DOI: 10.1002/ejic.200800323

Donor-Functionalised N-Heterocyclic Carbene Complexes of Group 9 and 10 Metals in Catalysis: Trends and Directions

Adrien T. Normand[a] and Kingsley J. Cavell*[a]

Keywords: N-Heterocyclic carbenes / Functionalised ligands / Homogeneous catalysis

This review focuses on the latest advances in homogeneous catalysis with donor-functionalised (donor = C, N, O, S or P) N-heterocyclic carbene complexes of group 9 and 10 metals. The applications of such complexes to C–C coupling reactions, alkyne and ketone hydrosilylation, olefin polymerisation, transfer hydrogenation, asymmetric hydrogenation and other catalysed reactions are discussed.

Introduction

In this short review we explore the more recent developments in the application of late-transition-metal complexes of chelating donor-functionalised N-heterocyclic carbenes (df-NHCs) in catalysis. By donor-functionalised NHCs we mean those ligands, containing at least another anionic or neutral 2e donor atom (e.g. C, N, O, S or P), which can act as a polydentate ligand upon coordination to a metal centre. The focus will be on apparent trends, and applications, which hopefully will provide a steer as to where the best opportunities lie for exploitation of these ligand systems. Since the first formative studies of Wanzlick,[1–6] Öfele[7–9] and Lappert[10–13] in the 1960's and 70's looking at the synthesis of N-heterocyclic carbene (NHC) complexes, investigations into their applications in catalysis have been initiated.[10,14,15] However, it was only after the isolation of the first free NHCs[16,17] and the subsequent catalytic studies by Herrmann that the field exploded into life.[18] Isolation of free NHCs meant that they could now be treated in much the same way as the ubiquitous phosphanes, in that they could be added to various metal compounds to form new complexes, or generated in situ to form the desired active catalyst. Following close behind these initial studies, investigations into chelating, df-NHCs and their application in catalysis were also reported in the literature, pointing to the scope and potential of these new ligand types.[19,20]

Because of the strong bonds between NHCs and transition metals, interest in these ligands for applications in catalysis grew rapidly. However, it soon became apparent that despite the strong bonding interactions, major problems existed. Electronic and structural factors associated with

Adrien Normand graduated from Ecole Européenne de Chimie Polymères et Matériaux de Strasbourg (France) and received a MSc in organic chemistry from Université Claude Bernard Lyon 1 (France) in 2004. He spent one year as an industrial trainee with Pfizer in the UK (2002–2003) and studied for a PhD in NHC chemistry with Prof. Kingsley J. Cavell in Cardiff University (2004–2007). He is currently a postdoctoral research associate with Sanofi-Aventis in France. His research interests include homogeneous catalysis, mechanisms in organometallic chemistry and metallodrugs.

Kingsley Cavell is Professor of Chemistry and, since 2006, Head of the School of Chemistry in Cardiff University. He did his PhD at La Trobe University in Melbourne (Australia) and undertook Post-doctoral studies at the University of Manchester (with Professor Hank Skinner and Dr. Geoff Pilcher) and at the University of Amsterdam (with Professor Kees Vrieze). This was followed by a period with the CSIRO (Div. Mats. Sci. Technol.), Melbourne, before moving to the University of Tasmania. He has been Guest Professor at the Institut für Chemie und Petrolchemie der RWTH Aachen, Germany (with Prof. Willi Keim), 1989–1990, and 1994, and in the Department of Chemistry, Huazhong University of Science and Technology, Wuhan, PR China (Prof. Li Guangxing), 1997. He was awarded the "2001 Royal Society of Chemistry Industrially-Sponsored Award in Homogeneous Catalysis, sponsored by Synetix". His research is focussed on ligand design in coordination and organometallic chemistry, homogeneous catalysis and elucidation of reaction mechanisms relating to catalytic processes and reaction steps.

---

[a] School of Chemistry, Main Building, Cardiff University,
51 Park Place, Cardiff CF10 3AT, UK
Fax: +44-(0)29-208-74075
E-mail: cavellkj@cf.ac.uk

NHC ligands generate conditions wherein they are particularly susceptible to reductive elimination.[21–26] The thermodynamically preferred arrangement for square planar NHC complexes containing hydrocarbyl-, hydrido- or acyl ligands is for these groups to be in *cis* positions to the carbene ligand. Furthermore, the plane of the NHC is inevitably at an angle to the coordination plane of the complex (normally in the range 65–80°), which, in turn, means the pπ-orbital of the NHC carbon is angled towards the *cis* hydrocarbyl group, ideally arranged to interact with orbitals on this ligand.[21–26] This leads to decomposition of the catalyst, in some instances before effective catalysis can take place. Computational studies have established the involvement of these orbitals, and d-orbitals on the metal centre, in the reductive elimination process.[24] When the nature of this decomposition pathway was unravelled it was apparent that one approach to limit the impact of the reaction is to reduce the dihedral angle between the plane of the carbene ligand and that of the coordination plane, thus reducing effective overlap of interacting orbitals. One obvious way to achieve this would be the use of relatively inflexible chelating NHC-based ligands. The ease of attaching functional groups to the nitrogens in heterocyclic carbenes makes them ideally suited to the synthesis of df-NHC chelating ligands. Thus the intense activity in the design and synthesis of df-NHCs, although undoubtedly motivated by a desire to develop exciting and innovative ligand systems, has also in part been driven by the need to circumvent the decomposition reaction and develop effective new catalysts. Many novel and varied ligands have thus been designed.

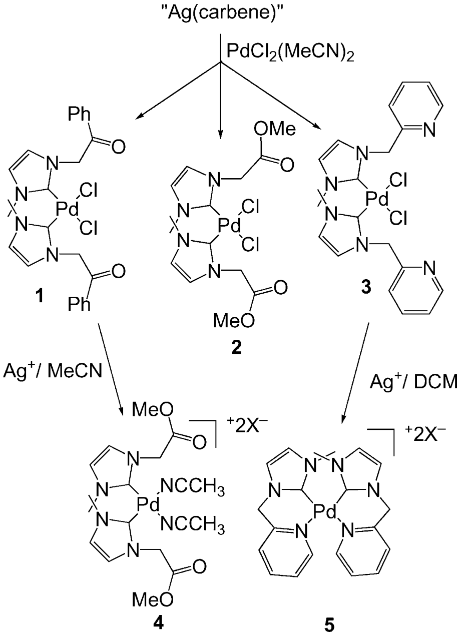
The field of chelating df-NHC ligands and their application in catalysis is now extremely large. To maintain the concept of a short focussed review it is necessary to restrict the breadth of the topic. The focus here is on groups 9 and 10 transition metals, their complexes with df-NHCs, and their application in catalysis. It is very clear that, apart from a few recent examples the literature has been concentrated on a small number of reaction classes. A number of important catalytic reactions, such as amination, telomerization etc. appear to be catalyzed by highly coordinatively unsaturated species of the type L–M(0).[27] Chelating ligands, unless suitably “hemilabile”, are therefore, generally inappropriate for such reactions and hence these processes will not be covered in this review.

Examples of df-NHCs were reported as long ago as the 1970’s.[28,29] This was followed by several further examples in the intervening years.[30–39] Functional groups, associated with the carbene, included P, O, S and N atoms as potential donors. In an early illustration of the application of df-NHCs in catalysis, Dixneuf et al. prepared Rh and Ru complexes of an NHC with a pendant (non-coordinating) methoxy group, and studied their application as catalysts in cyclopropanation reactions.[35] This microreview will concentrate on recent developments, in the period from 2000, which is in fact the period when most of the work in this area has been reported. There are now numerous reviews, and overview articles covering many aspects of NHC chemistry,[27,40–53] and hence, some overlap with these publications is inevitable. The ligand design has also encompassed the design of chiral-NHC systems, and an excellent review looking at chiral carbene ligands was recently published.[46] Therefore, this specific aspect of NHC chemistry will not be reviewed here, apart from the examples of chiral df-NHCs which obviously fall within the scope of the present review.

Cross-Coupling Reactions (Ni, Pd)

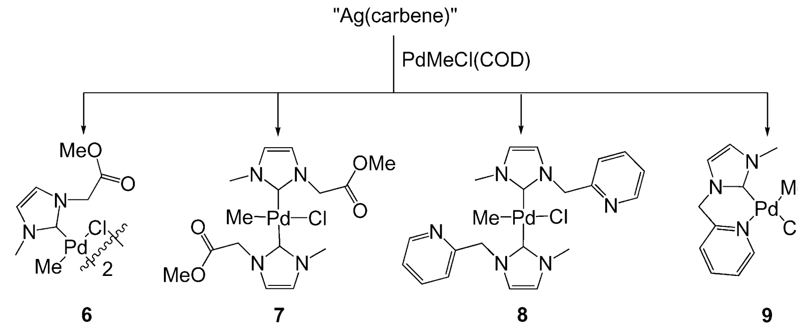
The vast majority of catalytic studies involving df-NHCs have focused on palladium-catalysed C–C coupling reactions, such as Heck, Sonogashira, Suzuki, and others−consequently a large part of this review will cover developments in this area.

In 2000 a comprehensive investigation of Pd–df-NHC complexes, and more importantly, Me–Pd–NHC complexes, and their catalytic performance in coupling reactions was reported for the first time.[19] The palladium complexes **1**–**5** (Scheme 1) and the methyl–Pd complexes **6**–**9** (Scheme 2) were prepared from the imidazolium ligand precursors through a silver-transfer process.



Scheme 1. Synthesis of df-NHCs by silver–NHC transfer.

The catalysts exhibited high stability and, at the time, exceedingly high turnover numbers for the Heck reaction between 4-bromoacetophenone and butyl acrylate, and for Suzuki coupling between 4-bromoacetophenone and $C_6H_5B(OH)_2$. Sonogashira and Stille coupling reactions were also studied, in which the catalysts showed only moderate performance. Amination reactions with these systems were largely unsuccessful. The complexes **7**, **8** and **9** gave rise to the best catalysts overall, with TON (turnover numbers) for Heck coupling of 0.6–1.7 × 10^6. The important features of this study were the performance of pyridine-functionalised NHCs, and the application of Me–Pd–df-



Scheme 2. Me–Pd complexes of df–NHCs.

carbenes in catalysis. Other reports along a similar theme appeared soon after.[20,54] A more recent report looked at the application of a Pd^{II} complex of a bulky *ortho*-substituted pyridinyl NHC ligand in the Heck and Suzuki coupling reactions; performance was modest and it appeared that the catalyst decomposed to give Pd nanoparticles as the active species.[55]

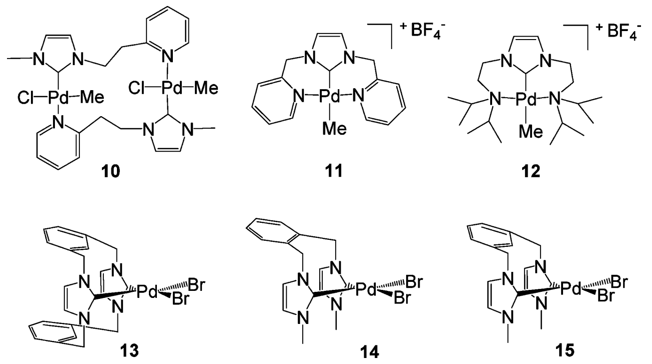


Figure 1. Pd complexes used in Heck and Suzuki coupling.

A novel series of df-NHCs and substituted NHCs and their Pd (and Me–Pd) complexes were investigated in the Heck reaction (coupling 4-bromoacetophenone with *n*-butyl acrylate) and in the Suzuki coupling reaction (4-bromoacetophenone with phenylboronic acid).[20] The new ligand types (Figure 1) included ethyl-bridged pyridine–NHC (**10**); pyridine–NHC–pyridine (**11**), and amine–NHC–amine (**12**) NCN pincer ligands; imidazol-linked cyclophanes, **13**, and half cyclophanes [*ortho*- and *meta*-aryl linked bis(carbenes), **14**, **15**]. The amino complex **12** was found to be very unstable and rapidly decomposed at room temperature to give 1,3-bis(diisopropyl-2-ethylamino)-2-methylimidazolium salt. However, other complexes demonstrated high stability (particularly the pincer complex **11**, and half cyclophane structure **15**), and when tested in Heck and Suzuki coupling showed good reactivity for coupling aryl bromides; high turnover numbers were obtained at low catalyst loadings. More recently Douthwaite et al. have investigated the preparation of amino-bridged bis-NHC ligands, and Pd complexes, synthesised by a Ag-transfer route.[56] The amino functionality was labile, and complexes in which the ligand behaved as a CNC pincer, and others in which the amino functionality was non-coordinating were prepared; examples of both types of complex were tested in Heck coupling, low loadings were used, and performance with aryl bromides was good, however, activity with aryl chloride was low. It appeared likely that colloidal Pd was involved in the catalysis, particularly at low loadings.

