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N-Heterocyclic Carbenes in Late Transition Metal Catalysis

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1. Introduction

N-Heterocyclic carbenes (NHCs) are cyclic carbenes bearing at least one α-amino substituent.[1] The most common subclasses of NHCs are represented in Chart 1.

Early work on these compounds, carried out independently by Öfele and Wanzlick,[2] dates back to the 1960s and was followed by important organometallic studies by Lappert and co-workers.[3] The real breakthrough facilitating forays into catalytic applications came from the Arduengo group with the isolation of "free" IAd (see Chart 2).[4] The discovery that some carbenes could be isolated and easily handled using classical inert atmosphere techniques triggered a true explo-

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Nicolas Marion received his M.Sc. in organic chemistry from the Université Pierre et Marie Curie (UPMC) in Paris where he worked under the supervision of Professors Louis Fensterbank and Max Malacria. He obtained his Ph.D. in 2008 in the group of Professor Steven P. Nolan at the ICIQ in Tarragona. He is currently pursuing postdoctoral studies at MIT with Professor Gregory C. Fu.

sion of interest in their coordination chemistry.[5] Rapidly, the realization of their outstanding potential as supporting ligands for homogeneous catalysis,[6] notably by Herrmann,[7] Enders,[8] and Dixneuf and Çetinkaya,[9] converted these laboratory curiosities into "broadly catalytically useful ligands comparable with cyclopentadienyls and phosphines".[10] Nowadays, the most common NHCs used in catalysis are five-membered ring imidazolylidenes, imidazolinylidenes, and triazolylidenes (the most frequently employed are depicted in Chart 2). The latter are exceptional organocatalysts,[11] while the two other families have proven impressively versatile in transition metal catalysis.[12] The success encountered by NHCs is often attributed to their strong σ-electron-donating properties,[13] which allow for very strong NHC−metal bonds[14,15] and prevent decomposition of the catalyst.

In this review, we describe the numerous, and ever-increasing, applications of NHCs as supporting ligands in late transition metal catalysis. This includes all elements of the d-block from group 7 to group 11.[16] We have considered both well-defined catalysts and in situ procedures using either an NHC or an azolium salt. On the other hand, we have excluded the two main applications of NHCs to date, namely, the ruthenium-catalyzed olefin metathesis and the palladium-catalyzed cross-coupling reactions, since each of these can be considered as an independent area of research that can warrant a sizable *Chemical Reviews* contribution. Additionally, since, along with the present review, another article entitled "Complexes with Poly(N-heterocyclic carbene) Ligands: Structural Features and Catalytic Applications"[17] will be published in this special issue on N-heterocyclic carbenes, we will mainly focus our discussion on monodentate NHCs and only mention briefly asymmetric developments.

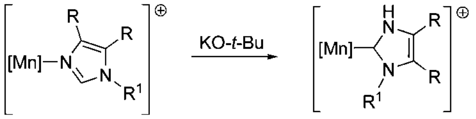
Steven P. Nolan received his B.Sc. in Chemistry from the University of West Florida and his Ph.D. from the University of Miami where he worked under the supervision of Professor Carl D. Hoff. After a postdoctoral stay with Professor Tobin J. Marks at Northwestern University, he joined the Department of Chemistry of the University of New Orleans in 1990. In 2006, he joined the Institute of Chemical Research of Catalonia (ICIQ) as Group leader and ICREA Research Professor. In early 2009, he joined the School of Chemistry at the University of St Andrews where he holds the Chair of Inorganic Chemistry.

2. Group 7: Manganese, Technetium, and Rhenium

NHC-containing manganese complexes were among the first isolated species within this family of ligands.[18] Compounds with manganese in the oxidation states I, II, and IV are known in the literature,[19] but no catalytic activity of such species has been reported to date. On the other hand, the first NHC−manganese(III) complexes have only been reported very recently.[20]

Nevertheless, different interesting processes observed in the coordination sphere of the manganese center might be converted into catalytic applications in the near future. Notably, [(NHC)Mn^I] complexes can be generated via the coupling of propargylamines (or alcohols) and isocyanides (Scheme 1).[21]

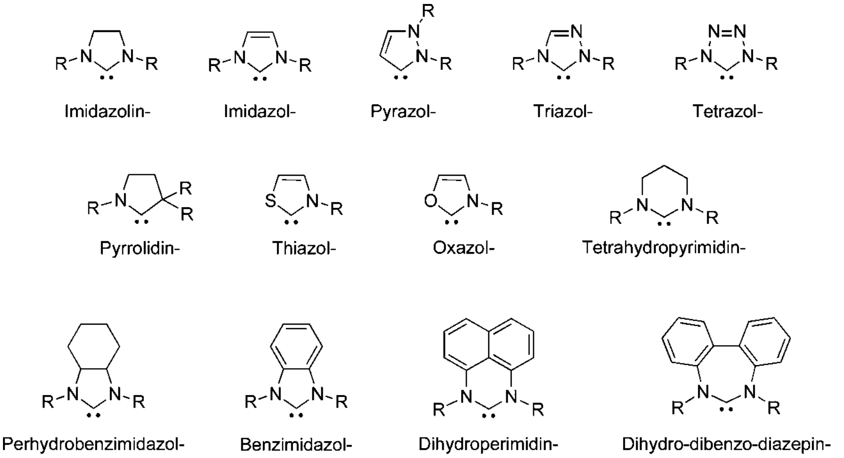
Alternatively, imidazole ligands can tautomerize to NHCs through a C−H bond activation process under basic conditions (eq 1).[22] These complexes might also find interesting applications as transmetalating agents or mediate the synthesis of unsymmetrical NHC ligands.



(1)

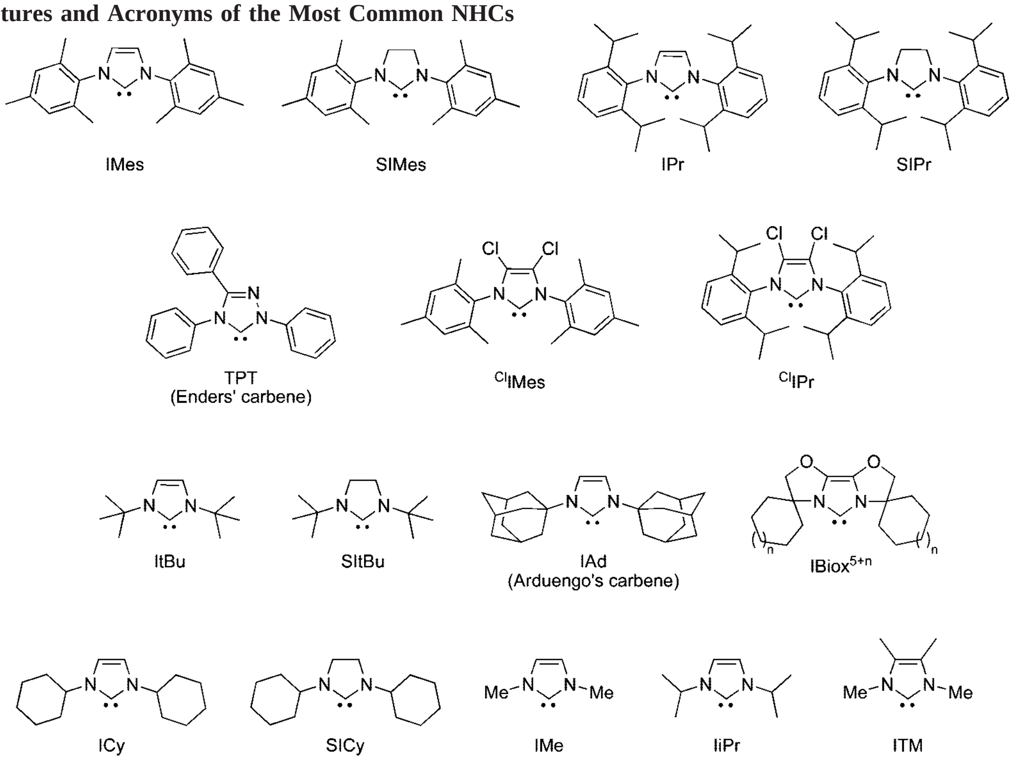
Even if more attention has been paid to rhenium coordination chemistry compared with manganese or technetium, this

Chart 1. Structures of the Most Encountered N-Heterocyclic Carbene Subclasses[a]

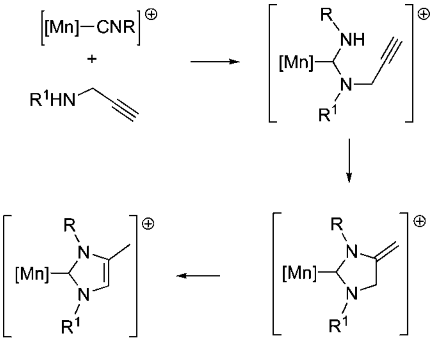


[a] The suffix "ylidene" should be added to obtain the generic name of each NHC subclass.

Chart 2. Structures and Acronyms of the Most Common NHCs



Scheme 1. Reactivity of Isocyanide−Mn Complexes with Propargyl Amines



field remains largely underdeveloped as well.[23] Several rhenium(I) tricarbonyl complexes have shown promising luminescent properties[24] or can undergo tautomerization from imidazole to carbene complexes.[25] NHC ligands have also allowed for the remarkable stabilization of rhenium(V) and technetium(V) species. In particular, silicon-based greases, considered as chemically inert, can be activated at room temperature by NHC−technetium nitrido species to form complexes with disiloxane coligands.[26]

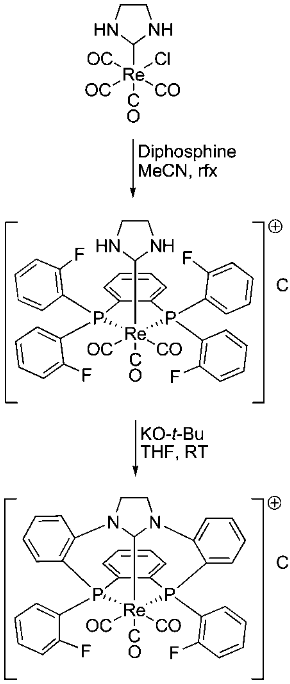
Furthermore, the synthesis of rhenium and manganese complexes bearing NHC−diphosphine macrocycles has also been reported.[27] These metal template-controlled macrocyclizations were performed in two steps: a diphosphine was introduced on an NH,NH-carbene complex, followed by intramolecular formation of two N−C bonds (Scheme 2).

3. Group 8: Iron, Ruthenium, and Osmium

3.1. Iron

Despite recent advances in iron chemistry,[28] iron remains one of the least studied late transition metals with NHCs.

Scheme 2. Synthesis of [(NHC)Re] Macrocyclic Complexes



The main area of investigation is to be found outside of catalysis, in the study of [FeFe] hydrogenase active site models,[29] where NHCs have allowed for a better understanding of the properties of these metalloenzymes, notably the oxidation states of both Fe atoms.[30] Iron carbonyl complexes have also been used to determine the electronic properties of NHCs.[31] In terms of catalytic applications, we are only aware of ten published reports to date.

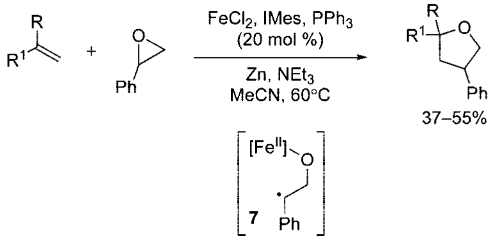
3.1.1. Polymerization Reactions

In 2000, the Grubbs group reported the first use of NHCs in homogeneous iron catalysis.[32] They synthesized two well-defined [$(IiPrMe)_2FeX_2$] (**1** and **2**; see Chart 3) complexes and tested their activity in atom transfer radical polymerization (ATRP)[33] of styrene and methyl methacrylate. Overall, polymerization activities were found to be comparable with those of anionic polymerizations as well as other metal-based systems for ATRP. The good activity of these complexes was rationalized as arising from the high electron-donating capabilities of the NHC ligand.

Gibson and co-workers synthesized a number of Fe^{II} and Fe^{III} complexes **3**−**5** bearing a bis(NHC)−pyridine tridentate ligand.[34] The three complexes were tested in ethylene oligomerization and polymerization and were all found totally inactive. In 2006, an NHC−phenoxide chelate compound **6** designed by Shen and co-workers was found to be an active initiator for the ring-opening polymerization of ε-caprolactone.[35] Nevertheless, this complex did not efficiently inhibit intramolecular transesterification reactions during the polymerization, as observed from the poor control on the number-average molecule weight of the obtained polymer.

3.1.2. Cyclization Reactions

In 2005, Hilt and co-workers disclosed that NHCs in combination with $FeCl_2$, PPh_3, and zinc powder allowed for the intermolecular ring expansion of epoxides with dienes (eq 2).[36]

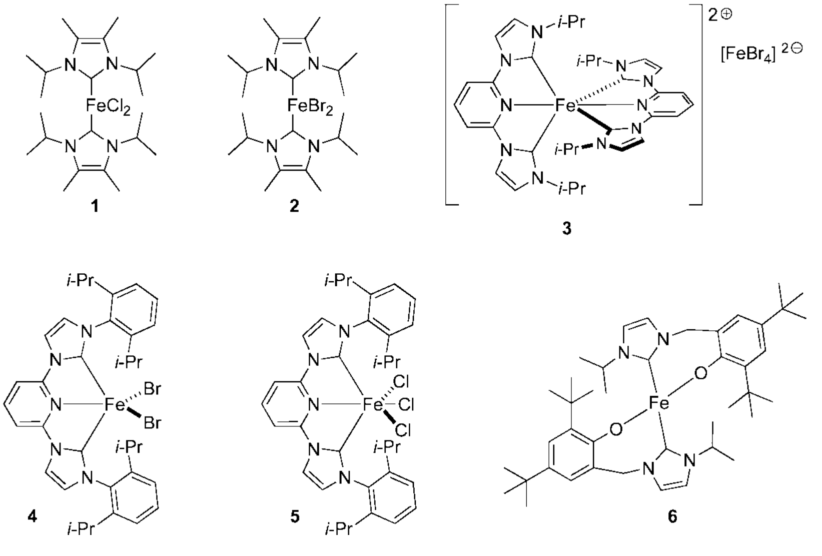


(2)

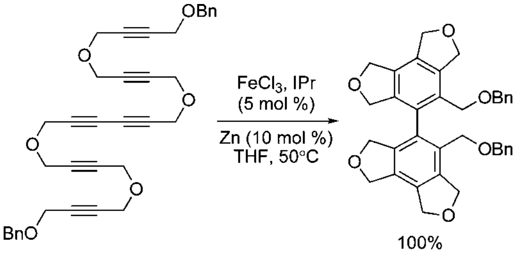
This interesting synthesis of tetrahydrofurans was applied to a broad variety of conjugated systems, including cyclic and acyclic dienes, styrene, acrylate, and enynes, but was efficient only with styrene oxide. The authors proposed a radical mechanism initiated by a single electron transfer step from the iron(I) catalyst, generated by the in situ Zn reduction of a Fe^{II} species, to the epoxide (see intermediate **7** in eq 2). Subsequent addition to the alkene and back electron transfer, regenerating the Fe^{I} catalyst, would lead to a zwitterionic intermediate prone to cyclization. The number of IMes or PPh_3 ligands in the coordination sphere of the iron center prior to and during the catalytic cycle remains to be elucidated.

Recently, Okamoto reported an efficient [(NHC)Fe]-catalyzed cyclotrimerization of triynes.[37] A number of benzene derivatives could be obtained in the presence of $FeCl_3$, an NHC, and Zn powder upon intramolecular cyclization of triynes; an example of bis-cyclotrimerization is

Chart 3. Structures of [(NHC)Fe] Complexes Tested in Polymerization Reactions



depicted in eq 3.[38] Comparison between IPr and IMes revealed the superiority of the former in this reaction. Of note, while a solution of IPr and $FeCl_3$ in THF could be stored for a few days under inert atmosphere without loss of activity, no well-defined [(NHC)Fe] complex could be isolated from this mixture.



(3)

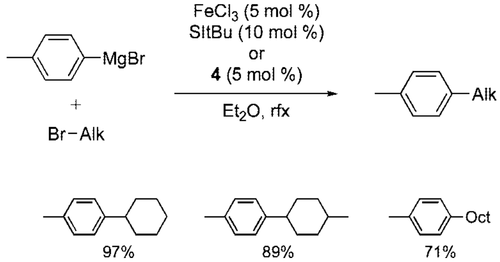
3.1.3. C−C Bond Forming Reactions

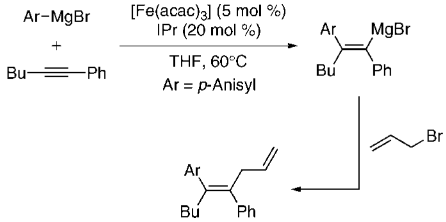
Despite the growing interest in NHCs for Pd- and Ni-catalyzed cross-coupling reactions,[39] there are only two reports making use of these ligands in iron-catalyzed cross-coupling. Bedford and co-workers showed, in 2006, that NHCs were indeed efficient supporting ligands for the Kumada coupling of primary and secondary alkyl electrophiles.[40,41] In addition to well-defined complex **4** (see Chart 3), different carbenes were tested including SICy, SItBu, SIMes, and SIPr. Besides SIMes, all NHCs performed well in the coupling of 4-tolyl Grignard and bromocyclohexane, yielding an extremely low amount of undesired β-elimination product. Cyclic and acyclic alkyl halides were coupled in good to excellent yields (Scheme 3). Only a handful of entries were reported but this study clearly demonstrated the high potential of NHCs for iron-catalyzed couplings.

More recently, Nakamura and co-workers reported the excellent activity of SIPr in mediating the Kumada coupling of aryl Grignard reagents with aryl chlorides.[42] This catalytic system, composed of anhydrous FeF_3 or $FeF_2 \cdot 4H_2O$ and SIPr·HCl, proved efficient at relatively low catalyst loadings (i.e., 3−5 mol %) and allowed for the coupling of both electron-rich and electron-poor aryl chlorides in good to excellent yields. Interestingly, the authors showed that replacement of the iron source with $CoF_2 \cdot 4H_2O$ or $NiF_2 \cdot 4H_2O$ provided the same level of efficiency in cross-coupled product.

Closely related to cross-coupling, Shirakawa and Hayashi disclosed an arylmagnesiation reaction of alkynes catalyzed by [Fe(acac)$_3$] and IPr.[43] Direct comparison with a set of alkyl and arylphosphines showed the superiority of IPr in this transformation, in terms of both yield and regioselectivity. A number of internal arylalkynes could be converted to the corresponding trisubstituted alkenes in good yields and *E*/*Z* ratio (typically 9:1), upon aqueous quench of the vinyl Grignard. Even more interesting from a synthetic point of view, the intermediate vinylmagnesium species could be used in situ for further functionalization such as electrophilic trapping (eq 4) or nickel-catalyzed cross-coupling.[44]

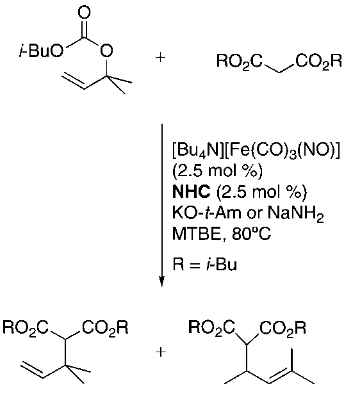
Scheme 3. [(NHC)Fe]-Catalyzed Cross-Coupling of Alkyl Electrophiles





(4)

Finally, Plietker and co-workers recently reported an intriguing behavior in allylic substitution reactions catalyzed by [(NHC)Fe] systems.[45] Hence, with $[Bu_4N][Fe(CO)_3(NO)]$[46] in MTBE, the regioselectivity of the addition of malonates onto allyl carbonates could be controlled by simply changing the structure of the NHC and modifying the base (eq 5). Hence, going from SIMes to SItBu allowed for a remarkable inversion of the selectivity (eq 5). In order to rationalize this observation, it was proposed that the reaction would occur via a π-allyl mechanism with the former NHC, while the latter ligand would promote a σ-allyl type mechanism.



(5)

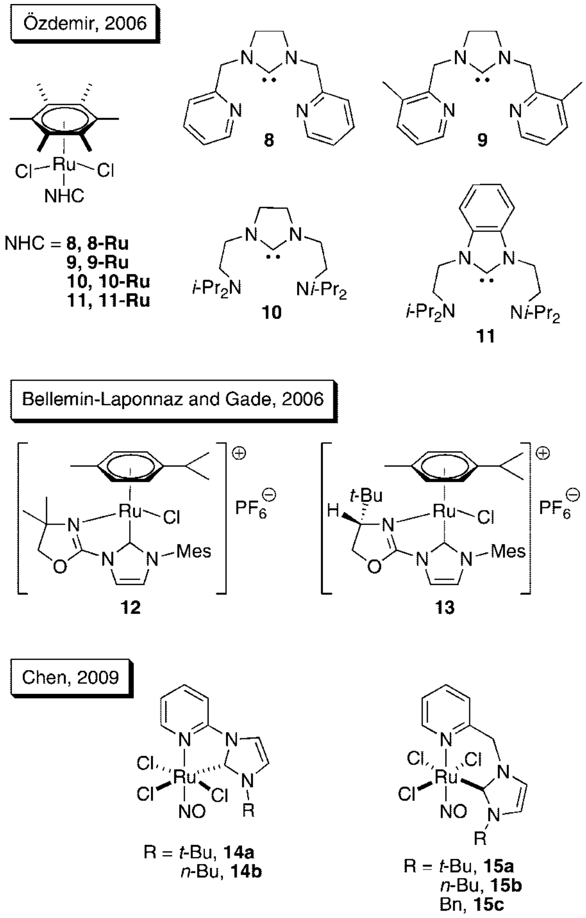
NHC = SIMes	9	98%	91
SIPr	33	38%	67
SItBu	91	74%	9

As stated previously, we are only aware of ten published reports on catalytic applications of [(NHC)Fe] systems.[47] We clearly believe that this is not representative of the potential of NHCs in iron catalysis. We note that N-heterocyclic carbenes have allowed for the stabilization of highly reactive organoiron species, such as molecular nitrogen adducts or iron nitride complexes.[48] This implies that the basic stereoelectronic properties of NHCs should support a number of elementary chemical steps taking place at the iron center.[49] We therefore foresee a strong surge, in parallel to the growing interest for iron catalysis, in the use of NHCs and iron species for organic transformations. Among others, cross-coupling chemistry appears as an ideal target for the development of [(NHC)Fe] catalytic systems.[50]

3.2. Ruthenium

Ruthenium's reign on the NHC chemistry of group 8 is the direct consequence of the immense interest raised by the thrilling triumph of [(NHC)Ru] complexes in olefin metathesis.[51] A downside of this success is that the other catalytic applications of [(NHC)Ru] compounds have long been

Chart 4. Structures of Well-Defined [(NHC)Ru] Catalysts Used in Transfer Hydrogenation of Ketones



overshadowed.[52] As mentioned in the Introduction of this review, we present here only non-metathetical transformations[53] and we invite the reader to consult specialized reviews,[54,55] including the one published in this special issue of *Chemical Reviews*,[56] for more information on the latest developments in the broad field of metathesis. Moreover, since comprehensive reviews on [(NHC)Ru]-catalyzed non-metathetical reactions already appeared,[57] we will only cover in this section the most recent reports published from 2006.

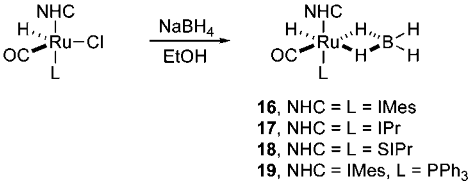
3.2.1. Hydrogenation Reactions

3.2.1.1. Transfer Hydrogenation. The reduction of carbonyl compounds using a hydrogen donor, typically isopropanol that is oxidized into acetone, has emerged lately as an attractive alternative to dihydrogen and metal hydride protocols.[58] In this context, [(NHC)Ru] complexes have proven to be excellent catalysts, and this transformation has become a benchmark for newly developed compounds.

Recently, a number of NHCs bearing *N*-donors were synthesized, along with their Ru complexes, by Özdemir (Chart 4, **8**−**11**),[59] by Bellemin-Laponnaz and Gade (Chart 4, **12**, **13**),[60] and by Chen (Chart 4, **14**, **15**).[61] All were tested in the transfer hydrogenation of aryl methylketones in the presence of isopropanol. Catalysts **8**−**13**, requiring chloride abstraction by a silver salt to free a coordination site, proved only moderately active. The nitrosyl series **14** and **15** showed better activity, producing benzyl alcohols with 0.4 mol % of catalyst when the most active complex, **15a**, was used.

Beller and co-workers evaluated the potential of a wide range of “common” N-heterocyclic carbenes in the transfer hydrogenation of acetophenone.[62] Among differently substituted aryl and alkyl NHCs, IPr proved to be the most active and furnished turnover frequencies up to 346 h^{-1} and turnover numbers up to 4150. Mechanistic investigations strongly supported the formation of a ruthenium dihydride species as reducing agent. Interestingly, while the Beller system displayed better activity with electron-poor acetophenones than with electron-rich ones, the reverse trend was observed with a tridentate pyridine−NHC ligand.[63]

3.2.1.2. H_2-Mediated Hydrogenation. Whittlesey and co-workers recently combined the potential of NHCs[64] with that of metal borohydrides[65] in molecular hydrogen-based reduction and undertook the synthesis of complexes **16**−**19** (eq 6).[66] Overall, these η^2-BH_4 ruthenium catalysts displayed good activities in the reduction of acetophenone derivatives under 10 atm of H_2. Similarly to Beller’s findings, the IPr-containing complex was found to be the most active.



(6)

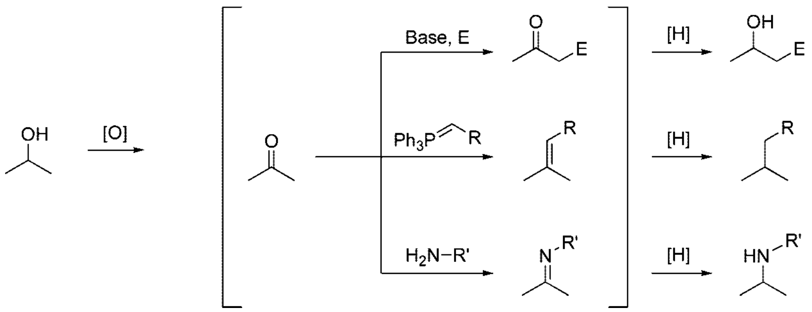
A comparative study recently published by Fogg demonstrated that complexes of the type [(IMes)RuHCl(L)-(PCy_3)][67] perform better in olefin hydrogenation when L = CO when compared with L = H_2.[68] This was attributed to the higher stability of the carbonyl complex under the reaction conditions. Other recent reports include a tethered NHC−η^6-arene ruthenium complex that displayed only moderate activity in the hydrogenations of styrene and carbon dioxide,[69] as well as an anchored [(NHC)Ru^{II}] that was found to be active in the hydrogenation of carbonyl compounds under both alcohol and aqueous reaction conditions.[70] Of note, very recently, Gunnoe, Cundari, and co-workers examined the activity of bis-NHC ruthenium(II) hydride complexes in the hydrogenation of alkenes, aldehydes, and ketones.[71]

Finally, the Beller group used a combination of [Ru-(COD)(2-Me-allyl)$_2$] and SIMes·HBF_4 to reduce nitriles under 35 bar of hydrogen.[72] The system was applied to the reduction of a number of aromatic nitriles and proved efficient with as low as 0.5 mol % ruthenium.

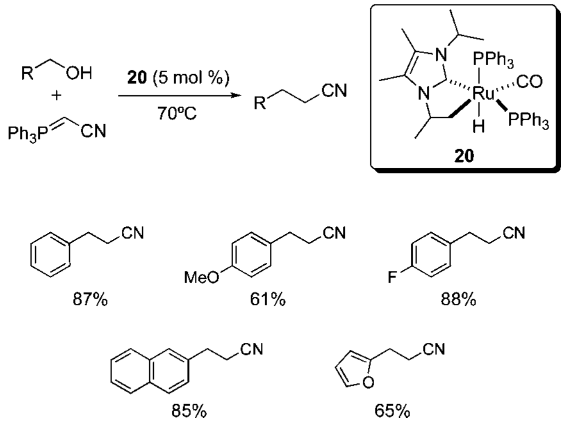
3.2.1.3. Borrowing Hydrogen Processes. The “borrowing hydrogen” strategy,[73] through a net neutral redox process, allows for C−C and C−N bond formation starting from a simple alcohol. Typically, it consists of the in situ oxidation of an alcohol to a carbonyl compound, subsequent bond formation (via enolate or carbonyl reaction), and reduction of the remaining π-bond (Scheme 4). These transformations are highly appealing since they circumvent the low reactivity of alcohols and represent an outstanding example of chemical efficiency (three steps in one pot).

Pursuing their initial studies,[74] Whittlesey and Williams reported an improved catalytic system for C−C bond formation involving an alcohol oxidation/Wittig olefination/alkene reduction sequence.[75] The authors capitalized on their key findings that a number of unsaturated [(NHC)Ru] compounds underwent $(C-H)^{NHC}$ activation at the ruthenium center to afford metalated Ru−H species,[76] which are thought to be involved in the catalytic cycle of these redox transformations. Hence, numerous NHCs were compared in different oxidation and reduction reactions prior to their use

Scheme 4. Most Common "Borrowing Hydrogen" Processes



Scheme 5. Applications of Cyclometalated [(NHC)Ru] in "Borrowing Hydrogen" Transformations



in a "borrowing hydrogen" process. The electron-rich alkyl-substituted NHCs were found to be the most efficient. More importantly, a well-defined cyclometalated complex **20** displayed the best activity of all catalysts tested, supporting the participation of C−H activated species in the catalytic cycle. A succinct scope of benzylic alcohols was examined and showed that electron-rich aromatics were more reluctant partners than electron-deficient ones (Scheme 5).

In 2007, Peris and co-workers reported the use of an unusual bis-carbene ligand in Ru-catalyzed β-alkylation of secondary alcohols with primary alcohols (Scheme 6).[77] This remarkable ligand,[78] where both carbenic carbons are located in the same triazole unit (see Scheme 6, **21**), permitted the formation of di- and tetranuclear ruthenium compounds **22** and **23**. Their activities in this reaction were found to be similar. A range of secondary alcohols could participate in this process, including usually reluctant secondary alkyl alkyl alcohols (Scheme 6). Overall, these catalysts compared extremely well to other ruthenium-based systems, performing at only 1 mol % Ru loadings. The Peris group recently disclosed an improved system, using a rare pyrazol-3-ylidene as NHC, for the β-alkylation of secondary alcohols.[79]

Along these lines, Crabtree and co-workers developed a pyrimidine−NHC chelate ligand, which showed only moderate activity in the β-alkylation of secondary alcohols with primary alcohols and the *N*-alkylation of amines with alcohols.[80] This ligand proved more active when placed on an iridium center (see section 4.3.1.3).

While the reaction of alcohols with amines under "borrowing hydrogen" conditions usually affords homologated amines (see Scheme 4), an interesting shift was recently reported by Madsen. It was found that the combination of a Ru^{II} source with an NHC and a phosphine allows for the direct formation of an amide from an alcohol and amine (Scheme 7).[81] An extensive screening of phosphines and NHCs was conducted and good to high yields of a wide array of amides were obtained in both inter- and intramolecular reactions. The surprising lack of formation of imines was tentatively explained by a tight coordination of the ruthenium center to the aldehyde (see **25**) and then to the aminal (see **26**), inhibiting their hydrolysis.

3.2.2. Isomerization Reactions

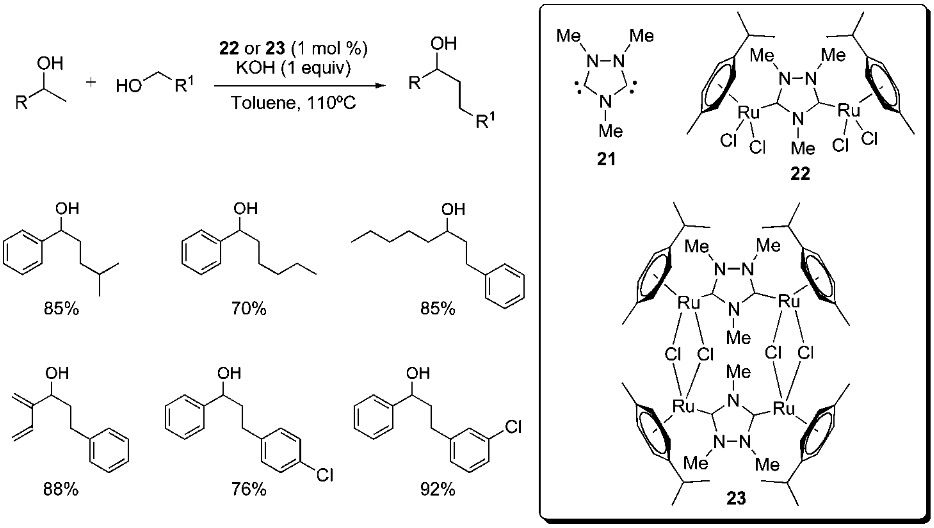
3.2.2.1. Olefin Isomerization. It was discovered early on, during the development of Ru-catalyzed olefin metathesis, that alkene isomerization could occur both on the substrate and on the product.[82] These observations have triggered a great deal of research, notably aimed at unraveling the modified structure of the ruthenium species catalyzing the isomerization.[83,84] While this process is considered parasitic for productive olefin metathesis, it can also be regarded as an interesting transformation in itself, provided that a good isomerization versus metathesis control can be obtained.

Most of the isomerization reactions were in fact observed while attempting metathesis reactions, and a catalytic system of preparative utility long remained elusive. Solving this problem, Hanessian and co-workers recently developed a self-standing [(NHC)Ru]-catalyzed olefin isomerization protocol.[85] Remarkably, the authors simply used Grubb's second generation catalyst **27** (Scheme 8). The switch in reactivity (i.e., isomerization vs self-metathesis) was attributed to the in situ formation of a carbonyl ruthenium hydride species from the decomposition of **27** in hot methanol.[86] A wide range of terminal allyl derivatives was efficiently converted into their 2-propenyl counterparts in good to excellent yields and selectivity (Scheme 8). In addition to its convenience, the main feature of this procedure is its high tolerance to diverse functional groups.

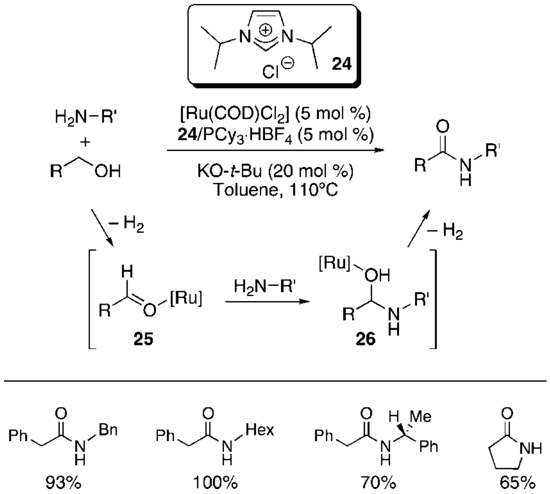
Another promising isomerization, the atom-economical conversion of allylic alcohols into aldehydes or ketones,[87] was recently reported by Joó.[88] The catalytic system, made of $[(BMIM)RuCl_2(\eta^6\text{-}p\text{-cymene})]$, aqueous phosphate buffer, and 1 bar of H_2, proved moderately efficient but could be reused up to four times upon recycling of the aqueous phase.

3.2.2.2. Cycloisomerization. The chemistry of ruthenium is rich in transformations involving polyunsaturated compounds.[89] Nevertheless, only a handful of examples can be found that employ N-heterocyclic carbenes. Following seminal work by Dixneuf on 1,1-diallyl compounds,[90] Arisawa and Nishida investigated the behavior of the *N*-tosyl diallyl amine in the presence of different olefin additives and observed that vinyl trimethylsilyl enolether allowed for the best yields of cycloisomerized product versus metathesis.[91] Hence, this olefin in conjunction with 10 mol % Grubbs II catalyst **27** allowed, via diene cycloisomerization, for the formation of diverse *exo*-methylene benzofurans and indolins.

