb reported by Trifonov in 2020.

14.2 Nd, Y-NHC Catalyzed Polymerization Reactions

In 2015, Ni and co-workers reported polymerization of *n*-hexyl isocyanate mediated by ring-expanded bis(phenolate) complexes **Ln3** and **Ln4** (**Scheme 81**) [218]. The yields of poly(hexyl isocyanate) obtained with a catalyst containing neodymium could reach 64% with a monomer/catalyst ratio of 1:700. In contrast, the yttrium analog was less reactive, however, it provided a narrower molecular weight distribution (M_w/M_n, **Ln3**: 2.23 vs. **Ln4**: 1.85) due to a smaller Y radius.



Scheme 81. Polymerization of isocyanates catalyzed by ring-expanded NHC-Nd and NHC-Y reported by Ni in 2015.

15. Miscellaneous

In addition to the complexes described above that have been validated in catalysis, several other ring-expanded NHC salts [219-238], and metal complexes, such as, K-NHC [239, 240], Dy-NHC [241], Cr-NHC [242-245], Mo-NHC [244, 246], W-NHC [244, 247], Fe-NHC [245, 248-254], Ru-NHC [255-259], Os-NHC [258], Co-NHC [245, 260], Rh-NHC [48, 50, 258, 261-280], Ir-NHC [48, 258, 267, 278-290], Ni-NHC [133, 290-297], Pd-NHC [43, 263, 298-307], Pt-NHC [308], Cu-NHC [39, 273, 308-327], Ag-NHC [38, 39, 43, 50, 190, 308, 313, 328-332], Au-NHC [32, 203, 308, 313, 328, 331-349], Zn-NHC [350, 351], Cd-NHC [350], B-NHC [152], Al-NHC [353, 354], Ga-NHC [354, 355], In-NHC [355], P-NHC [356], As-NHC [356] and Sb-NHC [356] have been reported.

16. Conclusions and Outlook

In this comprehensive review, we highlighted the remarkable progress made in the application of ring-expanded N-heterocyclic carbene metal complexes in catalysis. The distinct electronic and steric properties of ring-expanded NHC ligands, underscored by their enhanced σ-donation compared to the classic 5-membered imidazol-2-ylidene NHCs and their more pronounced steric effects of the N-wingtips, have played a pivotal role in the discovery and fine-tuning of reactivity that are unattainable using traditional ligands [357]. Consequently, these advancements have led to substantial progress in the already existing methodologies and the development of innovative cycles in catalysis. As highlighted in this review, the progress in the last two decades using ring-expanded NHC ligands has been significant. Furthermore, advancements have been made in harnessing the potential of ring-expanded NHC ligands across a wide range of transition metals and reaction mechanisms. This widespread success highlights the general potential of the ring-expanded NHC ligand platform. Notably, the development of asymmetric processes, facilitated primarily by the McQuade's chiral NHC-Cu complex, have emerged as a particularly exciting research direction. Furthermore, the exploration of NHCs with ring sizes exceeding 8 pioneered by the Hashmi group and the utilization of rare earth metal complexes as catalysts have opened new routes for catalytic transformations.

Although major advancements have been made in this field, there are still several challenges that require further progress:

(1) It is important to address the lack of commercial availability of ring-expanded NHC ligands, so that there is straightforward access to this ligand class by all interested researchers in academia and industry. In the long view, the limited availability of commercially accessible NHC ligands and their metal complexes hinders the widespread adoption and slows down the experimental screening and optimization processes.

(2) Furthermore, efforts should be made to develop readily scalable, divergent and user-friendly synthetic methods for ring-expanded NHC ligands, which would greatly enhance their practical utility and streamline applications in various processes.

(3) Ring-expanded NHCs with ring sizes larger than 8 are still rare. It is crucial to dedicate efforts towards exploring a wider range of diverse ring-expanded NHC ligands with larger ring sizes. When the scope of ring-expanded NHCs is broadened, including validation in catalysis, researchers would be able to uncover new ligand architectures and properties that could potentially enhance the catalytic performance and broaden the application of ring-expanded NHC-based systems. Mechanistically, this exploration will contribute to a more comprehensive understanding of ring-expanded NHC ligands and facilitate the development of innovative catalytic methodologies.

(4) Although ring-expanded NHCs have shown superior reactivity compared to classic NHCs in certain reactions, the underlying reasons for their enhanced performance often remain unclear. It is imperative to conduct ongoing investigations to determine whether the observed higher reactivity of NHCs is attributed to their electronic properties, steric effects, combination of both or other molecular effects. Understanding the precise factors that contribute to the reactivity of ring-expanded NHCs would allow for the rational design and optimization of ligands for specific catalytic applications, and apply the lessons from ring-expanded NHCs to their classical 5-membered counterparts [357].

At present, there is no doubt that the utilization of ring-expanded NHC metal complexes presents a compelling avenue for bolstering the toolbox of organic transformations and offering a wide range of possibilities in catalysis. We believe that it is critical that researchers involved in the development of new reactions routinely screen ring-expanded NHC ligands to identify the most suitable ligand for their desired transformation.

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Graphical Abstract