A comprehensive series of studies by Baker et al. has focused on imidazolium-linked cyclophanes, their coordination to Pd, structures, and catalytic testing in Heck and Suzuki coupling.[57–59] A range of ligand types (e.g. **16** and **17**) were synthesised, and treated with $Pd(OAc)_2$ or other Pd salts in the presence of base to give Pd-tetrakiscarbene [bis(cyclophane)] and bis(carbene) dihalide complexes, e.g. **13**, **14**, **18**, and **19** (Figure 1 and Figure 2).[57] Complexes of type **13** and **14** again showed high stability and the best catalytic performance in Heck and Suzuki coupling, between iodo- and bromoaryl substituents and acrylates or phenylboronic acid, respectively. In a follow-up paper, the same authors reported the synthesis of a series of Pd (**20**, **21**, **22**), Pt, and Rh complexes bearing similar carbene ligands that were substituted with heptyl or naphthyl groups in order to improve the solubility.[58] The catalytic performance was very similar to that previously reported for this type of compound, despite the addition of solubilising groups to the ligand framework. Very low catalyst loadings and high temperatures (140 °C) were used. However, the authors did not rule out the possible formation of colloidal-Pd species, which could be the active catalyst in these reactions.

In a slightly different approach to the usual pyridine-substituted df-NHC catalyst systems Shreeve et al. prepared a pyrazolyl-functionalised NHC complex of Pd, **23** (Figure 3) and tested it in the Heck coupling of aryl iodides and bromides with *n*-butyl acrylate, coupling of aryl iodides with styrene, and in the Suzuki coupling of aryl iodides with phenylboronic acid.[60] Of particular interest was the fact that catalytic reactions were carried out in an ionic liquid solvent (1-butyl-3-methylimidazolium hexafluorophosphate). Moderate conversions to coupled product were achieved with high selectivity, and the catalyst could be recycled up to six times with no decrease in catalytic performance. In a follow-up paper, the Shreeve group synthesised pyrazolyl-functionalised imidazolium ionic liquids, prepared a Pd complex of the resulting pyrazolyl-functionalised NHC, and tested the complex in Heck coupling reactions using the pyrazolyl-functionalised imidazolium ionic liquid as solvent.[61] The catalyst system was effective for

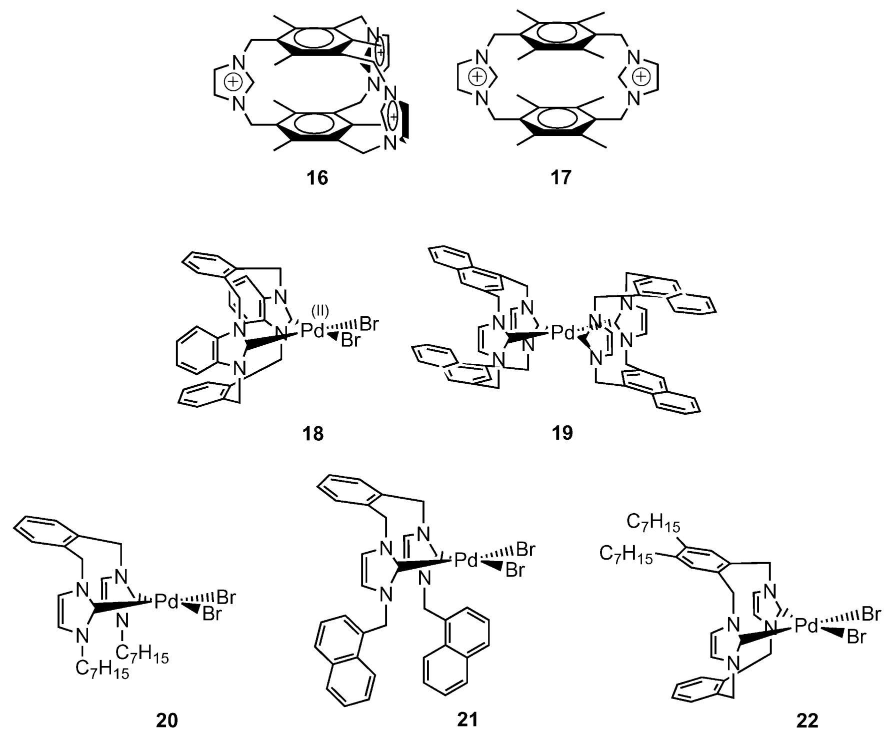
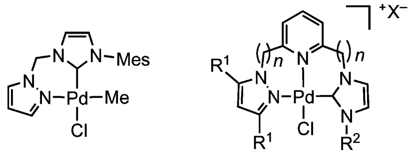

16 **17** **18** **19** **20** **21** **22**

Figure 2. Cyclophane based df-NHC complexes.

coupling aryl iodides but more interestingly, the catalyst system could be recycled up to 5 times with different substrates without loss in activity. Pd complexes of mixed donor tridentate ligands systems, incorporating an pyrazolyl donor connected to a NHC by a pyridine linker (**24**, Figure 3) have been used as catalysts in the Suzuki–Miyaura coupling of aryl halides (I, Br and Cl) with phenylboronic acids.[60] Catalytic performance was modest and the aryl chloride substrate required long reaction times and large catalyst loadings for effective conversions.

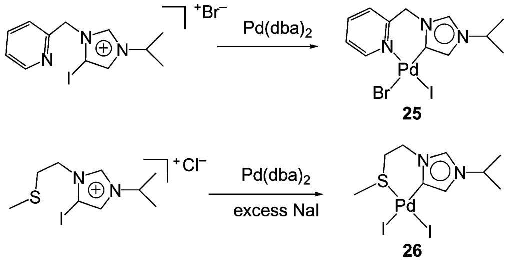

23 **24**

$n = 0$; $R^1 = Me$; $R^2 = nBu$, $n\text{-}C_7H_{15}$;
$X^- = BF_4^-$, PF_6^-

$n = 1$; $R^1 = Me$; $R^2 = Mes$;
$X^- = Cl^-$

Figure 3. Pd complexes of pyrazolyl-substituted NHCs.

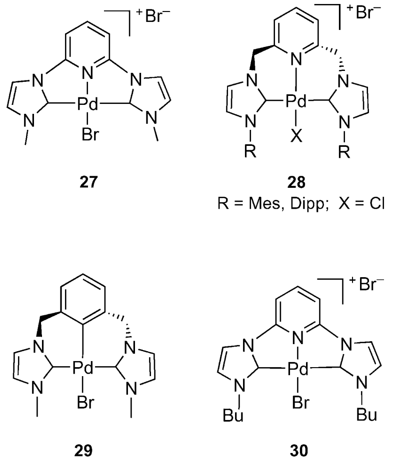
A particularly novel and interesting development is the synthesis of Pd complexes of functionalised C4-bound "abnormal" or non-classical carbenes; Albrecht et al. synthesised the pyridine- and thioether-functionalised systems **25** and **26**, respectively (see Scheme 3) and investigated the complexes in Heck olefination of aryl bromides.[62] Conversions and TONs were modest, and there was some indication that colloidal Pd may have been formed under the forcing conditions of the reaction–catalytic performance dropped quite significantly in the presence of excess Hg.



25 **26**

Scheme 3. Functionalised abnormal NHC complexes for Heck coupling.

Carbene-based pincers has become a very active area of study. Following from an earlier report,[20] a series of important publications by Crabtree et al. and Danopoulos et al., looking at different variations on the concept of NHC-based pincer ligands, has appeared.[63–65] The CNC pincer complex **27** (Figure 4) proved to be a robust catalyst for the Heck coupling that shows good activity for the conversion of aryl iodides and aryl bromides, at temperatures >180 °C, and in air.[64] Importantly, evidence was provided to show that the active catalyst was probably a homogeneous species, and not metallic palladium as often proposed for many of these "homogeneous" catalyst systems. The palladium catalysts **28** that were coordinated by 2,6-lutidinyl-bis(carbene) ligands were reported to be highly active and very stable catalysts for the Heck coupling.[63] This report also discussed the twisted, or helical symmetry of the complex. Further studies on complexes of type **28** (R = Me, X = Br), and **29**, which was the first reported CCC pincer, also commented on the twisted structure of the complexes, and on the fluxional behaviour of the structures.[65] The excellent air and thermal robustness of the complexes meant they could be used as Heck catalysts in refluxing DMA, allowing good conversions with aryl chloride substrate. In particular, complex **28** (R = Me, X = Br) proved to be an efficient catalyst. In defining studies on the robustness and effectiveness of Pd-pincer complexes in catalysis the complex **30** was synthesised.[66] The *N*-butyl substituents gave increased solubility, improved catalytic performance and high thermal stability (catalysis was carried out routinely at 145 °C and on occasions at 165 °C). The catalyst demonstrated some of the highest turnover numbers known for the Heck olefination of aryl chlorides. Furthermore, the catalyst showed complete air stability even when operated at 165 °C. The catalysts could be reused (6 cycles) with no obvious loss of activity. The catalyst was also tested in Suzuki and Sonogashira coupling reactions with modest success. Interestingly, preliminary studies looking at the possibility of a Pd^{II}/Pd^{IV} mechanism, rather than the generally accepted Pd^0/Pd^{II} mechanism, could not find any evidence to support the former.



27

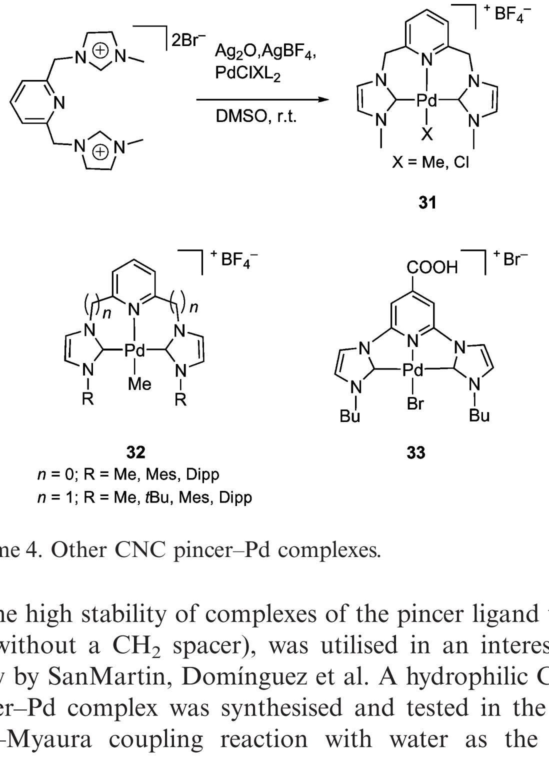
28
R = Mes, Dipp; X = Cl

29

30

Figure 4. CNC and CCC pincer–Pd complexes for Heck coupling.

A high-yielding one-pot synthesis of the first $Me–Pd^{II}$ pincer complex of type **31** via an intermediate Ag complex has been developed (Scheme 4).[67] Previous reports had specifically highlighted the high thermal stability of these pincer complexes.[64–66] However, as previously stated, a facile reductive elimination–decomposition route for *cis*-hydrocarbyl–M–carbene complexes (M = Pd, Ni) is known.[21–26] This tendency to reductively eliminate may be limited by; preventing the NHC donor and the hydrocarbyl group from adopting mutually *cis* geometry; and/or constraining the NHC ring to an orientation in which the carbene-pπ obital overlap with the hydrocarbyl group is limited, i.e. by forcing the plane of the carbene to approach coplanarity with the coordination plane.[67] A pincer-type structure addresses both these factors, and hence increased stability is expected, and is observed, for the $Me–Pd^{II}$ pincer complex **31** (X = Me). In an investigation of the thermal decomposition of the complex it was shown that decomposition only occurs with prolonged heating (15–18 h at 150 °C).[67] Intriguingly, the initial decomposition stage does appear to go via the ubiquitous reductive elimination mechanism. Consequently, higher temperatures may be used when applying these pincer complexes in catalysis. In a further study on Me–Pd complexes of this type of CNC pincers, a broad range of ligands, some with no bridge, and others with a CH_2 linker between the pyridine donor and the NHC components, were synthesised. The Pd complexes (**32**, Scheme 4) were tested in a model Heck coupling reaction to gain insight into ligand structural effects on catalytic performance.[68] The coupling of 4-bromoactophenone with *n*-butyl acrylate, with NaOAc as base, and 0.001 mol-% catalyst, was used as the standard reaction. It was apparent that there was, in general, no particular benefit derived from the presence or absence of the methylene spacer group. However, complexes with the more rigid ligand (without the spacer group), were slightly more active in the absence of an additive such as Bu_4NBr.[68] In general, additional steric bulk at the ligand "wingtips" (*N*-substituents) provided the most significant improvement in catalyst activity. Nevertheless, the complex with an extremely bulky *N*-substituent, the *t*Bu group, was notably less stable than other complexes.