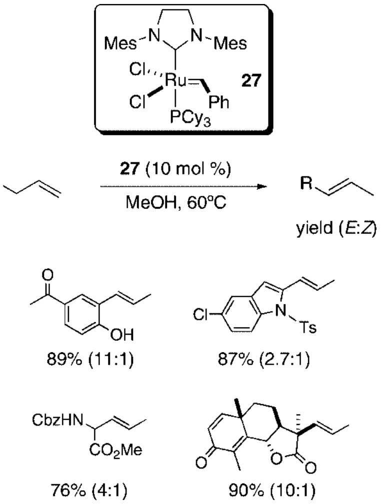
Scheme 6. Alkylation of Secondary Alcohols Using a Triazolediylidene−Ru System



Scheme 7. Amide Synthesis Catalyzed by a Ru/NHC/ Phosphine System

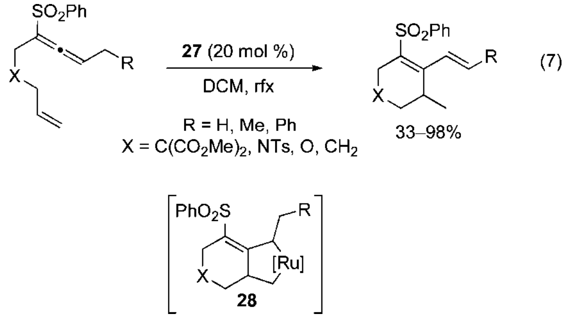


Scheme 8. Ruthenium-Catalyzed Isomerization of Terminal Allyls



It was shown that in the presence of the vinyl trimethylsilyl enolether, compound **27** decomposed into [(SIMes)-RuHCl(CO)(PCy$_3$)], which was believed to be the actual catalyst for the cycloisomerization process. Arisawa and Nishida subsequently applied their method to the synthesis of fistulosin (Scheme 9).[92]

Complementary to the aforementioned work on dienes, Mukai and co-workers examined the reactivity of 1,6-allenenes in the presence of Grubbs II catalyst **27**.[93] At high catalyst loadings, this system proved efficient for the cycloisomerization of a number of allenes (eq 7). The presence of heteroatoms was well tolerated. The authors proposed a mechanism going through ruthenacyclopentane **28** for this transformation.



(7)

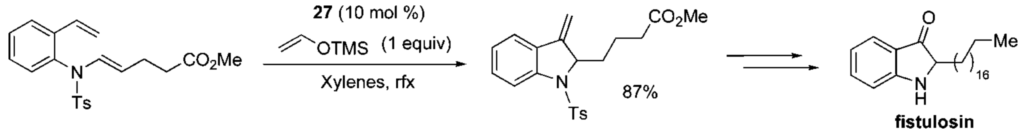
3.2.3. Polymerization Reactions

Despite the noticeable advances brought by the introduction of NHCs in Ru-catalyzed ATRP,[33,94] relatively few reports have appeared in this area, probably because most of the research efforts in [(NHC)Ru]-catalyzed polymerization have focused on ring-opening metathesis polymerization.[95]

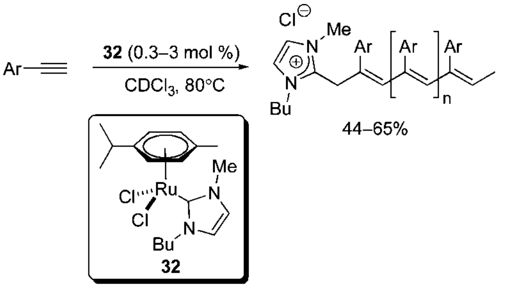
Following their early studies in ATRP,[94a,d,96] Delaude and Demonceau recently synthesized two homobimetallic ruthenium−NHC catalysts, **29** and **30** (Chart 5), and examined their activity in the polymerizations of methyl methacrylate, butyl acrylate, and styrene.[97] Both complexes led to controlled polymerization of MMA at 85 °C. Under these conditions, **29** outperformed **30** and **31** in terms of activity but a narrower polydispersity index was obtained with **31**. Attempts to polymerize butyl acrylate and styrene turned out to be a more difficult task, furnishing uncontrolled polymerization of the acrylate and almost exclusively self-metathesis of styrene. In both cases, phosphine-containing **31** proved more efficient and displayed good polymerization activities.

A mononuclear [(NHC)Ru(*p*-cymene)] complex was shown to catalyze the oligomerization of alkynes.[98] Complex **32**,

Scheme 9. Application of [(NHC)Ru]-Catalyzed Cycloisomerization in the Synthesis of Fistulosin



previously used by Joó and co-workers for the isomerization of allylic alcohols,[88] displayed interesting catalytic activity toward phenyl acetylene derivatives but was found to be inert in the presence of non-aromatic substituents and internal alkynes (eq 8). Remarkably, the oligomers were obtained with the imidazolium salt end group,[99] providing clear evidence for the decoordination of the NHC rather than of the *p*-cymene in this process.



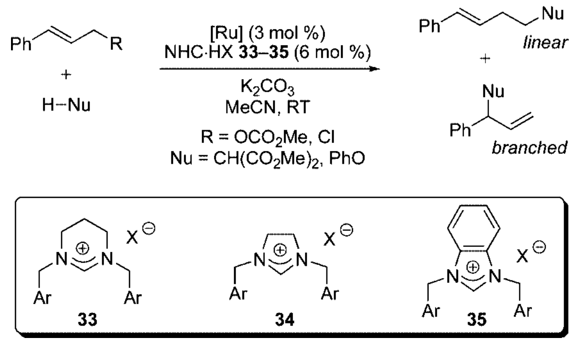
(8)

Of note, a series of [(NHC)RuCl$_2$(*p*-cymene)] complexes, recently reported by Peris, was shown to be active for the dimerization of phenyl acetylene.[79]

3.2.4. Miscellaneous Reactions

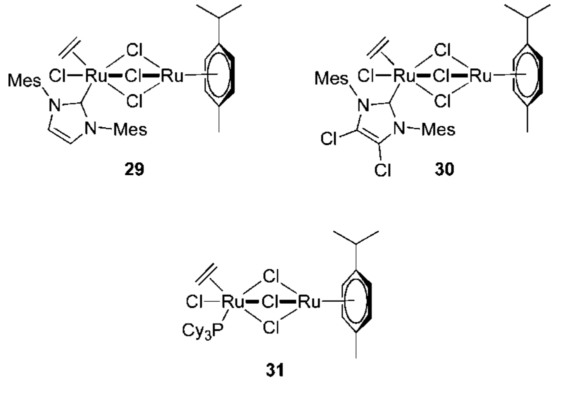
The allylic alkylation reaction is one of the most important C−C bond forming processes, and ruthenium is among the most efficient transition metals in this reaction.[100] Pursuing their initial studies in this field,[101] Özdemir, Çetinkaya, Renaud, and Bruneau published their recent progress toward a highly selective system. An impressive number of tetrahydropyrimidinium (**33**), imidazolinium (**34**), and benzimidazolium (**35**) salts were screened in different allylic substitution reactions (Scheme 10).[102] Unfortunately, linear versus branched selectivities were only modest, and a clear rationale for further ligand design remained elusive.

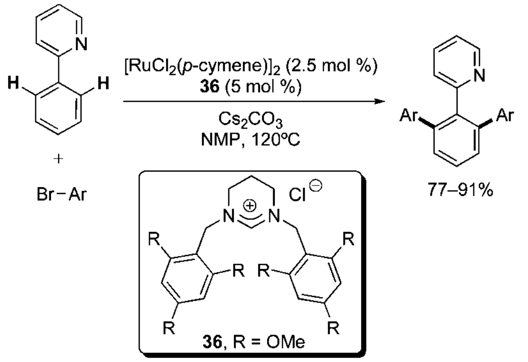
Scheme 10. Allylic Substitutions Catalyzed by [(NHC)Ru] Systems



Further investigation of the potential of these ligands revealed their high efficiency in direct C^{sp^2}−H arylation.[103] The direct arylation of “inert” C−H bonds is currently a field of high interest, notably for its faculty to minimize the organometallic waste produced with classical cross-coupling reactions.[104] Hence, Dixneuf and Maseras showed that ligands of the type **33** displayed the best activity toward di-*ortho*-arylation of 2-phenylpyridine (eq 9). More precisely, carbene precursor **36** proved remarkably efficient and allowed for the use of both electron-poor and electron-rich coupling partners. Subsequent studies showed that chelating bis-NHC complexes of ruthenium(III) are also active for this transformation, even with aryl chlorides.[105]

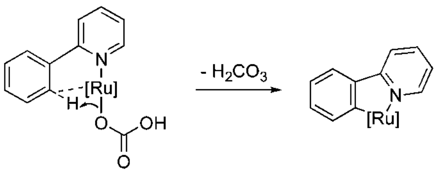
Chart 5. Structures of Homobimetallic [(NHC)Ru] Complexes Active in ATRP





(9)

Based on DFT studies of the possible mechanisms for the activation of the C^{sp^2}−H bond by the ruthenium center, a base-assisted Ru−C bond formation (eq 10) was proposed rather than oxidative addition of the C−H bond.

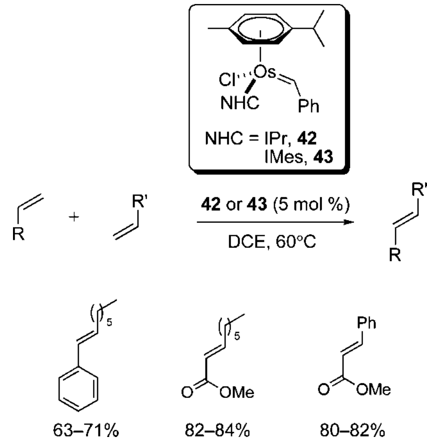


(10)

In addition to the transformations presented in this section on ruthenium, isolated reports have mentioned the use of [(NHC)Ru] catalytic systems for Diels−Alder reactions,[106] diazo cyclopropanation of olefins,[107] and the dehydrative coupling of allyl alcohol and benzimidazole.[108] Finally, a stoichiometric C^{sp^2}−F activation[109] at a ruthenium center bearing ICy as NHC was recently disclosed by Whittlesey and co-workers (Chart 6, **37**).[110] Modification of the NHC (i.e., from *N*-alkyl to *N*-aryl substituents) and the phosphine resulted in the development of a catalytic hydrodefluorination of polyfluoroarenes using complexes **38**−**41**.[111]

Overall, it can be stated that the non-metathetical chemistry of [(NHC)Ru] is already well developed, spanning over

Scheme 11. [(NHC)Os]-Catalyzed Olefin Cross Metathesis



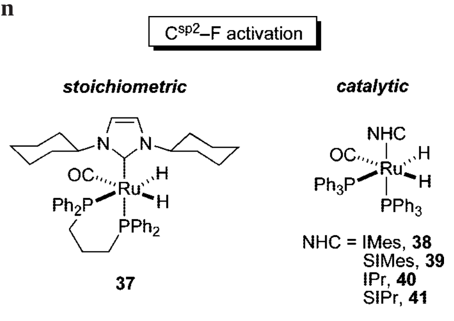
numerous and diverse areas of catalysis. Nevertheless, a closer look reveals that most of the developments were made as spin-off of the venerable olefin metathesis reaction.[112] However, this “metathesis dependence” seems to progressively fade away, and we are confident that, in the next few years, NHCs will break into the “treasure trove”[113] of ruthenium catalysis.

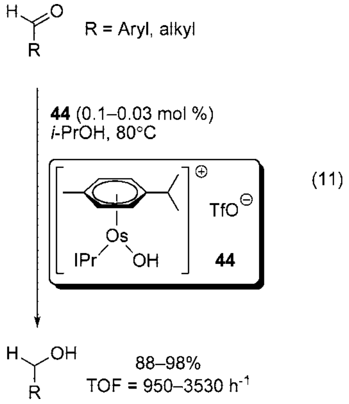
3.3. Osmium

Among the iron triad, osmium is the least studied element. It is therefore no surprise that, except for the pioneering work of Lappert in the 1970s and Herrmann in the 1990s,[114] [(NHC)Os] compounds attracted very little interest of the scientific community before 2005. As a matter of fact, even if the last three years have witnessed an increased activity, NHC-containing osmium complexes are still scarce[115] and catalytic applications only amount to two, to the best of our knowledge.

In 2005, the first brick of Esteruelas’ impressive work on [(NHC)Os] complexes was also the first catalytic application of an NHC-containing osmium compound.[116] Mimicking the structure of Grubbs’ metathesis catalysts,[117] Esteruelas and co-workers synthesized two osmium benzylidene complexes, **42** and **43**, bearing IPr and IMes ligands, respectively. These catalysts were benchmark tested in the ring-closing metathesis of diallyldiethylmalonate, the ring-opening metathesis polymerization of cyclooctene, and a variety of olefin cross metatheses (Scheme 11). The overall catalytic activity of **42** and **43**, even though not as good as ruthenium- or molybdenum-based metathesis catalysts,[118] was found to be fairly good, yielding crossed olefins in good yields and high selectivities. More importantly, in addition to being the first [(NHC)Os] catalytic application, this study constitutes a rare example of osmium catalysis for C−C bond formation.[119] Following this first report, Esteruelas recently disclosed the synthesis of [(IPr)Os(OH)(η^6-*p*-cymene)]OTf, **44**, which was found to be an efficient precatalyst for transfer hydrogenation.[120] The reactions were carried out in isopropanol, serving as hydrogen source, with 0.1−0.03 mol % of catalyst. Numerous aryl and alkyl aldehydes could be reduced in high yields and high TONs using this procedure (eq 11).

Chart 6. Structure of [(NHC)Ru] Catalysts for C−F Activation





(11)

Of note, under these conditions, acetophenone was reduced very slowly. Regarding the activation of the precatalyst, the authors provided strong evidence that, in isopropanol, **44** was converted into [(IPr)OsH(O*i*-Pr)]OTf, which is an active monohydride catalyst for transfer hydrogenation.

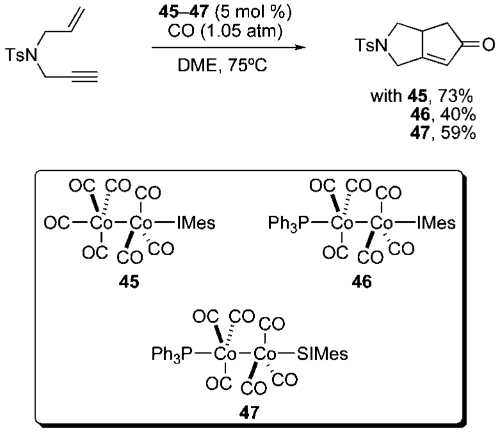
With only two reports to date, [(NHC)Os]-based catalysis can hardly be considered anything else than a curiosity. It is clear that the toxicity of osmium has played a crucial, and deleterious, role in this situation.[121] It is unfortunate though, since the two transformations explored so far, namely, olefin metathesis and transfer hydrogenation, are among the most important ones of modern organometallic catalysis. This underdeveloped potential will surely attract more consequent research in the near future.

4. Group 9: Cobalt, Rhodium, and Iridium

4.1. Cobalt

The NHC chemistry of cobalt is somewhat comparable to that of iron. Indeed, major breakthroughs have been achieved in organometallic chemistry rather than in catalysis. Since the 1970s and the pioneering work of Lappert,[122] N-heterocyclic carbenes have proven to be interesting ligands for the isolation of unusual organometallic cobalt species,[123] including the synthesis of cobalt imido complexes with the

Scheme 12. [(NHC)Co]-Catalyzed Pauson−Khand Reaction

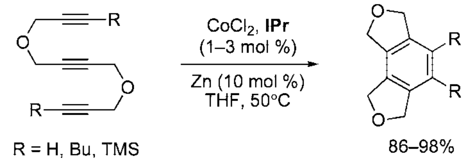


use of remarkable tripodal tris-NHC ligands.[124] On the other hand, catalytic applications only appeared recently, and we could find only nine reports, two of which present only a single catalytic trial, mentioning the use of NHCs in a Co-catalyzed transformation.[125]

4.1.1. Cyclization Reactions

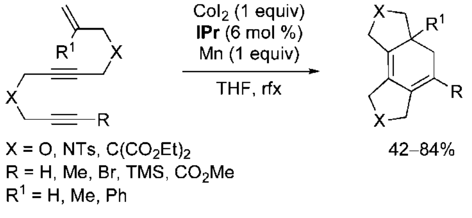
The first application of NHC ligands in cobalt catalysis was disclosed in 2003 by Gibson and Loch.[126] They synthesized a series of NHC-containing dinuclear cobalt complexes, **45**−**47**, and tested their activity in the Pauson−Khand reaction (Scheme 12). Only one enyne was examined, and the [(NHC)Co^0] systems showed lower activity than the simple [$Co_2(CO)_8$] complex, but it constituted the proof-of-concept that NHCs could be viable ligands in cobalt catalysis. Shortly after this report, the activity of an IPr-containing Nicholas-type cobalt−alkyne complex, used as stoichiometric reagent in the Pauson−Khand reaction, was disclosed.[127]

In 2005, Okamoto and co-workers,[38a] similarly to their findings with the iron-based system described in the same report, reported that the use of zinc powder and IPr in conjunction with $CoCl_2$ allowed for the efficient intramolecular cyclotrimerization of triynes (eq 12).



(12)

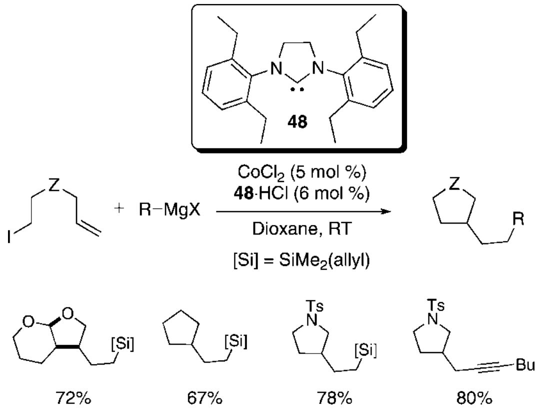
Very recently, Gandon and Aubert examined the effect of NHCs in the cyclization of enediyne precursors leading to fused polycyclic cyclohexadienes (eq 13).[128] Direct comparison with established catalytic systems, such as [(Cp)Co(CO)$_2$]/$FeCl_3$ and CoI_2/Mn/PPh_3, demonstrated the superior activity of the NHC ligand in this reaction. Of considerable importance, IPr could be used catalytically with 1 equiv of manganese, while 2 equiv of PPh_3 along with 10 equiv of Mn were generally required. Of note, substrates possessing terminal substituents on the olefin cyclized in a diastereospecific manner.



(13)

The propensity of cobalt to act as a single electron-donor was investigated in the context of a sequential cyclization/cross-coupling reaction by Yorimitsu and Oshima.[129] A number of haloalkenes could be cyclized to their corresponding five-membered rings and trapped for subsequent coupling with a Grignard reagent (Scheme 13). The reaction is thought to occur through Co-mediated generation of a carbon radical, 5-*exo*-trig cyclization, radical trapping by the cobalt complex, and reductive elimination. In this process, NHC **48** was found to be more efficient than IPr, IMes, and SIMes. Further development by the same group using halovinylsilyloxy derivatives permitted the synthesis of diverse 1,3-diols upon Tamao oxidation of the cyclized products.[130]

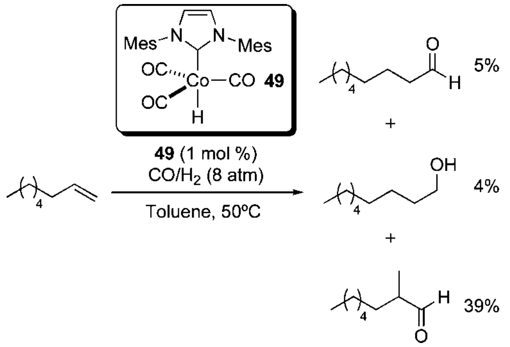
Scheme 13. [(NHC)Co]-Catalyzed Sequential Cyclization/Cross-Coupling



4.1.2. Miscellaneous Reactions

Continuing their investigations on [(NHC)Co]-mediated activation of carbon−halogen bonds, Yorimitsu and Oshima recently reported a remarkable dehydrohalogenation reaction (Scheme 14).[131] IMes was found to be optimal among a set of NHC, phosphine, and amine ligands. Bromo- and iodoalkanes participated in the reaction but not the corresponding chlorides and tosylates. The main feature of this transformation is its high regioselectivity favoring the formation of the less substituted alkene, unlike base-catalyzed elimination. The authors proposed a mechanism involving a single-electron transfer to generate an alkyl radical followed by C−Co bond formation and subsequent β-hydride elimination as depicted in Scheme 14.

Promising results were obtained by Llewellyn and co-workers in the hydroformylation of 1-octene using the hydrido cobalt complex [(IMes)Co(CO)$_3$H], **49**.[132] The unusual high selectivity for the branched hydroformylation[133] product versus linear 1-nonanal seems to indicate that the [(NHC)Co] complex catalyzes alkene isomerization prior to hydroformylation (eq 14).



(14)

In addition to the reports mentioned above, it should be noted that a handful of unsuccessful trials with [(NHC)Co] catalytic systems can be found in the literature. Hence, as part of a thorough optimization, the combination of $CoCl_2$ and IPr was found to catalyze the Kumada coupling of benzyl bromide with 1-hexynyl Grignard in good yield but with low selectivity.[134] An interesting dinuclear cobalt complex featuring a Co−Co bond, [(IMes)Co(CO)$_3$]$_2$, was tested in the hydroformylation of 1-octene without success.[135] Finally, the $CoCl_2$ analogue of complex **4** (see Chart 3, section 3.1.1) was tested in the oligomerization/polymerization of ethylene and proved totally inactive.[34a]

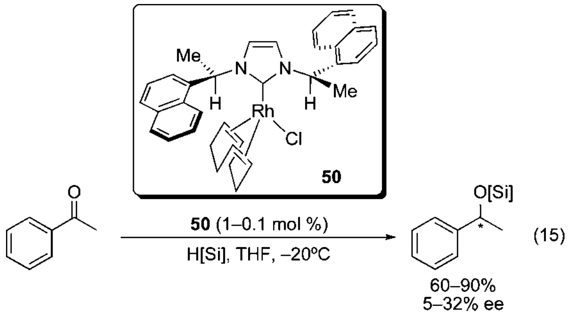
Despite the early interest of organometallic chemists, the successful use of [(NHC)Co] systems in catalysis only dates back to 2003. As of today, cobalt is still a minor player in the field of N-heterocyclic carbenes, and it seems premature to predict a surge of reports for the future.[136] Nevertheless, one of the most interesting aspects revealed by the published studies is that the NHC systems are often complementary with their phosphine analogues. This special feature, usually translated in different chemo- or regioselectivity, should be a strong incentive to "revisit" some of the [(R_3P)Co] chemistry with NHC ligands. We have no doubt that this type of development will ultimately lead to the discovery of unprecedented reactivity and novel organic transformations.

4.2. Rhodium

Rhodium holds a particular position in the late transition metal chemistry of NHCs. It belongs, along with Pd and Ni, to the "heavyweight category" in terms of catalytic applications and number of reports. It is also one of the very first late transition metals to have shown promising potential with NHCs, almost 15 years ago. The number of [(NHC)Rh] complexes synthesized to date is significant and their uses, outside of catalysis, are numerous, including notably a variety of biochemical applications.[137] NHC−rhodium complexes have also been used for the determination of key structural parameters of NHCs such as their electronic properties through infrared CO stretching correlations[138] and electrochemistry.[139] Finally, rhodium has served as an interesting platform for the development of polydentate NHC-based ligands. Most of these ligands have exhibited interesting catalytic properties worthy of note. Nevertheless, to minimize overlapping with another review published in this special issue on carbenes and dealing with "Complexes with Poly(N-heterocyclic carbene) Ligands: Structural Features and Catalytic Applications",[17] we will focus our discussion here on monodentate NHCs.

4.2.1. Hydrosilylation Reactions[140]

Hydrosilylation is arguably the most studied transformation with [(NHC)Rh]-based catalysts. Alkyne, alkene, carbonyl, and imine groups can be reduced with such systems in both racemic and asymmetric manners. Historically, it represents the first catalytic application where chiral inductions were obtained with an asymmetric NHC.[141] The hydrosilylation of acetophenone in the presence of diphenylsilane and a naphthyl-derived NHC−rhodium catalyst **50**, produced the corresponding enantio-enriched silyl ether in excellent yield (eq 15). Despite low ee's (∼30% ee at best), this report validated the possibility of asymmetric synthesis with NHC ligands.



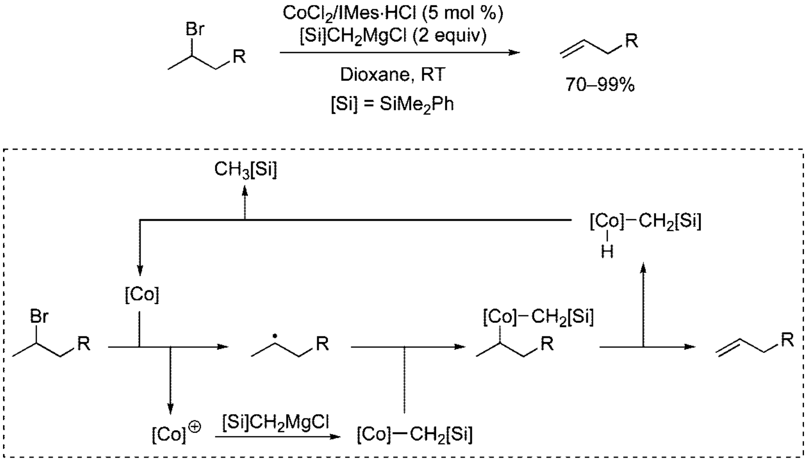
(15)

As a whole, the impressive number of reports in this area could warrant a review in itself. We will therefore mention here only the most recent advances with a strong focus on monodentate systems.[142]

4.2.1.1. Carbonyl Compounds. A number of polydentate NHC-based ligands have shown interesting catalytic activity for the reduction of carbonyl derivatives. Notably, the remarkable work of Bellemin-Laponnaz and Gade on oxazoline-NHC provided a high level of enantioselectivity in the reduction of aryl and alkyl ketones.[143] A number of CP,[144] CN,[145] and CC[146] bidentate ligands also proved active.

Most studies in this field have focused on the synthesis of well-defined complexes of the type [(NHC)Rh(COD)Cl]. The reduction of acetophenone has generally been used as a benchmark test for novel catalysts, but most systems are also active in the reduction of alkyl ketones. Scheme 15 shows some of the NHC structures that proved efficient.[147] All these carbenes displayed moderate to good activity in the reduction of aromatic ketones. In addition to **51**−**54**, Özdemir and coworkers examined the activity of NHCs **8**−**11**[148] (see Chart 4, section 3.2.1.1), as well as dinuclear rhodium complexes linked by bis-NHC ligands,[149] in the hydrosilylation of acetophenone derivatives for overall similar results. In terms of chiral induction, only moderate levels of enantioselectivity were obtained with the chiral NHCs depicted in Scheme 15. Carbenes **55**, **56**, and **61**−**63** afforded somewhat promising results (i.e., ∼40% ee), while **57** and **58** afforded a poor 7% and 28% ee, respectively. Of note, the two latter ligands did not prove more efficient when used with iridium. In the series developed by Fernández and Lassaletta, the thio-NHC chelate

Scheme 14. [(NHC)Co]-Catalyzed Dehydrohalogenation



Scheme 15. Structure of NHCs Active in Ketone Hydrosilylation

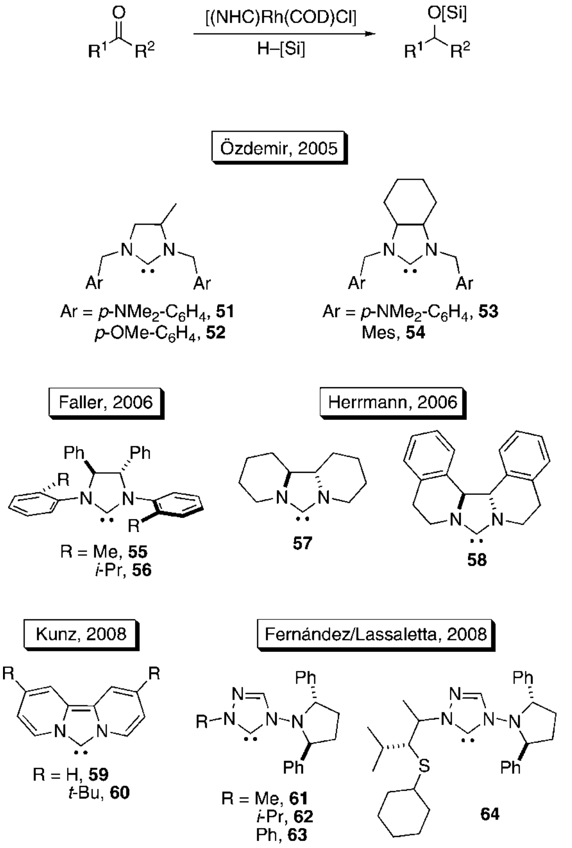
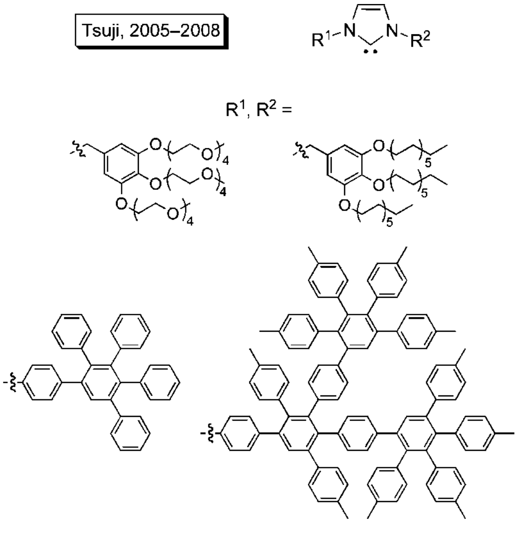


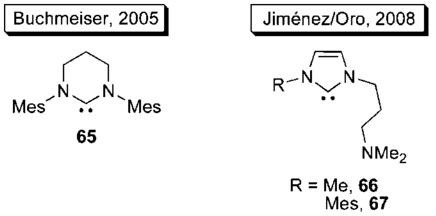
Chart 7. Structures of Dendrimeric NHCs Active in Ketone Hydrosilylation



64 allowed for the best ee values (i.e., up to 62%) in the reduction of acetophenone.

Interesting developments by Tsuji and co-workers have recently appeared. Several rhodium complexes bearing intriguing dendrimeric NHCs were synthesized and tested in hydrosilylation reactions. Different options were explored by the authors, including NHCs possessing hydrophilic or hydrophobic chains,[150] as well dendrimers made of polyphenyl[151] or polyphenoxy[152] groups (Chart 7). All of these proved catalytically active and even allowed for the reduction of dialkyl ketones and conjugated enones, generally favoring in the latter case 1,4-type hydrosilylation.

Chart 8. Structures of NHCs Active in Alkyne Hydrosilylation



4.2.1.2. Alkynes and Alkenes. Surprisingly, [(NHC)Rh] complexes have been much less studied in the hydrosilylation of alkenes and alkynes. Indeed, only a handful of chelating NHCs, including CC[153] and PCP[154] ligands, have been reported for the reduction of C−C unsaturated bonds.

Buchmeiser exploited the flexible scaffold of tetrahydropyrimidine-based NHCs such as **65** and synthesized the well-defined [(**65**)Rh(COD)]BF$_4$ cationic complex, which was further tested in the hydrosilylation of ketones, alkynes, and alkenes (Chart 8).[155] Internal and terminal alkynes could be reduced only in moderate yields but in good selectivity and at low catalyst loadings (i.e., as low as 0.05 mol %). This system also proved active in the hydrosilylation of internal and terminal olefins as well as ketones and aldehydes.

Good yields and fair to good selectivity were observed by Jiménez and Oro using **66** and **67** in [(NHC)Rh(COD)Cl] catalysts for the hydrosilylation of terminal alkynes.[156] Overall, the smaller NHC **66** was found to be more active than its mesityl counterpart.

Finally, it should be noted that only a few examples of [(NHC)Rh]-catalyzed hydroboration of olefins have been reported to date.[157]

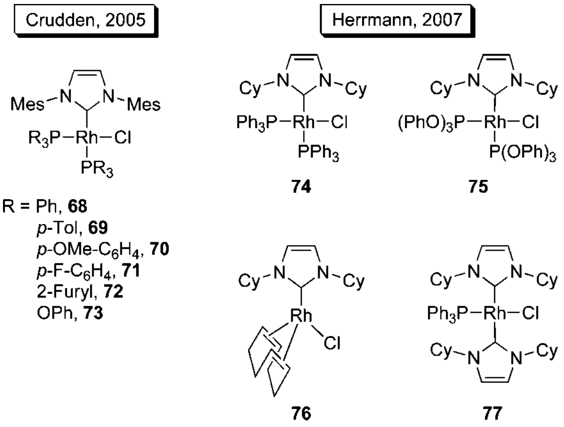
4.2.2. Hydrogenation Reactions

4.2.2.1. H$_2$-Mediated Hydrogenation. A number of NHC-based bidentate ligands, such as CC,[158] CP,[159] and CN[160] chelates, have shown interesting activity in the hydrogenation of alkenes. Monodentate NHCs are also active, but addition of phosphine ligands is generally required to avoid decomposition of the catalysts under hydrogenation conditions. Hence, Crudden and co-workers reported the synthesis of a series of [(IMes)Rh(PR$_3$)$_2$Cl] complexes that were tested in the hydrogenation of styrene derivatives.[161] Different aryl phosphines and phosphates were examined (Chart 9, **68**−**73**) in which **72** displayed the highest catalytic activity. Of note, the choice of solvent was found to be critical in handling these complexes since the same group showed in an earlier study that halogenated solvents promoted cleavage of the Rh−NHC bond and formation of Wilkinson-type complexes in the presence of excess phosphine.[162]

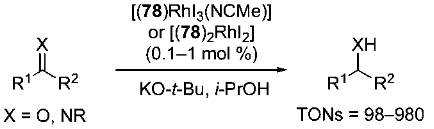
Recently, Herrmann studied the activity of ICy analogues **74**−**77** for the hydrogenation of aliphatic alkenes.[163] 1-Octene and cyclohexene were efficiently reduced with all complexes. It should be noted that these complexes did not really bring improvements of the catalytic activity when compared with Wilkinson's catalyst. Nevertheless, as mentioned by Herrmann, the observation that the Rh−NHC bond is not labile, under the right catalytic conditions, opens the possibility of asymmetric hydrogenations with chiral NHCs. A recent study also revealed that complexes of the type [(NHC)$_2$Rh(H)$_2$Cl], where NHC = IPr or IMes, catalyze the hydrogenation of 1-octene.[164]

4.2.2.2. Transfer Hydrogenation. In the context of NHCs, the reduction of unsaturated bonds using a hydrogen donor

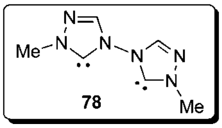
Chart 9. Structures of [(NHC)Rh] Catalysts Active in Olefin Hydrogenation



such as isopropanol has been much less studied with rhodium than with ruthenium and iridium (see sections 3.2.1.1 and 4.3.1.2). Following their early work in this field,[165] Peris and Crabtree recently reported the activity of the remarkable biscarbene **78**, where two triazolyl moieties are connected directly to each other without linker (eq 16).[166] Two well-defined rhodium complexes, bearing one and two ligands **78**, were investigated and showed good activity in the reduction of aryl and alkyl ketones, as well as imines. Of note, calculations on the electronic properties of **78** have predicted a somewhat electron-poor carbene, a feature that would distinguish this peculiar NHC from most of its relatives.