X = Me, Cl

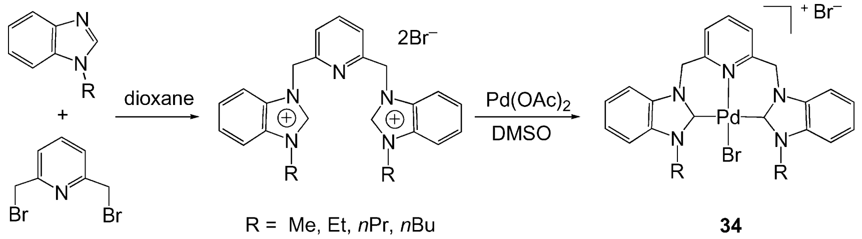
31

32
n = 0; R = Me, Mes, Dipp
n = 1; R = Me, *t*Bu, Mes, Dipp

33

Scheme 4. Other CNC pincer–Pd complexes.

The high stability of complexes of the pincer ligand type **33** (without a CH_2 spacer), was utilised in an interesting study by SanMartin, Domínguez et al. A hydrophilic CNC pincer–Pd complex was synthesised and tested in the Suzuki–Myaura coupling reaction with water as the solvent.[69] Water solubility was provided by a *p*-carboxy group on the backbone of the pincer. The reaction conditions consisted of: 0.1 mol-% catalyst, appropriate substrate, K_2CO_3, in pure water as solvent, refluxed for 2 h. A range of electron-rich, electro-neutral and electron-poor bromoarenes and arylboronic acids were tested, all giving 100% yield of



Scheme 5. CNC pincer–Pd complex used in Heck coupling.

product. Catalyst loadings as low as 10^{-7} gave >99% conversion after 6 h (TON: 1×10^9 and TOF: 1.67×10^8 were claimed). The catalyst system could be recycled 5 times without any discernible loss in activity and the authors argued against the formation of Pd-nanoparticles.[69]

A variation on the carbene-based CNC pincer ligand theme has been investigated by Hahn et al.[70] A range of pyridine-bridged bis(benzimidazolin-2-ylidene) pincers (**34**, Scheme 5) have been synthesised, coordinated to Pd, and tested as catalysts in the Heck olefination of various aryl bromides.[70] The stability of the catalysts was again a feature; the catalyst performance was similar to those CNC pincer systems previously reported. Very recently, Hahn et al. have also investigated the synthesis and catalytic performance of phenyl-bridged bis(benzimidazolin-2-ylidene) Pd, CCC pincer complexes. These catalysts, which could be operated under aerobic conditions, gave moderate performance in the Heck coupling of aryl bromides.[71]

An ether-bridged, quasi-pincer bis-NHC ligand has been synthesised and the Pd complex (**35**, Figure 5) prepared by a Ag transfer route. The resultant complex was studied in a model Heck coupling reaction (between 4-bromoacetophenone and *n*-butyl acrylate); the activity was modest.[72] The ether link does not coordinate and it is not clear what role it plays in the catalytic reaction. Other examples of O- and S-bridged bis(imidazolium) salts and their Ag complexes have been synthesised (**36**, Figure 5); the salts have been employed in situ as ligands in Pd-catalysed aryl coupling amination reactions; activity was low.[73] Pd and Au complexes of monodentate 3-*tert*-butylimidazol-1-(*o*-methoxybenzyl)-2-ylidene, containing a non-coordinating ether functional group, have been prepared.[74] The Pd complex was tested in Suzuki–Miyaura coupling and showed moderate performance with aryl iodides and bromides.

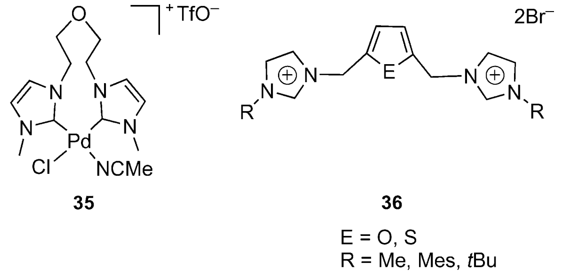
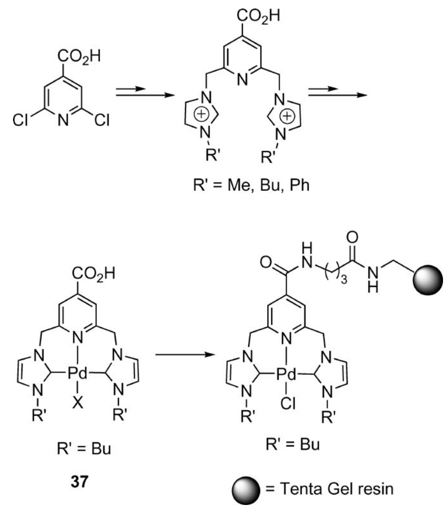
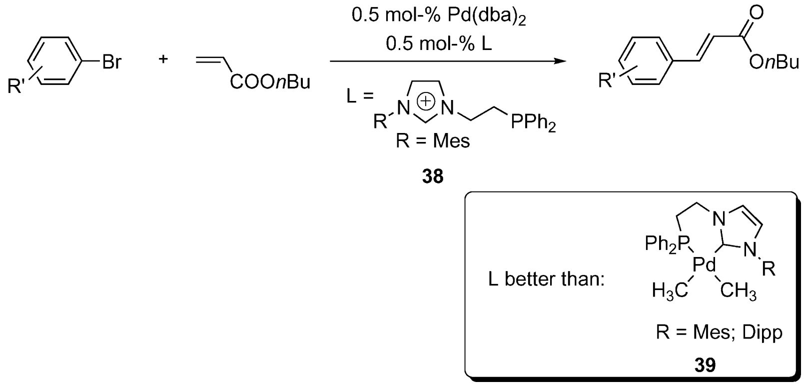


Figure 5. O- and S-donor ligands and their complexes.

The strong coordinating ability of NHCs and the high stability of NHC-based pincer ligands should make these pincer ligands ideal systems for immobilisation on various support materials. A number of valuable studies on the immobilisation of carbene-based pincers have been reported.[75–77] Peris and Claver et al. have immobilized the rigid pincer complexes, type **27** (Figure 4), in clays (montmorillonite and bentonite), and tested the resulting systems in the Heck olefination of aryl halides and Sonogashira coupling of aryl halides with terminal alkynes.[76,77] In the first example, Peris and Claver et al., employed the catalyst system to couple phenyl iodide and styrene at temperatures of 180 °C and recycled the system up to 10 times with little loss in activity.[76] Aryl bromides could also be coupled with good yields. In the second report, the same catalyst systems were tested for Sonogashira coupling and operated in refluxing pyrrolidine (87 °C) as both solvent and base.[48] The catalysts were tested for the coupling of aryl iodides and bromides with, in general, good yields. One catalyst system was recycled several times with little loss in activity. In a further study, by Steele and Teasdale, on immobilised Pd–CNC pincers, a preformed complex (**37**, Scheme 6) was attached to a polymer support.[75] The highly robust immobilised catalyst was applied in Heck and Suzuki coupling reactions and could be used at least 14 times with little or no loss in activity. The pincer complex was supported through



Scheme 6. Immobilisation of a CNC pincer–Pd complex for Heck and Suzuki coupling.



Scheme 7. Heck coupling catalysed by preformed and in situ catalysts.

caproate linkage to the amino-terminated polymer (Tenta Gel resin) giving approximately 0.22 mmol Pd g^{-1} catalyst. Very low levels of leaching were observed even after 14 recycles. Catalytic performance was modest, and aryl bromides and iodides were tested.[75]

A number of reports have appeared in which (diphenylphosphanyl)alkyl-functionalised NHC complexes have been synthesised and tested in coupling reactions.[78–81] In the first such study, Nolan et al. used ligand **38** (Scheme 7), in in situ catalytic studies on the Heck coupling of aryl bromides with n-butyl acrylate.[81] Catalytic performance was promising and in general high yields were obtained in short reaction times. Danopoulos et al. studied preformed complexes of the same ligand systems, **39**, as catalysts in coupling reactions.[80] It was found that the preformed complexes were not as effective in the coupling reaction as the in situ catalyst system, although catalyst loadings were lower. Such variation between preformed and in situ reaction behaviour is not uncommon and has been reported on a number of occasions. A key feature of the catalysis with preformed complexes was the generation of Pd-colloids, due to catalyst decomposition, possibly via reductive elimination enabled by the flexible and highly labile –PPh_2 arm of the ligand. Brief mention was also made of the application of this catalytic system in ethylene/CO copolymerisation.

Palladium complexes of similar phosphane-functionalised NHC ligands have been investigated in the Suzuki coupling of aryl bromides with phenylboronic acid.[79] Ligands with a variety of different N-substituents were studied. The catalysts showed modest performance, and no mention is made of the catalyst stability. However, it is noted that prolonged reaction times gave relatively small improvement in product yields, indicating that catalyst deactivation is occurring. The same group investigated the application of PCP pincer–Pd complexes **40** and **41** (Figure 6) in Heck and Suzuki coupling.[78] The catalysts showed modest performance. Catalysts stability is not discussed, however, the observation that TONs improve significantly on reduction of catalyst concentration (down to 10^{-6} mol-%) suggests that Pd-colloids may be forming. Hahn et al. have synthesised phosphane-functionalised benzimidazolin-2-ylidenes, and a variety of Pd and Pt complexes of these ligands were prepared by the Ag-transfer route.[82] The Pd complexes were investigated in Heck-type reactions coupling aryl bromides with styrene and *n*-butyl acrylate. Both bidentate (**42**) and pincer-type (**43**) ligand systems were studied, good catalyst performance was noted and high yields of products obtained.

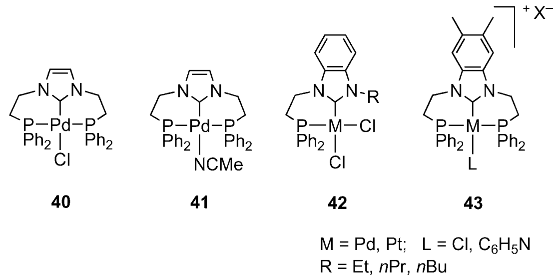


Figure 6. P-donor functionalised NHC complexes of Pd used in Heck and Suzuki coupling.

Shi et al. have synthesised a phosphanyl(ferrocenyl)imidazolium salt (**44**, Figure 7) which was used in situ, with a suitable Pd precursor complex, to give a robust catalyst for the Suzuki–Miyaura coupling of aryl bromides with phenylboronic acid.[83] In general, $Pd(OAc)_2$ was employed as the precursor complex and loadings between 0.5 and 0.005 mol-% were employed to good effect. The pre-formed Pd complex **45** was also an effective catalyst giving similar performance to the in situ systems. Sterically congested substrate and substrate with electron-withdrawing groups were successfully investigated, as were activated aryl chloride substrate (although higher loadings of catalyst were required in this case).[55]

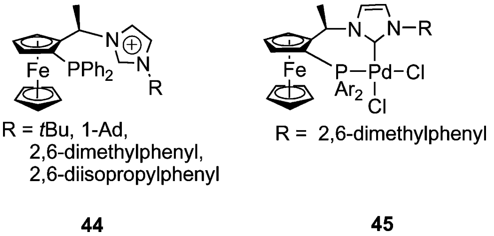


Figure 7. Other P-functionalised NHC Pd complexes.

Several novel tridentate NHC-based ligands have been prepared and their Pd complexes applied in catalytic coupling reactions. Yagyu et al. have prepared the neutral Pd complexes **46** and **47** (Figure 8) and investigated their activity in Heck coupling of iodobenzene with styrene. Not surprisingly, given the reactivity of aryl iodides, the catalysts were quite effective in this coupling reaction even at low catalyst concentration.[84] Shi et al. have synthesised a Pd complex **48** of an unusual tridentate ligand containing a binaphthyl backbone. The complex showed moderate activity in Suzuki- and Heck-type coupling reactions. Aryl iodides and aryl bromides were used as substrate and in general long reaction times and quite high temperatures were required to obtain high yields.[85] Chelating *o*-hydroxyaryl-functionalised NHC ligands and their Pd complexes **49** have also recently been prepared and tested in Suzuki coupling of phenyl halides with phenylboronic acid.[86] The catalytic performance for aryl bromides was modest but poor for aryl chlorides.