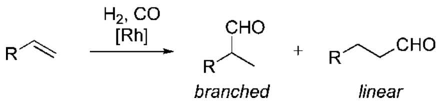
(16)



Albrecht and co-workers reported the efficient reduction of several ketones using another unusual type of carbene.[167] A bis-C(4)-bound carbene complex of rhodium was indeed shown to be active in transfer hydrogenation. Interestingly, while the catalytic performances of this carbene are comparable to those of **78** in this reaction, it should be noted that C(4)-bound NHCs are among the most electron-rich known carbenes, in sharp contrast to the electronics calculated for **78**.

4.2.3. Hydroformylation Reactions

The hydroformylation of alkenes (eq 17) is one of the most important processes of the chemical industry and the largest, in terms of volume, employing homogeneous catalysts.[168]



(17)

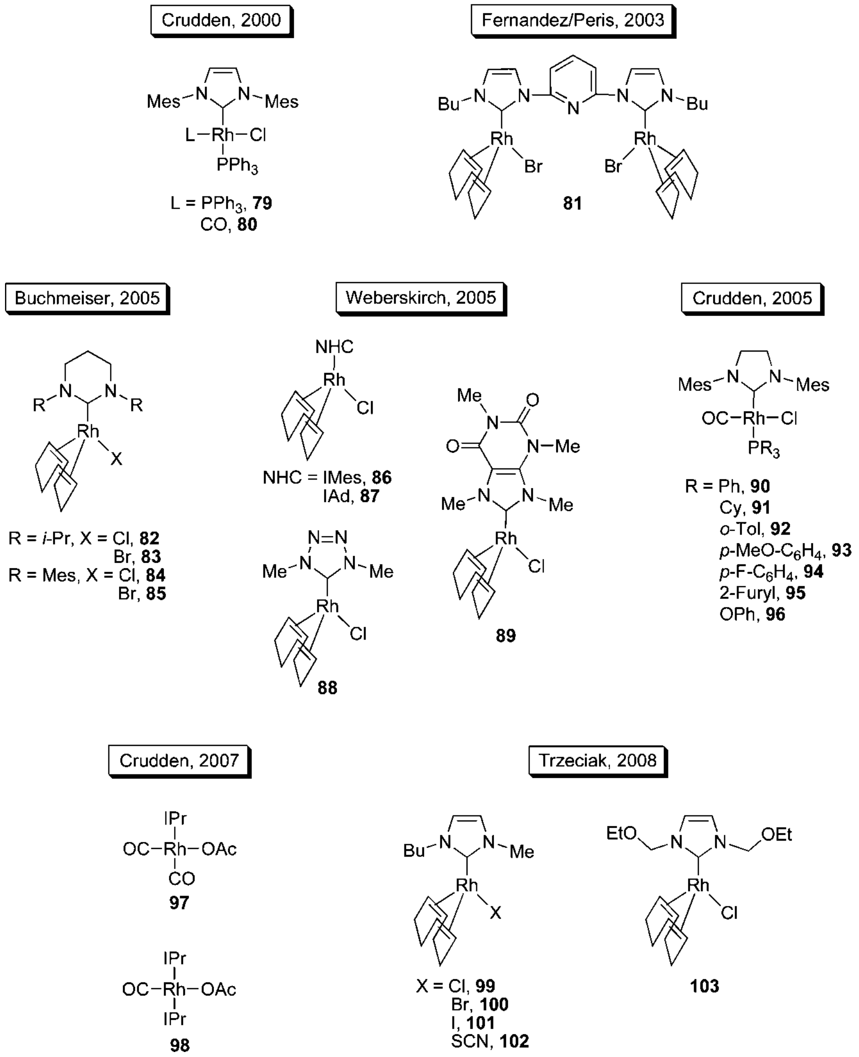
The principal catalytic systems used for this reaction are phosphine/rhodium complexes, such as the Wilkinson catalyst. Therefore, it comes as no surprise that a number of [(NHC)Rh] species were examined as potential alternatives for this reaction. Since an excellent and comprehensive review on this topic by Crudden was published recently,[169] we will only briefly discuss this facet of [(NHC)Rh]-based catalysis. Also, it should be noted that different NHC-related systems, which will not be discussed further here, such as a CN bidentate ligand,[170] a cyclopropenylidene ligand,[171] and cyclic thioureas[172] have been used in hydroformylation reactions.

As can be seen from Chart 10, most studies published so far have focused on variations of the structure of the NHC. Hence, with the exception of Crudden's work, all [(NHC)Rh] catalysts for hydroformylation are templated on [(NHC)Rh(COD)X], where X is a halogen. Fernandez and Peris reported the activity of the dirhodium complex **81** in the hydroformylation of alkyl and aryl alkenes and observed high selectivity for the branched products (see eq 17).[173] Buchmeiser explored the performance of tetrahydropyrimidinylidenes as NHCs (**82**−**85**),[174] while Weberskirch looked at very different NHC architectures (**86**−**89**).[175] Interestingly, it was shown in the latter study that electron-poor NHCs, such as in complex **88**, increase the overall catalytic activity.[176] Despite low selectivity between linear and branched products, catalyst **88** is, to date, the most active NHC-based system for Rh-catalyzed hydroformylation reactions with TOFs up to 3540 h^{-1}. The same group also reported interesting catalytic activity for a supported [(NHC)Rh(COD)Cl] species, where the NHC was immobilized on an amphiphilic block copolymer.[177] More recently, Trzeciak and co-workers synthesized a series of complexes **99**−**102** differing only by the halide on the rhodium center.[178] Little difference in activity was observed among these catalysts.

Moving away from cyclooctadiene complexes of rhodium, the work of Crudden and co-workers has focused on mixed NHC/phosphine carbonyl complexes **79**−**80** and **90**−**96**.[179] This type of complex, which is closer to catalytic intermediates than the COD-containing ones, has also allowed for high selectivity in the formation of the branched isomer. Further developments by the same group led to the synthesis and evaluation of rhodium−acetate compounds **97** and **98** that furnished promising results.[180] Recently, a rhodium monocarbonyl complex bearing an NHC−indenyl chelate ligand was reported by Danopoulos and Cole-Hamilton and their co-workers to be active in the hydroformylation of 1-octene and in the carbonylation of methanol.[181]

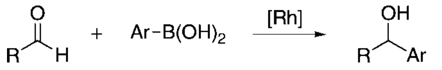
Finally, Beller and co-workers, using IMes- and IPr-derived NHCs, including ^{Cl}IMes, examined a set of [(NHC)Rh(COD)Cl] complexes in the hydroaminomethylation reaction of a wide range of amines and olefins.[182] This process, which combines alkene hydroformylation and imine reduction, allows for the straightforward formation of homologated linear amines from readily available starting materials (i.e., CO, H_2, and an olefin).[183] Overall, excellent catalytic activity was observed with [(IMes)Rh(COD)Cl], **86**, with as low as 0.1 mol % catalyst loadings. Remarkably, the linear versus branched selectivities, arising from the hydroformylation step (see eq 17), were extremely good (i.e., typically >99:1) in favor of the linear isomer.

Chart 10. [(NHC)Rh] Catalysts Active in the Hydroformylation of Alkenes



4.2.4. Arylation of Carbonyl Compounds with Boron Reagents[184]

Along with reduction reactions, the addition of aryl boron derivatives to carbonyl compounds (eq 18) is the most fertile field of research for [(NHC)Rh] catalysts. In this section, we will again focus the discussion on homogeneous systems with monodentate NHCs.[185]



(18)

As early as 2001, Fürstner screened a number of "common" NHCs in the Rh-catalyzed addition of phenyl boronic acids to *p*-anisaldehyde, making use of azolium salts in an in situ procedure.[186] The authors notably observed that unsaturated NHCs performed better than their saturated analogues. Direct comparison with trialkyl phosphines revealed that, even though both ligand classes afforded similar yields, NHCs led to reactions that were 5−8 times faster. The optimized catalytic system, comprised of IPr·HCl and $RhCl_3$, allowed for the arylation of numerous alkyl and aryl aldehydes in moderate to excellent yields. Of note, vinyl boronic acids could be used with this catalyst and afforded the corresponding allylic alcohols. Another "common" imidazolium salt, IAd·HCl, in conjunction with $[RhCl(COD)]_2$, proved active in the arylation of *N*-sulfonyl and *N*-phosphinoyl arylimines.[187]

Buchmeiser, pursuing the examination of the potential in catalysis of tetrahydropyrimidine-based NHCs,[155,174] tested complexes **82**, **84**, and **85** (see Chart 10) in the arylation of benzaldehyde derivatives.[188] All these compounds were found to be active, and the best results (i.e., TONs up to 1230) were obtained with a modified catalyst of the type **84**/**85**, where the halogen was replaced by a trifluoroacetato ligand. This catalytic system is the most efficient to date. It should be noted that iridium analogues of the aforementioned rhodium catalysts performed poorly in these arylation reactions.

Over the last five years, Özdemir and co-workers have synthesized an impressive number of [(NHC)Rh(COD)Cl] complexes and tested their catalytic activities in the addition of phenyl boronic acid to benzaldehyde derivatives. Different scaffolds, such as imidazolidinylidenes **104**−**107**[189] and **124**−**127**,[190] tetrahydropyrimidinylidenes **108**−**113**,[191] benzimidazolylidenes **114**−**119**,[192] and perhydrobenzimidazolylidenes **120**−**123**[190] were employed and found active in this transformation (Chart 11). All these rather diverse NHC architectures proved efficient at 80 °C with 1 mol % catalyst loading for differently substituted benzaldehydes.

The synthesis and use in arylation reactions of an important family of [(NHC)Rh] complexes, encompassing dinuclear complexes $[(NHC)Rh(OAc)_2]_2$ **128** and **129** (Chart 12), were recently described by Gois and co-workers.[193] Relying on

Chart 11. Structures of [(NHC)Rh(COD)Cl] Complexes Active in Carbonyl Arylation

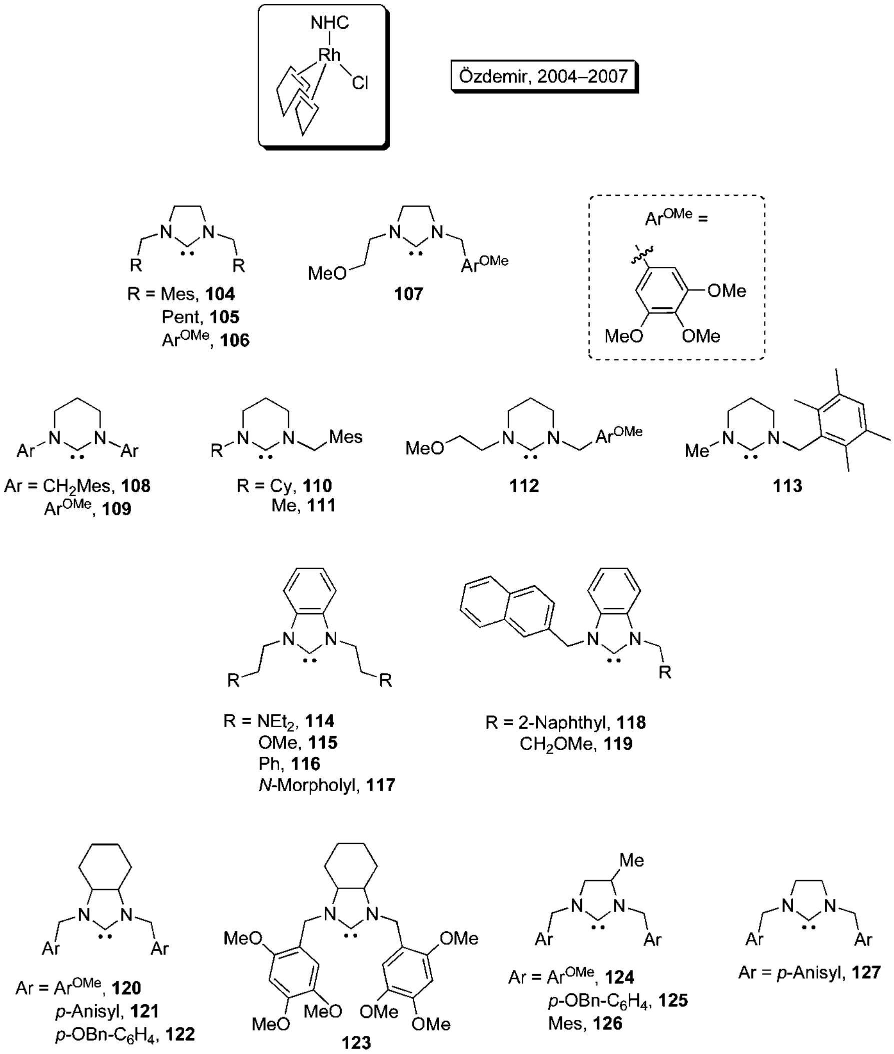
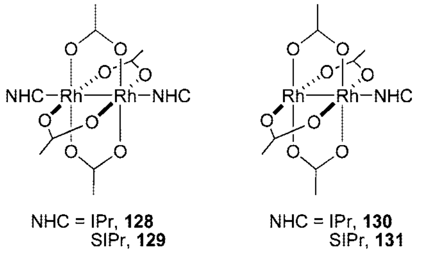
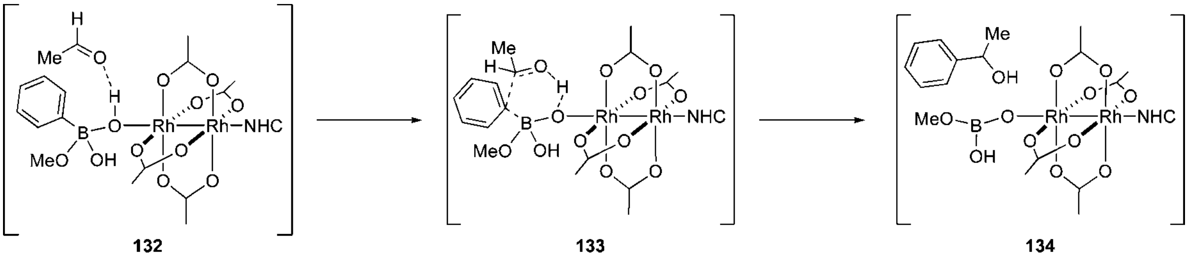


Chart 12. Structures of Dirhodium(II) Complexes Active in Carbonyl Arylations



DFT calculations showing that the active species was probably a mono-NHC complex, the same group isolated complexes **130** and **131** (Chart 12) via simple elution of the corresponding bis-NHC complexes on preparative thin-layer chromatography. It was found that the mono-SIPr **131** is the most efficient catalyst among the four tested.[194] A number of secondary alcohols could be formed at 60 °C, and **131** proved particularly active for the conversion of aliphatic aldehydes. Of note, the use of conjugated enals resulted exclusively in 1,2-addition products (some examples of 1,4-additions are briefly discussed at the end of this subsection). Mechanistic studies and DFT calculations performed by the authors point to an unusual mechanism where transfer of the aryl moiety from the boron to the aldehyde would occur without direct participation of the metal. Instead, coordination to the rhodium center of a borate formed in situ (Scheme 16, **132**), and subsequent approach of the aldehyde stabilized by hydrogen bonding (Scheme 16, **133**) would be favored for the C–C bond forming step (Scheme 16, **133** → **134**). It should be noted that this catalytic system provides an intriguing example of through-bond stabilization (e.g., along

Scheme 16. Aryl Transfer Step Using 131 According to DFT Calculations

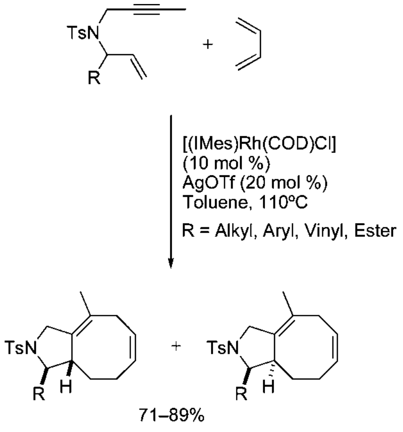


the NHC−Rh−Rh axis), the NHC lying far from the reactive center where bond formation occurs.

Finally, it should be noted that asymmetric versions of this reaction have also been published. Notably, enantiopure cyclophane-containing NHC ligands have been used by Bolm and co-workers for the enantioselective addition of $PhB(OH)_2$ to aryl aldehydes.[195] Despite good overall yields in secondary alcohols, only low enantioselectivities were obtained (up to 38% ee). The use of dicyclophane NHCs by Andrus and co-workers in the related 1,4-addition of aryl boronic acids to cyclic conjugated enones displayed much higher level of enantioselectivity, up to 98% ee.[196]

4.2.5. Cyclization Reactions

In addition to their excellent activity in hydrosilylation, hydroformylation, and carbonyl arylation (see sections 4.2.1, 4.2.3, and 4.2.4), [(NHC)Rh(COD)Cl] complexes have also shown promising behavior in different carbocyclizations. Evans notably reported the [4 + 2 + 2] cycloaddition of differently substituted 1,6-enynes with 1,3-butadiene catalyzed by [(IMes)Rh(COD)Cl] (eq 19).[197] The main feature of this system lies in its high diastereoselectivity, the *cis* isomer **135** being largely favored over the *trans*, that was shown to arise from the formation of an unexpected metallacycle intermediate.[198]



(19)

135.............>19:1.............**136**

Recently, Chung and co-workers disclosed their results on intramolecular [4 + 2] and [5 + 2] cycloadditions catalyzed by [(IPr)Rh(COD)Cl] in conjunction with a silver(I) salt.[199] Overall, this catalytic system was found to be highly efficient for these two cyclizations, producing, respectively, bicyclo[4.3.0]octadiene and bicyclo[5.3.0]nonadiene derivatives in high yields (Scheme 17). Of note, despite the high activity observed for these intramolecular transformations, this system was not effective for the corresponding *intermolecular* [5 + 2] cycloaddition.

Other [(NHC)Rh]-based compounds proved efficient for a number of cyclization and cycloaddition reactions (Chart 13). Hence, BMIM-based catalyst **137**, which is also a good catalyst for the polymerization of acetylene,[200] was found to be active for the hydrosilylation/cyclization of 1,6-enynes,[201] while **138** catalyzed [5 + 2] and [4 + 2] cycloadditions similar to the ones presented in Scheme 17.[202] Recently, complex **141**, the most efficient within the series of quinoline−NHCs **139**−**142**, displayed interesting activity in the [3 + 2] cycloaddition of diphenylcyclopropenone with alkynes.[203]

Scheme 17. [(NHC)Rh]-Catalyzed Cycloaddition Reactions

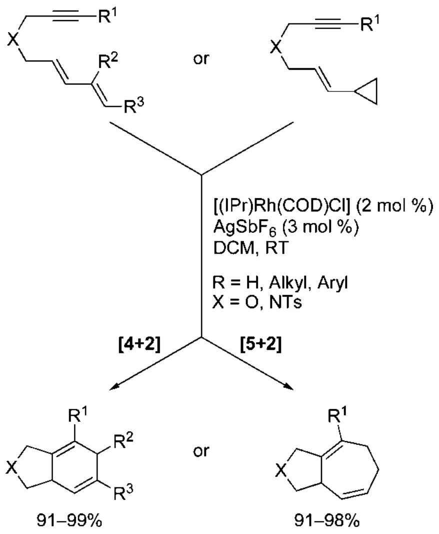
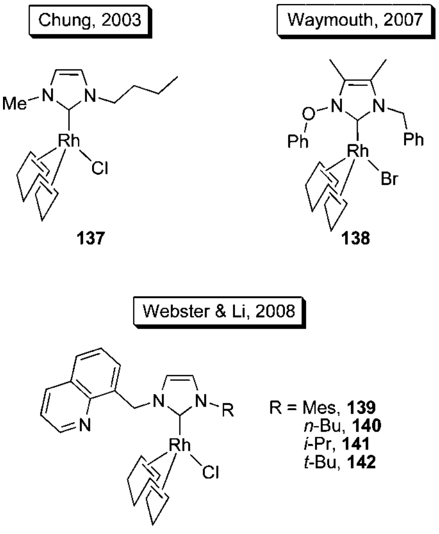
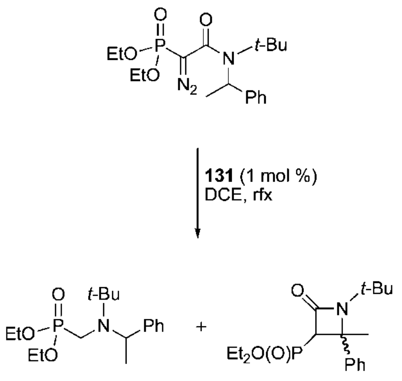


Chart 13. Structures of [(NHC)Rh(COD)X] Catalysts Efficient for Different Cyclizations



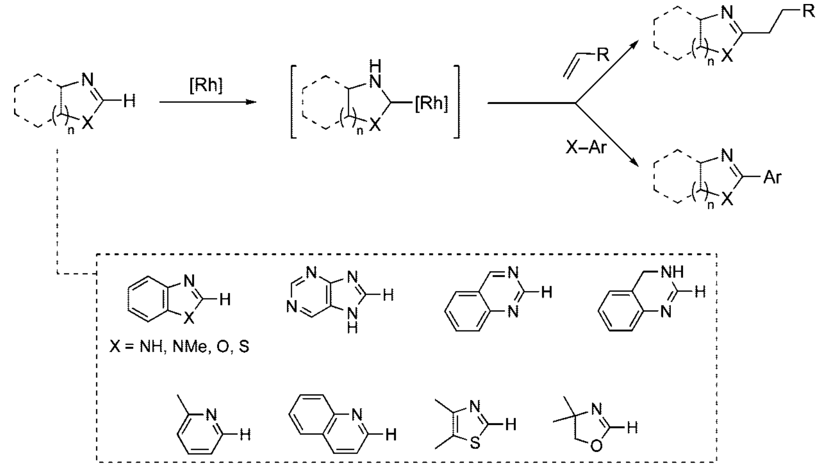
Finally, dinuclear rhodium complexes **130** and **131** (see Chart 12) were shown to promote intramolecular C−H insertions of α-diazoamides leading to the formation of β- and γ-lactams as a function of the precursor or the catalyst employed.[204] Of note, a surprising decarbonylation reaction, affording linear amines such as **143**, was also observed in certain cases (eq 20).



(20)

143, 51% 23%

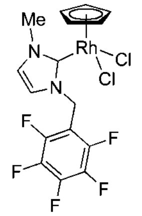
Scheme 18. Rhodium-Catalyzed Direct Functionalization of *N*-Heterocycles via [(NHC)Rh] Species



4.2.6. Miscellaneous Reactions

Other important classes of organic reactions can be performed with [(NHC)Rh] systems. We will only highlight here some of these applications, the most peculiar ones, again focusing on monodentate NHCs. Nevertheless, it should be noted that a number of NHC bidentate ligands have been found to be active for intramolecular alkyne hydroamination,[205] cyclization of acetylenic carboxylic acids,[206] and diazo olefin cyclopropanation.[207]

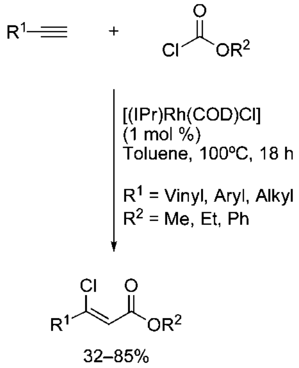
Aryl−aryl cross-coupling and dynamic kinetic resolution of alcohols (DKR) are among the "classical" organic transformations feasible with [(NHC)Rh] catalysts. Hence, a mixture of IMes·HCl and $[Rh(COD)Cl]_2$ was shown to catalyze the coupling of numerous aryl tosylates with aryl boronic acids.[208] A large number of phosphines and NHCs were tested in this reaction, but only IMes proved satisfactory. The DKR[209] of secondary aryl and alkyl methyl alcohols was efficiently achieved using complex **144**, which serves here as a racemization catalyst, in conjunction with lipase B as the acylation catalyst.[210] The main feature of this system is that, unlike with other DKR catalysts, a base is no longer required to ensure good conversions and enantioselectivities.



144

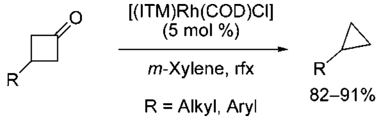
Even though it does not involve, strictly speaking, NHCs as *supporting* ligands, an interesting Rh-catalyzed C−H activation/coupling process has been reported by Bergman and Ellman. It consists of a C−H activation at the rhodium center, leading to the formation of an [(NHC)Rh] intermediate, which participates in a subsequent reductive elimination to form a new C−C bond at C(2) of the transient NHC (Scheme 18).[211] A number of different *N*-heterocycles are viable substrates for this transformation. The fruitful Bergman−Ellman collaboration[212] has resulted in the impressive development of this methodology for intra- and intermolecular coupling with alkenes,[213,214] as well as intermolecular coupling with aryl halides.[215] These synthetic tools were eventually applied to different total syntheses.[216]

Pursuing their examination of the potential of [(NHC)Rh] systems in homogeneous catalysis,[199,201] Chung and co-workers recently reported [(IPr)Rh(COD)Cl] as an efficient catalyst in the chloroesterification of alkynes (eq 21).[217] It should be noted that IPr was found to be superior to both IMes and PPh_3 in this transformation. Evaluation of the alkyne scope revealed that conjugated terminal alkynes (i.e., 1,3-enynes or phenylacetylenes) were necessary for the reaction to proceed, alkyl acetylenes affording only poor yields of products and internal alkynes being unreactive under these conditions.



(21)

An intriguing [(ITM)Rh(COD)Cl]-catalyzed decarbonylation reaction of cyclobutanone derivatives leading to the corresponding cyclopropyl-containing compounds was reported by Murakami and co-workers (eq 22).[218] Remarkably, highlighting the chemoselectivity of this process, an aldehyde present in the starting cyclobutanone remained intact while the cyclobutanone underwent decarbonylation.

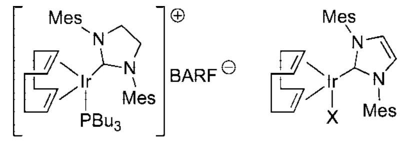


(22)

The chemistry of [(NHC)Rh]-based complexes is undoubtedly one of the richest of all the late transition metals. Even though clearly dominated by extremely important processes such as hydrosilylation, hydroformylation, and carbonyl arylation, the field of [(NHC)Rh] homogeneous catalysis covers multiple other applications, encompassing C−H bond activation, cycloadditions, and diazo transfer to only name a few.

Nevertheless, one should not believe that nothing else is to be done in this area. Primarily, a number of known Rh-mediated transformations have yet to be reported with NHC-containing catalysts. It is very likely that by doing "old chemistry" with new NHC-containing catalysts, not only

Chart 14. NHC−Iridium Catalysts for Hydrogenation Reactions



145, Buriak, 2006

X = Cl, $OSiMe_3$
146, Marciniec, 2008

improvements in terms of yields and reaction conditions could be obtained but, more importantly, new reactivity modes will probably be uncovered along the way. Second, a closer look at the structures of [(NHC)Rh] catalysts reveal the almost univocal utilization of [(NHC)Rh(COD)X], where X is a halogen, as rhodium(I) precatalysts composition. Hence, we believe that, following the impressive work done on varying the NHC scaffolds, looking at modifications of the rhodium complexes structures could be an equally rewarding task in terms of potential applications in homogeneous catalysis.

4.3. Iridium

The chemistry of [(NHC)Ir] complexes is very close to that of [(NHC)Rh]. Most efforts in catalysis with these compounds have been focused on reduction reactions, with iridium hydride species as key intermediates. Interestingly, such species can also be isolated and are typically prepared directly from imidazolium salts via oxidative addition,[219] which could broaden the scaffolds available for catalysis.

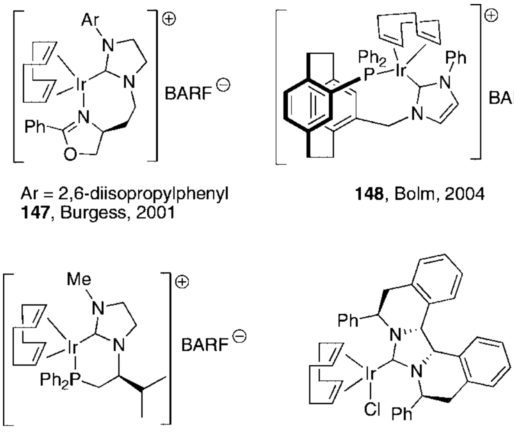
The most studied inner sphere process with [(NHC)Ir] is undoubtedly C−H bond activation (aromatic or aliphatic),[220] but equally attractive tautomerization reactions have also been reported: isomerization of pyridines to NHCs[221] or, alternatively, from NHC to *N*-bound imidazole.[222] Furthermore, the formation and applications of C(4)-bound (also called abnormal) NHCs is also an active field of research,[223] although it falls outside the scope of this review.[224]

4.3.1. Reduction Reactions

4.3.1.1. Hydrogenation Reactions. Reduction reactions, and hydrogenation in particular, are arguably the most popular reaction with [(NHC)Ir]-based complexes. Since the pioneer reports by Burgess[225] and Nolan[226] in 2001, numerous architectures have been explored in this context.

Two closely related families have been studied for the achiral hydrogenation of alkenes (Chart 14). Cationic NHC/phosphine mixed complex **145** led to good conversions for unfunctionalized substrates under 1 atm of H_2 at room temperature.[227] Furthermore, the robustness of this catalyst allowed the hydrogenation of several equivalents of olefins added at different times. Neutral complexes **146** showed similar activities in the hydrogenation of (*Z*)-cyclooctene and (*E*)-stilbene, although with the silyl-containing catalyst higher TOFs were observed.[228]

Chart 15. [(NHC)Ir] Catalysts for Asymmetric Hydrogenation Reactions



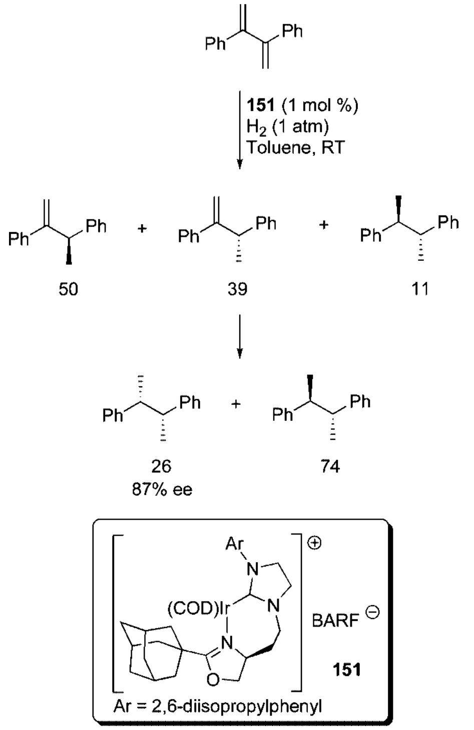
Ar = 2,6-diisopropylphenyl
147, Burgess, 2001

148, Bolm, 2004

149, Pfaltz, 2006

150, Herrmann, 2007

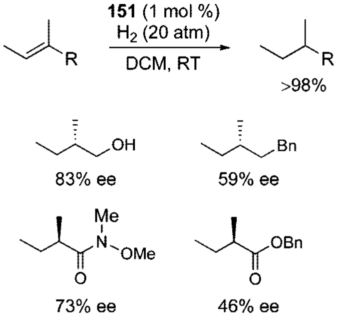
Scheme 19. [(NHC)Ir]-Catalyzed Hydrogenation of a Diene



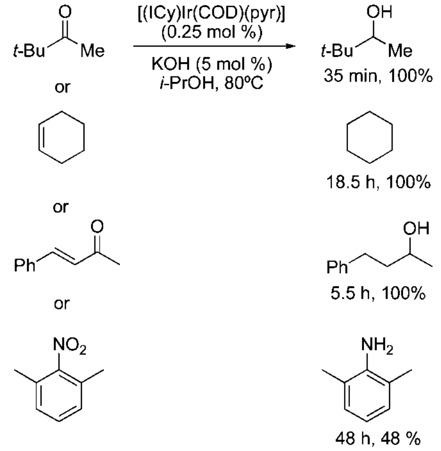
For the asymmetric version of this transformation, bis-chelating NHC ligands have focused most reported investigations. NHC/oxazoline ligands, first studied by Burgess and co-workers,[225] have displayed particularly high activity in this context (see compound **147**, Chart 15).[229] Complex **148**, containing a paracyclophosphane/NHC ligand was studied by Bolm and co-workers.[230] With this catalyst, moderate ee's were obtained after long reaction times. In these reactions, the level of chiral induction was strongly dependent on the alkene geometry but not the absolute configuration. Related catalyst **149** required high hydrogen pressure to induce only moderate enantioselectivities.[231] However, it showed a remarkable activity in the hydrogenation of an allylic alcohol and an imine. Alternatively, Herrmann and co-workers applied NHC ligands with restricted flexibility to this transformation.[232] However, complex **150** only induced 66% ee in the hydrogenation of acetamido acrylate (Chart 15).

Among the families studied, **147**-type complexes have undoubtedly displayed the most interesting reactivity. Catalyst **151** in particular has been applied to the hydrogenation of a variety of interesting substrates. In the case of a prochiral diene, it was shown that the reaction takes place in two distinct phases (Scheme 19).[233] Initially, the substrate is transformed into a mixture of enantiomers of its mono-reduced analogue and a meso-dihydrogenated product. This step is relatively slow and poorly stereoselective. Once all

Scheme 20. Hydrogenation Reactions Catalyzed by 151



Scheme 21. [(NHC)Ir]-Catalyzed Transfer Hydrogenation



the starting diene is consumed, the reaction accelerates, and the enantioface preference is reversed.

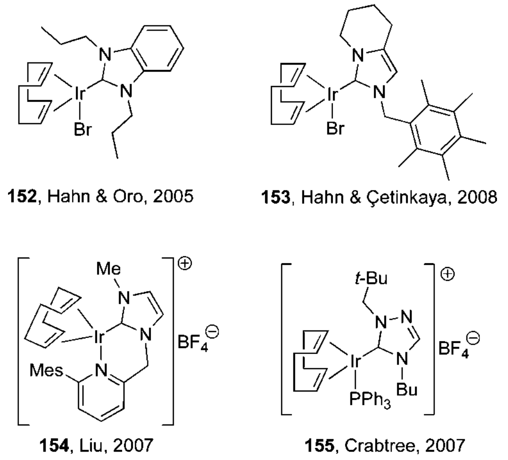
Furthermore, catalyst **151** has displayed very interesting activity in the hydrogenation of diversely functionalized substrates.[234] More precisely, the face selectivities for hydrogenation depend exclusively on the substrate ability to coordinate the metal center.[235] Hence, allylic alcohol derivatives were reduced to the same isomer as simple olefins, whereas α,β-unsaturated carboxylic acid derivatives produced the corresponding enantiomer (Scheme 20).

4.3.1.2. Transfer Hydrogenation Reactions. Nolan and co-workers reported the first [(NHC)Ir] catalyst active in transfer hydrogenation reactions.[236] The cationic [(ICy)Ir(COD)(pyr)]PF_6 complex showed remarkable activity in the reduction of ketones and, after prolonged reaction times, alkenes (Scheme 21). Furthermore, an α,β-unsaturated ketone cleanly produced its corresponding saturated alcohol and an aromatic nitro compound could partially be transformed into the corresponding aniline.

Since then, other iridium(I) complexes have been studied in this context (Chart 16). Of note, all these systems were effective with low base loadings, typically 0.5−5 mol %. Compounds **152**[237] and **153**,[238] displayed activities somewhat lower than Nolan's system in the catalytic transfer hydrogenation of cyclohexanone.[239] Compounds **154** and **155** were tested with more challenging substrates. Whereas lutidinyl complex **154** allowed for the reduction of nitro functionalities into either amine or azo derivatives,[240] triazolylidene-containing **155** was found to be active for the generation of amines and alkanes from imines and alkenes, respectively.[241]

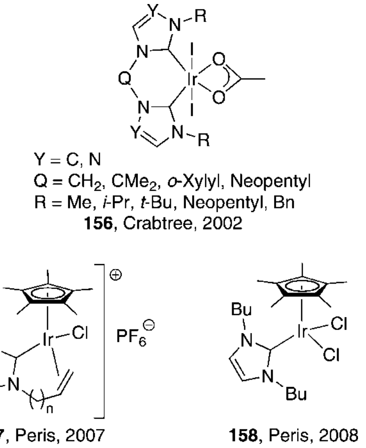
Two single reports are available up to now for asymmetric transfer hydrogenation reactions. Disappointingly, neither chiral ferrocenyl-NHC[242] nor mixed phosphine-NHC ligands[243] have allowed so far for satisfactory chiral inductions.