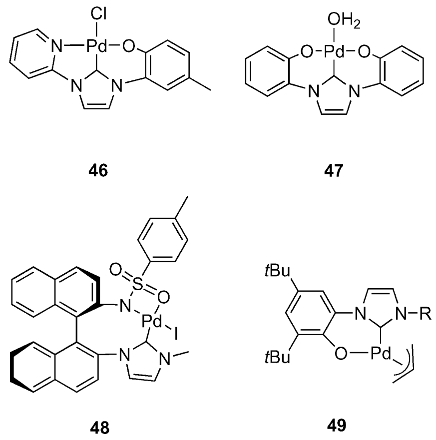


Figure 8. Various aryl-functionalised Pd–NHC complexes for Heck and Suzuki coupling.

A diverse array of other functional groups have been attached to NHCs, coordinated to metal centre and tested in catalytic coupling reactions.[87–93] Batey et al. have synthesised the Pd complex **50** (Figure 9) with a non-chelating carbamoyl-substituted NHC.[87] When operated at room temperature the complex formed an effective catalyst for the Sonogashira cross-coupling of aryl iodides with a variety of primary alkynes. For effective cross-coupling of aryl bromides, heating to 80 °C was necessary. Sames et al. have investigated the Pd complex of a closely related carbamoyl-functionalised NHC in the catalytic C–H arylation of substituted indoles and imidazoles with aryl iodides and bromides.[88] Complex **51** was used in 0.15–5 mol-% to give moderate to high yields of coupled product. As with the previous complexes **6**, **7** and **50**, the carbonyl group was not observed to chelate, however, it is possible that a weak interaction may occur during catalysis. Imido-functionalised NHCs have recently been prepared and tested in situ and as preformed Pd complexes in Suzuki coupling with aryl bromides – catalytic performance was poor.[89]

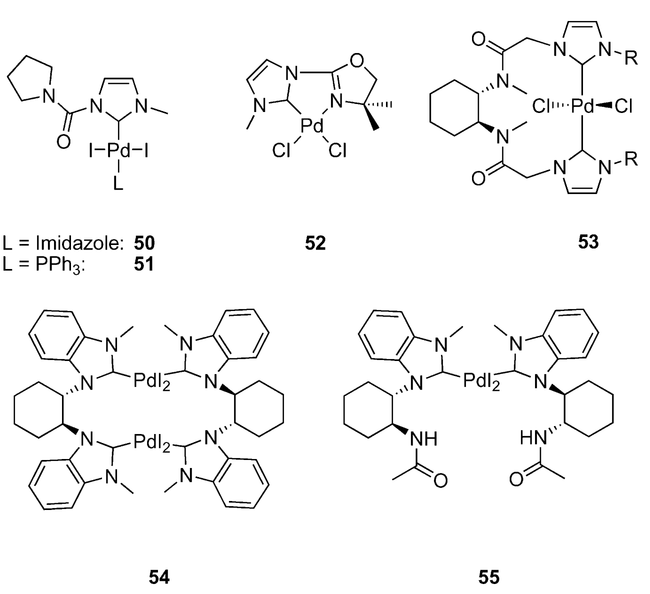
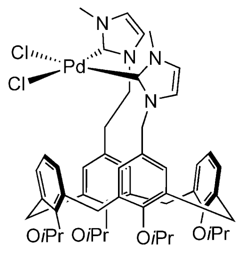


Figure 9. Other df-NHC complexes used in C–C coupling reactions.

Gade et al. have prepared a Pd complex **52** of an oxazole-functionalised NHC, which was synthesised by direct coupling of mesitylimidazole with bromodimethyloxazoline, and found that the resulting complex is an effective catalyst for Heck and Suzuki coupling of activated and deactivated bromoarenes.[90] Higher catalyst loadings (3 mol-%) also gave very good product yields even with aryl chlorides. The Heck coupling of styrene with aryl halides showed the catalyst to be highly selective for the *trans* product. Two reports have appeared describing Pd complexes of bis-NHC ligands, connected by different linking groups, and their catalytic performance in coupling reactions.[91,92] In the first example the ligand forces the complex **53** to adopt a *trans* configuration. The complex was tested in intramolecular asymmetric Heck coupling with poor yields and enantioselectivities; it is clear that the *trans* configuration and the strong coordinating ability of NHCs disfavour a reaction requiring a reductive elimination step.[92] In the second example a dimeric complex, **54**, is formed which shows activity in Suzuki and Heck coupling reactions.[93] Complex **54** has also been applied in the homocoupling of terminal alkynes using Cu^I as a cocatalyst. Moderate to good yields of coupled product were obtained for a range of terminal alkynes under mild conditions and 0.5 mol-% Pd catalyst. A similar catalytic performance was noted for the related system based on complex **55**.[93]

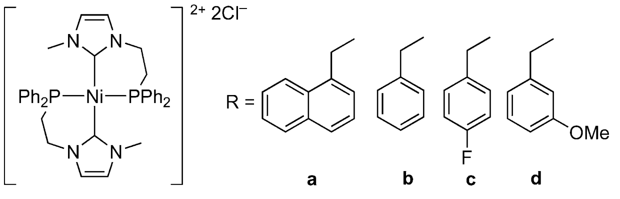
Although not strictly belonging to the category of donor-functionalised NHCs, one novel approach to "functionalisation" has been the studies of Schatz et al.[94,95] and Dinarès, Alcande et al.,[96] in which bidentate NHC–Pd complexes are attached to a calix[4]arene framework such as in **56** (Figure 10). Both in situ (using imidazolium salts with a variety of R groups), and preformed Pd catalysts were used for the Suzuki coupling of aryl halides with phenylboronic acid – the catalyst systems were effective for the coupling of aryl chlorides.[94,95]



56

Figure 10. Calix[4]arene-based NHC–Pd complex used in Suzuki coupling.

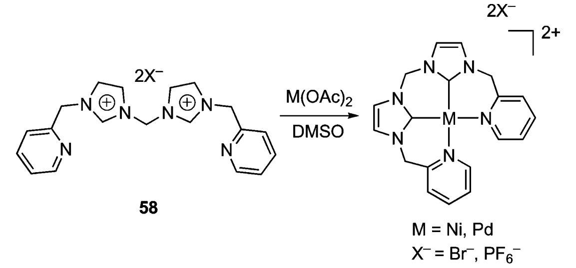
In an interesting series of studies, Ni^{II} complexes of df-NHC ligands have been investigated in various coupling reactions. A Ni^{II} complex of a CNC carbene based pincer of the type described for Pd has been tested in Heck and Suzuki coupling. The catalyst was be operated at 150 °C and in air.[97] The activity of the catalyst in Heck olefination is considerably lower than its Pd counterparts, but both electron-rich and electron-poor aryl bromides could be converted into the coupled product. Activated aryl chlorides could also be converted. However, the catalytic behaviour of the system and the total loss of activity on the addition of Hg suggests that a heterogeneous catalyst system is generated and is the active species.[97] Ni^{II} complexes of an ethyl-bridged diphenylphosphanyl-NHC ligand, of the type previous designed by Nolan et al.[81] and Danopoulos et al.,[80] has been tested in aryl Grignard cross-coupling of aryl chlorides and in the Kumada–Corriu coupling reaction.[98,99] In one particular study worthy of note, Lee et al. have investigated cationic Ni^{II} complexes of ethyl-bridged diphenylphosphanyl-NHC ligands **57** (Figure 11). The complexes are air stable and the complex **57a** was found to be a very effective catalyst (1–3 mol-% loading, 80 °C, 2 h) for the Suzuki cross-coupling of aryl chlorides with phenylboronic acid.[100] For unreactive aryl chlorides, at low catalyst loading, the addition of PPh_3 accelerated the reaction. Activities are superior to those of other reported Ni and Pd–NHC complexes.



57

Figure 11. *P*-functionalised Ni–NHC complexes used in Ni-catalysed Suzuki coupling.

A tetradentate NHC precursor (**58**, Figure 12) has been synthesised, complexes with Ni and Pd prepared, **59**, and the Ni complex tested in Suzuki coupling between aryl halides and phenylboronic acid.[101] The tetradentate chelate ring has a highly twisted helical coordination, however, the ligand undergoes a rapid fluxional ring-twisting process. The catalytic activity of the Ni complex in the Suzuki reaction, including some activity with the coupling of aryl chlorides would suggest a degree of hemilability for the ligand under reaction conditions.

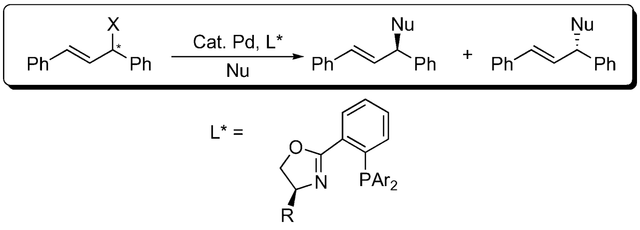


58 **59**

Figure 12. Tetradentate Ni and Pd–NHC complexes used in Suzuki coupling.

Asymmetric Allylic Alkylation (Pd)

Asymmetric allylic alkylation (AAA, Scheme 8) is a well-established methodology for the synthesis of chiral molecules.[102] Very efficient ligands for this reaction have been developed by Helmchen and Pfaltz, the most prominent being phosphanyloxazoline ligands (a.k.a. PHOX, **60**).[103,104]



60

Scheme 8. Popular benchmark allylic alkylation reaction and ligand.

The key to the high enantioselectivities displayed by **60** lies in the different electronic properties of P- and N-donor ligands. Pfaltz et al. have shown that nucleophilic attack on the π-allyl system occurs selectively *trans* to P.[104] On this basis, a variety of functionalised NHC catalysts have been developed.

Fernández et al. have synthesised the Pd complex **61** (containing a chiral imidazo[1,5-*a*]pyridin-3-ylidene thioether ligand) by Ag transfer, and tested the complex in AAA, giving good yields of product and moderate to good *ee* values (ranging up to 91% *ee*).[105] Visentin and Togni have investigated phosphanyl-ferrocenyl-carbene–Pd catalysts **62**, and tested them in allylic amination coupling reactions.[106] Poor conversions and low enantioselectivities were observed. Canac, Duhayon and Chauvin have synthesised a NHC with a phosphonium ylide functional group, coordination to Pd gives a novel CC chelating ligand:[107] complex **63** was tested in the allylation of dimethyl malonate with 3-acetoxy-1,3-diphenylpropene, with 100% conversion and 100% selectivity under mild conditions. This encouraging result should prompt the development of chiral analogues of **63**. In a short note Douthwaite et al. have demonstrated the potential of carefully designed functionalised NHC in asymmetric C–C bond-forming catalysis.[108] An imine-functionalised imidazolium salt **64** has been synthesised and investigated under similar conditions to those employed with **63**. In one case >99% conversion was achieved with 92% *ee*. Finally, while the present manuscript was being finalised, Buono et al. reported NHC precursors **65** in a very interesting study investigating synergic effects between NHCs and chiral P-ligands.[109] Whilst **65** afforded 71 to 89% *ee*, the authors demonstrated that the combination of bulky NHCs and P-donor ligands can reach even higher enantioselectivities (in excess of 95%) (Figure 13).

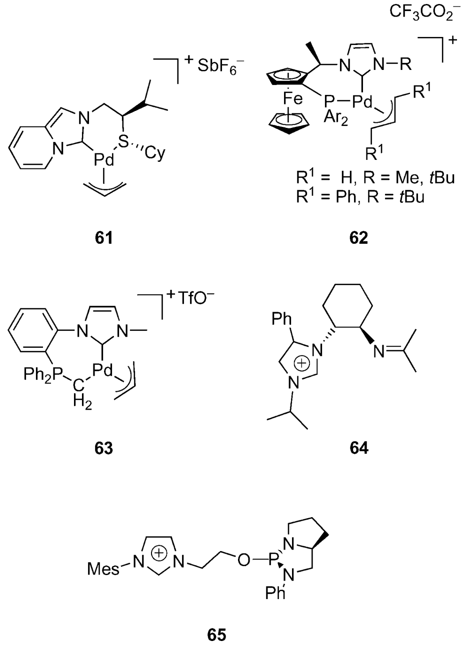


Figure 13. Examples of df-NHCs used in allylic alkylation.

In related examples, Gischig and Togni have synthesised complexes of tridentate PCP ligands containing phosphanyl-ferrocenyl functional groupings on the ring nitrogen atoms **66**.[110] The complexes were tested in asymmetric hydroamination, and in the asymmetric addition of thiomorpholine to methacrylonitrile, giving *ee* values of up to 63 and 75%. Shi et al. have prepared axially chiral chelating binaphthyl-bridged NHC complexes of Pd, **67**, and tested the catalysts for the oxidative kinetic resolution of secondary alcohols; only modest yields of products were obtained but with good *ee* values (Figure 14).[111]

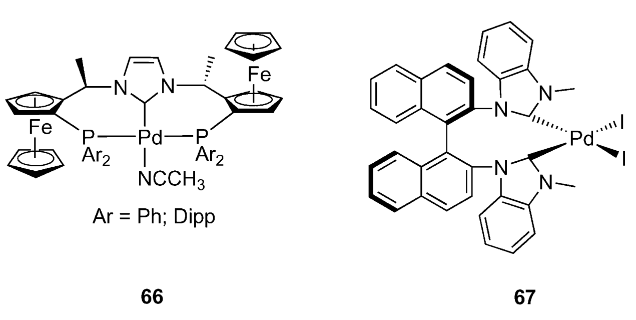


Figure 14. Chiral df-NHC–Pd complexes used in asymmetric catalysis.

Olefin Polymerisation (Ni, Pd)

A limited number of complexes of df-NHC ligands have been tested in catalytic reactions other than standard coupling reactions. For example, Chen and Lin prepared a variety of Pd complexes of the tridentate NCN, pyridine–carbene–pyridine ligand and undertook preliminary testing in the copolymerisation of CO/norbornylene with complex **68** (Figure 15).[112] In all complexes the ligand acts as either a bidentate or monodenate ligand, no tridenate (pincer) complexes were isolated. Of importance is the fact that the catalyst is stable enough to show some activity and does not decompose immediately by reductive elimination. In a further study on olefin polymerisation Jin et al. have found that the Pd complex **69** shows high activity for the polymerisation of norbornene [up to 10^8 g of PNB per mol of NB per hour] when activated with methylaluminoxane (MAO).[72] Interestingly, the trinuclear Ag–carbene complex, which was formed and used in the preparation of the Pd complex, was also found to be active for the polymerisation of ethylene.

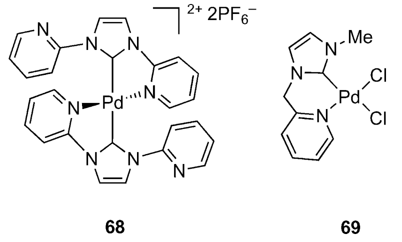
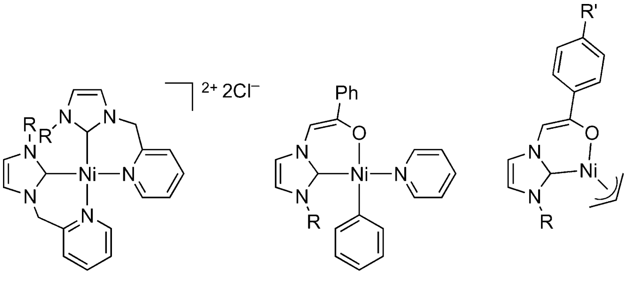


Figure 15. Functionalised Pd–NHC complexes used in copolymerisation.

A number of examples of chelating functionalised NHC complexes of Ni^{II} have been synthesised and tested in olefin polymerisation.[86,113–116] These key studies demonstrate that chelating ligand systems can provide a degree of stability against the facile reductive elimination process previously noted for monodentate NHC complexes of Ni.[24] However, it appears that the reductive elimination from these hemilabile systems may still lead to catalyst deactivation. Complexes **70** (Figure 15), when activated with methylaluminoxane (MAO) showed high catalytic activities for the polymerisation of norbornadiene and moderate activity for the polymerisation of ethylene.[113] Maximum activity was obtained at 80 °C, however stability decreased as the temperature was raised. Even at 30 °C the catalyst deactivates quite rapidly. Toluene solutions of the neutral Ni^{II} complex **71**, containing a novel anionic NHC-enolate ligand formed single component catalysts (no cocatalyst necessary) for the polymerisation of ethylene to linear polyethylene, with high α-olefin end groups.[115] However, the catalysts were short-lived, and a possible decomposition mechanism was proposed, involving chain-transfer by β-elimination, generating a carbene–Ni–H intermediate, which decomposed by reductive elimination. In related studies, Ni^{II}–allyl complexes of NHC-enolate ligands were prepared and tested in ethylene polymerisation.[116] Toluene solutions of complex **72b**, activated with diethylzinc yielded a catalyst with modest activity, but high linearity, and greatly improved stability compared with previous Ni–NHC-based polymerisation catalysts. This improved catalyst stability is an important breakthrough in the application of functionalised carbene in catalysis (Figure 16).



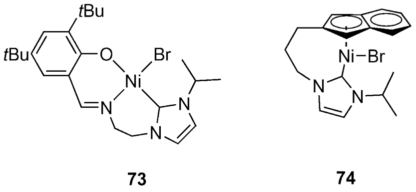
R = Me; Ar **70**

R = Mes; Dipp **71**

R = Dipp
R' = H **72a**
R' = NO_2 **72b**

Figure 16. Functionalised Ni–NHC complexes used in ethylene polymerisation.

In the same way that phosphane-based ligands have undergone important design stages, novel df-NHC ligands are now being designed and their performance investigated; in further polymerisation studies, the Ni^{II} complex **73** (Figure 17) was treated with $NaBPh_4$ and tested as a catalyst for the polymerisation of styrene, at 80 °C in toluene.[114] On the basis of the relatively high average molecular weight of the resultant polymer it was suggested that the catalysts with a tridentate salicylaldiminato-carbene demonstrate higher stability. The same group also studied the polymerisation of styrene using a Ni^{II} complex containing an NHC functionalised with a C3-bridged indenyl group, **74**.[117] The indenyl group also appeared to improve the stability of the catalyst.

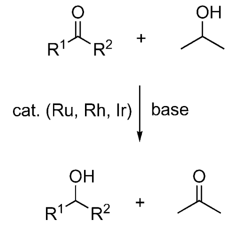


73 **74**

Figure 17. Ni–NHC complexes of df-NHCs used in styrene polymerisation.

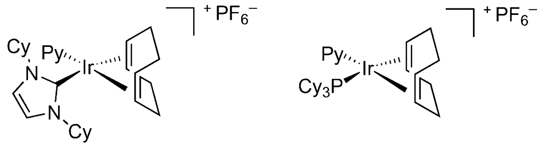
Catalytic Transfer Hydrogenation (Rh, Ir)

Rh and Ir are known to be effective catalysts for the transfer hydrogenation of unsaturated subtrates by hydrogen donors (e.g., cyclohexene or 2-propanol).[118] In particular, transfer hydrogenation of carbonyl compounds in *i*PrOH (Scheme 9) is a popular benchmark reaction to test the catalytic properties of Rh and Ir complexes as it is a very simple protocol. The driving force is provided by the use of the hydrogen donor as solvent. In the case of unsymmetrical ketones, one generates two enantiomers and it is thus possible to test chiral complexes.



Scheme 9. Catalytic transfer hydrogenation of carbonyl compounds.

Nolan first reported the use of a cationic Ir^{I}–NHC complex, $[Ir(COD)(Py)(ICy)]PF_6$ (ICy = *N*,*N′*-dicyclohexylimidazol-2-ylidene) **75** in catalytic transfer hydrogenation of unsaturated substrates such as carbonyl compounds.[119] This catalyst is an NHC analogue of Crabtree's catalyst **76** (Figure 18; a general use hydrogenation catalyst). Since this initial report, several Rh and Ir complexes of donor-functionalised NHCs have been applied to catalytic transfer hydrogenation.



75 **76**

Figure 18. Crabtree's catalyst and its NHC analogue.

In 2002, Crabtree et al. reported the use of bis(carbene) complexes of Rh^{III} and Ir^{III} **77a–d**.[120,121] The two NHC moieties in these complexes are linked by a methylene bridge. Interesting activities were obtained with 0.005–0.1 mol-% catalyst, in particular **77c** enabled the hydrogenation of acetophenone at room temperature (Figure 19). Also, this catalyst was found to be more active by four orders of magnitude than similar complexes with different alkyl substituents.[121] In a subsequent paper,[122] the same group expanded the linker and the resulting Ir complex was applied to the transfer hydrogenation of aldehydes (a more challenging reaction due to possible decarbonylation and aldol side reactions in the presence of base) at low catalyst loading (0.1 mol-%). Finally, other chelating bis(carbene) complexes were tested in transfer hydrogenation,[123] notably a bitriazole NHC,[124] however activities were low.

An intriguing tripodal NHC complex of Rh^{III} (**78**, Scheme 10) was described by Peris, displaying good activities (loadings down to 0.001 mol-%) for a range of substrates including imines.[125] The stability profile of this complex (24 h reaction in refluxing *i*PrOH) is consistent with the favourable thermodynamics of its formation, for which no mechanism was proposed.

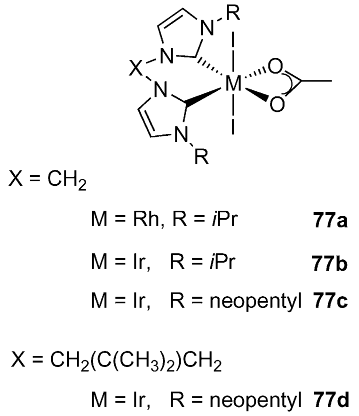
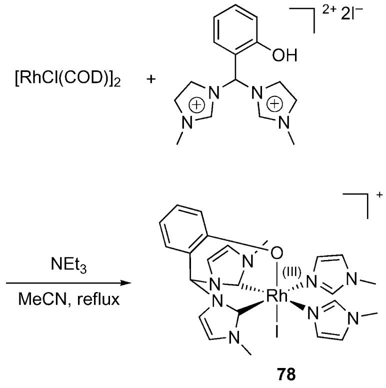
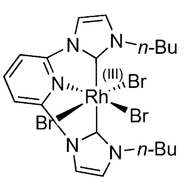


Figure 19. Bis(carbene) Rh and Ir complexes for transfer hydrogenation.



Scheme 10. Synthesis of a tripodal NHC complex of Rh.

Peris et al. also reported the use of a CNC pincer complex **79** (Figure 20), obtained by the same method as **78**. The activity of this complex in the hydrogenation of cyclohexanone, acetophenone and benzophenone was slightly lower than that of **78**, with loadings of 0.06–0.006 mol-%.



79

Figure 20. CNC-pincer NHC–Rh^{III} complex.

Transfer hydrogenation catalysts discussed so far are likely to remain firmly chelated during catalysis. In the view of the success of the concept of hemilability in catalysis,[126–128] it is quite surprising that hemilabile NHC ligands only display moderate catalytic activity in transfer hydrogenation. Complexes based on such ligands (Figure 21) have been described by Oro (**80**),[129] Peris (**81**)[130,131] and Liu (**82**),[132] with relatively high catalyst loading (0.1–5 mol-%) and/or limited substrate scope.

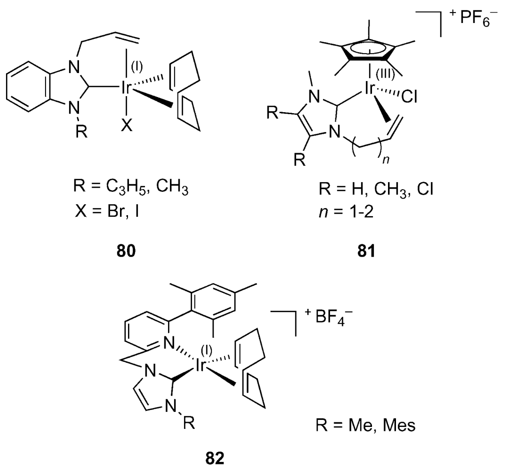
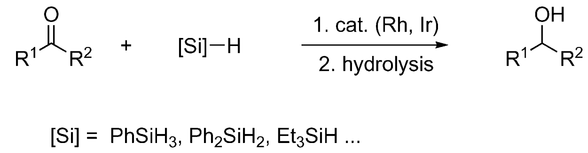


Figure 21. Hemilabile NHC complexes for transfer hydrogenation.

Hydrosilylation of Ketones (Rh, Ir)

The hydrosilylation of ketones (Scheme 11) by silanes is similar to transfer hydrogenation in that chiral secondary alcohols can be generated from prochiral substrates (after hydrolysis; alternatively, the silyl ether can be used as a protected alcohol).[133]



Scheme 11. Hydrosilylation of carbonyl compounds.

Spectacular achievements in this field have been accomplished with ligands **83**–**85** (Figure 22),[134–136] reaching *ee* values in excess of 95% at 1 mol-% Rh loading.