Chart 16. [(NHC)Ir^{I}] Complexes for Transfer Hydrogenation Reactions



152, Hahn & Oro, 2005
153, Hahn & Çetinkaya, 2008
154, Liu, 2007
155, Crabtree, 2007

Chart 17. [(NHC)Ir^{III}] Complexes for Transfer Hydrogenation Reactions

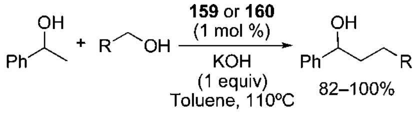


Y = C, N
Q = CH_2, CMe_2, o-Xylyl, Neopentyl
R = Me, i-Pr, t-Bu, Neopentyl, Bn
156, Crabtree, 2002

157, Peris, 2007
158, Peris, 2008

Iridium(III) complexes are also efficient catalysts for this transformation. Crabtree and co-workers first reported the activity of **156**-type complexes, bearing different CC bidentate NHC ligands (Chart 17).[244] These species have the advantage of being air- and moisture-stable and have been reported to mediate the reduction of ketones, aldehydes, and imines. Alternatively, Peris and co-workers investigated the activity of [(Cp*)Ir^{III}] complexes (Chart 17). Complex **157**, active with ketones and imines, would be activated in the reaction media via hydrogenation of the hemilabile alkene moiety, generating a vacant site in the iridium coordination sphere.[245] Related complex **158** was shown to be active under base-free conditions, an important feature for the reduction of sensitive compounds.[246]

4.3.1.3. "Borrowing Hydrogen" Reactions.[73] The β-alkylation of secondary alcohols (see Scheme 4, section 3.2.1.3) in the presence of an [(NHC)Ir] complex was first explored with iridium(III) complex **159** bearing a Cp* ligand with a pendant NHC (eq 23).[247] Very similar activities were observed with another Cp*−iridium compound but this time bearing an NHC ligand with a chelating pyrimidine substituent (**160**).[248] In both cases, improved catalytic results were obtained when compared with the parent [(Cp*)$IrCl_2$]$_2$ system.[249] Moreover, optimization of the reaction time was found to be crucial to avoid the undesirable dehydrogenation of the obtained alcohol into the corresponding ketone.[250]



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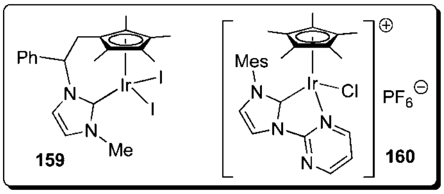
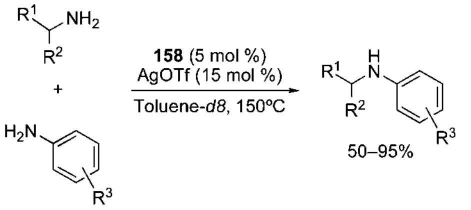


159

160

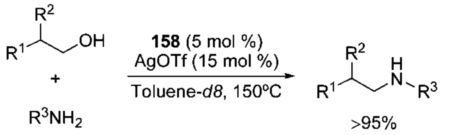
The pyrimidine-containing catalyst was also applied to the *N*-alkylation of amines with alcohols. Interestingly, in this case a weak base such as $NaHCO_3$ was sufficient to ensure the turnover of the reaction. This feature could be explained by an internal base effect of the pyrimidine or, alternatively, by the cationic nature of the complex, expected to facilitate the alcohol deprotonation.

Additionally, catalyst **158** (see Chart 17, section 4.3.1.2) has also been reported as an excellent mediator in the *N*-alkylation of amines.[251] Excellent conversions were obtained for the alkylation of diverse anilines with aliphatic amines (eq 24).



(24)

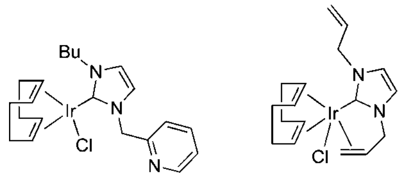
Under the same reaction conditions, alcohols could also be used in this context with, generally, good to total selectivities (eq 25).[252] As for the transfer hydrogenation reactions,[246] no base or other additive was required in these transformations.



(25)

4.3.1.4. Hydrosilylation Reactions.[140] Several [(NHC)Ir] systems have been developed for the hydrosilylation of terminal alkynes or ketones. In the first case, complex **161**, bearing a pyridine-functionalized carbene, has allowed for the detection and characterization via ESI-MS of all relevant reaction intermediates (Chart 18).[253] This study notably showed that under stoichiometric conditions, only the hydrosilylation product was formed. However, when the conditions were closer to those during catalysis, both hydrosilylation and silylation mechanisms were operative. Other pendant substituents on the NHC, such as alkenes, also led to active catalytic systems. Hence, complex **162** displayed a remarkable activity and selectivity in the hydrosilylation of alkynes at room temperature (Chart 18).[254] Interestingly, this catalyst could be used up to three times with no sign of deactivation.

Chart 18. [(NHC)Ir] Complexes for Alkyne Hydrosilylation Reactions

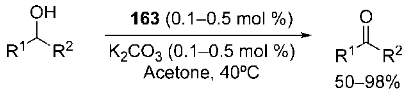


161, Peris, 2005 **162**, Mata, 2008

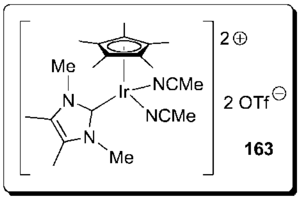
On the other hand, axially chiral BINAM-derived and bowl-shaped NHC ligands have been applied to the hydrosilylation of aryl methyl ketones. Whereas only moderate ee's (up to 60%) were reached in the first case,[255] dendrimer-like ligands allowed for promising substrate specificity in the competitive hydrosilylation of structurally different ketones.[256]

4.3.2. Oxidation Reactions

In contrast to reduction processes, oxidation reactions have only attracted scarce attention with [(NHC)Ir]-based catalytic systems. Yamaguchi and co-workers reported the activity of cationic Cp*-containing complexes in the Oppenauer-type oxidation of alcohols. Under optimized conditions, secondary alcohols were efficiently converted into the corresponding ketones with only 0.1 mol % of catalyst when acetone was used as oxidant (eq 26).[257] More challenging primary alcohols could also be transformed into aldehydes, albeit using higher catalyst loadings.



(26)



163

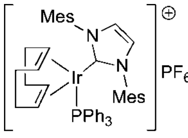
In these reactions, the strong electron-donating ability of NHCs would facilitate the hydride transfer to acetone as hydrogen acceptor. Moreover, the postulated active species, an iridium monohydride complex, would deactivate via dimerization. In order to stabilize the active species and avoid deactivation, a related complex with an amino pendant function on the Cp* ligand was developed.[258] Not only did this catalyst outperformed the previous systems, but the addition of an external base was no longer required, which notably enlarged the scope of the reaction to highly sensitive substrates.

4.3.3. Hydrogen/Deuterium Exchange Reactions

Besides their application in reduction and oxidation processes, $[(NHC)Ir^{III}(Cp^*)]$ complexes have also been shown active in H/D exchange reactions. In particular, the air-stable complex **158** (see Chart 17) displayed a generally higher activity than its PMe_3-containing analogue. Notably, the use of 2 mol % **158** at 100 °C led to high incorporation from deuterated methanol in challenging substrates such as diethyl ether, THF, or isopropanol.[259]

Kerr and co-workers showed that iridium(I) complexes are also active in this transformation. Stable mixed NHC/phosphine complex **164** was successfully applied to the deuteration of aromatic substrates under D_2 atmosphere.[260]

In these reactions, ketyl, amido, and nitro groups were tolerated, and outstanding selectivity was obtained.

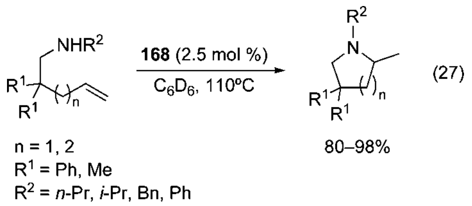


164, Kerr, 2008

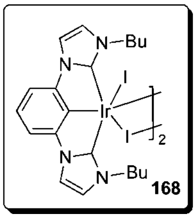
4.3.4. Miscellaneous Reactions

Different [(NHC)Ir(Cp*)] complexes have been reported as active catalysts in diverse catalytic transformations (Chart 19). Complex **165** was applied to the addition-type polymerization of norbornene upon activation by MAO, although it only displayed moderate activity.[261] Alternatively, compound **166** was found to be a good mediator racemization catalyst in base-free dynamic kinetic resolution of secondary alcohols, and under optimized conditions, aryl alkyl and dialkyl alcohols (even hindered ones) could be efficiently converted.[262] Complex **167**, with a stereogenic center at the metal atom, represents the first application of iridium derivatives to the diboration of alkenes.[263] In these reactions, NaOAc had to be used as additive, most probably to favor the heterolytic cleavage of the diboron reagent. Additionally, a silver salt was required to produce any chiral inductions, although they did not surpass 10% ee.

Finally, a CCC−NHC pincer iridium complex has shown remarkable activity in the intramolecular hydroamination of unactivated alkenes.[264] The reactions were carried out in refluxing benzene, although the catalyst was equally active with water as solvent. In all cases, *exo−trig* cyclized products were exclusively formed in high yields and isomerization of the starting material was competitive only with primary amines (eq 27). Of note, the rhodium-containing analogue displayed a very similar activity in this transformation.

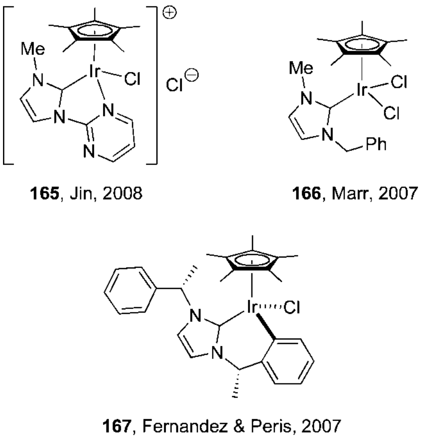


(27)



Reduction reactions have been the center of most studies on [(NHC)Ir] species in catalysis. Despite their remarkable activity, similar to rhodium-based systems and sometimes even better, this success may have hindered further investigations in other organic transformations. Furthermore, NHC ligands have shown an outstanding ability for making iridium-containing complexes highly stable toward air and moisture, which should help to broaden their scope.

Chart 19. [(NHC)Ir(Cp*)] Catalysts



165, Jin, 2008

166, Marr, 2007

167, Fernandez & Peris, 2007

5. Group 10: Nickel, Palladium, and Platinum

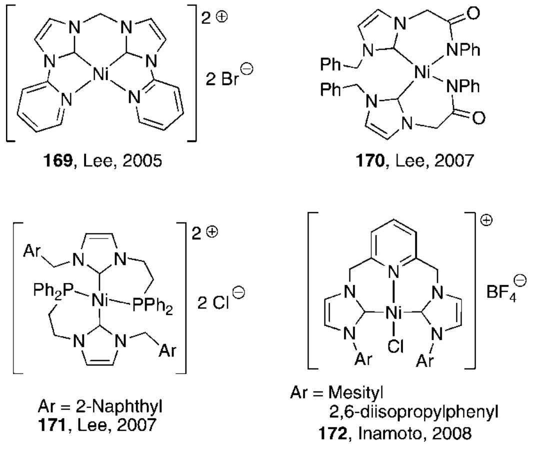
5.1. Nickel

[(NHC)Ni]-based catalytic systems are sometimes not given so much publicity as palladium, ruthenium, or even rhodium. However, [(NHC)Ni] catalytic systems have already found application in a vast number of organic transformations. This is not surprising if we consider the rich reactivity of [(NHC)Ni], which are notably capable of activating small molecules such as oxygen[265] or CO_2.[266] Furthermore, several unusual bond cleavages have been reported with these systems: C−N bond in an NHC ligand,[267] C−S bond in sulfoxides,[268] or C−C bond in organonitriles.[269] Finally, the first biomedical study with [(NHC)Ni] complexes appeared very recently. A number of tetradentate NHC−nickel complexes notably displayed subdued cytotoxicity, which could find application in the development of new agents for inducing acquired cellular tolerance toward cytotoxic metals.[270]

5.1.1. Cross-Coupling Reactions

5.1.1.1. Carbon−Carbon Bond Forming Reactions. The Suzuki−Miyaura reaction is arguably one of the most powerful methodologies for the formation of carbon−carbon bonds.[271] Whereas [(NHC)Pd] systems are outstanding catalysts for this transformation,[272] nickel-based complexes have only shown moderate activities. Mainly bi- and tridentate ligands have been studied in this context with catalyst loadings ranging from 1 to 3 mol % (Chart 20).[273] High temperatures (80−120 °C) were required even for the

Chart 20. [(NHC)Ni] Complexes for Suzuki−Miyaura Coupling



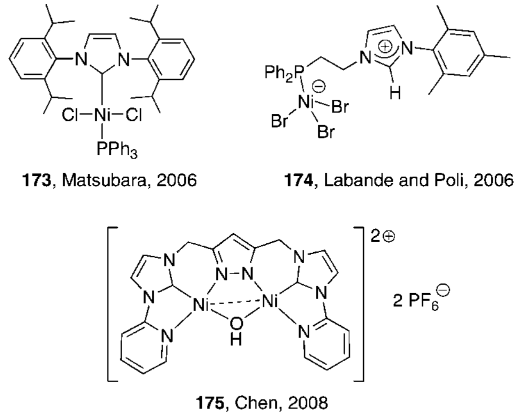
169, Lee, 2005

170, Lee, 2007

Ar = 2-Naphthyl
171, Lee, 2007

Ar = Mesityl
2,6-diisopropylphenyl
172, Inamoto, 2008

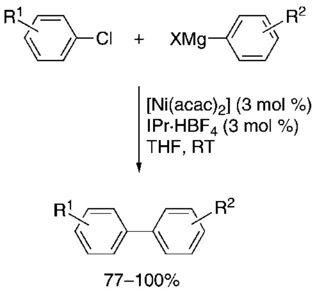
Chart 21. [(NHC)Ni] Complexes for Kumada−Corriu Coupling



coupling of aryl bromides, along with the use of a tertiary phosphine (i.e., PPh_3) as coligand in order to ensure good conversions. For catalysts containing a phosphane ligand such as complex **171**, the need for additional phosphine was restricted to the most challenging aryl chlorides. This catalyst was notably shown to be more effective than the benchmark $[NiCl_2(dppe)]/PPh_3$ system.[274] Alternatively, complex **172** has been applied to the coupling reactions of aryl or alkenyl tosylates or mesylates and boronic acids.[275] Moderate yields in the corresponding biaryl derivatives were obtained under rather harsh reaction conditions (4−36 h at 120 °C in a sealed tube). All these catalytic systems were particularly sensitive to hindrance, and only mono-*ortho*-substituted biphenyl products could be prepared.

The possible coupling partners were not restricted to aryl halides. More "exotic" ammonium salts,[276] imidazoles, and triazoles[277] have also been successfully coupled using monodentate NHCs as ancillary ligands (Scheme 22). Even if phosphine addition was no longer required for carrying out these transformations, the catalyst loading had to be increased to 10 mol %. The ammonium Suzuki couplings were shown to be particularly broad in scope and notably allowed for the preparation of di-*ortho*-substituted products in good yields.

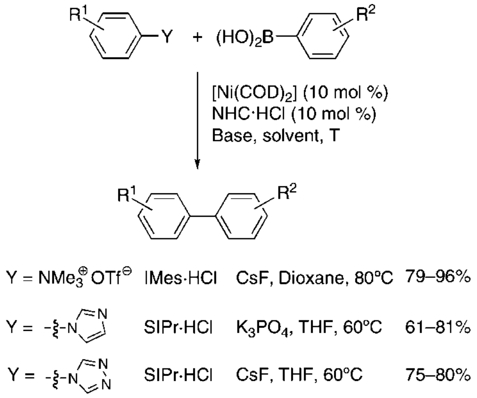
The most efficient nickel-catalyzed C−C bond forming cross-coupling reaction is undoubtedly the Kumada−Corriu reaction. Even if Grignard reagents are air- and moisture-sensitive, it should be borne in mind that most boronic acids, organozincs, and stannanes are actually prepared from the corresponding organomagnesium (or lithium) compounds. The first [(NHC)Ni]-based catalytic system was reported by Herrmann and co-workers, and it already allowed for the coupling of aryl chlorides at room temperature in the presence of 3 mol % of metal source (eq 28).[278] This system notably permitted the preparation of tri-*ortho*-substituted biaryl compounds, a result not matched yet by subsequent reports.



(28)

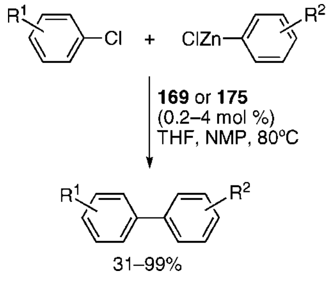
A number of mixed NHC/phosphine systems have been studied for this transformation (Chart 21).[279] Complex **173**, only effective with aryl iodides or bromides, was actually a better catalyst than its bis-NHC and bisphosphine derivatives. Improved catalytic results could be obtained with *cis* chelating dicarbenes[280] and with pyridine- or quinoline-based carbenes.[281] Bifunctional phosphine−imidazolium ligands as in **174** led also to enhanced activity. This phosphine−nickel compound possesses a pendant imidazolium moiety that is deprotonated by the Grignard reagent to generate the corresponding carbene complex, which catalytic activity is almost comparable to Herrmann's pioneer work. Complex **175** could couple diverse aryl chlorides with loadings down to 0.1 mol %. Regrettably, only the formation of mono-*ortho*-substituted biaryls was tested. The observed efficiency might be due to a bimetallic cooperativity[282] of both nickel centers in **175**. Similar scope and outcome was found for complex **169**, previously presented as a Suzuki catalyst (see Chart 20).[283]

Scheme 22. Nickel-Catalyzed Suzuki−Miyaura Reaction with Non-halogenated Coupling Partners



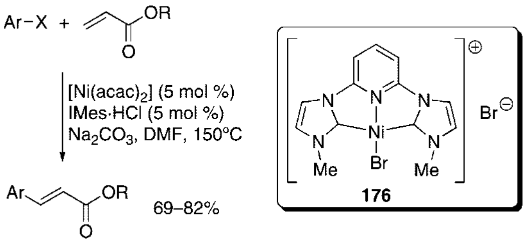
Far less interest has been focused on the study of the Heck reaction. The first [(NHC)Ni]-based system for this transformation was only reported with acrylates in 2005.[284] An $IMes\cdot HCl/[Ni(acac)_2]$ combination allowed for the coupling of aryl iodides and bromides at 150 °C (Scheme 23). One year later, the authors succeeded in coupling aryl chlorides with **176**, a complex bearing a CNC pincer ligand instead of the IMes salt.[285] However, the presence of iodine salt and extended heating periods (up to 7 days) were required to ensure product formation.

The Negishi coupling in the presence of nickel/NHC systems has only been recently reported.[286] Complexes **169** and **175** showed a wide scope in the formation of biaryl compounds from organozinc reagents. Good yields were generally reached from aryl chlorides in the presence of 0.1−4 mol % of catalyst (eq 29). Again, a bimetallic cooperative effect was postulated to explain the enhanced activity of **175** when compared to **169**.



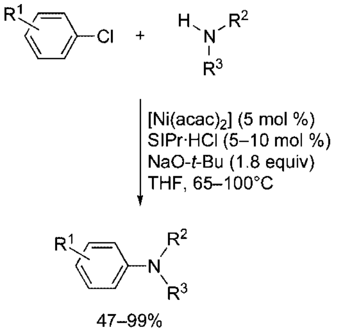
(29)

Scheme 23. [(NHC)Ni]-Catalyzed Heck Reaction



Further approaches to the formation of carbon–carbon bonds rely on the cross-coupling of aryl bromides and chlorides with organomanganese reagents using IPr as ligand,[287] the α-arylation of ketones by complex **173** (see Chart 21),[288] or on the Ullman homocoupling of aryl bromides in the presence of benzimidazol-based carbenes.[289]

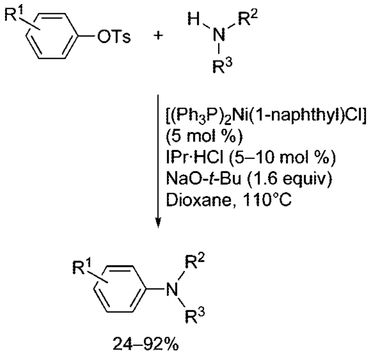
5.1.1.2. Carbon–Heteroatom Bond Forming Reactions. Fort and co-workers first reported the [(NHC)Ni]-catalyzed amination of aryl chlorides.[290] The *in situ* formed nickel(0) species, in the presence of SIPr as ligand, allowed for the general coupling of secondary cyclic or acyclic amines and anilines under relatively mild conditions (eq 30).



(30)

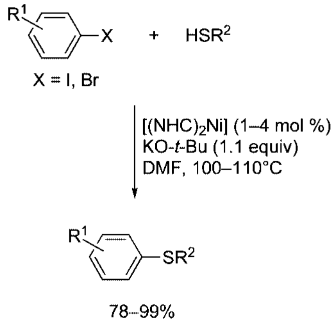
Recently, Matsubara and co-workers have shown that $[(NHC)_2Ni]$ complexes can be easily synthesized from $[Ni(acac)_2]$.[291] Furthermore, catalytic experiments with these nickel(0) species showed that these homoleptic complexes are certainly very close to the active catalytic species in this coupling reaction.

Other NHC-containing complexes have also been investigated in this context. Whereas [(NHC)Ni(Cp)Cl] complexes only showed moderate activity in this reaction,[292] the use of nickel(II)–aryl complexes allowed for the unprecedented amination of aryl tosylates (eq 31).[293] The reactions were surprisingly fast when compared with precedent systems (15–30 min instead of 5–12 h), although heating was still required. The obtained yields were usually high even if the undesirable O–S cleavage of the starting tosylate was competitive in all entries.



(31)

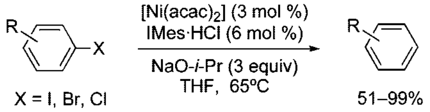
Finally, the reaction of aryl halides with thiols has also been reported.[294] In this case, $[(NHC)_2Ni]$ complexes were used for the coupling in high yields of aryl iodides or bromides with aryl or alkyl thiols (eq 32).



(32)

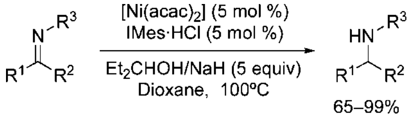
5.1.2. Reduction Reactions

The dehalogenation of aryl halides, often regarded as an undesirable process especially in cross-coupling reactions, is actually of great chemical and environmental importance due to their high toxicity.[295] Concomitant with their work on the amination of aryl chlorides, Fort and co-workers reported the effective reduction of halogenated arenes using IMes as the ligand of choice (eq 33).[292,296] Noteworthy, the developed catalytic system could partially induce the reduction of a carbon–fluorine bond.



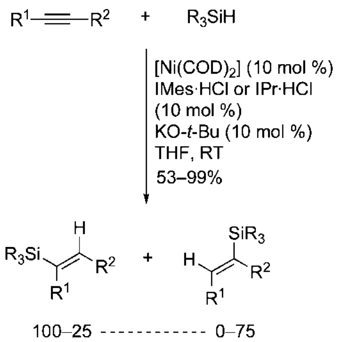
(33)

A very similar catalytic system was reported by the same group for the transfer hydrogenation of imines.[297] Different aldimines and ketimines were efficiently reduced in fairly short reaction times with a remarkable tolerance to functional groups, except, as expected, for halogens (eq 34).



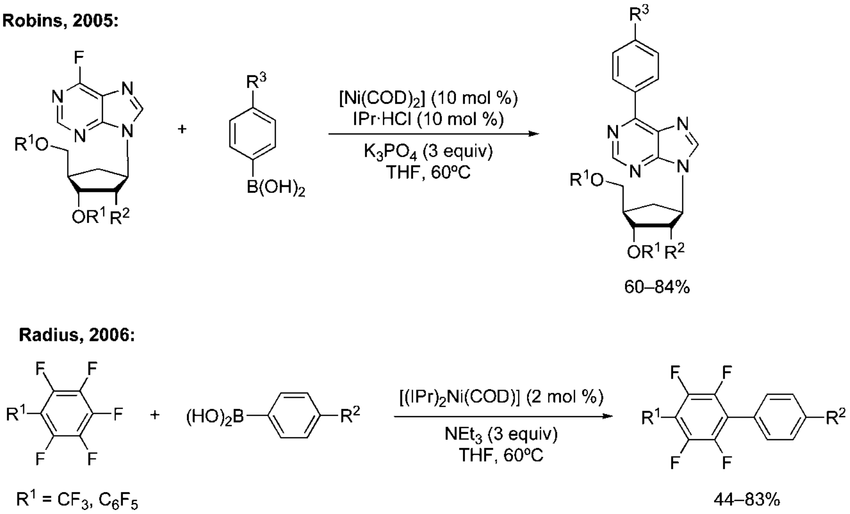
(34)

Finally, Montgomery and co-workers reported the hydrosilylation of alkynes in the presence of Ni/NHC species at room temperature (eq 35).[298] Slow addition of the starting alkyne to the reaction mixture was required to avoid the major formation of adducts of the 2:1 coupling of the alkyne and the silane. This system was applicable to different alkynes and silanes, and the observed selectivities (usually very high) were extremely dependent on the nature of the alkyne, the silane, and the NHC ligand used.



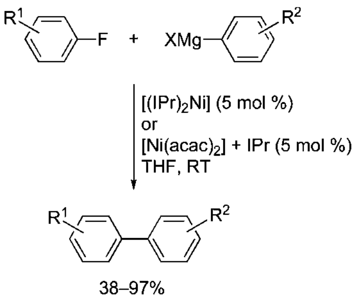
(35)

Scheme 24. Suzuki−Miyaura Couplings from Fluoroarenes



5.1.3. Activation of Inert Bonds

5.1.3.1. Activation of C−F Bonds. NHC-containing nickel complexes have shown outstanding activity in the activation of carbon−fluorine bonds, a particularly challenging process due to the strength/stability of these bonds.[109] Already in 2001, Herrmann and co-workers reported the [(NHC)Ni]-catalyzed Kumada reaction with aryl fluorides.[299] The reaction cleanly proceeded at room temperature in the presence 5 mol % of metal complex, the major byproduct being due to the homocoupling of the Grignard reagent (eq 36). Mono-NHC nickel(0) species were postulated as the most probable active catalysts since the in situ system (Ni/NHC, 1:1) was actually superior to the well-defined system (Ni/NHC, 1:2).

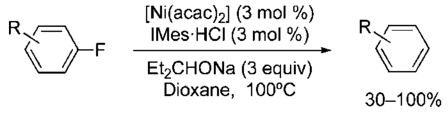


(36)

The Suzuki−Miyaura coupling through C−F activation has also been studied. While Robins and co-workers studied the coupling reactions of different nucleosides,[300] Radius and co-workers explored the activity and selectivity of NHC−nickel complexes in the activation of perfluorinated arenes (Scheme 24).[301]

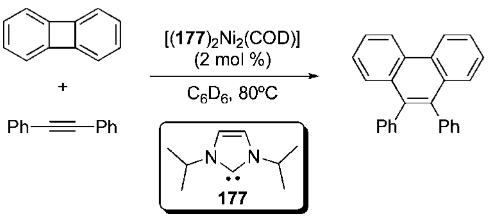
Radius' system (also active in Kumada coupling although to a lesser extent) was extremely selective, and only the fluorine *trans* to the CF_3 or C_6F_6 groups reacted under those conditions. Complete selectivity was also observed with differently substituted starting materials.[302] Mechanistic studies allowed for the isolation of intermediate species with the aromatic fluorine coordinated in an η^2-fashion. DFT calculations were in good agreement with the observed regio- and chemoselectivities (only C−F bonds were activated in the presence of C−H bonds).

The activation of C−F bonds has also been applied to the reduction of fluoroarenes. Further screening[296] allowed Fort and co-workers to effectively defluorinate a variety of arenes in the presence of an alkoxide base containing a β-hydrogen (eq 37).[303]



(37)

5.1.3.2. Activation of C−C and C−H Bonds. A dimeric NHC−nickel complex has shown a notable activity in the activation of C−C bonds.[304,305] Under optimized conditions, the reaction of biphenylene with diphenylacetylene led to the corresponding phenanthrene quantitatively at 80 °C within 30 min (eq 38).[306] This transformation also proceeded at room temperature, although a reaction time of three days was required. Remarkably, the chosen catalyst did not convert the alkyne in the absence of biphenylene even after 3 days of heating. On the other hand, biphenylene dimerization was not competitive either since it was too slow with respect to the catalytic cycle.

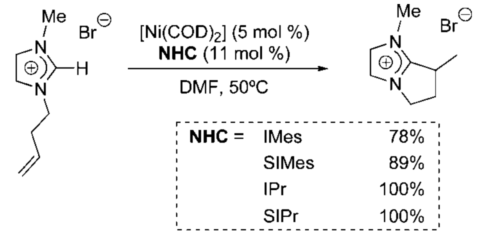


(38)

This reaction was extended to aliphatic alkynes, although overnight reactions were required. In this case, no excess of alkyne had to be used to avoid the undesired cyclo-oligomerization processes.

Imidazolium salts bearing an alkenyl chain can be converted into fused-ring imidazolium and thiazolium salts in the presence of [(NHC)Ni] systems (Scheme 25).[307] This reaction is believed to proceed through the oxidative addition of the C(2)−H bond to a nickel(0) center followed by intramolecular insertion of the double bond into the formed nickel hydride.

Scheme 25. [(NHC)Ni]-Catalyzed Annulation of Heterocycles



Finally, it is important to note that [(NHC)Ni]-based systems have even been reported to activate silicon−oxygen bonds of vacuum grease (supposedly chemically inert) at room temperature.[308]

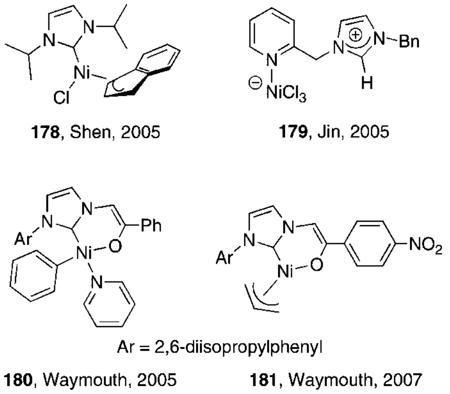
5.1.4. Polymerization and Related Reactions

The activity of [(NHC)Ni]-based catalytic systems was first tested in the dimerization of 1-butene. [$(NHC)_2NiI_2$] species were found to be far more active than the [$(Cy_3P)_2NiCl_2$] analogue at room temperature, although the selectivity in terms of branched dimers was disappointingly low.[309] Of note, the reactions only proceeded in ionic liquids, the complexes being mostly inactive in toluene.

Diverse scaffolds have been studied for the dimerization/oligomerization of ethylene with limited success (Chart 22). Complex **178** only showed very modest reactivity in the oligomerization of ethylene using MMAO as cocatalyst.[310] Alternatively, complex **179** can be activated with MAO to afford polyethylene of high molecular weight ($M_v = 10^4$ g/mol).[311] The best results were obtained under 5 atm of ethylene at 40 °C. In contrast, the optimized conditions for complex **180** did not include any activator.[312] In this case, the most plausible reaction pathway is chain-transfer by β-H elimination to generate a nickel hydride whose instability might explain the mitigated activity of this species. The related complex **181** required the use of Et_2Zn as activator at 80 °C under 15 bar of ethylene in order to generate linear polyethylenes of low molecular weights and broad polydispersities.[313]

For the norbornene polymerization, complex **182**, once activated by MAO treatment, afforded polynorbornene (PNB) through an exclusive vinyl addition pathway (Chart 23).[314] At 80 °C, the resulting PNB presented a high molecular weight, although with a moderate molecular weight distribution. Higher activities were reached with catalyst **183** without the need for any activator.[315] Alternatively, complex **184** was applied to styrene polymerization.[316] In this case, the presence of non-hindering groups on the NHC ligand led to higher yields, although bulkier substituents were needed in order to increase the product molecular weight. [(NHC)Ni(Cp)Cl] complexes have also been screened in this context,[317] although the best performance reported to date corresponds to salicylaldiminato-containing complex **185**.[318] Upon activation with $NaBPh_4$, polystyrene could be quantitatively formed with an number-average molecular weight of 17 600 after 12 h of reaction at 80 °C.

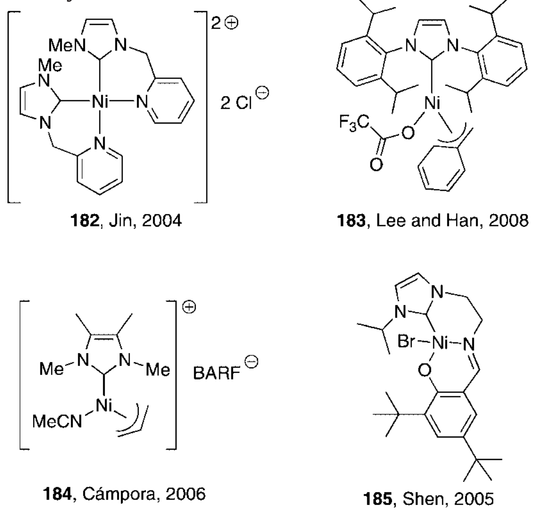
Chart 22. [(NHC)Ni] Complexes for Ethylene Polymerization



178, Shen, 2005 **179**, Jin, 2005

180, Waymouth, 2005 **181**, Waymouth, 2007

Chart 23. [(NHC)Ni] Complexes for Norbornene and Styrene Polymerization

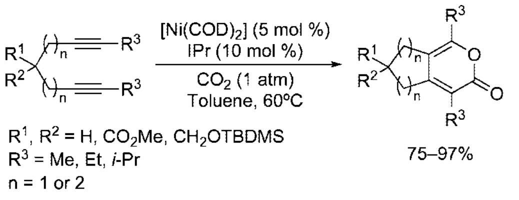


182, Jin, 2004 **183**, Lee and Han, 2008

184, Cámpora, 2006 **185**, Shen, 2005

5.1.5. Cycloaddition Reactions

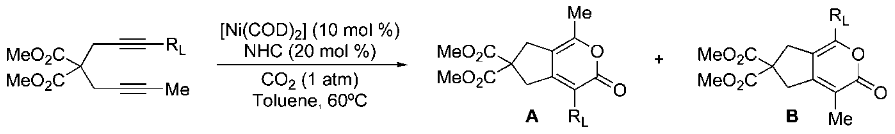
[2 + 2 + 2] Cycloadditions are the most extensively studied [(NHC)Ni]-catalyzed cycloaddition reactions. In 2002, Louie and co-workers reported the efficient [2 + 2 + 2] nickel-catalyzed cycloaddition of diynes and CO_2.[319] Among the ligand families tested, only NHCs led to the formation of the desired cycloadducts, and under optimized conditions, both acid- and base-sensitive functions were tolerated in the formation of diverse fused five- and six-membered rings (eq 39). Of note, the catalyst loading could be decreased to 1 mol % using the well-defined complex [$(IPr)_2Ni$].