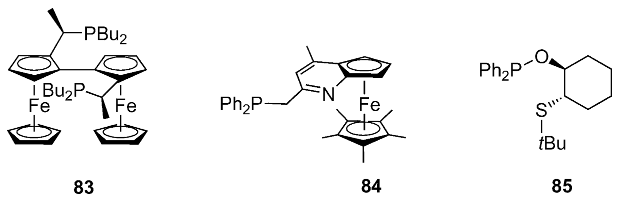
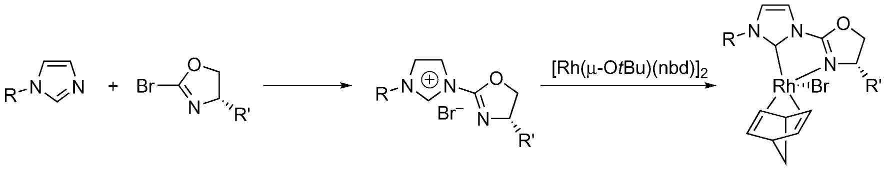


Figure 22. P-, N- and S-donor functionalised phosphanes for the asymmetric hydrosilylation of ketones.

Gade et al. have synthesised a library of NHC-oxazoline Rh^I complexes, taking advantage of the availability of a variety of imidazoles and their reactvity towards bromooxazolines (Scheme 12).[137,138]

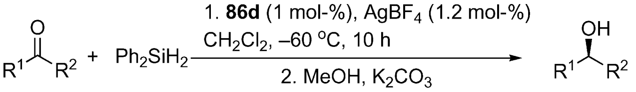
These complexes were investigated for their activity in the asymmetric hydrosilylation of acetophenone. Complex **86d** was found to give the best results, and the reaction conditions were systematically optimised (silane, temperature and activating silver salt). Very good activities (conversions between 65 and 99% at 1 mol-% Rh loading) and enantio-



86a-j

86d: R = Mes, R' = *t*Bu

Scheme 12. Synthesis of oxazoline–NHC Rh^I complexes.



65-99% yield

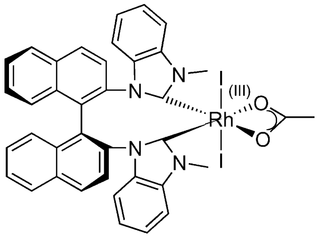
R^1 = aryl, alkyl
R^2 = alkyl

19 examples, up to 95 % *ee*

Scheme 13. Hydrosilylation of ketones catalysed by **86d**.

selectivities (between 53 and 95%) where obtained for a wide range of arylalkyl and dialkyl ketones (Scheme 13).

Shi et al. reported the use of complex **87**, with a bis(imidazol-2-ylidene) ligand derived from (*S*)-BINAM, for the hydrosilylation of ketones[139] and β-keto esters[140] (Figure 23).



87

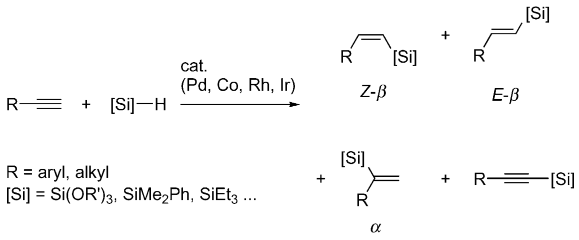
Figure 23. Rh^{III} complex with BINAM-based bis(carbene) ligand.

Near complete conversions and excellent enantioselectivities (up to 98%) were obtained for a variety of substrates at 2 mol-% Rh loading. This is higher than the loading used with **86d**, but an advantage of this system over that of Gade is that the reaction can be conducted at 15 °C instead of –40 °C.

In addition to **86d** and **87**, other catalytic systems have been investigated: Bolm et al. reported several chiral ferrocene-based oxazoline–NHC Rh^I complexes,[141] whilst a family of chiral binaphthyl alkoxy-NHC–Rh^I and Ir^I complexes were reported by Crabtree.[142] However, these complexes did not give satisfactory enantioselectivities. Finally, achiral ligands were applied to the hydrosilyation of ketones by Poli (ferrocene-based phosphanyl-NHCs),[143] Shi (derived from 2,2′-diaminobiphenyl),[144] and Tsuji [dendritic bis(carbenes)].[145]

Hydrosilylation of Alkynes (Rh, Ir, Pt)

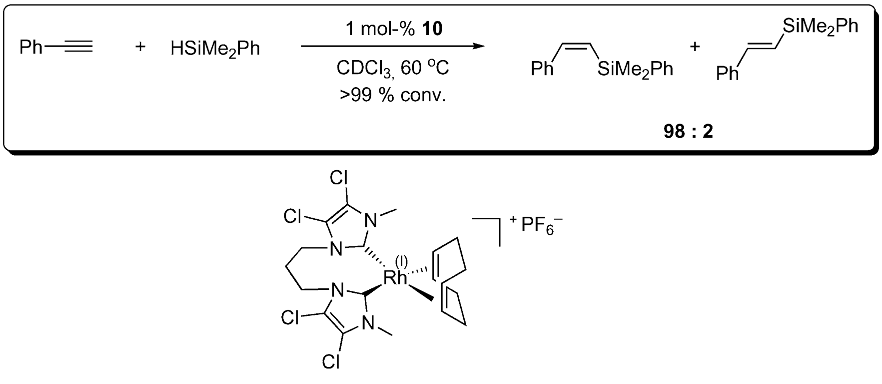
The reaction of silanes with terminal alkynes is a remarkably challenging reaction in which to test new catalysts. Indeed, no less than four types of silylated products [i.e. (*E*) and (*Z*) β-silylalkenyls, α-silylalkenyls and silylalkynes, Scheme 14] can be obtained, making it a very difficult process to optimise. Remarkably, NHC–Rh complexes were used by Hill[14] and Lappert[15] in the hydrosilylation of olefins and alkynes long before the isolation of the first stable free NHC by Arduengo.[16]



Scheme 14. Hydrosilylation of alkynes.

It is generally accepted that the reaction proceeds by oxidative addition of the silane to the metal, followed by insertion of the alkyne in the metal–hydrogen (so called Chalk–Harrod mechanism[146]) or the metal–silicon bond (so called modified Chalk–Harrod mechanism[147]), followed by reductive elimination of the silylated product.[148]

Peris et al. reported several NHC complexes active in alkynes hydrosilylation, including bimetallic NHC–Rh^I,[76,149] bis-NHC–Rh^I,[149–151] bis-NHC–Ir^I[149,150,152] and pyridine-functionalised Ir^I and Rh^I complexes.[131] For example, complex **88** enabled the reaction of phenylacetylene with $HSiMe_2Ph$ with 98% selectivity for the (*Z*)-β-silylalkenyl product at 1 mol-% loading (Scheme 15). By contrast, the same complex only gave the dehydrogenative si-

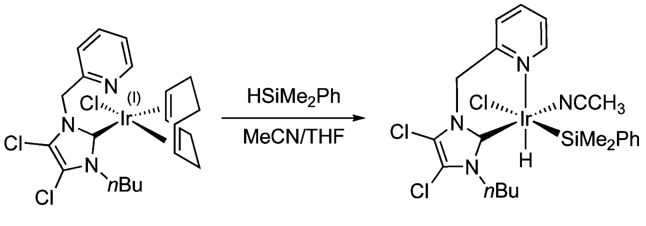


88

Scheme 15. Hydrosilylation of phenylacetylene with a bis-NHC–Rh^{I} complex.

lylation product (silylphenylacetylene) when $HSi(OEt)_3$ was used, highlighting the importance of the choice of silane.

The same group also found that Ir complexes were generally less active than their Rh counterparts.[150] Thus, taking advantage of the lower activity of the Ir complexes, a mechanistic study (by ESI-MS[153]) of the hydrosilylation of terminal alkynes was conducted with the complexes **89a** and **89b** (Scheme 16).

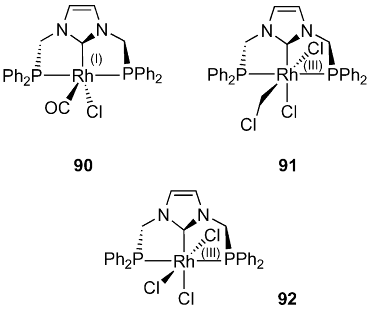


89a **89b**

Scheme 16. Pyridine-functionalised NHC–Ir complexes used in mechanistic studies.

The authors identified all the expected intermediates for both the M–H and M–Si insertion pathways, and concluded (in accordance with previous studies by Crabtree[148]) that higher alkyne/silane ratios favored the latter, which in turns increases the amount of undesired silylalkyne product.

Perhaps the most interesting results in terms of catalytic activity were reported by Lee et al.[154] These authors synthesised Rh^{I} and Rh^{III} complexes **90–92**[155] containing a PCP-pincer carbene ligand (Figure 24).



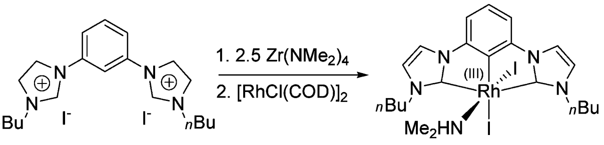
90 **91**

92

Figure 24. Pincer NHC–Rh complexes for alkyne hydrosilylation.

The complexes **90–92** all dislayed high activities, enabling the reaction of phenylacetylene with $HSiMe_2Ph$ at 0.1–0.001 mol-% loading with >80% selectivities on average for the (*E*)-β-silylalkenyl product. The very close activities of **90–92** led the authors to conclude that the catalytic active species was the [RhCl(PCP)] fragment.

Another pincer carbene Rh^{III} complex was reported by Hollis et al. Whilst most functionalised NHC complexes are obtained by transfer from a Ag^{I} complex[156] or in situ deprotonation of an imidazolium salt precursor followed by coordination to a metal,[157] complex **93** was prepared by transmetalation from a Zr^{IV} complex (Scheme 17). This catalyst gave 95% selectivity for the (*Z*)-product at 2 mol-% loading in the reaction of phenylacetylene with $HSiMe_2Ph$.[158]

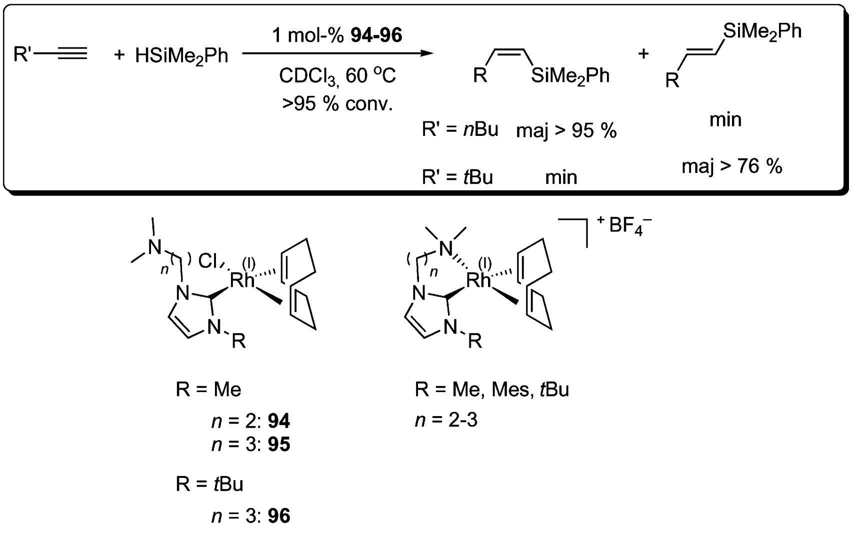


93

Scheme 17. Synthesis of a pincer NHC–Rh^{III} complex for alkynes hydrosilylation.

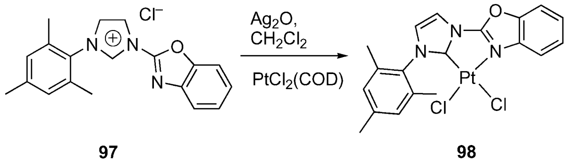
Finally, Oro et al. recently reported several neutral and cationic dimethylamino-NHC–Rh^{I} complexes (Scheme 18) and tested them against a range of alkynes.[159] Neutral complexes were generally more selective and more active than cationic ones. Interestingly, complexes **94–96** displayed almost complete selectivities (> 95%) for the (*Z*)-product in the case of hex-1-yne whilst *tert*-butylacetylene mostly gave the (*E*)-product (> 76%).[160]

There has been relatively few publications where Pt complexes of df-NHCs have been applied in catalysis.[161,162] An oxazole-NHC ligand precursor (**97**, Scheme 19) has been synthesised, and coordinated to Pd, Rh, and to $PtCl_2(COD)$ via a silver transfer route.[162] Both the Rh, and Pt complexes were tested in hydrosilylation. The Pt complex **98** was investigated in the hydrosilylation of phenylacetylene and styrene with various silanes; the hydrosilylation of 1-octene was also investigated. In all cases ac-



Scheme 18. Alkyne hydrosilylation with amino-NHC–Rh^{I} complexes.

tivity was modest, however, selectivity was generally good, and favoured the linear product. Of significance, very little isomerisation or dehydrogenative silylation of the alkene substrate was observed.