(39)

The postulated mechanism for this transformation involves the initial [2 + 2] cycloaddition of carbon dioxide and an alkyne, followed by the insertion of the second unsaturation and subsequent reductive elimination to form a carbon−oxygen bond. Accordingly, hindered alkynes did not react under the aforementioned conditions. On the other hand, the reaction of asymmetrically substituted diynes showed that the regioselectivity of the reaction depended not only on the terminal groups size but also on the NHC ligand of choice.[320] In all cases, the major product formed presented the larger sub-

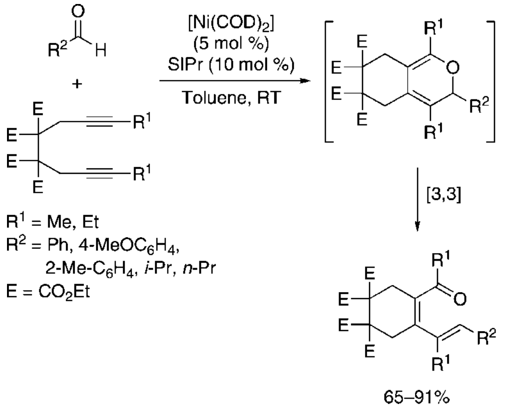
Scheme 26. Regioselectivity for Unsymmetrically Substituted Diynes



NHC = IMes	R_L	A:B	NHC = IPr	R_L	A:B
	i-Pr	56:44		*i*-Pr	80:20
	t-Bu	64:36		*t*-Bu	100:0

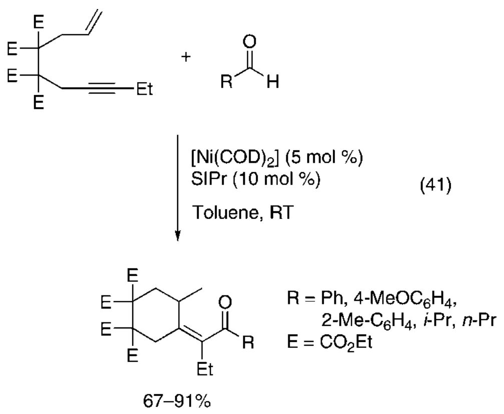
stituent of the diyne precursor in the position 3 of the resulting pyrone product (Scheme 26).

The use of carbonyl compounds (aldehydes or ketones) instead of CO_2, allowed access to a great variety of structures under mild reaction conditions.[321] The reaction of diynes with aldehydes led to the formation of dienones upon electrocyclic ring opening of the [2 + 2 + 2] cycloadduct (eq 40). Noteworthy, no reaction was observed with a variety of phosphane ligands. This reaction was not restricted to aromatic aldehydes, although alkyl substrates had to be used in excess (up to 5 equiv) and with higher nickel loadings (10 instead of 5 mol %).



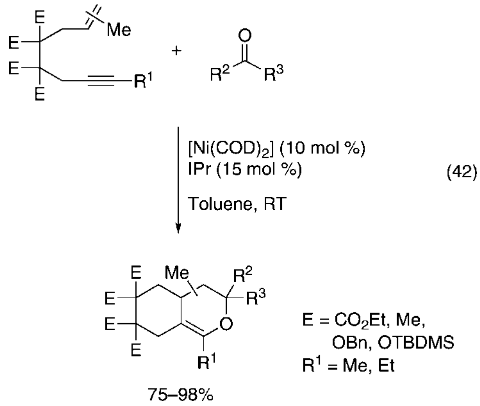
(40)

Alternatively, the reaction of substrates presenting a disubstituted alkyne and a terminal alkene moiety with aldehydes under identical conditions led to the sole formation of enones provided that the substituent on the starting alkyne was bigger than a methyl group (eq 41).

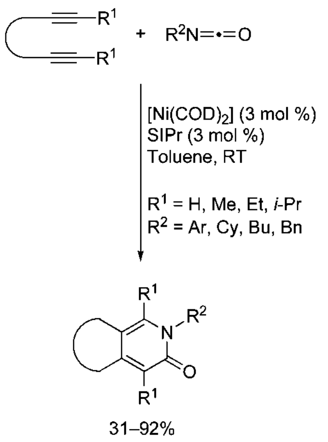


However, for unsubstituted or methyl-substituted alkynes, the product from the aldehyde addition on the alkene moiety was also isolated (Scheme 27). The substituent on the olefin also plays an important role on the chemoselectivity of the reaction and can notably lead to the formation of pyrans. In all cases, the aldehyde reacted preferentially with the more sterically hindered unsaturation in order to reduce the steric interaction between the NHC ligand and the substrate substituent in the intermediate oxanickelacycle (Scheme 27, box).

Remarkably, the reaction of enynes with ketones led to the unprecedented and general formation of pyrans in good yields. In contrast with the aldehyde reactions, the substitution pattern of the substrate had little influence on the reaction outcome and the carbonyl carbon was bound to the olefin, regardless of the alkyne substitution (eq 42).

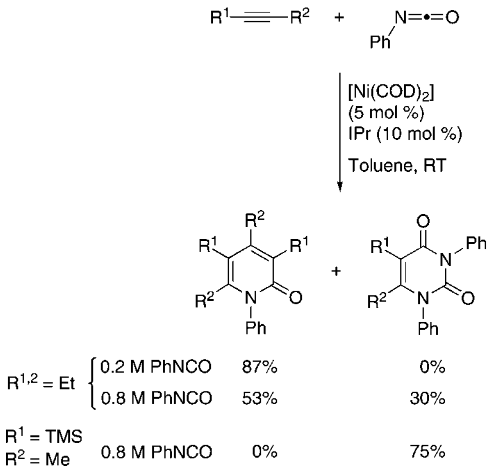


On the other hand, a very similar catalytic system has been reported to mediate the [2 + 2 + 2] cycloaddition reaction of diynes and isocyanates, affording a series of 2-pyridones in high yields (eq 43).[322]



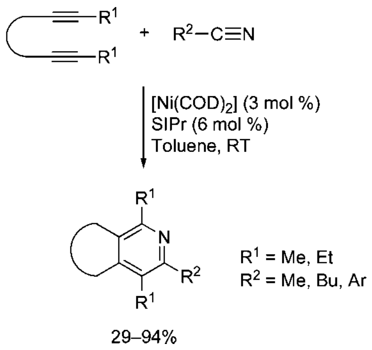
(43)

This reaction has also been explored with untethered alkynes. For these three component reactions, pyridones or pyrimidines can be formed depending on the alkyne substitution and the individual concentrations of the substrates in the reaction media (eq 44).[323]



(44)

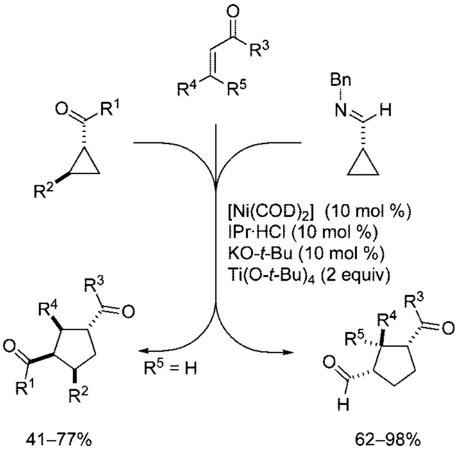
Nitriles have also been used in these cycloadditions to provide an effective nickel-catalyzed approach to pyridines (eq 45).[324] Of note, untethered alkynes also provided the expected pyridines, and a single regioisomer was obtained from the reaction of an unsymmetrical diyne.



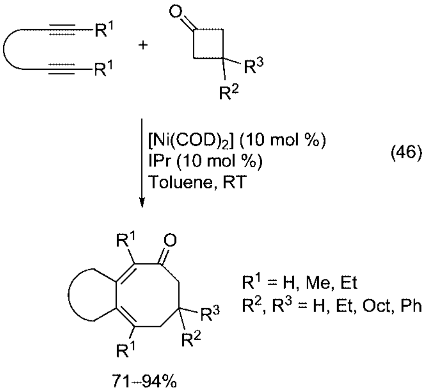
(45)

[(NHC)Ni]-based catalysts have also shown remarkable activities in other annulation reactions. In particular, a direct route to bicyclic eight-membered ring ketones has been developed through [4 + 2 + 2] cycloaddition of diynes and cyclobutanones (eq 46).[325] This transformation, which goes through a β-carbon elimination to expand the cyclobutane ring, is general for a variety of tethers but was shown to be very sensitive to alkyne substitution. Whereas excellent yields were obtained with alkynes bearing a methyl or an ethyl group, no reaction was observed in the case of isopropyl or phenyl groups. Of note, NHCs were clearly superior to phosphines in this transformation in terms of reactivity (room temperature reactions instead of 100 °C) and selectivity for unsymmetrical substrates. However, phosphine ligands provided better results in the reaction of enynes with cyclobutanones.[326]

Scheme 28. [(NHC)Ni]-Catalyzed [3 + 2] Cycloadditions[a]



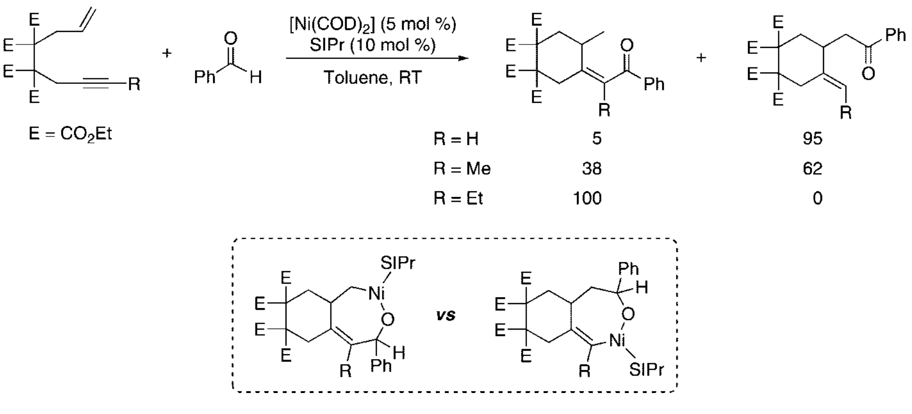
[a] Only the major diastereoisomer is shown.



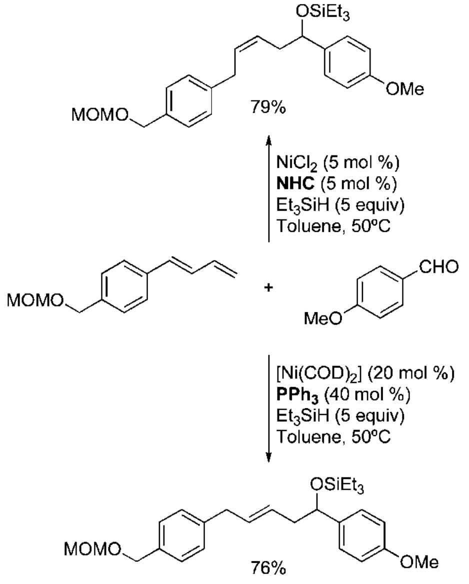
(46)

Finally, Montgomery and co-workers reported a remarkable nickel-catalyzed cycloaddition from simple cyclopropyl ketones. Capitalizing on the unexpected dimerization of such compounds in the presence of [(NHC)Ni] systems, the authors developed the [3 + 2] cycloaddition of enones with cyclopropyl ketones (Scheme 28).[327] Even tetrasubstituted

Scheme 27. Chemoselectivity of the Reaction Depending on the Alkyne Substitution



Scheme 29. Reductive Coupling of Dienes and Aldehydes



cyclopentanes could be prepared in fair to good yields, and the use of titanium alkoxides, although not mandatory, was beneficial for both reaction rates and yields. Noteworthy, cyclopropyl imines showed an improved reactivity in this context despite their lower electrophilicity and displayed a larger scope (Scheme 28).[328] In all cases, a low enone concentration had to be maintained in the reaction mixture to avoid inhibition of the reaction.

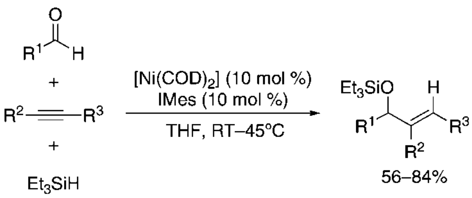
Stoichiometric experiments showed that both reactions are not really diastereodivergent. The selectivity was kinetically controlled, and in both cases the cis/trans diastereisomer was preferentially formed. However, the imine-derived aldehyde underwent epimerization upon hydrolysis.

5.1.6. Reductive Couplings and Related Transformations

Pioneering work by Mori and co-workers showed that [(NHC)Ni]-based systems not only could effectively catalyze the coupling of 1,3-dienes and aldehydes[329] but also provided the corresponding homoallylic silyl ether with reversed *E*/*Z* selectivity when compared with phosphine-based systems (Scheme 29).[330]

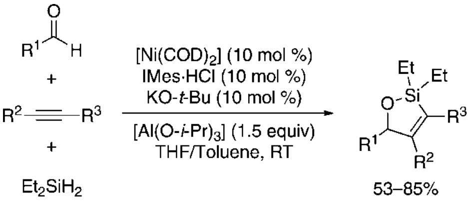
This methodology has been applied to the preparation of allylsilanes from silylated 1,3-dienes.[331] Again an inversed selectivity was observed between NHCs and phosphines as ancillary ligands. Interestingly, the addition of PPh_3 to an [(NHC)Ni]-catalyzed reaction improved the obtained yield without erosion of the stereoselectivity. The role of the phosphine would be to stabilize the proposed unstable active species: [(NHC)Ni^0]. Additionally, the use of a chiral NHC ligand allowed for the efficient asymmetric three-component coupling of 1,3-diene, aldehydes, and silanes with ee's up to 97%.[332]

The reductive coupling of aldehydes and alkynes has also been studied with NHC-containing systems to efficiently produce allylic alcohols protected as silyl ethers (eq 47).[333] This transformation was explored in its intermolecular version and included monosubstituted alkynes, the two main limitations of phosphine-based catalytic systems. The reaction is broad in scope,[334] regioselective, and displays fair to good enantioselectivities (up to 88% ee) upon the use of a chiral NHC.[335]



(47)

This process has been successfully applied to the construction of macrocycles[336] (intramolecular reaction) and to the preparation of oxasilacyclopentanes from aldehydes, alkynes, and dihydrosilanes (eq 48).[337] Theses silacycles were prepared as a sole regioisomer (except for 2-octyne) presenting the bulkier substituent in the α position to silicon, as had been previously observed for reactions with triethylsilane. This selectivity is opposite to that observed for the related copper-catalyzed addition of silacyclopropenes to aldehydes.[338] Whereas in the latter case a silylene transfer reaction is the most plausible reaction pathway, the intermediacy of a metallacycle was proposed for the nickel-catalyzed reaction.

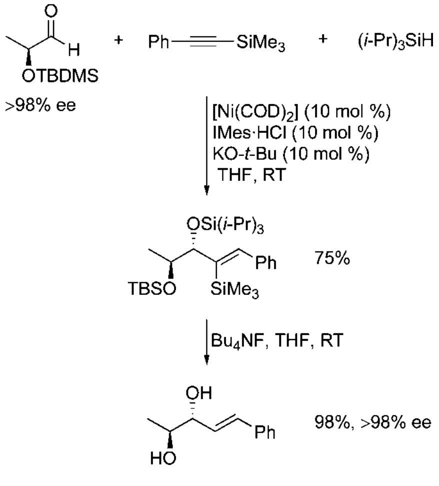


(48)

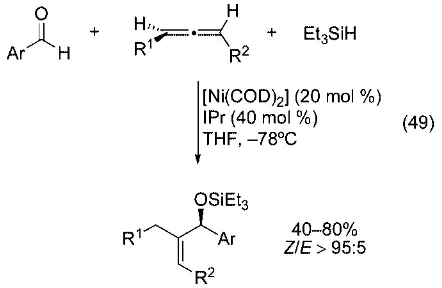
Furthermore, the use of α-silyloxy aldehydes in these reactions provides general access to *anti*-1,2-diols.[339] Interestingly, when an enantiopure aldehyde was employed, no stereochemistry erosion was observed in the final product (Scheme 30).

Allenes, instead of alkynes, could also be used in these multicomponent couplings.[340] The reactions proceeded at low temperature with total *Z* selectivity and transfer of the allene axial chirality (eq 49). Of note, catalytic species containing tricyclopentylphosphine were also active in this transformation although they led to an important erosion of the enantiomeric purity. Interestingly, the observed selectivity

Scheme 30. [(NHC)Ni]-Catalyzed Addition of Alkynes to α-Silyloxyaldehydes

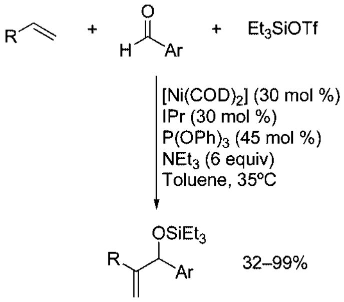


corresponds to the addition of the aldehyde to the more hindered face of the allene.



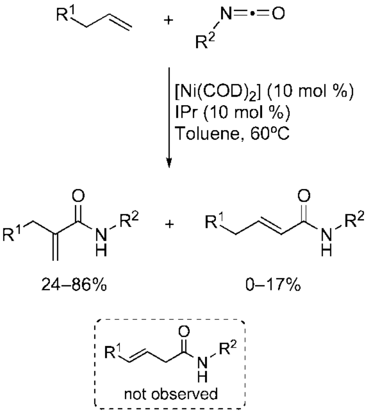
(49)

When similar reaction conditions were applied to the reaction of aldehydes and alkynes with silyl triflates, no turnover was observed. In this case, the use of an additional strong π acceptor ligand was required to render the reaction catalytic.[341] Phosphites were found to be the most effective additives, and under optimized conditions a large variety of allylic alcohols were prepared (eq 50). Not only was this catalytic system much broader in scope than the related nickel/phosphine-based one, but it also led to a total selectivity and the undesired formation of homoallylic alcohols was hampered.[342] In the present catalytic system, the NHC ligand is assumed to accelerate the oxidative coupling of the alkene and the aldehyde thanks to its highly electron-donating nature and to render the reaction highly selective thanks to its steric hindrance. Synergistically, the phosphite would reduce the electron density on the nickel center, facilitating the subsequent reductive elimination.



(50)

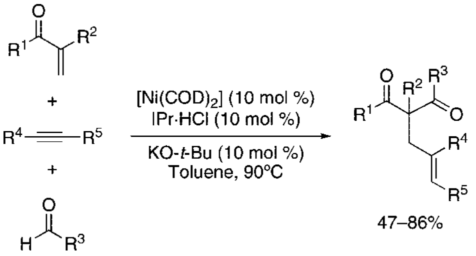
In a related transformation, isocyanates could be used instead of aldehydes.[343] This coupling reaction, of special interest in polymer science,[344] provided the corresponding acrylamides in good yields from bulky, electron-rich alkyl isocyanates (eq 51). The observed selectivity (preference for the carbon–carbon bond formation at the 2-position of the olefin) is again opposite to the one observed with phosphine ligands, which favors the formation of (*E*)-disubstituted enamides. In no case was the formation of homoallylic products observed.



(51)

Finally, the coupling of α,β-unsaturated aldehydes, alkynes, and alcohols in the presence of [(NHC)Ni] species led to the formation of unsaturated esters as a result of an internal redox process and therefore does not require the presence of a reducing agent (Scheme 31).[345]

Similarly, enones, alkynes, and aldehydes can also be coupled into 1,3-diketones with a striking chemoselectivity (eq 52). The ligand of choice (NHC or phosphine) had an effect not only on the regioselectivity of the alkyne coupling but also on the aldehyde scope: whereas aromatic aldehydes can be used with either ligand family, aliphatic substrates required a phosphane ligand.

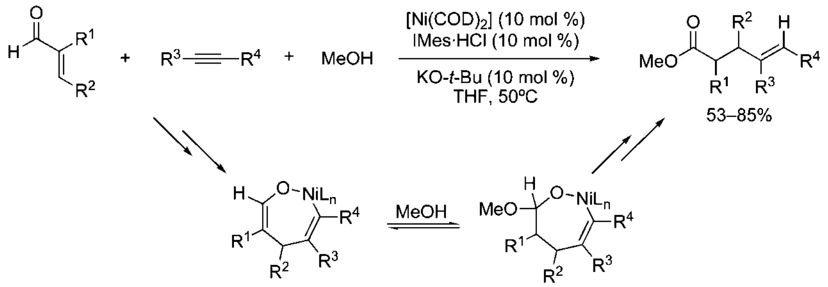


(52)

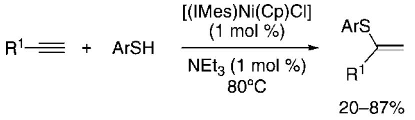
5.1.7. Miscellaneous Reactions

[(NHC)Ni] complexes have been found to be good candidates for the dehydrogenation of chemical hydrogen storage agents. A 1:2 combination of [Ni(COD)₂] and NHC at 60 °C allowed for the dehydrogenation of amine-borane to a soluble cross-linked borazine to an unprecedented extent.[346] Theoretical calculations on this catalytic system showed that the dehydrogenation process starts with a proton transfer from nitrogen to the carbenic carbon coordinated to the nickel.[347] The newly formed C–H bond is then activated by the metal center and delivers the hydrogen atom to the nickel. The final dihydrogen formation is achieved by H transfer from another borane molecule.

Scheme 31. [(NHC)Ni]-Catalyzed Three-Component Redox Couplings



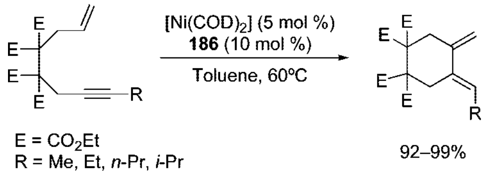
[(NHC)Ni(Cp)Cl] complexes are excellent catalysts for the regioselective hydrothiolation of alkynes to form the corresponding vinylsulfides in good yields (eq 53).[348] Of note, these Markonikov-type olefins did not isomerize under catalytic conditions. Mechanistic studies showed that the three main steps involved are substitution of the chloride on the nickel center by a SAr group, followed by alkyne insertion on the newly formed Ni−S bond and protonolysis of the Ni−C bond.



(53)

On the other hand, a combination of [Ni(COD)]/IMes·HCl has successfully been applied to the borylation of aryl cyclopropyl ketones.[349] Under optimized conditions, the corresponding 4-oxoalkylboronates could be prepared at room temperature in good yields.

During their studies on nickel-catalyzed cycloaddition reactions (see section 5.1.5), Louie and co-workers observed that in the absence of an adequate partner, enynes could actually be cycloisomerized under mild conditions (eq 54).[350] These reactions were postulated to proceed through hydrometalation of the alkyne moiety by a nickel hydride species followed by insertion of the pendant alkene. Interestingly, the Ni−H intermediate was found to be formed by orthometalation of the NHC ligand.



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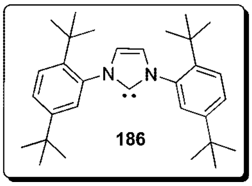
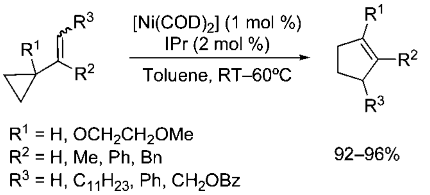


186

The same research group reported in 2004 the [(NHC)Ni]-catalyzed isomerization of a range of activated and unactivated vinylcyclopropanes to afford the corresponding cyclopentenes in good yields (eq 55).[351] Interestingly, mechanistic studies discarded nickel hydride species as mediators in this transformation, in contrast with previously known nickel-based catalytic systems.[352]



(55)

Additionally, more complex architectures could be accessed by simply tethering the vinylcyclopropane to an alkyne chain.[353] The expected oxacyclopentanes were selectively obtained when ItBu was used as ancillary ligand (Scheme 32). Remarkably, the use of SIPr instead, led also to the formation of bicyclic cycloheptadienes, the selectivity being controlled by the nature of the alkyne substitution. The formation of these different products could be rationalized from a common nickelacyclooctadiene intermediate **187** (Scheme 32). From **187**, β-hydride elimination followed by reductive elimination would produce the expected cyclopentanes. In contrast, when both the ligand and R are sterically hindered, the β-hydride elimination would be disfavored and a direct reductive elimination would yield a bicyclic seven-membered ring. However, since both SIPr and ItBu ligands are extremely encumbered ligands, this hypothesis does not explain why no cycloheptadiene products were formed with ItBu as ligand. Sigman and co-workers proposed that this difference in reactivity between SIPr and ItBu in these reactions would arise from the preference of the latter to induce square-planar coordination, which minimizes the steric hindrance around the metal center.[354]

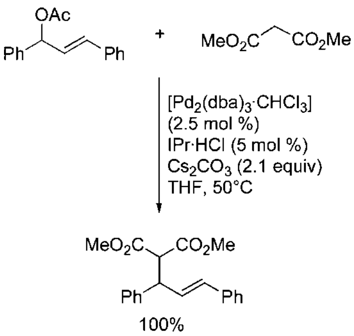
Finally, a number of [(NHC)$_2$Ni]-type complexes bearing N/O-functionalized NHCs have been applied to the Michael addition of β-dicarbonyl, β-keto ester, and α-cyano ester to activated ethylene compounds.[355] These reactions were carried out in air and at room temperature, but more importantly, no base was required for the reactions to proceed.

5.2. Palladium

Palladium, along with ruthenium, is undoubtedly the most commonly used transition metal with NHC ligands. This family of ligands has notably allowed for major breakthroughs in C−C and C−N forming cross-coupling reactions. This success has certainly overshadowed other applications of [(NHC)Pd] systems, which are actually numerous and remarkable. As stated in the Introduction, only transformations other than cross-coupling reactions will be covered here, since the latter have been comprehensively reviewed very recently.[39,356]

5.2.1. Allylic Alkylation Reactions[100]

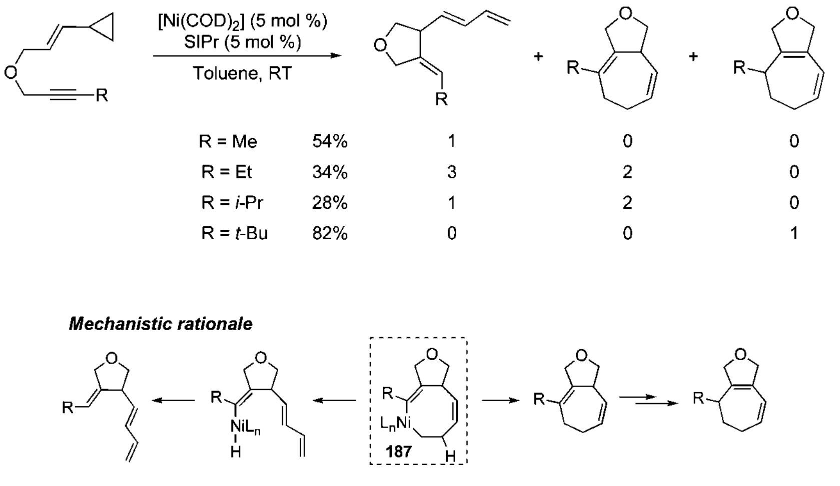
Allylic substitution has become the most popular palladium-catalyzed method for carbon−carbon bond formation along with cross-coupling reactions. However, despite the success of NHCs in palladium-catalyzed cross-coupling reactions, the first report on allylic alkylations with NHCs only appeared in 2003.[357] IPr was found to be a suitable ligand for allylic substitution with soft nucleophiles. [Pd$_2$(dba)$_3$] as palladium source and Cs$_2$CO$_3$ as base completed the catalytic system (eq 56). These reactions proceeded with overall retention of stereochemistry, as for phosphine-based catalytic systems.



(56)

Significantly, mixed phosphine/NHC systems have shown important synergetic effects. Whereas NHC/phos-

Scheme 32. [(NHC)Ni]-Catalyzed Rearrangements of Cyclopropylenynes



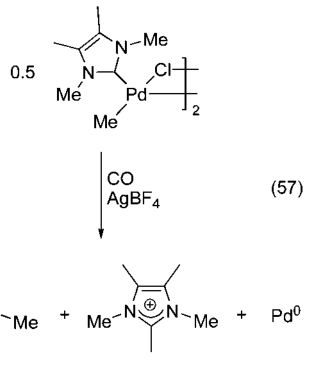
R = Me	54%	1	0	0
R = Et	34%	3	2	0
R = *i*-Pr	28%	1	2	0
R = *t*-Bu	82%	0	0	1

phine palladium complexes were shown to catalyze the alkylation of 1,3-diphenyl allyl acetate with diethyl malonate[358] or with diverse nitrogen nucleophiles[359] at room temperature, the addition of an NHC to a reaction mixture containing a palladium/chiral phosphine system led to an enhancement of the enantioselectivity.[360] However, the reported attempts to apply NHC in asymmetric allylic alkylations have only found limited success, despite the variety of monodentate[361] or bidentate (CN,[362] CP,[243] or CS[363]) NHC families explored.

5.2.2. Polymerization Reactions

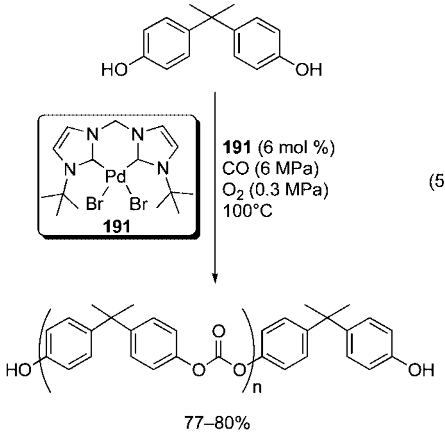
The virtual unlimited availability of CO makes it extremely attractive as monomer in copolymerization reactions. Herrmann and co-workers first reported the copolymerization of CO and ethene using dicationic chelating carbene complexes of palladium(II) **188** (Chart 24).[364] Considering the large molecular weight of the obtained copolymer and the relatively modest TONs observed, the authors postulated that only a small percentage of palladium precatalyst actually participated in the production of copolymer.

An explanation for this deactivation during the copolymerization process was provided by Cavell and co-workers who demonstrated the feasibility of the CO insertion in a (NHC)methylpalladium complex,[365] the resulting acyl-palladium complex being prone to decomposition to yield acylimidazolium salts and Pd^0 species (eq 57).



(57)

A system related to **188** allowed for the synthesis of aromatic polycarbonates (PCs) via oxidative carbonylation of a biphenol.[366] High yields (~80%) with close to industrially useful molecular weight (M_n = 94 000) were obtained in this case (eq 58).



(58)

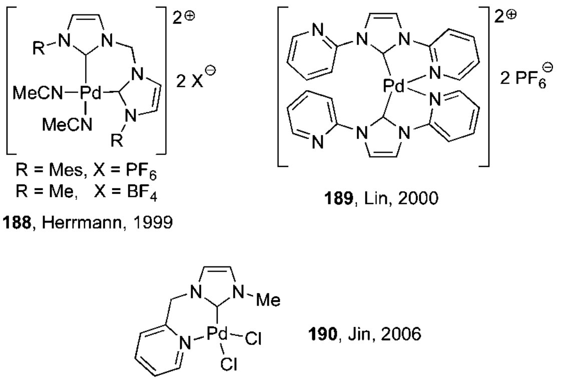
Good catalytic behavior was also observed for palladium complexes bearing hemilabile pyridylcarbene ligands: complexes **189**[367] for the copolymerization of CO and norbornadiene and **190** for the polymerization of norbornene (see Chart 24).[368] The latter process could alternatively be mediated by η^3-allyl complexes such as [(IPr)Pd(allyl)Cl].[369] Interestingly, as observed for cross-coupling reactions,[272c,e] the substitution of the allyl moiety had a beneficial effect on the reaction outcome.[370] Finally, [(IPr)Pd(OAc)$_2$] has been used for the polycondensation of 4′-halopropiophenones to produce polymers with modest number-averaged molecular weights.[371]

5.2.3. Carbonylation Reactions

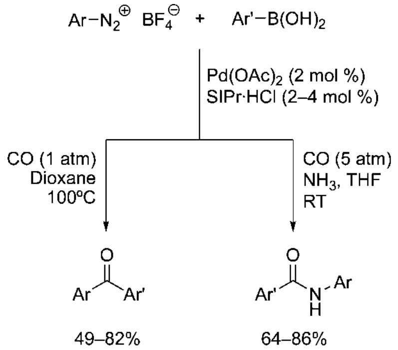
Carbonylative coupling reactions represent a straightforward method for the preparation of diversely functionalized ketones. A combination of Pd(OAc)$_2$/SIPr·HCl has been reported to efficiently catalyze the coupling of diazonium salts with boronic acids to yield ketones[372] or amides[373] in the presence of CO or CO/ammonia, respectively (Scheme 33). Optimization studies showed that CO pressure had to be maintained at 5 atm during the amide formation to minimize the formation of byproduct such as anilines or biaryl compounds. Not only boronic acids but also boranes and borate salts can be used as coupling partners with this catalytic system.

Oxidative carbonylations can also be carried out using NHC ligands. Sugiyama and co-workers reported the trans-

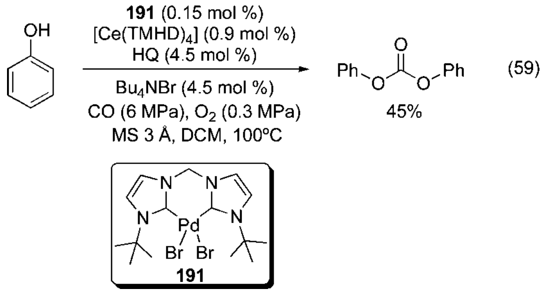
Chart 24. [(NHC)Pd] Systems for Copolymerization Reactions



Scheme 33. [(NHC)Pd]-Catalyzed Carbonylative Couplings

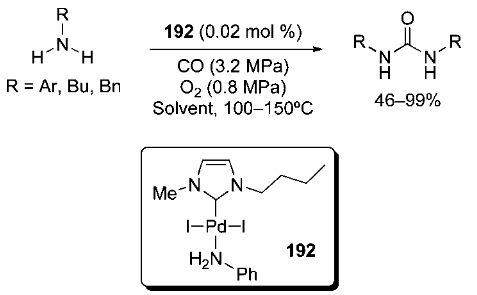


formation of phenol into diphenyl carbonate in the presence of [(NHC)Pd] complexes.[374] This catalytic system consisted of an inorganic redox cocatalyst, an organic cocatalyst, an organic onium salt, and a dehydrating agent (eq 59). Under optimized conditions, the highest TOF reached was 50.7 h^{-1}, giving a 45% yield in diphenyl carbonate.



(59)

Alternatively, [(NHC)Pd]-based systems can catalyze the oxidative carbonylation of amines to ureas.[375] In this case, no cocatalyst was required and the reactions were carried out in DMF at 150 °C for anilines or in diglyme at 100 °C for aliphatic amines (eq 60).

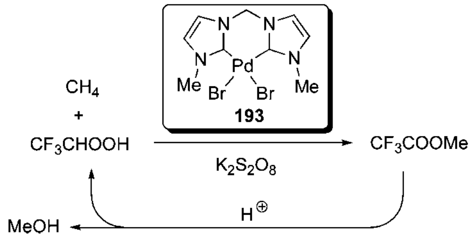


(60)

5.2.4. C–H Bond Activation Processes

5.2.4.1. Oxidation of Methane to Methanol. The extreme thermal stability of NHC–palladium(II) complexes combined

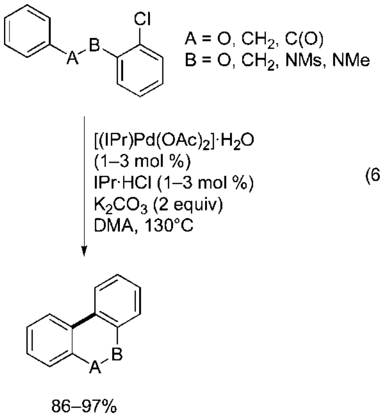
Scheme 34. [(NHC)Pd] Activation of Methane



with their surprising resistance to strong acids and oxidative conditions make these species excellent candidates for C–H bond activation. Whereas the catalytic conversion of methane into methanol is still one of the major challenges for synthetic chemists, it has been efficiently achieved in trifluoroacetic acid using a complex bearing a bidentate NHC.[376] This system has the advantage that it can be run in a closed loop: the formed ester can be distilled from the reaction mixture and hydrolyzed, and the acid along with the remaining methane can be transferred back to the reactor (Scheme 34).

Interestingly, analogous platinum complexes decomposed under these acidic conditions. Even if the optimized yield is still below industrial expectations, adequate tuning of the carbene, the nature of the counterion, and the reaction conditions should allow for major improvements.[377]

5.2.4.2. Direct Arylation Reactions. [(IPr)Pd(OAc)$_2$] has recently been shown to efficiently promote the intramolecular direct arylation of aryl chlorides (eq 61).[378] Interestingly, the use of IPr·HCl as additive led to enhancement of the reactivity, probably due to the preventive effect on catalyst decomposition at high reaction temperatures. These conditions allowed for the formation of five- and six-membered rings bearing ether, amine, amide, or alkyl tethers.

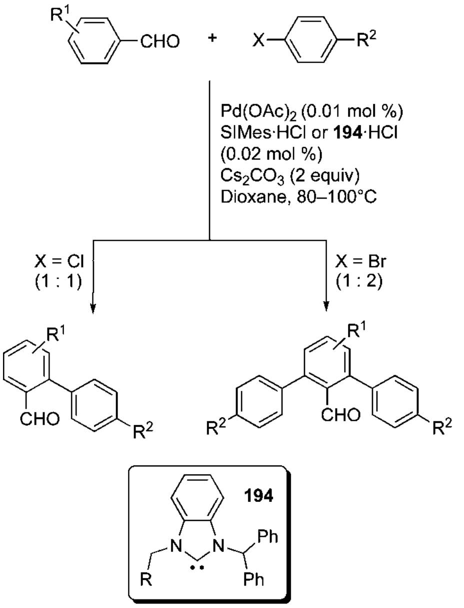


(61)

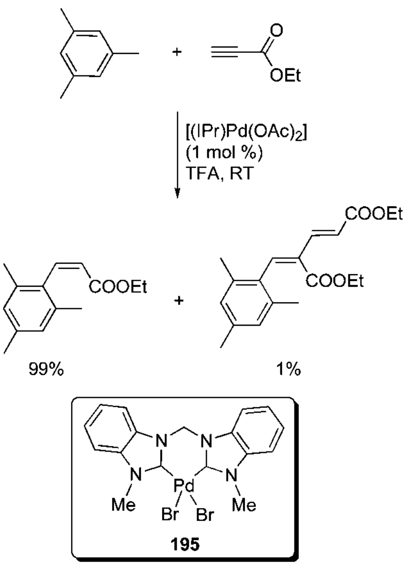
The *o*-arylation of aromatic aldehydes in the presence of a combination of Pd(II)/saturated imidazolium salt has also been reported.[379] Remarkably, the formation of the mono- or di-*ortho*-substituted product could be easily controlled as a function of the nature of the aromatic halide employed (Scheme 35). Both electron-donating and electron-withdrawing substituents were well tolerated by this catalytic system, and heteroaromatic aldehydes could also be coupled.

5.2.4.3. Hydroarylation of Unsaturated Compounds. [(IPr)Pd(OAc)$_2$] was the first reported example of NHC-based system for the hydroarylation of ethyl propiolate in TFA to generate stilbene derivatives at room temperature (eq 62).[380] Arenes bearing alkoxy and halide substituents or internal alkynes could also be used in this reaction. However,

Scheme 35. [(NHC)Pd]-Catalyzed *o*-Arylation of Benzaldehyde Derivatives



enhanced catalytic activity and broader scope was observed under similar reaction conditions using complex **195**.[381]



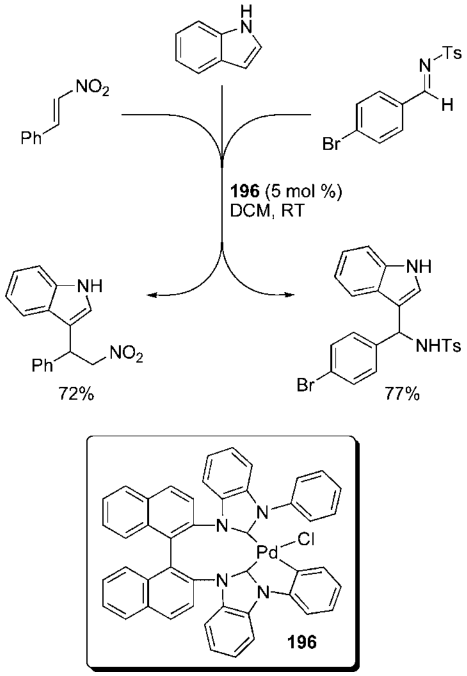
(62)

It is important to note that under the same conditions, ligandless [Pd(OAc)$_2$] led only to poor conversions after extended reaction times. To date, the catalytic cycle of this transformation is not fully understood. It is thought to be based on palladium(II) exclusively,[382] and the latest evidence point toward a Friedel–Crafts-type alkenylation.[383] Such transformation has also been tested with cyclometalated bidentate NHC ligands with which the reactions of indole with a nitrovinyl derivative or a tosyl imine smoothly proceeded at room temperature (Scheme 36).[384]

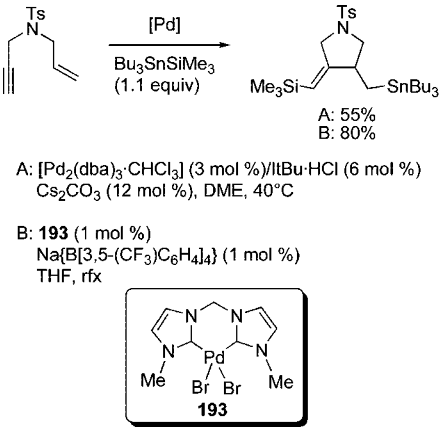
5.2.5. Cycloisomerization Reactions

The transition metal-catalyzed cycloisomerization of enyne systems is a powerful synthetic tool for the construction of a variety of architectures.[385] The bismetalative cyclization of enynes has the added advantage that the reaction products can be further functionalized thanks to the newly formed metal–carbon bonds. Two different systems with N-heterocyclic carbenes as ligands have been reported to be efficient in the Pd-catalyzed bismetalative cyclization of enynes in the presence of Bu$_3$SnSiMe$_3$. The combination [Pd$_2$(dba)$_3$]/imidazolium salt/Cs$_2$CO$_3$[386] or **193**/NaB[3,5-(CF$_3$)$_2$C$_6$H$_4$]$_4$[387] could convert nitrogen-containing enynes into cyclized products containing a vinylsilane moiety and a homoallylstannane (Scheme 37). The synthetic utility of this strategy was highlighted by the transformation of the cyclized products into cyclopropanol derivatives.[388]

Scheme 36. [(NHC)Pd]-Catalyzed Friedel–Crafts Reaction

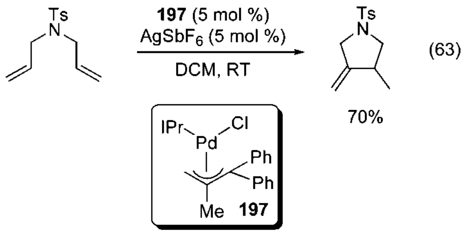


Scheme 37. [(NHC)Pd]-Catalyzed Bismetalative Cyclization of Enynes



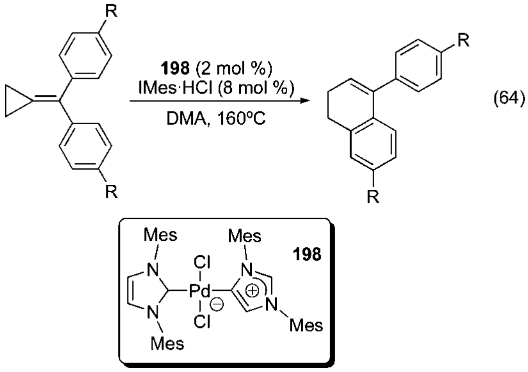
On the other hand, cationic [(NHC)Pd^{II}] complexes have been reported to be efficient catalysts for the cycloisomerization of dienes.[389] The reactions proceeded at room temperature with complete regioselectivity for the formation of *exo*-methylene-containing products (eq 63). However, only nitrogen tethers were suitable for this catalytic system.

Another family of compounds that undergoes a cycloisomerization process in the presence of NHC–palladium species is the alkylidenecyclopropanes.[390] This process produced the corresponding 1-aryl dihydronaphthalenes with high selectivity at room temperature (eq 64). The proposed mechanism involves hydropalladation of the alkene by a



(63)

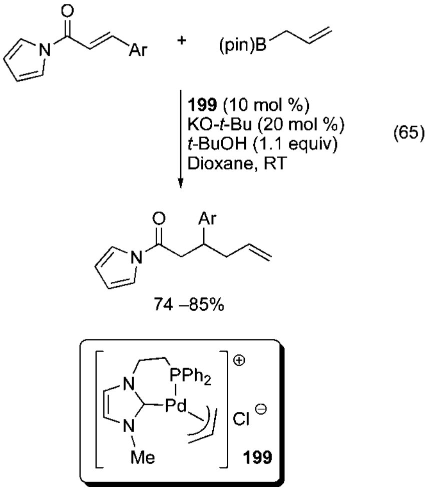
palladium hydride species, β-carbon elimination, then C−H insertion of the phenyl ring to provide the cyclic product.



(64)

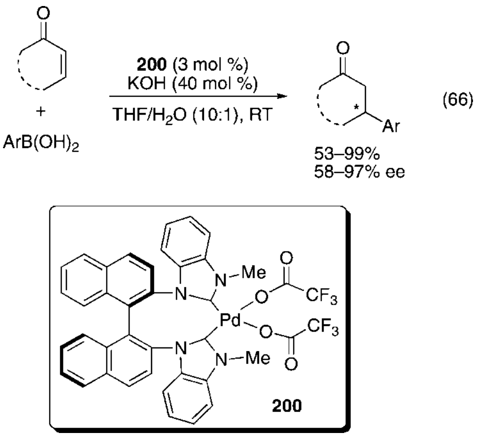
5.2.6. Addition Reactions

5.2.6.1. 1,4-Addition Reactions. The conjugate allylation of α,β-unsaturated *N*-acylpyrroles by allylboronic esters has been reported in the presence of a palladium center coordinated by a bidentate NHC ligand.[184,391] This transformation was carried out at room temperature with 10 mol % catalyst loading with a variety of *N*-acylpyrroles (eq 65). Mechanistic studies pointed toward nucleophilic allylpalladium species as intermediates in this process. The related conjugate allylation of alkylidene malononitriles has also been investigated. In this case, [(IMes)Pd(allyl)Cl] was found to be the catalyst of choice and the allylation by boron reagents could be conducted at room temperature for a variety of malononitriles.[392]



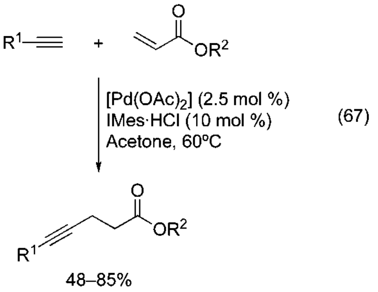
(65)

More general was the asymmetric reaction of cyclic enones with diverse boronic acids catalyzed by a palladium complex bearing a BINAM-tethered bidentate NHC ligand (**200**).[393] The corresponding adducts were recovered in good to excellent yields with ee's up to 97% (eq 66). In this case, the reaction of the precatalyst with the base would generate the corresponding hydroxopalladium species, activated toward transmetalation with the boronic acid.



(66)

Alkynes have also been used for the 1,4-addition to unsaturated carbonyl compounds.[394] Whereas a phosphine ligand was optimal for the conjugate addition of terminal alkynes to enones, NHC ligands were clearly superior in the addition to acrylate esters (eq 67).

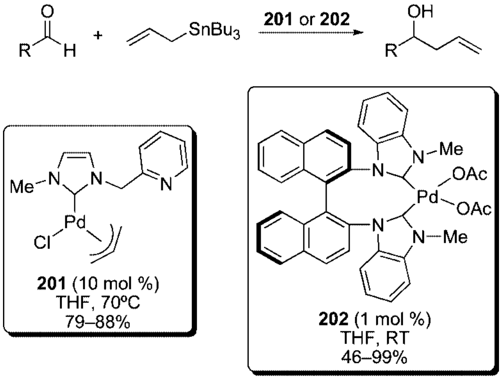


(67)

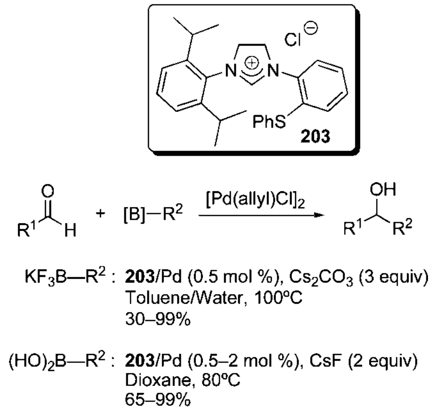
5.2.6.2. 1,2-Addition Reactions. Bidentate [(NHC)Pd]-based systems have been reported to efficiently catalyze the allylation of aldehydes. This transformation was carried out at 70 °C using 10 mol % palladium complex **201** bearing a pyridine-functionalized NHC (Scheme 38).[395] Better results were obtained with the BINAM-tethered NHC ligand in **202**,[396] and in this case, the reactions were run at room temperature with only 1 mol % catalyst. Furthermore, this catalytic system was also shown effective for the allylation of imines and glyoxalates.

Additionally, the 1,2-addition of boron reagents to aldehydes has been recently reported. Notably, a thioether-functionalized NHC was found to be efficient for the reactions with potassium trifluoroborates[397] and boronic acids.[398] Both transformations proceeded under similar

Scheme 38. [(NHC)Pd]-Catalyzed Allylation of Aldehydes

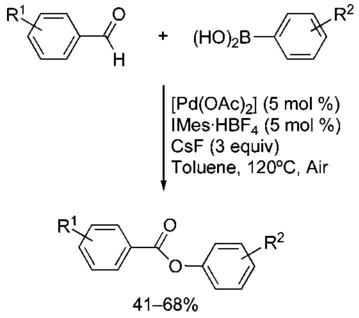


Scheme 39. [(NHC)Pd]-Catalyzed Addition of Boron Reagents to Aldehydes



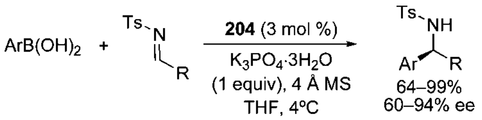
conditions and were broad in scope in terms of aldehyde and boron reagent (Scheme 39), although boronic acids were determined to be more suitable substrates for the addition to aliphatic aldehydes.

When this transformation was carried out in air, the formation of the corresponding ester was obtained instead (eq 68).[399] The incorporation of atmospheric oxygen in the final product was evidenced by labeling studies. This methodology represents a versatile alternative to classic esterification reactions, even though its scope is limited to aldehydes bearing neutral or electron-donating groups.



(68)

Alternatively, the arylation of *N*-tosylimines with arylboronic acids can also be carried out in the presence of an [(NHC)Pd]-based catalytic system.[400] Again in this case, a BINAM-derived NHC led to remarkable activity and good to high enantioselectivities (eq 69).[401] Notably, even aliphatic imines reacted to yield the corresponding amine in more than 60% ee.



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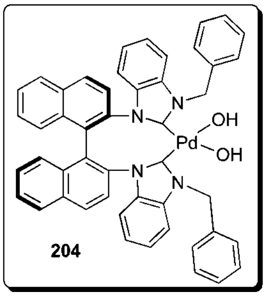

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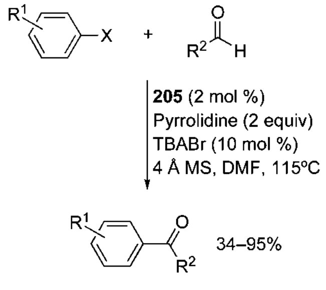
Finally, the direct acylation of aryl iodides or bromides with aldehydes has been achieved in fair to high conversions in the presence of a triazolyldiylidene−palladium complex (eq 70).[402] Of note, under these reaction conditions, no α-arylation of the aldehyde was observed.



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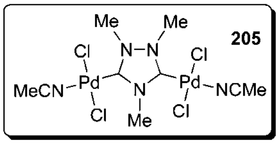

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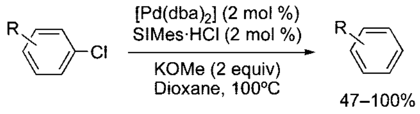
5.2.7. Reduction Reactions

A palladium/imidazolinium salt (SIMes·HCl) mixture proved efficient for the dehalogenation of aryl bromides and chlorides at relatively high temperature (eq 71).[403] In this case, the formation of the actual active species, a palladium hydride intermediate, was postulated to occur through oxidative addition of the imidazolidinium salt to the palladium(0) precursor.



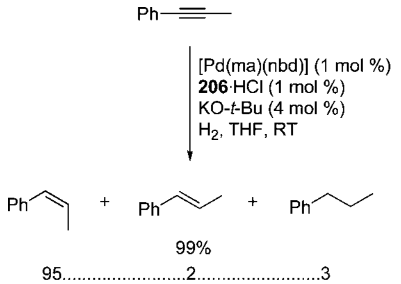
(71)

A well-defined complex, [(IPr)Pd(allyl)Cl],[404] provided an improved system for this transformation.[405] The dehalogenation of aryl chlorides could be carried out at 60 °C using very low catalyst loading (0.5−0.025 mol %) in less than 2 h or in 2 min when microwave irradiation was used.

Despite the successful use of NHCs in a number of palladium-catalyzed reactions, no system for hydrogenation was reported until 2005. This can be easily explained by the previous observation that imidazolium salts can be formed from decomposition of NHC−Pd^{II} species, probably through reductive elimination of the corresponding NHC−hydridopalladium(II) intermediates.[406]

However, Cavell and co-workers also showed that the oxidative addition of imidazolium salts to bis-carbenic palladium complexes leads to isolable NHC-hydridopalladium compounds,[407] putting into evidence the remarkable stabilizing effect of NHC ligands in otherwise reactive species. This study led to the development of the first NHC/palladium(0) catalyst for hydrogenation.[408] Not only was such a system stable under hydrogenation conditions, but it could also semihydrogenate 1-phenyl-1-propyne with remarkable efficiency and selectivity (eq 72).

This transformation has also been studied under transfer hydrogenation conditions. Very high conversions and selectivities were again achieved (eq 73). Of note, the unprecedented chemoselective reduction of alkynes bearing carbonyl functions was possible with this catalytic system.



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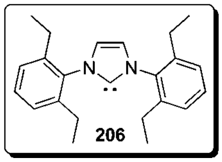

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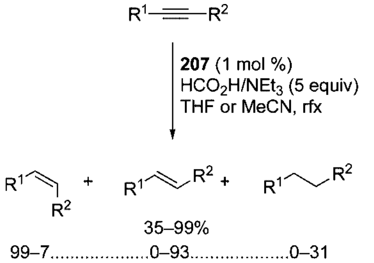
Furthermore, the selectivity could be further enhanced by carrying out the reactions in acetonitrile at 65 °C.



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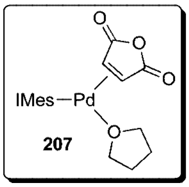

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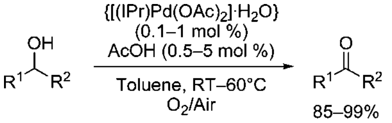
Recently, a number of mixed NHC/phosphine palladium(0) systems of the type [(NHC)Pd(PR$_3$)] have been synthesized by Nolan and co-workers.[409] Interestingly, these highly unsaturated 14-electron complexes were shown to react with small molecules such as dioxygen, dihydrogen, and HCl. They have notably allowed for the isolation and characterization of tetracoordinated NHC−phosphine peroxo-palladium(II) complexes as well as an unprecedented *trans*-NHC−phosphine dihydrido-palladium(II) species, [(IPr)Pd(H)$_2$(PCy$_3$)].[410] The synergy between the NHC and the phosphine on the palladium center was found to be crucial for the isolation of the dihydride species since the use of any other combinations than IPr/PCy$_3$ (i.e., IPr/PPh$_3$, SIPr/PCy$_3$, IPr/IPr, and PCy$_3$/PCy$_3$) led to recovery or decomposition of the starting material.

Further developments by Cazin and co-workers established the high catalytic activity of [(SIPr)Pd(PCy$_3$)] in hydrogenation and semihydrogenation of a variety of unsaturated substrates.[411] Remarkably, these transformations can be carried out using very low catalyst loadings (as low as 10 ppm) and under 1−4 bar of dihydrogen.

5.2.8. Oxidation Reactions

5.2.8.1. Oxidation of Alcohols. Metal-catalyzed oxidation of alcohols has attracted much attention as an alternative to "traditional" methods, since employing molecular oxygen as oxidant still represents an important challenge for catalysis. Sigman and co-workers pioneered the use of NHCs in this field and explored the scope of [(IPr)Pd^{II}] complexes at low catalyst loadings and mild temperatures.[412] Noteworthy, air could be used as oxidant instead of molecular oxygen by simply increasing the amount of acid in the reaction mixture. Diversely functionalized benzylic, aliphatic, and allylic alcohols could be transformed under these conditions (eq 74).



(74)

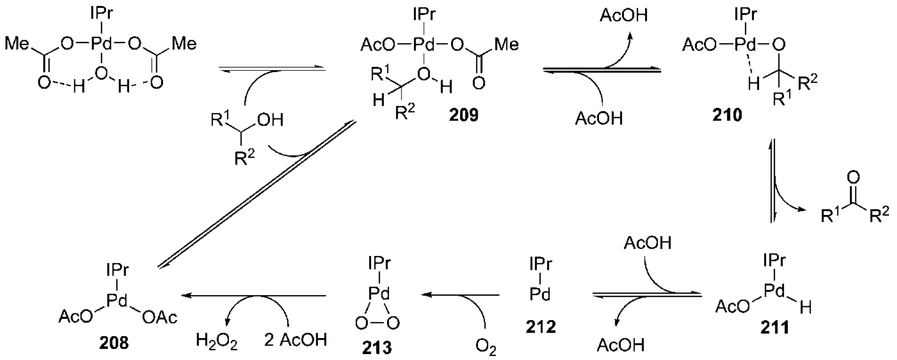
The initial postulated mechanism for this transformation is depicted in Scheme 40. Coordination of the substrate with concomitant loss of water would start the catalytic cycle, then an intramolecular deprotonation of the alcohol would generate the alkoxide **210**, which would yield hydride **211** upon β-hydride transfer. A reductive elimination of acetic acid would lead to a palladium(0) species **212**, which would be oxidized by oxygen to generate the corresponding peroxo complex **213**. Protonation of this species would regenerate **208**, closing the catalytic cycle.

Outstanding efforts aimed at fully validating and understanding this proposal have been undertaken by several research groups.[413] Theoretical and experimental mechanistic studies by Sigman and co-workers showed that, under optimized conditions, β-hydride transfer to generate palladium hydride **211** is the rate-limiting step.[414] Furthermore, the role of acetic acid is multiple: it modulates the rates of the oxidation reaction and regeneration of the palladium-based catalyst. In the absence of acid, reprotonation of peroxo complex **213** is kinetically competitive with β-hydride elimination. This can be translated into reversible oxygenation and subsequent decomposition of palladium(0) intermediate **212** to undesired palladium black.

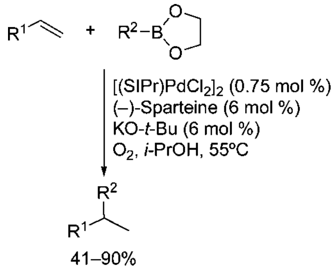
On the other hand, Stahl and co-workers isolated and characterized a related dioxygen-derived palladium(II)−hydroperoxide complex.[415] The capability of IMes ligands to undergo *cis*−*trans* isomerization was pointed out as essential for the formation of this complex (Scheme 41). Surprisingly, theoretical calculations on this system showed that solvent plays an essential role on the reversibility of the oxygenation step.[416] More precisely, nonpolar solvents, such as toluene used in this catalysis, promote this reversibility and therefore contribute to catalyst decomposition. Alternatively to the pathway proposed in Scheme 40, reoxidation of the catalyst could also occur via direct reaction of molecular oxygen with a **211**-type palladium(II)−hydride complex. Stahl and co-workers demonstrated that such transformation proceeded smoothly for a bis-NHC-containing palladium complex (Scheme 41).[417] Interestingly, this reaction was significantly accelerated by the presence of carboxylic acids in the media. Extensive mechanistic studies showed that in this system the reaction of oxygen with a palladium hydride takes place via an AcOH oxidative addition process, followed by oxygen coordination and Pd−O protonolysis to yield the hydroperoxo species.[418] However, this conclusion cannot be extended to other catalytic systems since the preferred pathway is dependent on the ligand of choice and reaction conditions.

These oxidation reactions have also been applied to the kinetic resolution of secondary alcohols using oxygen as terminal oxidant[419] and to the alkene hydroarylation with

Scheme 40. Proposed Mechanism for the Aerobic Oxidation of Alcohols



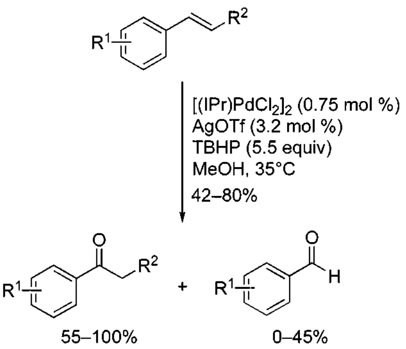
boronic esters (eq 75).[420] In this transformation, oxidative conditions are required for the oxidation of the alcoholic solvent to generate the active palladium(II) hydride species and for reoxidazing the palladium(0) to palladium(II) after the bond-forming process.



(75)

5.2.8.2. Wacker Oxidation and Related Transformations.

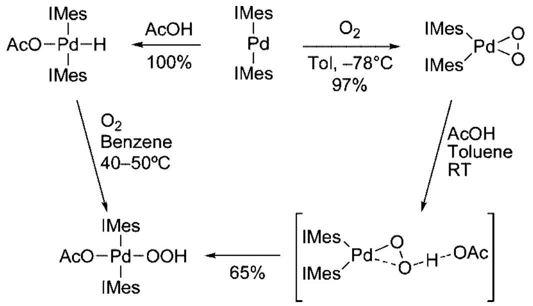
The palladium-catalyzed oxidation of terminal olefins to methyl ketones, or Wacker oxidation, is a common transformation even on an industrial scale.[421] However, the classic use of $CuCl_2$ as cocatalyst inherently limits the choice of ligands for the palladium center and leads to the formation of chlorinated byproduct.[421a] A highly efficient [(NHC)Pd] catalytic system was developed for this transformation by Sigman and co-workers.[422] A number of styrene derivatives were oxidized to the corresponding acetophenones under mild conditions (eq 76). It is important to note that, with this system, only internal olefins led to the significant formation of benzaldehyde derivatives, because of an undesired oxidative cleavage.



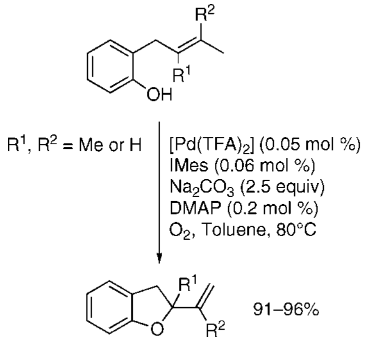
(76)

The authors proposed that $[(IPr)Pd(OH_2)_3 \cdot (OTf)_2 \cdot (H_2O)_2]$ is the actual catalyst because similar catalytic results were obtained directly from this complex. Moreover, mechanistic studies showed that TBHP rather than water acts as oxygen source in this process.

Scheme 41. Preparation of Peroxo and Hydroperoxo Complexes

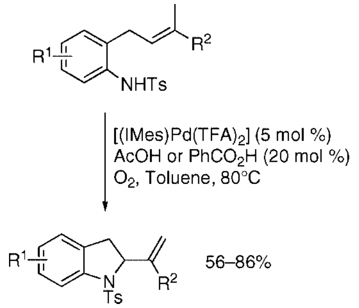


Alternatively, Wacker-type oxidative cyclization is a versatile approach for the construction of oxygenated stereocenters. The synthesis of a number of dihydrobenzofurans catalyzed by an in situ-formed carbene/palladium complex has been reported by Muñiz.[423] When $[Pd(TFA)_2]$ in combination with IMes was employed, high yields of pure cyclized products were obtained after simple workup (eq 77). Of note, palladium salts containing chloride or acetate ligands led to the formation of mixtures containing the desired product and its six-membered ring isomer.



(77)

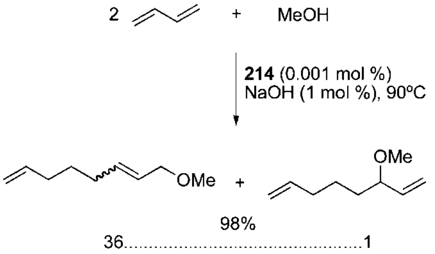
IMes was also the ligand of choice for the related intramolecular oxidative amination of alkenes.[424] In this case, a very closely related well-defined system was employed and the reaction was not limited to aromatic-tethered substrates (eq 78). Interestingly, the use of carboxylic acids as cocatalysts generally improved the reaction outcome. Even if the role of this additive remains elusive, it was proposed that the acid might react with palladium(0) species to generate palladium(II)-hydride derivatives, less prone to aggregation into inactive palladium black. Extensive mechanistic studies showed that this transformation generally proceeds through a *cis*-aminopalladation.[425] However, *trans*-aminopalladation is also possible and can become the major pathway depending on the reaction conditions, substrate, and catalyst. Remarkably, N-heterocyclic carbenes were found to be particularly efficient in promoting *trans*-aminopalladation processes.



(78)

5.2.9. Telomerization Reactions[426]

5.2.9.1. Telomerization of Dienes with Alcohols. Beller and co-workers first employed monocarbene–palladium(0) complexes **214** bearing a dvds group for the telomerization of butadiene with alcohols.[427] Unprecedented reaction rates in the reaction of butadiene and methanol were obtained, and in addition, better chemoselectivity and better linear to branched product ratios were observed when compared with phosphine-based systems (eq 79).[428]



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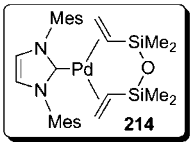
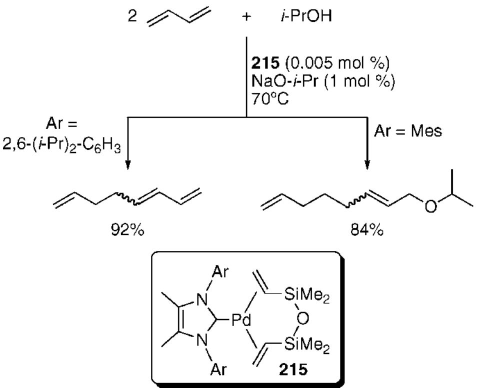


Having prepared diverse [(NHC)Pd(dvds)] complexes, the authors made a systematic structure/activity comparison for this telomerization reaction.[429] This study showed that electron-withdrawing substituents on the carbene backbone destabilize the precatalyst and therefore enhance its reactivity. These complexes permitted the use of primary and secondary alcohols as well as phenols and represent the first industrially viable catalytic system for palladium-catalyzed telomerization of butadiene with alcohols.[430]

Alternatively, the combination of IMes·HCl/[Pd(acac)$_2$] has shown a remarkable activity in the telomerization of isoprene with glycerol and PEG to efficiently yield new terpene derivatives.[431] The most outstanding feature of this catalytic system is the complete selectivity toward the formation of linear monotelomer products.

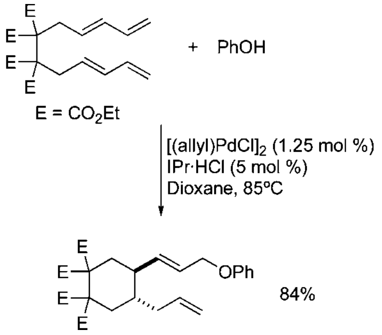
The reactivity of the palladium complexes can be finely tuned depending on the chosen ligand. With butadiene and isopropanol and under the same reaction conditions, different groups on the nitrogen atoms of the carbene ligand led to different major products (Scheme 42).[432] When Ar = mesityl, the linear alkoxyoctadiene was isolated in high yield, but the presence of diisopropylphenyl groups on the ligand directed the major formation of the corresponding octatriene. Even though this kind of compound is normally considered as a byproduct of the telomerization reaction, it is actually an interesting synthon.

Scheme 42. Telomerization versus Dimerization Reaction



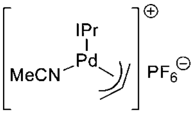
Similar shifts in reactivity between NHC ligands have been observed for the telomerization of isoprene with methanol. Whereas the presence of an IMes ligand on the palladium center led to the preferential formation of head-to-head telomerization products, SIPr-containing species promoted the trimerization of isoprene to produce sesquiterpenes.[433]

For the related cyclization/trapping of bis-dienes, it was found that IPr was somewhat superior to IMes.[434] This is unexpected since in the precedent examples IPr/SIPr ligands favored dimerization without alcohol trapping processes. Extensive optimization studies allowed for the reaction to proceed at 85 °C with 1.25 mol % palladium precursor (eq 80).



(80)

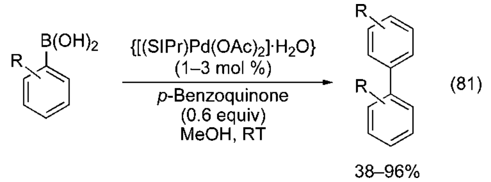
5.2.9.2. Telomerization of Dienes with Amines. Far less attention has been paid to the use of amines as nucleophiles in telomerization reactions. Nolan and co-workers first showed that well-defined cationic palladium complexes such as **216** were efficient catalysts for the telomerization of butadiene with amines under mild conditions.[435] In the case of primary amines, the concentration of the reactants and their steric hindrance dictated the formation of a mono- or bis-alkylated product. More recently, Beller and co-workers used palladium(0) complexes in this context.[436] In particular, complex **214**, also used for the telomerization of butadiene and methanol (see eq 79), allowed for catalyst loadings as low as 0.0005 mol % and furnished good yields of the corresponding linear telomerization product, which was formed exclusively even for primary amines. Furthermore, the reactions were faster in methanol, though it is a competitive nucleophile.

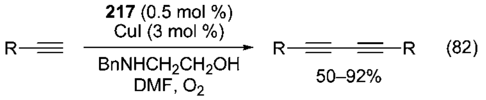


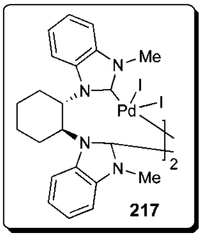
216

5.2.10. Miscellaneous Reactions

[(NHC)Pd] systems have been applied to different coupling reactions under oxidative conditions, such as the homocoupling of arylboronic acids[437] (eq 81) or terminal alkynes[438] (eq 82).

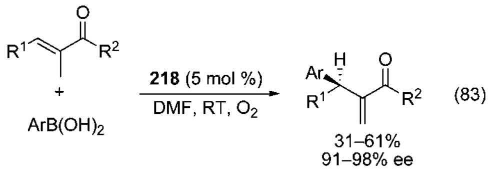


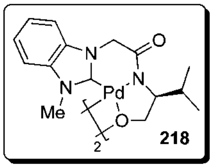




217

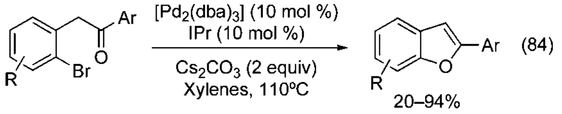
For these reactions, *p*-benzoquinone and oxygen, respectively, were used as oxidants to ensure catalyst turnover. Oxygen was also used for the oxidative Heck-type reaction of aryl boronic acids with acyclic alkenes catalyzed by **218** (eq 83).[439,440] Different NHC−amidate ligands as in **218** have also found application in the palladium-catalyzed hydrogen/deuterium exchange in hydrocarbons,[441] and the Strecker reaction of aldehydes and ketones.[442]





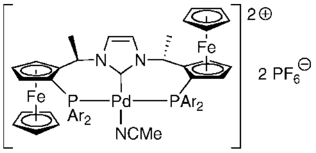
218

The synthesis of 2-arylbenzofurans via the ring closure of aryl 2-bromobenzyl ketones has been recently achieved in the presence of IPr/[$Pd_2(dba)_3$] (eq 84).[443] Nevertheless, the outcome of the reaction was strongly dependent on the nature of the aryl, although a clear trend could not be established.