Scheme 19. Benzoxazole-based NHC–Pt complex used in hydrosilylation.

Despite the advances made in the design of selective and highly active catalysts for alkyne hydrosilylation, there is to date no clearly defined direction which would hold much promise to achieve this goal. This is in contrast with other reactions, such as asymmetric olefin hydrogenation (vide infra), for which very efficient families of catalysts have been identified.

Asymmetric Olefin Hydrogenation (Rh, Ir)

The asymmetric hydrogenation of functionalised olefins, pioneered by Knowles and Noyori,[163–165] was first developed with Ru and Rh. Inspired by the success of Crabtree's Ir^{I} catalyst **76** (Figure 18) in the hydrogenation of unfunctionalised, polysubstituted olefins, Pfaltz et al. have developed extremely efficient Ir^{I} systems containing the PHOX (**60**) and SimplePHOX P,N ligands (**99**).[103,166] More recently, phosphanyl-oxazoline ligands **100** were reported to efficiently catalyse the hydrogenation of tetrasubstituted substrates (Figure 25).[167]

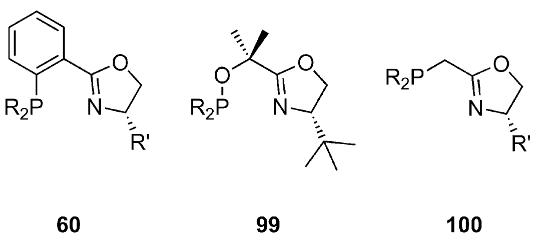
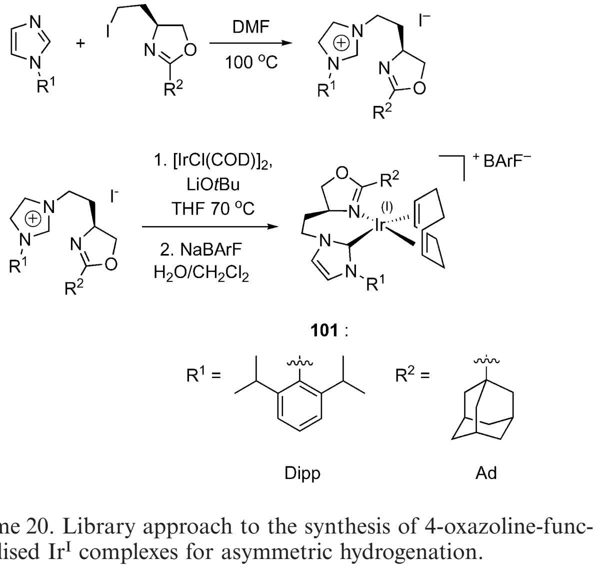


Figure 25. P,N-ligands for the asymmetric hydrogenation of unfunctionalised olefins.

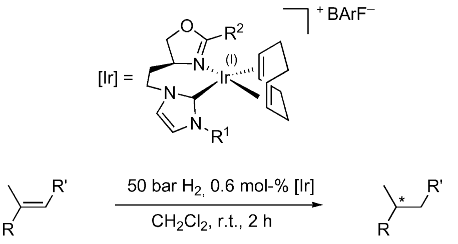
Burgess developed a library approach to 4-oxazoline-functionalised NHC ligands from which **101** emerged (Scheme 20). Complex **101** is an air-stable cationic Ir^{I} catalyst displaying excellent activities and enantioselectivities in the hydrogenation of trisubstituted arylalkenes.[168,169]



Scheme 20. Library approach to the synthesis of 4-oxazoline-functionalised Ir^{I} complexes for asymmetric hydrogenation.

Compared to other complexes of the same family, **101** is both much more active and selective (Table 1).

Table 1. Hydrogenation of trisubstituted alkenes.[168]



Entry[a]	R	R′	R¹	R²	Conv. (%)	*ee* (%)
1	Ph	Ph	Dipp	Ph	25	13
2	Ph	Ph	Dipp	*t*Bu	81	50
3	Ph	Ph	Dipp	Bz	12	25
4	**Ph**	**Ph**	**Dipp**	**Ad**	**99**	**98**
5	*p*-C_6H_4OMe	Ph	Dipp	*t*Bu	45	45
6	***p*-C_6H_4OMe**	**Ph**	**Dipp**	**Ad**	**99**	**97**
7[a]	*p*-C_6H_4OMe	Me[b]	Dep[c]	Ad	84	27
8[a]	***p*-C_6H_4OMe**	**Me**[b]	**Dipp**	**Ad**	**100**	**79**

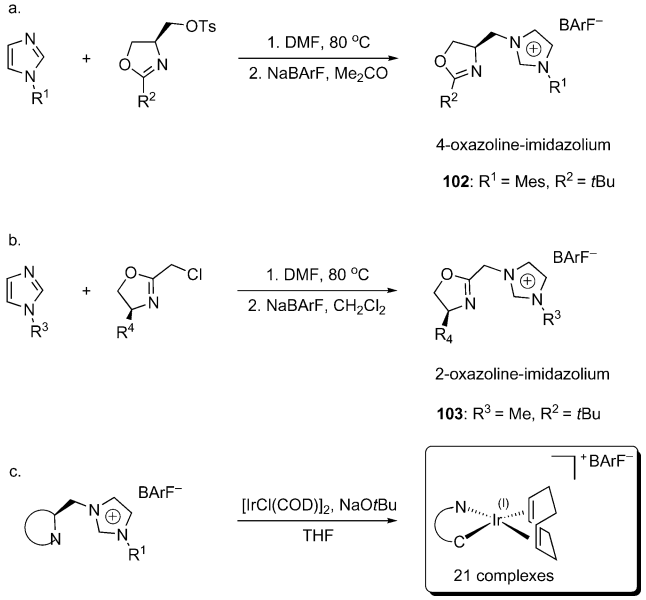
[a] 1 bar H_2. [b] (*Z*)-Alkene. [c] 2,6-Diethylphenyl.

The exquisite selectivity of **101** appears to arise from a combination of electronic and steric effects. Electronic effects drive the alkene substrate *trans* to the NHC, enabling steric effects (mainly adamantane/alkene interaction) to efficiently control enantioface discrimination.[170] The application of **101** to the hydrogenation of more complex functionalised dienes has also been described,[171,172] whilst a pyrimidine analogue was recently described.[173]

In direct line with the work of Burgess, Pfaltz has reported a library approach to 2- and 4-oxazoline-NHC cationic Ir^I complexes (Scheme 21). A large number of imidazolium precursors were generated (e.g., **102** and **103**) and the NHC–Ir^I complexes were tested in the hydrogenation of a range of di- and trisubstituted alkenes, with results (essentially complete conversions at 1 mol-% loading, *ee* values up to 90%) approaching those obtained with **101** and the best SimplePHOX ligand.[174]

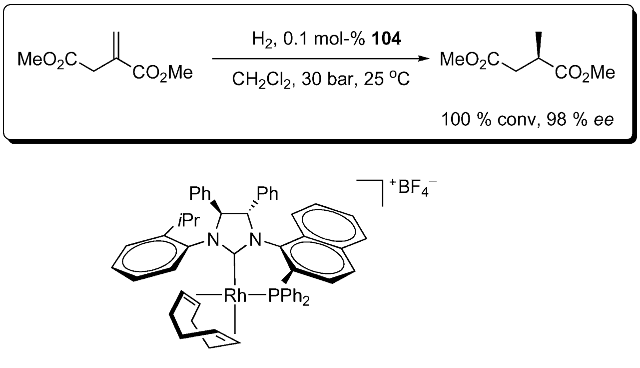
The obvious advantage of library approaches to functionalised ligands is that a wide variety of substituents can be investigated, allowing for fine-tuning of the catalyst, depending on the substrate and/or reaction conditions. Also, as pointed out by Burgess,[172] and Pfaltz,[174] Ir-catalysed asymmetric hydrogenation is a complex process, the mechanism of which can vary according to a wide range of parameters (including stirring speed!). This makes rational catalyst design almost impossible, hence the need for such approaches.

Other, more isolated examples of *N*-functionalised NHC–Ir^I complexes for olefin hydrogenation have been reported by Bolm (planar-chiral paracyclophane-based ligand),[175] Messerle (pyrazole-functionalised NHC),[176] and Andersson (thiazole-functionalised NHC)[177] whilst *P*-functionalised NHC–Ir^I complexes were reported by Pfaltz (ligands structurally close to **99** and **100**)[178] and Bolm (planar-chiral phosphanyl-NHC).[179]



Scheme 21. Synthesis of libraries of functionalised NHC–Ir^I complexes for asymmetric olefin hydrogenation.

Finally Helmchen reported a *P*-functionalised Rh^I complex (**104**, Scheme 22).[180] This catalyst displayed both high activities (0.1 to 1 mol-% loading) and enantioselectivities (*ee* values from 63 to 99%) for a range of functionalised olefins.



104

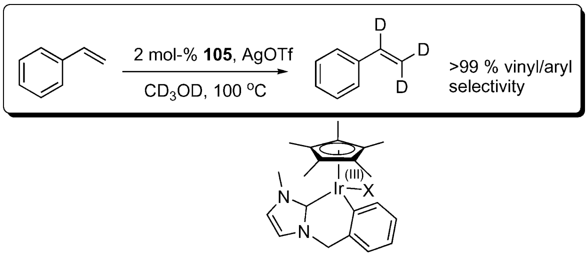
Scheme 22. *P*-functionalised NHC–Rh^I complex for asymmetric olefin hydrogenation.

Miscellaneous Reactions

Functionalised NHC complexes have been applied to a number of less systematically investigated reactions. For example, **104** (see Scheme 22) was applied to the conjugate addition of arylboronic acids to cyclic enones with *ee* values reaching 94%.[181] Peris et al. also reported the application of a CNC pincer dimetallic Rh^I complex to the hydroformylation of olefins.[182] Other reactions include the following steps.

H/D Exchange (Ir)

Complex **105** was reported by Peris et al. amongst other [Ir(Cp*)Cl(NHC)] complexes.[183] The ability of these complexes to undergo reversible metalation/solvolysis of the substituents on the NHC seem to make them very active in deuteration reactions.[184] Interesting selectivities were obtained (Scheme 23), and these complexes certainly deserve more investigation. The same group recently reported a chiral analogue of **105** and tested it in the chiral diboration of olefins. The activity was modest, and *ee* values were low (10%).[185]



105 (R = I, Cl)

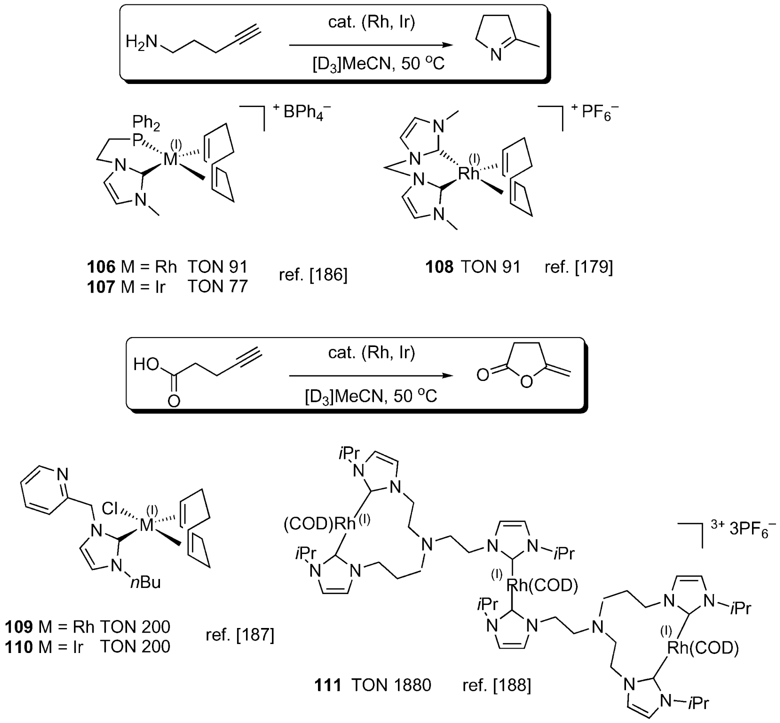
Scheme 23. Rare NHC–Ir^{III} complex active in deuteration.