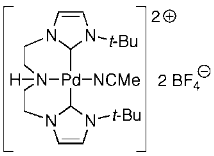


Several [(NHC)Pd] complexes have been investigated for the hydroamination of cyanoolefins (Chart 25).[444] Although very high yields were generally obtained with 2−5 mol % of these palladium complexes at room temperature, no or low asymmetric induction was achieved with catalysts **219** and **221**.

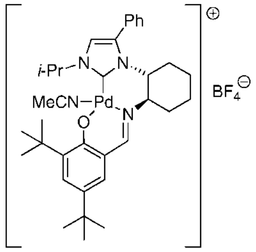
Chart 25. [(NHC)Pd] Complexes for Hydroamination Reactions



219, Togni, 2005

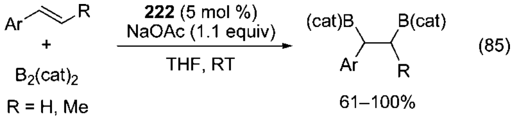


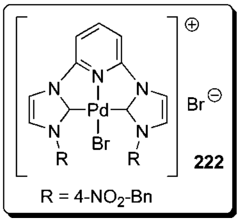
220, Douthwaite, 2007



221, Douthwaite, 2008

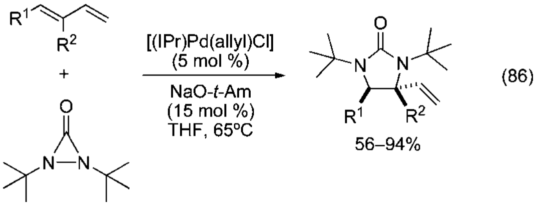
Finally, [(NHC)Pd] complexes like **222** have been reported to catalyze the diboration of aromatic alkenes.[445] The reactions proceeded in good conversions at room temperature in the presence of a mild base (eq 85). DFT calculations led the authors to propose that a heterolytic cleavage of the B−B bond, rather than oxidative addition of the diboron to the metal, was the key step for this transformation. The related diamination of conjugated dienes (and trienes) by a diaziridinone was achieved with [(IPr)Pd(allyl)Cl] at 65 °C (eq 86).[446]





222

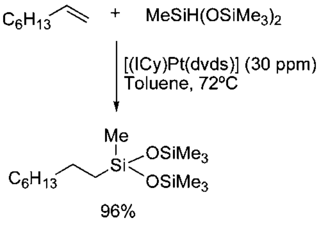
Less than 15 years after the first report of an NHC/palladium-mediated reaction,[7] these catalytic systems have been applied to a plethora of transformations. Even if their exploration remains at an early stage when compared with phosphorus-based systems, NHCs have certainly proven to be more than alternative ligands for cross-coupling reactions. Undoubtedly, more exciting applications are just waiting to be discovered.



5.3. Platinum

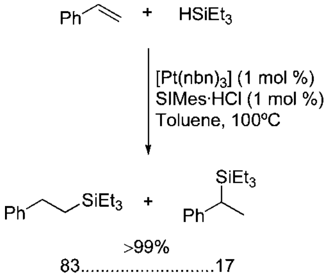
5.3.1. Hydrosilylation Reactions[140]

Mono-NHC/platinum complexes have shown outstanding catalytic activity in the hydrosilylation of unsaturated carbon−carbon bonds. In 2002, Markó and co-workers reported that dvds-containing platinum(0) complexes were active in the hydrosilylation of 1-octene with just 30 ppm catalyst loading (eq 87).[447] With this catalyst, the formation of byproduct and colloidal platinum was minimized, and only primary alkylsilane was produced. Furthermore, this catalytic system was tolerant to a number of functional groups such as free or protected alcohols, epoxides, ketones, and esters.[448] Related benzimidazolylidene-containing complexes also showed similar catalytic activity.[449]



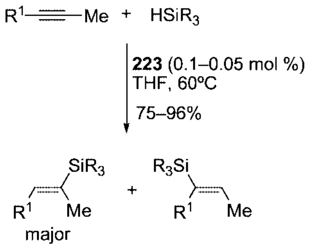
(87)

Complementarily, Elsevier and co-workers studied the activity of other olefin-coordinated platinum(0) complexes.[450] For a challenging substrate such as styrene, an in situ generated SIMes-containing complex was found to be the most effective catalyst (eq 88). Quantitative yields were obtained in hydrosilylated products, although as a mixture of β- and α-silylated products.



(88)

The exceptional activity of [(NHC)Pt(dvds)] complexes in the hydrosilylation of alkenes led naturally to their study in the reduction of alkynes. Among all the ligands tested, IPr was found to best meet the stereoelectronic requirements of the reaction.[451] The best results were obtained using allyl ether as olefinic ligand, and under optimized conditions, terminal and internal alkynes could be regioselectively hydrosilylated, up to 100:1 (eq 89).[452]



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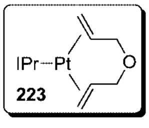

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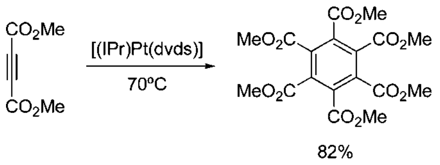
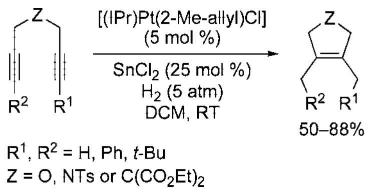
Interestingly, when [(IPr)Pt(dvds)] was reacted with an activated disubstituted alkyne the corresponding cyclotrimerized aryl derivative was obtained in good yields (eq 90).



(90)

5.3.2. Miscellaneous Reactions

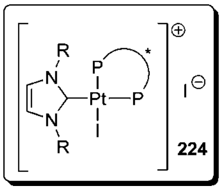
[(NHC)Pt(allyl)Cl] complexes were shown to be efficient catalysts for the reductive cyclization of diynes.[453] Under hydrogen atmosphere, a number of diynes could be converted into the corresponding 2,5-dihydrofurans, -pyrroles, and -cyclopentenes in fair to high yields (eq 91). Enynes could also be used as starting materials to afford the same reaction products, although the reaction temperature had to be raised to 70 °C. Of note, in the absence of NHC or upon phosphine coordination to the platinum center, no conversion was observed. When the reaction was carried out under D_2 atmosphere, a rare four-hydrogen addition to the substrate was evidenced. Furthermore, under mixed H_2/D_2 atmosphere, the formation of crossover products (among others) pointed toward heterolytic activation of hydrogen in this process.



(91)

Additionally, a carbene/diphosphine platinum(II) complex was shown to be active in the cycloisomerization reaction of a nitrogen-tethered enyne.[454] The most important feature of this transformation is that the catalyst is a chiral-at-metal square-planar platinum species, capable of promising chiral induction (eq 92).

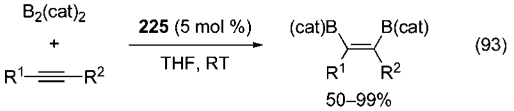
(92)



224

The activation of carbon−hydrogen bonds, a transformation often performed with platinum-based systems, has only met with limited success with [(NHC)Pt] complexes. Despite the straightforward stoichiometric C−H activation of imidazolium salts to generate bis-carbene/platinum(0) species,[455] poor results were obtained for the oxidation of methane to methanol[456] or the alkyne hydroarylation reaction.[381] On the other hand, [(NHC)Pt^0] complexes have been found to be catalytically active in the diboration of unsaturated C−C bonds.[457] *cis*-Alkene bis(boronate) esters were prepared from the corresponding alkynes in good to excellent yields with 5 mol % of [(NHC)Pt] catalyst (eq 93). Aromatic alkenes (including allylic sulfones) also yielded the corresponding bis(boryl)alkanes in fair yields under identical reaction conditions.

The same NHC−platinum complex was found to be active in the hydroboration of alkenes.[458] However, for the transformation of aromatic alkynes, more interesting substrates in this context, a related complex (**226**) was found to be optimal (eq 94). The presence of a platinum catalyst allowed the reaction temperature to be lowered with respect to the uncatalyzed version. The selectivity, though, was only moderate under these conditions, and styrene derivatives were also formed as main byproduct. Alternatively, this catalytic system could be employed in a tandem hydroboration/Suzuki coupling reaction, although low yields were obtained in this case.



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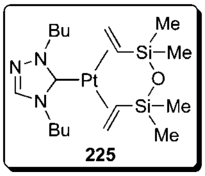

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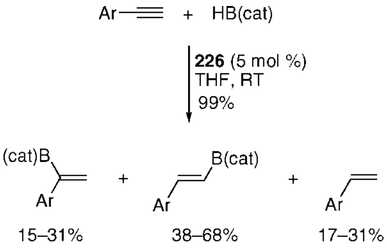

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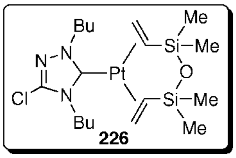


226

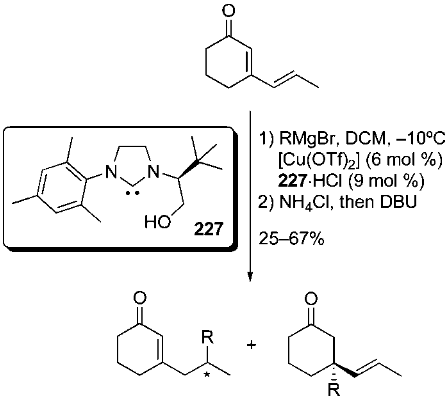
6. Group 11: Copper, Silver, and Gold

6.1. Copper

[(NHC)Cu] species have been known in the literature since 1993,[459] and their first application in homogeneous catalysis, in conjugate additions more precisely, appeared in 2001.[460] Eight years later, this is a very active field of research. Actually, the preparation and application in catalysis of [(NHC)Cu] complexes have been reviewed very recently.[461] Therefore, only an update on the latest advances will be presented in this section.

These species are not only of interest in the context of catalysis. For instance, [(NHC)Cu] complexes have displayed a remarkable toxicity against human tumor cells.[462] NHC−copper complexes are also good candidates for processes of important industrial interest such as reduction of CO_2 to CO[463] or hydrogen storage.[464] It is also significant that studies dealing with structure and molecular orbitals of such derivatives revealed the existence of non-negligible π-interaction between copper (and other group 11 metals) and NHC ligands,[465] which, at the time, shattered the general assumption that NHC ligands were pure σ-donors.

Scheme 43. [(NHC)Cu]-Catalyzed 1,4-Conjugate Addition



R = Et	1	99
R = Bu	4	96
R = Butenyl	5	95
R = *i*-Pr	35	65
R = *i*-Bu	44	56

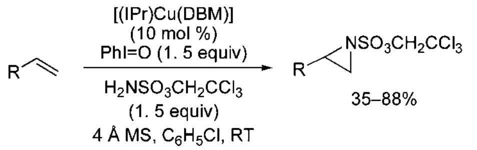
6.1.1. Conjugate Addition Reactions

Since Woodward's pioneer work on [(NHC)Cu]-catalyzed 1,4-addition of diethylzinc to enones,[460] this transformation has been a very active field of study.[466] The most recent advances in this context include the enantioselective conjugate addition of alkyl and aryl aluminum reagents to cyclic enones to generate all-carbon quaternary stereogenic centers[467] or the regiodivergent copper-catalyzed 1,4- versus 1,6-conjugate addition of Grignard reagents.[468] Whereas with different phosphoramidites 1,6-addition products were exclusively formed, NHC ligands led to the preferential formation of 1,4-adducts from conjugated dienones (Scheme 43). Remarkably, this observation corresponds to a conjugate addition at the most hindered position to generate an all-carbon stereogenic center with high enantioselectivity.

On the other hand, the use of NHC in the addition of diethyl zinc to *N*-sulfonylimines[469] and aldehydes[470] has also been reported.

6.1.2. Carbene Transfer Reactions

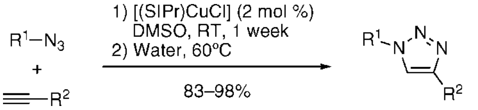
Considering the remarkable activity of [(NHC)Cu] complexes, and [(IPr)CuCl] in particular, in the cyclopropanation of alkenes,[471] it was natural to broaden their scope to related reactions such as aziridination. Surprisingly, two applications in total synthesis[472] were reported before a proper methodological study.[473] Under optimized conditions, a number of aziridines were prepared in moderate to high yields in the presence of 10 mol % copper catalyst (eq 95). The most remarkable features of this catalyst are that the nitrene was generated in situ and that a large excess of the starting material was not required. In this context, phenoxyimine-functionalized NHC-containing copper complexes have also been studied, and moderate activities were observed at room temperature in the presence of PhI═NTs as nitrene source.[474]



(95)

6.1.3. [3 + 2] Cycloaddition Reactions

The copper-catalyzed reaction of organic azides and terminal alkynes to yield 1,2,3-triazoles has attracted increasing attention and become the best Click reaction to date.[475] The screening of [(NHC)CuX] complexes for this transformation allowed for the reaction to proceed under neat conditions with only 0.8 mol % copper catalyst.[476] Furthermore, this catalytic system allowed for the unprecedented use of internal alkynes in this context.[477] More recently, this family of complexes has been reported to be efficient latent catalysts under simple reaction conditions.[478] Whereas a number of azides and alkynes did not react in DMSO in the presence of [(SIPr)CuCl] under ambient conditions, the reactions proceeded smoothly at 60 °C upon addition of water (eq 96). This study should broaden the applications of this transformation, especially in biology and material science.



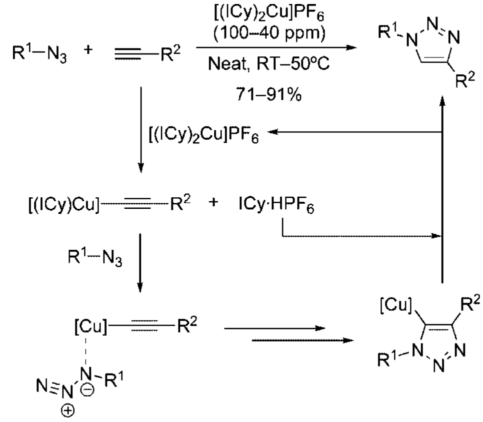
(96)

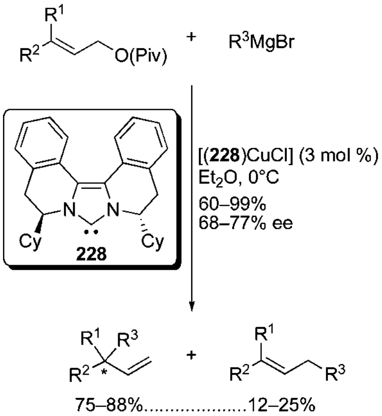
Alternatively, another family of [(NHC)Cu] complexes was shown to be active even at very low catalyst loadings.[479] With only 40−100 ppm of $[(ICy)_2Cu]PF_6$, an array of triazoles could be efficiently prepared (Scheme 44). Mechanistic studies showed that one of the NHC ligands on the copper center acts as a base, deprotonating the starting alkyne to generate a copper acetylide and start the catalytic cycle. The enhanced catalytic activity of this system was attributed to the efficiency of the formed azolium salt to protonate the copper triazolide intermediate, closing the catalytic cycle (Scheme 44).

6.1.4. Allylic Alkylation Reactions

As is the case for the conjugate addition, binaphthol-derived NHC ligands developed by Hoveyda and co-workers have been shown to be particularly efficient for allylic alkylation reactions.[480] However, the search for new ligand architectures is continuous. Thus, Hong and co-workers recently reported the activity of biisoquinoline-based chiral NHCs in this context.[481] Under optimized conditions, good to excellent yields and enantioselectivities around 75% ee were obtained (eq 97). The observed regioselectivity (i.e., ~5:1) was in favor of the γ product, except when an aromatic Grignard reagent was employed. In this case, the α isomer represented 98% of the final products, pointing toward distinct mechanistic pathways.

Scheme 44. $[(NHC)_2Cu]X$-Catalyzed [3 + 2] Cycloaddition Reaction

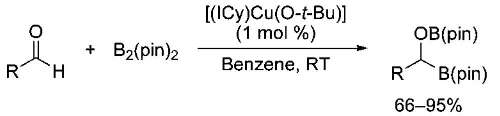




(97)

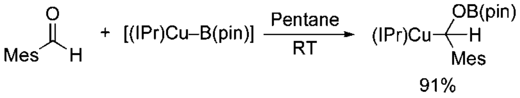
6.1.5. Diboration Reactions and Related Transformations

Sadighi and co-workers reported in 2006 that [(ICy)Cu(O-*t*-Bu)] was a performing catalyst for the 1,2-diboration of aldehydes (eq 98).[482] The actual active species, [(NHC)Cu(boryl)], was shown to be formed under these catalytic conditions.[483]



(98)

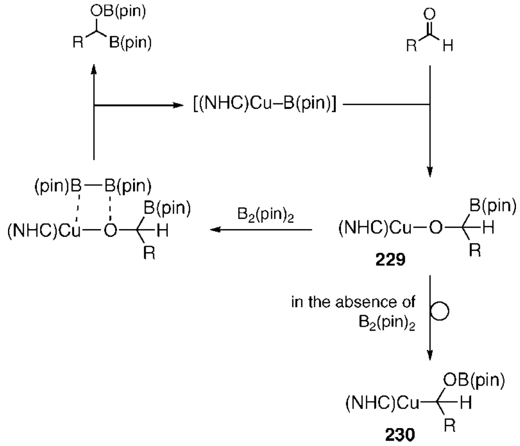
However, when an aldehyde was reacted with a stoichiometric amount of this species, a complex containing a Cu−C bond (and not Cu−O as expected) was formed (eq 99).



(99)

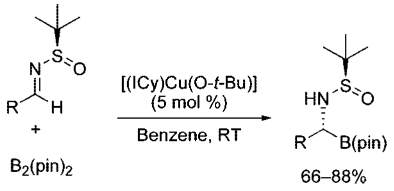
DFT calculations pointed toward aldehyde insertion into the Cu−B bond to form a Cu−O−C species **229** as the initial step of the catalytic cycle (Scheme 45).[484] This intermediate would undergo a σ-bond metathesis with the diborane to generate the reaction product and close the cycle. Additionally, it

Scheme 45. Mechanism of the [(NHC)Cu]-Catalyzed Diboration Reaction



would be only in the absence of diborane that **229** could undergo isomerization into the thermodynamic complex **230**.

On the other hand, the extension of this methodology to aldimines allowed for the preparation of α-amino boronic acid derivatives in good yields and excellent diastereoisomeric ratios of at least >95:5 (eq 100).[485] In these reactions, the sense of induction is consistent with an open transition state with the boryl group delivered to the least hindered face.

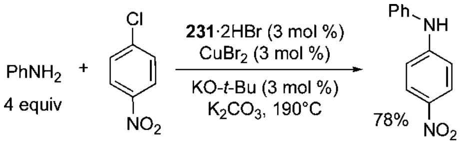


(100)

Finally, [(SIMes)CuCl] has recently been applied to the hydroboration of styrene derivatives.[486] High to excellent yields in the corresponding boronates were obtained when the reactions were carried out at room temperature in the presence of 0.5−5 mol % catalyst.

6.1.6. Cross-Coupling Reactions

NHC ligands have only been scarcely studied for copper-catalyzed cross-coupling reactions. The first example was reported in 2004, when a biscarbene−copper complex was found to be active and selective in the monoarylation of aniline (eq 101).[487] However, biphenyldialkylphosphines delivered higher conversions under identical reaction conditions.



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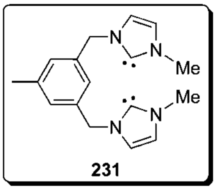
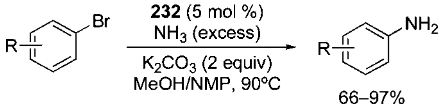


231

On the other hand, NHC/copper complexes have been reported to be efficient catalysts for the preparation of anilines via the coupling of aromatic and heteroaromatic bromides with ammonia.[488,489] The reactions proceeded in good to high yields with 5 mol % catalyst at 90 °C (eq 102). Even if the reaction was less effective with electron-rich substrates, these conditions were compatible with different functional groups such as nitro, cyano, trifluoromethyl, amide, and ketone.



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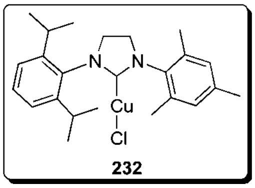

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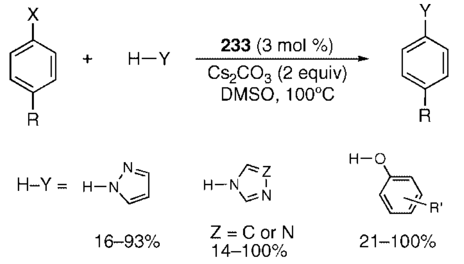
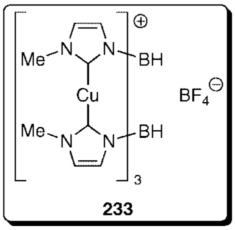
Scheme 46. [(NHC)Cu]-Catalyzed Cross-Coupling Reactions





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Additionally, a triscarbene-containing cationic complex has been employed as catalyst for the arylation of azoles, amides, and phenols.[490] Even if aryl iodides and bromides were mainly screened, this catalytic system could activate several aryl chlorides to produce the corresponding coupling products in around 50% yield (Scheme 46). Remarkably, all reactions could be carried out under identical conditions.

6.1.7. Miscellaneous Reactions

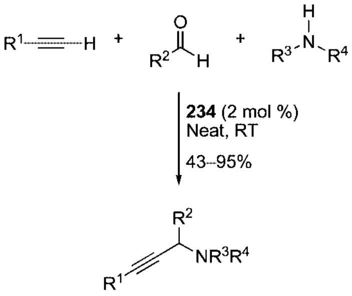
[(IPr)CuCl] has shown a remarkable activity in the carbonylation of boronic esters.[491] Hence, these boron reagents were converted into their corresponding carboxylic acids in refluxing THF in high to excellent yields (Scheme 47). The proposed actual active species is the in situ formed [(IPr)Cu(O-*t*-Bu)]. Its reaction with a boronic ester would generate a [(IPr)CuR] intermediate that would undergo a nucleophilic addition to CO_2 to produce a copper carboxylate, followed by a σ-metathesis with the base to close the catalytic cycle (Scheme 47). Remarkably, the authors could isolate and fully characterize every postulated intermediate in this reaction using two model substrates.

A combination of [(IPr)CuI] and IPr·HCl has shown remarkable activity in the double carbonylation of aryl iodides and secondary amines.[492] Interestingly, in this case a $[(NHC)_2Cu]$ species was postulated as the active species.

[(IPr)CuF] has been reported to catalyze the allylation of an aldehyde at room temperature (Scheme 48).[493] This reaction, which proceeds by a transmetalation mechanism, is possible thanks to the outstanding ability of the NHC complex to form organocopper compounds from a wide variety of silanes.

Related $[(NHC)Cu(CF_3)]$ complexes have been recently prepared and applied to the trifluoromethylations of aromatic iodides and bromides, albeit with stoichiometric amounts of copper.[494]

A silica-immobilized [(NHC)Cu] complex has been reported to mediate the three-component coupling of aldehydes, alkynes, and amines to yield the corresponding propargyl amines (eq 103).[495] Not only did the reactions proceed smoothly in the absence of solvent at room temperature for a variety of aromatic and aliphatic substrates but also the catalyst could be recycled and reused for up to ten cycles.



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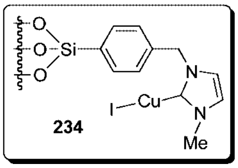

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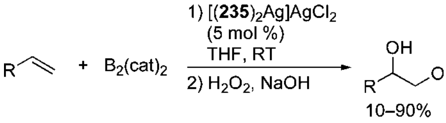
6.2. Silver

[(NHC)Ag] Complexes have attracted important attention as potential pharmaceuticals[496] or NHC transfer agents in the preparation of carbene complexes.[497] However, their application in catalysis remains so far scarcely explored, and the first report in this field only appeared in 2005. One year earlier, Hedrick and Waymouth had reported the activity of silver/NHC systems in the living polymerization of lactide.[498] Nevertheless, these complexes simply served as delivery agents of free NHCs, the actual active species in this reaction.[11]

The first true application in catalysis of [(NHC)Ag] complexes was the diboration of alkenes, reported by Peris and Fernandez.[499] A well-defined silver complex was shown to mediate the transformation of terminal alkenes at room temperature (eq 104). Even if only low conversions were obtained with disubstituted or electron-poor alkenes, it should be noted that no reaction was observed when using phosphine or diphosphine ancillary ligands. Disappointingly, no chiral induction was observed with this catalytic system nor with other related NHC ligands.[500]



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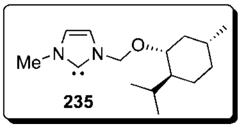

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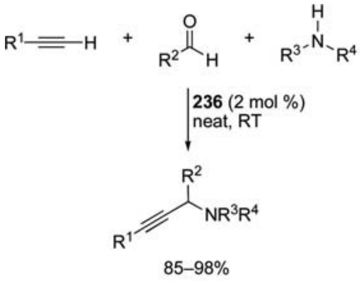
The silver-catalyzed hydrosilylation[501] of aldehydes is also possible with NHC-based systems.[502] However, just one example was reported by Stradiotto and co-workers in which benzaldehyde was reduced in 94% yield in the presence of 3 mol % AgOTf and 20 mol % NHC ligand.

Wang and co-workers reported the efficient coupling of aldehydes, alkynes, and amines to yield the corresponding propargyl amine catalyzed by a PS-supported [(NHC)Ag] complex.[503] Similarly to their copper-based system,[495] very high yields and reusabilities were observed when neat reactions were carried out at room temperature (eq 105).



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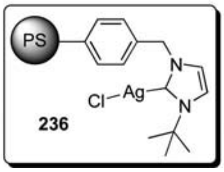

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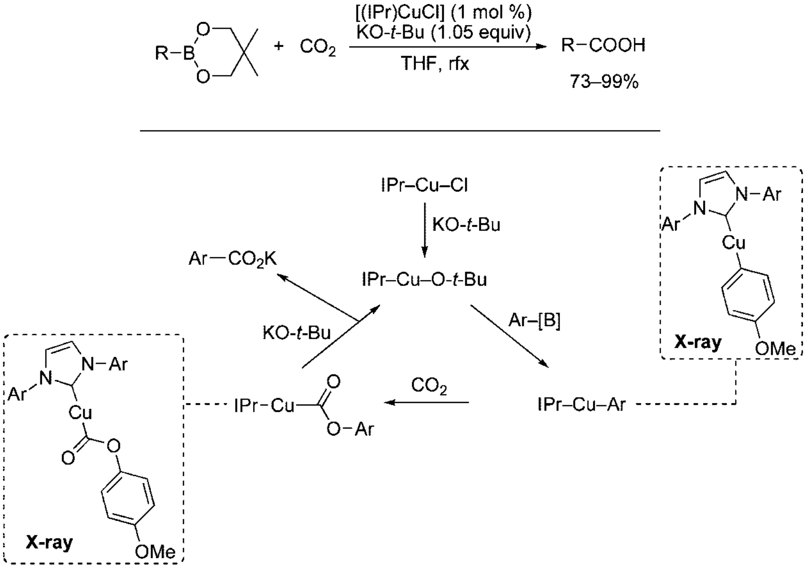
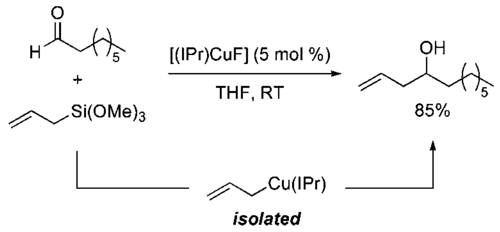
[(IMes)AgCl] has been reported to catalyze the regioselective carbomagnesiation of terminal alkenes with alkyl

Scheme 47. [(NHC)Cu]-Catalyzed Carboxylation of Boronic Esters



Scheme 48. [(NHC)Cu]-Catalyzed Allylation Reaction



Grignard reagents in the presence of 1,2-dibromoethane as reoxidizing reagent.[504] When enynes were used as substrates, good regioselectivities were also obtained, provided an electrophile was present in the reaction media to trap the propargyl and allenyl Grignard intermediates (Scheme 49). However, a related NHC complex did not show any activity in the carbostannylation of alkynes.[505]

Despite the wide use of [(NHC)Ag] complexes in other fields, their use in homogeneous catalysis is still certainly underdeveloped. Considering their stability and straightforward preparation, we foresee an increasing amount of applications in the near future for these families of compounds, especially considering the growing interest for Ag-based homogeneous catalysis.[506]

6.3. Gold

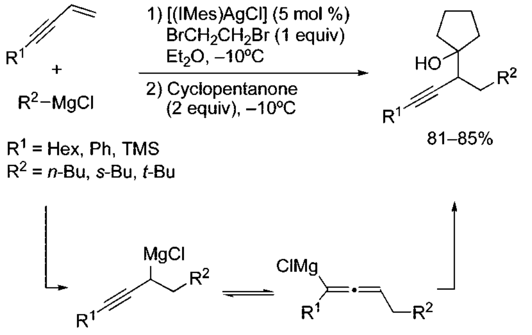
Long thought to be catalytically inert as a late transition metal,[507] gold started to attract the attention of the "homogeneous catalysis community" only recently.[508] As early as 1973, the first diaminocarbene−gold(I) complex was isolated,[509] but it is only recently that NHC−Au chemistry has gained in importance, benefiting from straightforward synthetic routes to [(NHC)Au^{I}] complexes developed lately.[510] NHCs have allowed for important breakthroughs in the isolation of unstable gold species, such as the first gold(I) fluoride and gold(I) hydride by Sadighi.[511] [(NHC)Au] complexes have proven interesting also as potential drugs[512] and luminescent devices[513] and have allowed important information to be gathered on the nature of the metal−NHC bond.[514]

Gold homogeneous catalysis has become in the past few years a topic of intense research.[515] Alongside ligandless systems, phosphines and NHCs are the most employed ligands in this field. Since a comprehensive review that includes references up to early 2008 dealing with N-heterocyclic carbenes in gold catalysis was recently published,[516] we will focus, in this section, on the most recent applications of NHC−gold catalysts. Of note, reports making use of a NHC-containing gold catalyst only during optimization studies are mentioned here for the reader's convenience and will not be discussed later.[517]

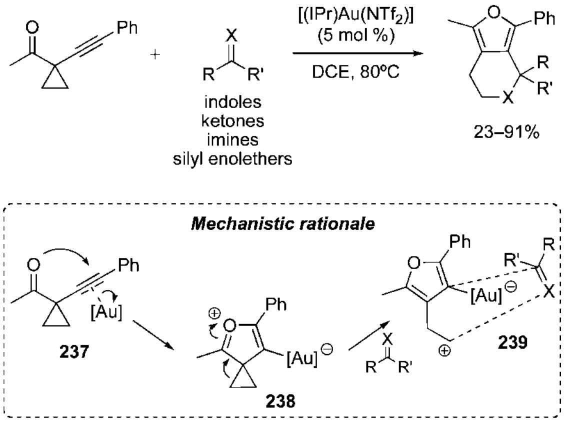
6.3.1. Cycloisomerization Reactions

Prior to 2008, cationic [(NHC)Au] compounds were notably shown to catalyze a number of "classical" enyne skeletal rearrangements[518] involving the formation of an auracarbene.[519,520] More recently, Zhang and co-workers, replacing the olefin of an enyne by a carbonyl group, took advantage of the particular reactivity of ynones in the presence of gold[521] to generate interesting dipoles. A first approach allowed for the construction of furan-fused polycyclic compounds (Scheme 50).[522] Gold-promoted cycloisomerization of the ynone scaffold (**237** → **238**) triggers the opening of the adequately placed cyclopropane ring, generating an all-carbon 1,4-dipole **239** that further reacts with a number of dipolarophiles.

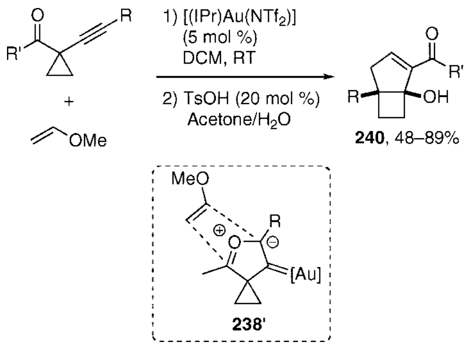
Scheme 49. [(NHC)Ag]-Catalyzed Carbomagnesiation of Enynes



Scheme 50. Gold-Catalyzed [4 + 2] Cycloadditions



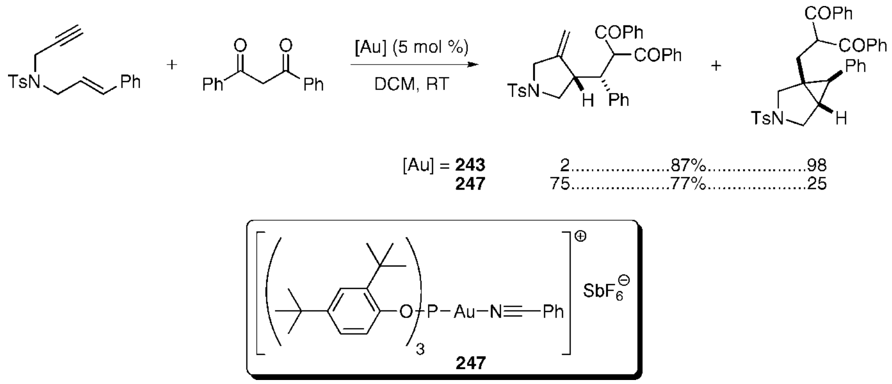
The same research group observed an interesting shift in reactivity when ethyl vinyl ether was used as dipolarophile.[523] The electron-rich olefin preferentially reacts with intermediate **238′** (i.e., a resonance structure of **238**) to form a bridged bicyclic ether, which, upon rearrangement and cyclopropyl ring enlargement, leads to hydroxy enones **240**, after acidic workup (eq 106). This method represents an attractive entry to the synthesis of compounds possessing the highly strained bicyclo[3.2.0]heptene skeleton.



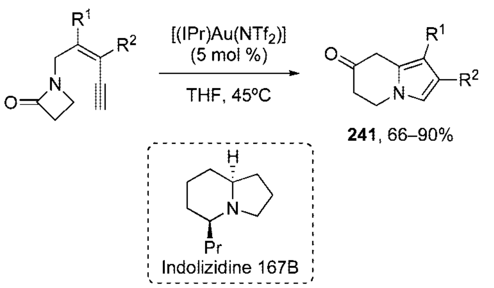
(106)

Subsequent studies by Zhang making further use of [(IPr)Au(NTf$_2$)] focused on the reactivity of β-lactams bearing a pendant conjugated enyne group.[524] It was proposed that, upon alkyne activation by the cationic [(IPr)Au] catalyst, the lactam nitrogen would add to the C≡C bond and trigger an intramolecular rearrangement producing dihydroindolizinones **241** (eq 107). As for the two aforementioned transformations (see Scheme 50 and eq 106), optimization revealed the superiority of the IPr ligand over PPh$_3$ in these

Scheme 51. NHC and Phosphite Ligands in the Addition of Diketones to Enynes



reactions. Of note, the β-lactam cyclization was applied to the formal total synthesis of indolizidine 167B (eq 107).



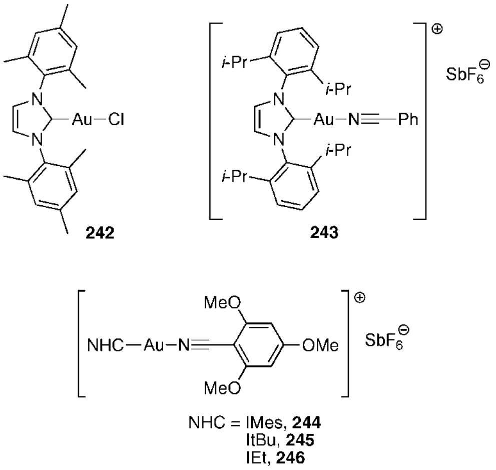
(107)

Echavarren and co-workers, following their initial lead in [(NHC)Au]-catalyzed enyne cycloisomerization,[525] synthesized a number of cationic gold(I) complexes and studied their activity in the intermolecular addition of carbon nucleophiles to enynes.[526] Complexes **242**–**246** (Chart 26) displayed good catalytic activities in this addition of electron-rich arenes and other activated *C*-nucleophiles,[527] the IPr-containing **243** yielding the most interesting results.

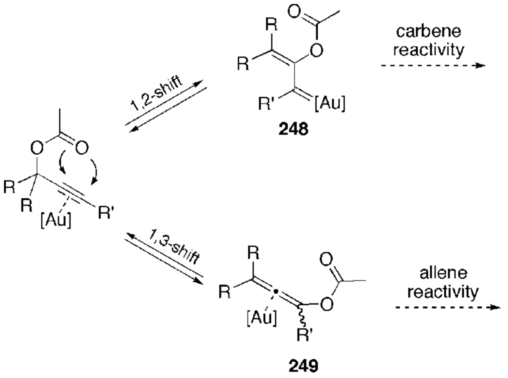
Remarkably, in specific cases where two types of cycloisomerized products could be obtained, NHC and phosphite ligands were found to afford opposite selectivity (Scheme 51).

Finally, an interesting [4 + 3] cycloaddition of allenedienes making use of [(IPr)AuCl] was disclosed very recently.[528] In this particular case, it was shown that the [(NHC)Au] complex efficiently catalyzed the reaction at room temperature while prolonged heating at 110 °C in toluene was required with $PtCl_2$ as catalyst.[529]

Chart 26. Structure of [(NHC)Au] Complexes Active in Enyne Cycloisomerization



Scheme 52. Gold-Promoted Reactivity of Propargylic Acetates



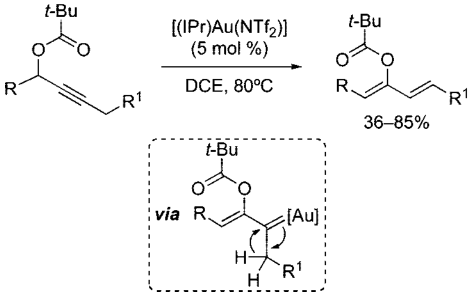
6.3.2. Reactivity of Propargylic Esters and Related Substrates

Initially considered as part of the "enyne cycloisomerization chemistry", propargylic esters have recently gained their own position in the field of gold catalysis. This is mainly due to the ability of the ester moiety to undergo 1,2- or 1,3-migration upon alkyne activation by a π-carbophilic metal such as gold, leading to an array of very diverse products (Scheme 52).[530]

DFT studies by Cavallo and co-workers showed that the starting alkyne, the Au–carbene **248** resulting from the 1,2-OAc shift, and the allene **249** from the 1,3-OAc shift are all in rapid equilibrium.[531] An illustration of this concept can be found in the formation of products **251**–**253** from dienyne **250**,[532] where NHCs proved more selective than phosphines for the formation of **253** (Scheme 53).[533,534]

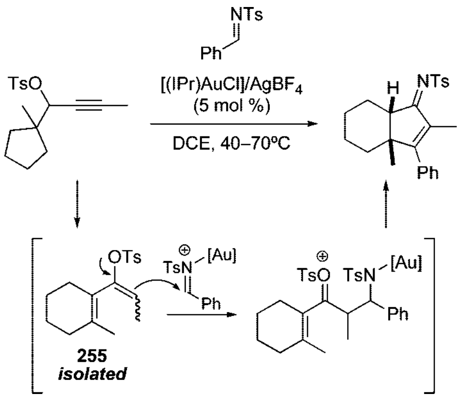
In a recent study, it was shown that **251** and **252** were likely formed via a 1,2-migration of the acetate, while **253** would be produced via initial 1,3-OAc migration.[535] Based on combined experimental and theoretical studies, an unprecedented 1,3-OAc shift/allene–ene cyclization/1,2-OAc shift sequence was proposed (Scheme 54). Supporting this hypothesis, which translates the apparent 1,2-OAc shift from **250** to **253** in a 1,3-OAc migration followed by a 1,2-OAc "retromigration", the cyclization of allenenyl acetate **254** afforded a greater proportion of **253** over **251** and **252** (Scheme 54).

Intermediates **248** and **249** (see Scheme 52) generally only constitute a first step toward the construction of more complex structure upon inter- or intramolecular reaction with different chemical groups. Nevertheless, if no adequate functional group is present, carbene **248** can be trapped by 1,2-H migration, affording 2-acyloxy-1,3-dienes (eq 108).[536] This reaction requires the presence of a propargylic proton opposite to the propargylic ester and is not tolerant to functional groups such as alkenes, alcohols, or aryls, which react more rapidly with **248** or **249**.[537] Despite these considerations, it remains a straightforward method for the construction of conjugated dienes.[538] Of note, the IPr carbene proved more efficient in this transformation than IMes, which yielded an important amount of conjugated enone.[539]



(108)

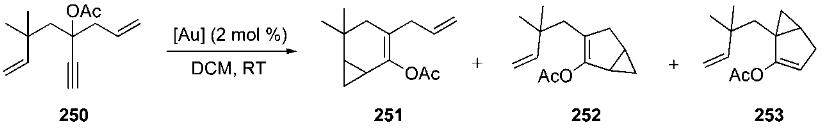
Other functional groups have been found to participate in this migration process.[540] Notably, González and co-workers have reported the successful involvement of propargylic tosylates[541] in an unsual [4 + 1] cycloaddition with imines catalyzed by [(IPr)AuCl].[542] The net result of this reaction is the formation of conjugated cyclopentimines after incorporation of the imine moiety and loss of the tosylate (eq 109). The authors, based notably on the isolation of diene **255**, proposed a mechanism involving a dual activation by the gold catalyst. Hence, after π-activation of the alkyne leading, upon 1,2-shift of the tosylate, to the formation of a 1,3-diene, the gold catalyst would be released and would promote nucleophilic addition of the diene through σ-activation of the imine. Subsequent rearrangements and Nazarov cyclization would produce the cyclopent-2-imines.



(109)

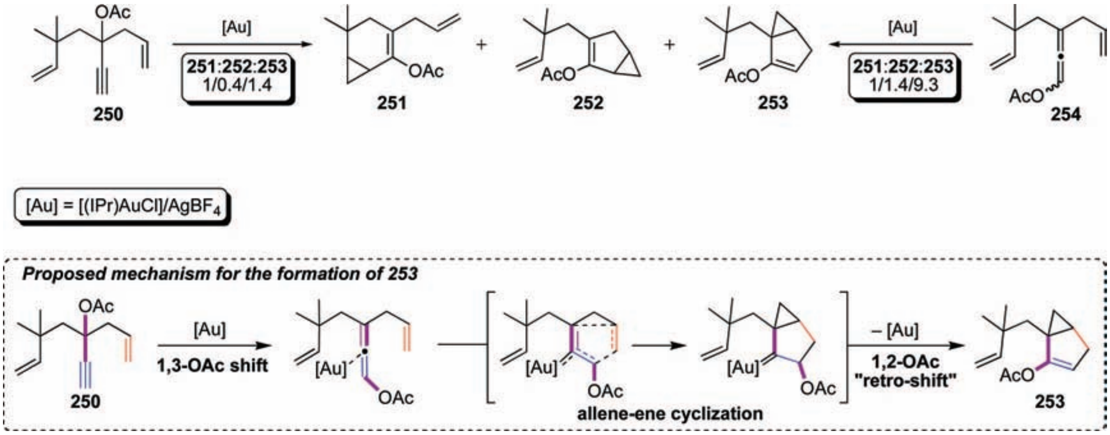
Allylic esters, even though less studied than their propargylic counterparts, have received increased attention lately in the context of gold catalysis.[538b,543] The combination [(IPr)AuCl]/AgBF$_4$ was notably found to catalyze efficiently the [3,3] rearrangement of a variety of allylic esters.[544] A subsequent study by the same group used this allylic rearrangement as a benchmark reaction to evaluate the catalytic activity of a series of cationic NHC−gold(I) complexes (Scheme 55).[545] Complexes **256**−**261** proved all active to some extent. Of interest, this study allowed for a strict comparison of both the counteranion and the neutral ligand bound to the gold center in addition to the NHC. The difference between weakly coordinating perfluoro anions was found to be negligible (compare **256**−**259**). On the other hand, the nature of the neutral ligand greatly affected the reactivity. While complexes **256**−**260**, bearing acetonitrile, required 48 h to reach high conversion, the norbornadiene gold catalyst **261** needed 5 days to reach a lower conversion. The pyridine-containing complexes **262**−**264**[546] did not yield any trace product, even after 10 days. The authors rationalized these observations by the necessity for the gold center to free a coordination site in order to bind to the olefin. A correlation between the catalytic activity and the affinity of a given ligand for the cationic gold(I) atom can therefore be

Scheme 53. Cycloisomerization of Enyne 250

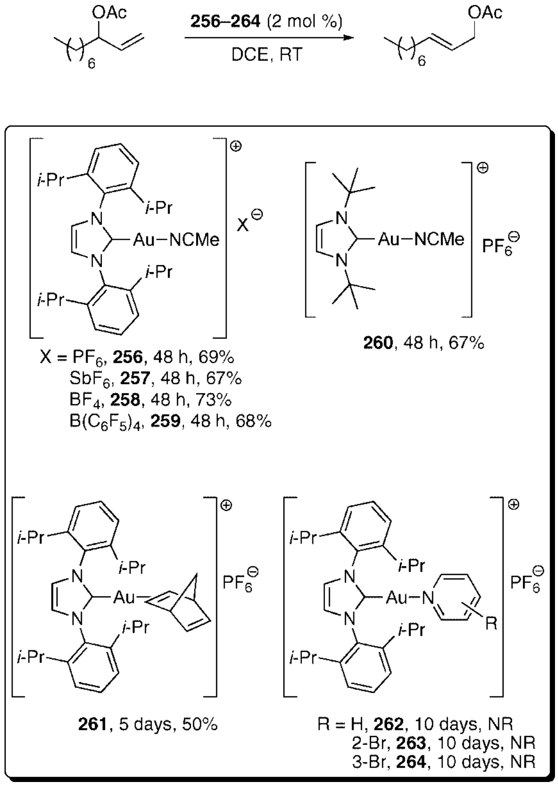


	251	252	253
[(Ph$_3$P)AuCl]/AgBF$_4$	49%	5%	10%
[(IPr)AuCl]/AgBF$_4$	30%	12%	42%

Scheme 54. [(NHC)Au]-Catalyzed Cycloisomerization of Enyne versus Allenene

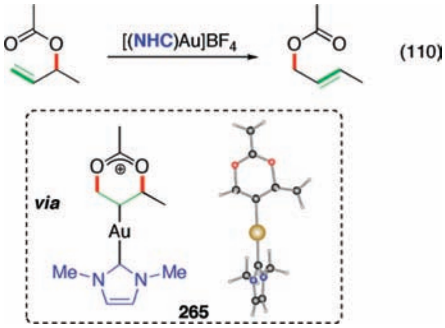


Scheme 55. [(NHC)Au(L)]X-Catalyzed Allylic Rearrangement



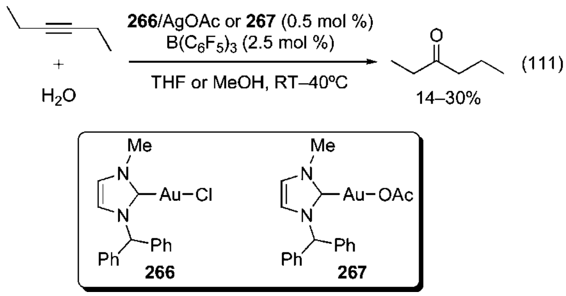
envisioned. In this study, the strength of the Au−pyridine bond was notably highlighted. Of interest also in this report, the authors observed the decomposition of a cationic NHC−gold species through P−F activation, leading to the isolation of a rare PF_4-containing complex {(μ-PF_4)[(IPr)Au]$_2$}PF_4.[547] This unusual observation is evidently of high relevance for catalytic applications since the vast majority of counteranions used in cationic gold(I) homogeneous catalysis is made of perfluoro anions, such as PF_6^-.

Of note, the mechanism of the reaction, proposed to be a cyclization induced rearrangement,[548] was recently the subject of a DFT study by Maseras and co-workers.[549] These calculations, where an NHC was placed as ancillary ligand on gold, supported coordination of the gold center to the olefin,[550] and formation of a cyclic oxonium **265** (eq 110). Based on their results, the authors ruled out the possibility of a mechanism involving ionization of the allylic ester.



6.3.3. Hydrofunctionalization of Alkynes, Allenes, and Alkenes

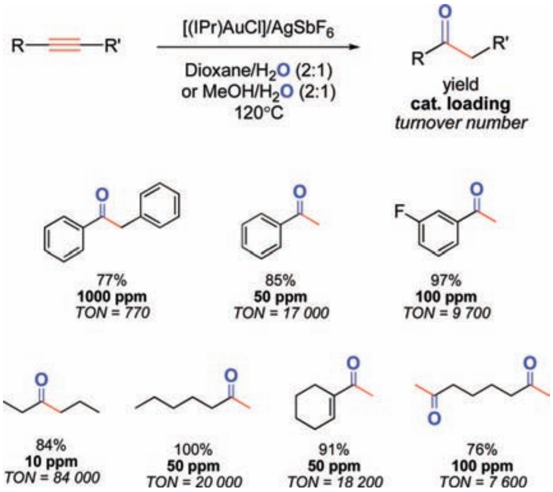
6.3.3.1. *O*-Nucleophiles.[551] The addition of the simplest *O*-nucleophile (i.e., water) to alkynes was the first application of NHC ligands in gold catalysis.[552] It is not surprising since, regardless of the ligand, the alkyne hydration reaction[553] has become a benchmark test for new gold catalysts,[554] which can beneficially replace toxic mercury salts. In the context of NHCs, this hydration reaction was first reported by Herrmann in 2003 using complexes **266** and **267** (eq 111).[555] Despite modest results, it provided a proof-of-concept for the use of NHCs in homogeneous gold catalysis.



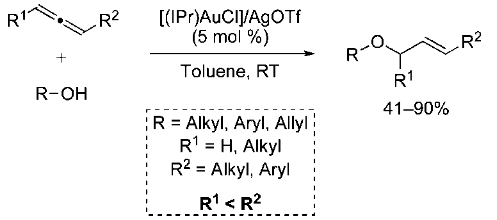
The recent interest in gold homogeneous catalysis arises mainly from the increased molecular complexity usually obtained in one step from simple (poly)unsaturated precursors. This aspect has somewhat overshadowed a crucial feature of any catalytic system: the catalyst loading.[556] Typically, gold-catalyzed reactions are carried out with 1−5 mol % gold complex. In this regard, alkyne hydration is the most studied reaction at low loadings, and NHCs recently provided the most efficient system to date. Hence, [(IPr)AuCl] allowed for the use of only 10−100 ppm of gold in the hydration of a wide array of alkynes (Scheme 56).[557] Screening of different NHC ligands demonstrated the superiority of IPr over IMes and ItBu under these acid-free conditions. In addition to its efficiency at very low catalyst loadings, the main feature of this system lies in its high versatility, allowing for the hydration of both terminal and internal alkynes possessing any combination of alkyl and aryl substituents (alkyl/H, aryl/H, alkyl/alkyl, alkyl/aryl, and aryl/aryl). Of note, preliminary mechanistic studies revealed that two distinct mechanisms are probably at play in this reaction as a function of the solvent (i.e., MeOH versus 1,4-dioxane).

[(NHC)AuCl] complexes have also been shown to catalyze efficiently the much less studied hydration of allenes. Wiedenhoefer and co-workers disclosed that the combination of 5 mol % [(IPr)AuCl] and AgOTf in dioxane was optimal for this reaction, leading in fair selectivity to allylic alco-

Scheme 56. Hydration of Alkynes at Low Catalyst Loadings



hols.[558] Using a similar catalytic system, the intermolecular hydroalkoxylation of allenes was reported by the same group (eq 112).[559] Excellent regioselectivity was obtained for the addition of the alcohols at the less hindered terminal carbon of the allene, providing a straightforward entry to allylic ethers.



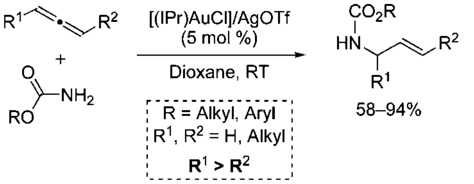
(112)

Closely related to NHCs, P-heterocyclic carbene ligands (PHCs) were recently reported to form stable complexes of the type [(PHC)Au(O-*t*-Bu)], which were found to be active in the addition of phenol and methanol to acrylonitrile.[560]

6.3.3.2. *N*-Nucleophiles.[561] The hydroamination of unsaturated carbon–carbon bonds is one of the most efficient methods for C–N bond formation.[562] Nevertheless, the use of simple ammonia is still a great challenge in this reaction.[489] A real breakthrough in this area came from the use of cyclic alkyl amino carbene (CAAC)[563] by Bertrand and co-workers. Complex **268**, which showed excellent activity in the gold-catalyzed synthesis of allenes from terminal alkynes and enamines,[564] proved efficient for the ammonia addition to 3-hexyne (Scheme 57).[565] The use of the more stable **269** in the presence of K[B(C_6F_5)$_4$] allowed for comparable results. Interestingly, the authors isolated the ammonia adduct **270**, which also proved efficient in this catalytic hydroamination.

The scope of the reaction was tested with alkynes, diynes, and allenes.[566] Addition of ammonia to 1,3- and 1,5-diynes resulted in the formation of pyrrole derivatives (Scheme 57). Of note, mechanistic studies led to the proposal of an insertion mechanism rather than an outer-sphere attack of ammonia onto a gold-activated alkyne.

Capitalizing on their initial results in the [(IPr)AuCl]-catalyzed intramolecular hydroamination of alkenes,[567] Widenhoefer and co-workers developed an efficient intermolecular hydroamination of allenes.[568] The reaction proved quite versatile and a number of allylic amines could be formed in good to excellent yields (eq 113). It should be noted that while the catalytic system is similar to the one used for the addition of alcohols (see eq 112), the regioselectivity of the nucleophilic attack is reversed going from alcohols to amines. As acknowledged by the authors, the reasons for such a dichotomy are still unclear.[569]



(113)

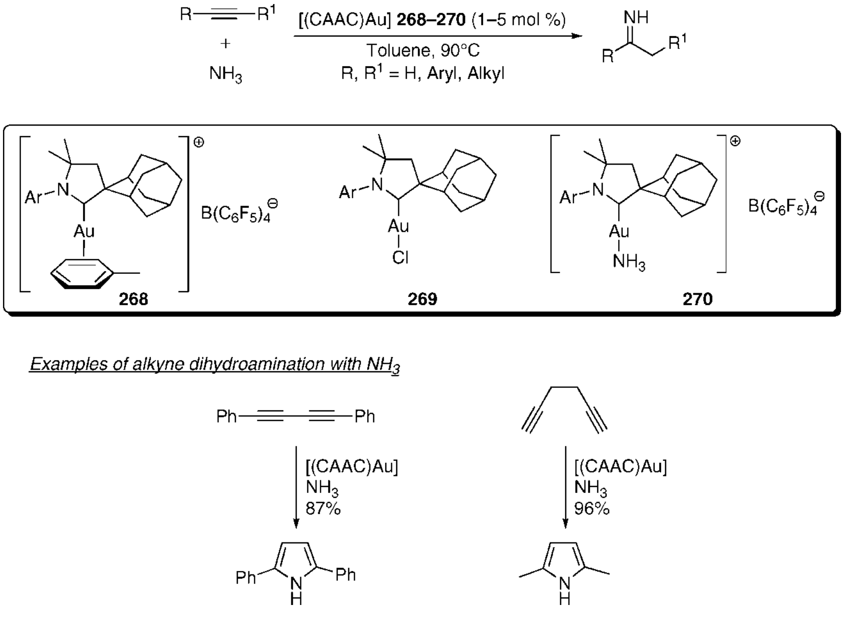
Heterogenized systems are also a topic of intense research for hydroamination reactions. Hence, two reports making use of [(NHC)Au] catalysts where the NHC is linked to a solid support were recently published. Corma and Sánchez used a tin-silicate MCM-41 support, where the tin Lewis acid site acts as cocatalyst in the hydroamination of both alkynes and alkenes.[570] Alternatively, Bochmann and Wright developed an α-zirconium phosphonate-based support that proved efficient in the addition of aniline to phenyl acetylene.[571]

6.3.3.3. Other Nucleophiles. N-Heterocyclic carbene ligands have allowed for the efficient use of more exotic H–X substrates in the hydrofunctionalization of carbon–carbon multiple bonds. An outstanding achievement in this area was reported by Sadighi and co-workers, who developed a catalytic hydrofluorination of alkynes (Scheme 58).[572] Gold complexes **271** and **272**, along with [(IPr)AuCl], were found to be the most active ones among a series of NHC–Au catalysts that notably included ICy, SICy, and SIMes. The isolation of vinyl NHC–gold species **273** provided strong support to an inner-sphere alkyne fluoroauration pathway.[573]

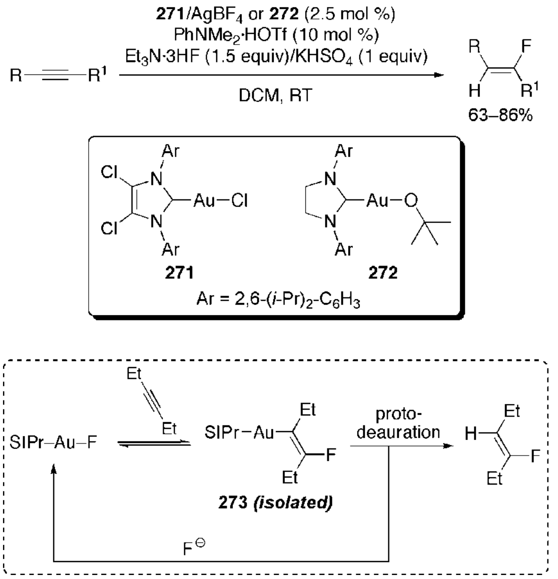
The addition to an unsaturated C–C bond of aryl compounds, namely, the hydroarylation reaction, also falls in the category of hydrofunctionalization.[574] Gold catalysts, including NHC–gold compounds,[575] have met with success in this reaction since seminal work by Reetz and Sommer.[576]

Following their lead in this area,[577] Widenhoefer and co-workers recently published a study on the intermolecular

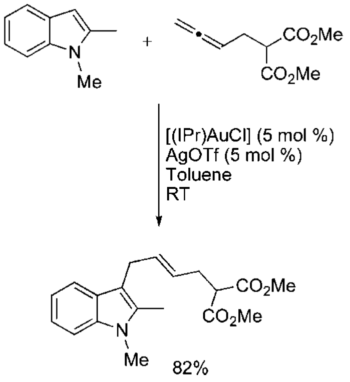
Scheme 57. Hydroamination of Alkynes with Ammonia



Scheme 58. Hydrofluorination of Alkynes



hydroarylation of allenes with indoles (eq 114).[578] Again, IPr proved to be an excellent supporting ligand for this transformation.



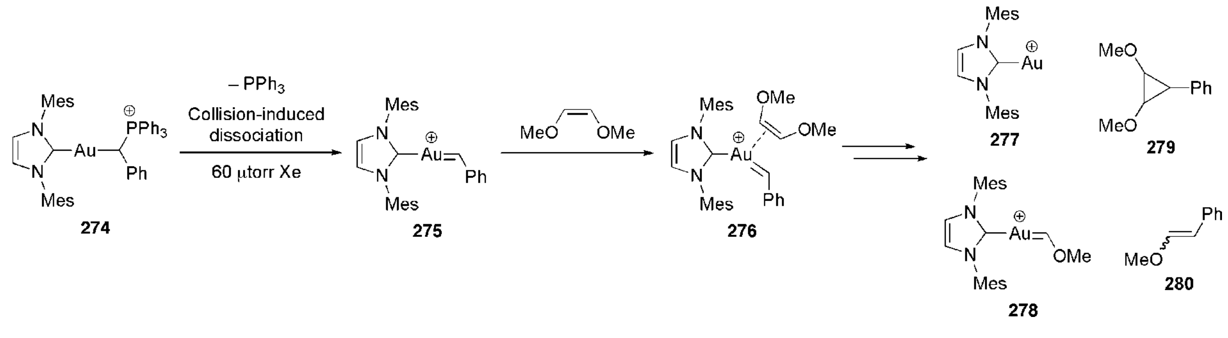
(114)

Of note, even though mechanistically different, the addition of H–Si across C=C and C=O bonds in the presence of a NHC–gold catalyst has also been reported.[501,579]

6.3.4. Miscellaneous Reactions

As previously described for cycloisomerizations and related reactions (see sections 6.3.1 and 6.3.2), the intermediacy of gold carbenoid species has often been postulated.[580] Therefore, the recent observation in the gas phase of IMes-supported gold–carbene complex **275** generated from the gold ylide adduct **274** (Scheme 59) shed some light onto the complex bonding description of these gold species.[581]

Scheme 59. Gas-Phase Generation of a Gold–Carbene Species



Upon addition of an olefin, the bare [(IMes)Au] cationic fragment **277** could be observed along with cyclopropanation product **279**. More striking, Chen and co-workers observed the formation of the cross-metathesis product **280**, as well as the corresponding gold–carbene **278**. Of course, these gas-phase observations should await confirmation from benchtop homogeneous catalysis to be fully exploited. Nevertheless, this study allows one to think that gold-catalyzed olefin metathesis might be a future rewarding direction of research.[582]

The decomposition of diazo compounds can be catalyzed by NHC–gold complexes and lead to the corresponding carbenoid species. The in situ formed NHC–gold carbene has been shown to perform olefin cyclopropanations,[583] Buchner reactions,[584] and insertions into C–H, N–H, and O–H bonds.[585]

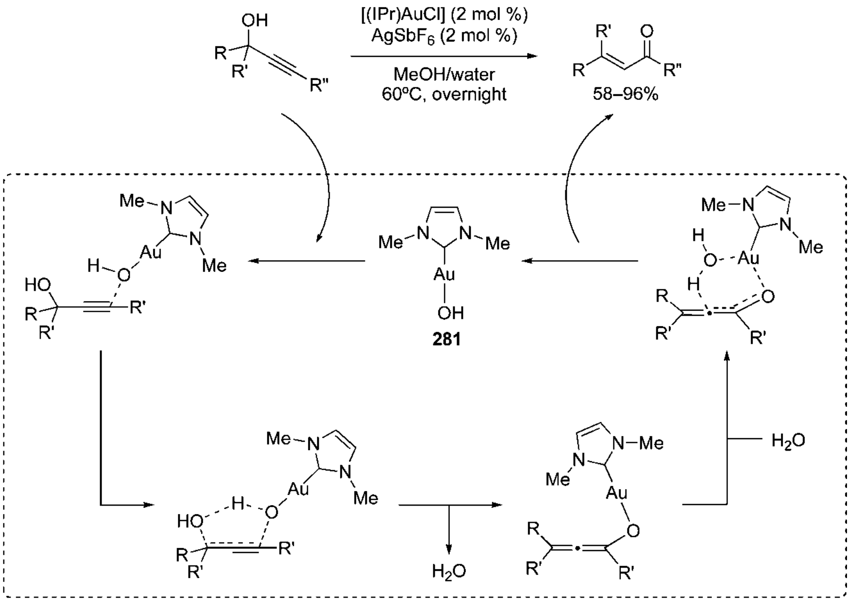
An example of gold-induced olefin polymerization was reported with NHC–gold(III) compounds.[586] Different styrene-type monomers could be polymerized at room temperature in the presence of a series of [(NHC)AuBr$_3$][587] complexes and NaBARF. The study showed that in contrast to NHC–gold(III), NHC–gold(I) compounds were not effective precatalysts. The influence of the NHC ligand was further investigated as well as the possibility of an acid-catalyzed polymerization. The authors finally concluded that a cationic, rather than radical, polymerization was at play since both the metal center and the ligand influenced the physical properties of the polymeric material produced. This mechanistic hypothesis is in accordance with the generation, via π–alkene activation, of a gold-stabilized carbocation. Even though mechanistically diverse, it should be noted that the polymerization of L-lactide in the presence of a [(NHC)AuCl] initiator has also been studied.[588]

The renewed interest for the Meyer–Schuster reaction[589] has placed gold at the forefront of new catalyst development in this area.[590] Based on previous investigations with propargylic acetates,[539a] a [(NHC)AuCl] catalytic system was recently developed for the rearrangement of propargylic alcohols into conjugated enones (Scheme 60).[591] The scope was found to be broad and compatible with diverse substitution patterns at both the propargylic and acetylenic positions. A possible mechanism proposed by the authors, where the active catalyst is the gold-hydroxo species **281** (Scheme 60), relies on DFT calculations made for their previous work involving propargylic acetates.[539a]

Finally, as a testimony to the versatility of [(NHC)Au] catalysts, it should be noted that interesting reports from the Corma group have explored successfully their activity in olefin hydrogenation[592] and in cross-coupling reactions.[593]

The chemistry of homogeneous gold catalysis is developing at a mind-blowing pace and seems to be "still accelerat-

Scheme 60. [(NHC)Au]-Catalyzed Meyer−Schuster Reaction



ing".[594] Great achievements have already been made in the fields of cycloisomerization and hydrofunctionalization, and the most interesting areas for future research are probably to be found in clearly underdeveloped topics such as cross-coupling, oxidation, reduction, or carbene transfer reactions, to only name a few. In this context, NHCs, which have participated since the beginning in this examination of novel reactivity, seem well suited for *supporting* further gold catalysts in this exploratory journey. The ability of NHCs to stabilize important catalytic intermediates and yet to promote subsequent reaction in the coordination sphere of gold will surely lead to exciting discoveries.[595]

7. Conclusion

Less than 20 years after the isolation of IAd by Arduengo[4a] and less than 15 years after their first application in homogeneous catalysis by Herrmann,[7] N-heterocyclic carbenes have tremendously marked the field of late transition metal catalysis. They now belong to the classical ligand kit any organometallic chemist considers. Their ability to stabilize otherwise highly reactive intermediates and yet promote and enhance constructive chemical steps at the metal center has been key in their extremely rapid development. Even if IPr/SIPr and IMes/SIMes hold a prominent place in the gallery of NHCs, the flexibility of their general architecture has also played a crucial role in this success story.

Presently, in terms of catalytic applications with NHCs, late transition metals can be divided into four categories: (1) the *heavyweights* (Ru, Rh, Ni, and Pd), (2) the *well-established* (Ir, Pt, Cu, and Au), (3) the *underdeveloped* (Fe, Os, Co, and Ag), and (4) the *nonexistents* (Mn, Tc, and Re). Catalytic applications for the first two categories will surely continue to develop at a rapid pace, thanks to, among other things, the commercial availability of a growing number of well-defined NHC-containing catalysts with these elements. The *underdeveloped* metals are at a critical stage where each of them needs a showcase catalytic application that would serve as a strong incentive to help attract broader attention. The *nonexistents*, the entirety of group 7, are still at a "pre-catalysis stage" where general synthetic procedures leading to catalytically useful complexes are required. Clearly, it is within these last two categories that major breakthroughs are expected that will strengthen even further the position of N-heterocyclic carbenes in late transition metal catalysis.

8. Abbreviations

Ac	acyl
acac	acetylacetonato
Ad	adamantyl [tricyclo[3.3.1.1^{3,7}]decyl]
Alk	alkyl
Am	amyl
atm	atmosphere
Ar	aryl
ATRP	atom transfer radical polymerization
BARF	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
BINAM	1,1′-binaphthyl-2,2′-diamine
BMIM	*N*-butyl-*N*′-methyl-imidazol-2-ylidene
Bn	benzyl
Bu	butyl
Bz	benzoate
cat	catecholate
Cbz	carbobenzyloxy
CAAC	cyclic alkyl amino carbene
COD	1,5-cyclooctadiene
Cp	cyclopentadiene
Cp*	pentamethylcyclopentadiene
Cy	cyclohexyl
dba	dibenzylideneacetone
DBM	dibenzoylmethanoate
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DCM	dichloromethane
DFT	density functional theory
DKR	dynamic kinetic resolution
DMA	dimethylacetamide
DMAP	4-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dppe	bis(diphenylphosphino)ethane
dvds	1,1,3,3,-tetramethyl-1,3-divinylsiloxane
eq	equation
equiv	equivalent
Et	ethyl
ESI-MS	electrospray ionization mass spectroscopy

Hex	hexyl
HQ	hydroquinone
i	iso
IAd	*N*,*N*′-diadamantylimidazol-2-ylidene
ICy	*N*,*N*′-dicyclohexylimidazol-2-ylidene
IEt	*N*,*N*′-diethylimidazol-2-ylidene
IiPr	*N*,*N*′-diisopropylimidazol-2-ylidene
IiPrMe	*N*,*N*′-diisopropyl-4,5-dimethylimidazol-2-ylidene
IMe	*N*,*N*′-dimethylimidazol-2-ylidene
IMes	*N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IPr	*N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
ItBu	*N*,*N*′-di-*tert*-butylimidazol-2-ylidene
ITM	1,3,4,5-tetramethyl-imidazol-2-ylidene
LTM	late transition metal
m	*meta*
ma	maleic anhydride
MAO	methylaluminoxane
Me	methyl
Mes	mesityl [1,3,5-trimethylphenyl]
MMA	methyl methacrylate
MMAO	modified methylaluminoxane
M_n	number-average molar mass
mol %	molar percentage
MOM	methoxymethyl ether
MS	molecular sieves
MTBE	*tert*-butylmethyl ether
M_v	viscosity-average molar mass
nbd	norbornadiene
nbn	norbornene
NHC	N-heterocyclic carbene
NMP	*N*-methylpyrrolidinone
NR	no reaction
o	*ortho*
Oct	octyl
p	*para*
PC	polycarbonate
PEG	poly(ethylene glycol)
Pent	pentyl
PHC	P-heterocyclic carbene
Ph	phenyl
pin	pinacolato
Piv	pivalate
PNB	polynorbornene
Pr	propyl
PS	polystyrene
pyr	pyridine
RT	room temperature
rfx	reflux
s	*sec*
SICy	*N*,*N*′-dicyclohexylimidazolin-2-ylidene
SIMes	*N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene
SIPr	*N*,*N*′-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
SItBu	*N*,*N*′-bis(*tert*-butyl)imidazolin-2-ylidene
t	*tert*
TBA	tetrabutylammonium
TBHP	*tert*-butylhydroperoxide
TBDMS	*tert*-butyldimethylsilyl
Tf	triflyl [trifluoromethylsulfonyl]
TFA	trifluoroacetic acid
TIMEN	tris[2-(3-arylimidazol-2-ylidene)ethyl]amine
THF	tetrahydrofuran
TMHD	2,2,6,6-tetramethyl-3,5-heptanedionate
TMS	trimethylsilyl
TOF	turnover frequency
Tol	tolyl [4-methylphenyl]
TON	turnover number
TPT	1,3,4-triphenyltriazol-5-ylidene
Ts	tosyl [(4-methylphenyl)sulfonyl]
vs	versus

9. Acknowledgments

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(15) We have chosen to represent the NHC−M bond as a single bond, without resonance structure within the NHC. It is a pure formalism adopted to obtain clear drawings. It should be noted that the nature of the NHC−M bond varies tremendously as a function of the NHC itself, the metal center, and the other ligands. For more discussion on this highly interesting aspect of NHCs, see refs 13 and 14.

(16) We have not included the elements of group 12 (i.e., Zn, Cd, Hg) since they are not considered transition metals according to the IUPAC definition, which states that a transition metal is “an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell”. Definition taken from the *IUPAC Compendium of Chemical Terminology*, Internet Edition; see: http://old.iupac.org/goldbook/T06456.pdf.

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