Cyclisation of Alkynes (Rh, Ir)

Amino and carboxylato alkynes can be cyclised by an intramolecular addition of NH or OH across the carbon–carbon triple bond.[131,186–188] These reactions produce interesting cyclic imines or lactones in an atom economical process. Amongst other cationic Rh^{I} and Ir^{I} complexes, trimetallic complex **111**, containing a tertiary amino functionality, displayed high activity towards pentynoic acid cyclisation (Scheme 24).

Conclusions

It is clear from this brief overview of chelating df-NHC ligands and their complexes that many opportunities still exist for the design and development of novel and potentially very useful ligand systems for catalysis. In the case of group 10 metals, the facile reductive elimination reaction that NHC ligands undergo does present a problem, however, compared with the extensive investigations and ligand design studies carried out, over many years, on phosphane ligands it is still very early in the design process for these NHCs. Because of the inherently strong NHC–M bond, key opportunities exist in the design of pincer ligands encompassing NHCs, and immobilised ligand systems offer some key areas for development. The use of these ligand systems in ionic liquid solvents based on imidazolium salts also offers an interesting approach to forming stable complexes and catalysts. The investigation of Pd complexes of df-NHCs has been heavily focused on catalytic coupling reactions, particularly Heck and Suzuki coupling processes. The design of suitably hemi-labile ligand systems may allow the application of df-NHCs in reactions such as amination or telomerization – reactions in which it is believed that the active catalyst is a monodentate, zero-valent intermediate. In the case of Rh and Ir systems, df-NHCs have benefited from considerable groundwork with phosphane analogues. The ease with which large libraries of complexes can be



Scheme 24. Alkynes cyclisation-mediated by functionalised NHC–Rh and Ir complexes.

obtained, allowing for extensive ligand optimisation, is key to the success of these catalysts in reactions such as asymmetric hydrogenation and ketone hydrosilylation. As the understanding of NHCs and their complexes progresses, and new synthetic methods emerge, df-NHCs might enable the development of industrially viable catalytic processes in a not-so-distant future.

---

[1] H.-W. Wanzlick, H. J. Kleiner, *Angew. Chem.* **1961**, *73*, 493–493.

[2] H. W. Wanzlick, F. Esser, H. J. Kleiner, *Chem. Ber.* **1963**, *96*, 1208–1212.

[3] H.-W. Wanzlick, H. J. Schönherr, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141–142.

[4] H. J. Schoenherr, H. W. Wanzlick, *Justus Liebigs Ann. Chem.* **1970**, *731*, 176–179.

[5] H. J. Schoenherr, H. W. Wanzlick, *Chem. Ber.* **1970**, *103*, 1037–1046.

[6] R. Walentowski, H. W. Wanzlick, *Chem. Ber.* **1970**, *103*, 1421–1423.

[7] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42–P43.

[8] K. Öfele, *Angew. Chem. Int. Ed. Engl.* **1969**, *9*, 739–740.

[9] K. Öfele, C. G. Kreiter, *Chem. Ber.* **1972**, *105*, 529–540.

[10] D. J. Cardin, M. J. Doyle, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1972**, 927–928.

[11] D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1973**, 514–522.

[12] D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, E. W. Randall, E. Rosenberg, *J. Chem. Soc., Dalton Trans.* **1973**, 1982–1985.

[13] B. Cetinkaya, E. Cetinkaya, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1973**, 906–912.

[14] J. E. Hill, T. A. Nile, *J. Organomet. Chem.* **1977**, *137*, 293–300.

[15] M. F. Lappert, R. K. Maskell, *J. Organomet. Chem.* **1984**, *264*, 217–228.

[16] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[17] I. Anthony, J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.

[18] W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309.

[19] D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748.

[20] A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White, B. W. Skelton, *J. Organomet. Chem.* **2001**, *617–618*, 546–560.

[21] D. S. McGuinness, M. J. Green, K. J. Cavell, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1998**, *565*, 165–178.

[22] D. S. McGuinness, K. J. Cavell, B. W. Skelton, A. H. White, *Organometallics* **1999**, *18*, 1596–1605.

[23] D. S. McGuinness, K. J. Cavell, B. F. Yates, B. W. Skelton, A. H. White, *J. Am. Chem. Soc.* **2001**, *123*, 8317–8328.

[24] D. S. McGuinness, N. Saendig, B. F. Yates, K. J. Cavell, *J. Am. Chem. Soc.* **2001**, *123*, 4029–4040.

[25] S. Caddick, F. G. N. Cloke, P. B. Hitchcock, J. Leonard, A. K. d. K. Lewis, D. McKerrecher, L. R. Titcomb, *Organometallics* **2002**, *21*, 4318–4319.

[26] D. S. McGuinness, W. Mueller, P. Wasserscheid, K. J. Cavell, B. W. Skelton, A. H. White, U. Englert, *Organometallics* **2002**, *21*, 175–181.

[27] D. J. Nielsen, K. J. Cavell, Pd–NHC Complexes as Catalysts in Telomerization and Aryl Amination Reactions, in *N-Heterocyclic Carbenes in Synthesis* (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2006**; pp. 73–102.

[28] A. N. Nesmeyanov, T. N. Sal'nikova, Y. T. Struchkov, V. G. Andrianov, A. A. Pogrebnyak, L. V. Rybin, M. I. Rybinskaya, *J. Organomet. Chem.* **1976**, *117*, C16–C20.

[29] W. K. Dean, R. S. Charles, D. G. VanDerveer, *Inorg. Chem.* **1977**, *16*, 3328–3333.

[30] L. K. Johnson, R. J. Angelici, *Inorg. Chem.* **1987**, *26*, 973–976.

[31] J. A. Chamizo, P. B. Hitchcock, H. A. Jasim, M. F. Lappert, *J. Organomet. Chem.* **1993**, *451*, 89–96.

[32] D. Sellmann, W. Prechtel, F. Knoch, M. Moll, *Inorg. Chem.* **1993**, *32*, 538–546.

[33] W. A. Herrmann, C. Köcher, L. J. Gooßen, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 1627–1636.

[34] C.-Y. Liu, D.-Y. Chen, G.-H. Lee, S.-M. Peng, S.-T. Liu, *Organometallics* **1996**, *15*, 1055–1061.

[35] B. Cetinkaya, I. Ozdemir, P. H. Dixneuf, *J. Organomet. Chem.* **1997**, *534*, 153–158.

[36] W. A. Herrmann, L. J. Gooβen, M. Spiegler, *J. Organomet. Chem.* **1997**, *547*, 357–366.

[37] D. Sellmann, C. Allmann, F. Heinemann, F. Knoch, J. Sutter, *J. Organomet. Chem.* **1997**, *541*, 291–305.

[38] H. Lang, J. J. Vittal, P.-H. Leung, *J. Chem. Soc., Dalton Trans.* **1998**, 2109–2110.

[39] W. A. Herrmann, L. J. Goossen, M. Spiegler, *Organometallics* **1998**, *17*, 2162–2168.

[40] W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187.

[41] D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.

[42] F. K. Zinn, M. S. Viciu, S. P. Nolan, *Annu. Rep. Prog. Chem. B* **2004**, *100*, 231–249.

[43] K. J. Cavell, D. S. McGuinness, *Coord. Chem. Rev.* **2004**, *248*, 671–679.

[44] E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239–2246.

[45] C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2005**, *248*, 2247–2273.

[46] V. Cesar, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619–636.

[47] K. J. Cavell, D. S. McGuinness, Palladium Complexes with Carbonyl, Isocyanide and Carbene Ligands. In *Comprehensive Organometallic Chemistry III* (Eds.: R. H. Crabtree, D. M. P. Mingos, A. J. Canty), Elsevier, **2007**, vol. 8, pp. 197–268.

[48] D. Pugh, A. A. Danopoulos, *Coord. Chem. Rev.* **2007**, *251*, 610–641.

[49] R. E. Douthwaite, *Coord. Chem. Rev.* **2007**, *251*, 702–717.

[50] L. H. Gade, S. Bellemin-Laponnaz, *Coord. Chem. Rev.* **2007**, *251*, 718–725.

[51] J. A. Mata, M. Poyatos, E. Peris, *Coord. Chem. Rev.* **2007**, *251*, 841–859.

[52] W. J. Sommer, M. Weck, *Coord. Chem. Rev.* **2007**, *251*, 860–873.

[53] F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.

[54] A. A. D. Tulloch, A. A. Danopoulos, S. M. Cafferkey, S. Kleinhenz, M. B. Hursthouse, R. P. Tooze, *Chem. Commun.* **2000**, 1247–1248.

[55] C.-Y. Wang, Y.-H. Liu, S.-M. Peng, J.-T. Chen, S.-T. Liu, *J. Organomet. Chem.* **2007**, *692*, 3976–3983.

[56] J. Houghton, G. Dyson, R. E. Douthwaite, A. C. Whitwood, B. M. Kariuki, *Dalton Trans.* **2007**, 3065–3073.

[57] M. V. Baker, M. J. Bosnich, C. C. Williams, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1999**, *52*, 823–825.

[58] M. V. Baker, B. W. Skelton, A. H. White, C. C. Williams, *J. Chem. Soc., Dalton Trans.* **2001**, 111–120.

[59] M. V. Baker, D. H. Brown, P. V. Simpson, B. W. Skelton, A. H. White, C. C. Williams, *J. Organomet. Chem.* **2006**, *691*, 5845–5855.

[60] R. Wang, B. Twamley, J. M. Shreeve, *J. Org. Chem.* **2006**, *71*, 426–429.

[61] R. Wang, Z. Zeng, B. Twamley, M. M. Piekarski, J. n. M. Shreeve, *Eur. J. Org. Chem.* **2007**, 655–661.

[62] E. Kluser, A. Neels, M. Albrecht, *Chem. Commun.* **2006**, 4495–4497.

[63] A. A. D. Tulloch, A. A. Danopoulos, G. J. Tizzard, S. J. Coles, M. B. Hursthouse, R. S. Hay-Motherwell, W. B. Motherwell, *Chem. Commun.* **2001**, 1270–1271.

[64] E. Peris, J. Mata, J. A. Loch, R. H. Crabtree, *Chem. Commun.* **2001**, 201–202.

[65] S. Grundemann, M. Albrecht, J. A. Loch, J. W. Faller, R. H. Crabtree, *Organometallics* **2001**, *20*, 5485–5488.

[66] J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 700–706.

[67] D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2002**, *327*, 116–125.

[68] D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2006**, *359*, 1855–1869.

[69] F. Churruca, R. SanMartin, B. Inés, I. Tellitu, E. Domínguez, *Adv. Synth. Catal.* **2006**, *348*, 1836–1840.

[70] F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, *Organometallics* **2005**, *24*, 6458–6463.

[71] F. E. Hahn, M. C. Jahnke, T. Pape, *Organometallics* **2007**, *26*, 150–154.

[72] D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, *Organometallics* **2006**, *25*, 4850–4856.

[73] D. J. Nielsen, K. J. Cavell, M. S. Viciu, S. P. Nolan, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2005**, *690*, 6133–6142.

[74] L. Ray, M. M. Shaikh, P. Ghosh, *Organometallics* **2007**, *26*, 958–964.

[75] P. G. Steel, C. W. T. Teasdale, *Tetrahedron Lett.* **2004**, *45*, 8977–8980.

[76] M. Poyatos, F. Marquez, E. Peris, C. Claver, E. Fernandez, *New J. Chem.* **2003**, *27*, 425–431.

[77] E. Mas-Marza, A. M. Segarra, C. Claver, E. Peris, E. Fernandez, *Tetrahedron Lett.* **2003**, *44*, 6595–6599.

[78] H. M. Lee, J. Y. Zeng, C. H. Hu, M. T. Lee, *Inorg. Chem.* **2004**, *43*, 6822–6829.

[79] H. M. Lee, P. L. Chiu, J. Y. Zeng, *Inorg. Chim. Acta* **2004**, *357*, 4313–4321.

[80] N. Tsoureas, A. A. Danopoulos, A. A. D. Tulloch, M. E. Light, *Organometallics* **2003**, *22*, 4750–4758.

[81] C. Yang, H. M. Lee, S. P. Nolan, *Org. Lett.* **2001**, *3*, 1511–1514.

[82] F. E. Hahn, M. C. Jahnke, T. Pape, *Organometallics* **2006**, *25*, 5927–5936.

[83] J.-C. Shi, P.-Y. Yang, Q. Tong, Y. Wu, Y. Peng, *J. Mol. Catal. A* **2006**, *259*, 7–10.

[84] T. Yagyu, S. Oya, M. Maeda, K. Jitsukawa, *Chem. Lett.* **2006**, *35*, 154–155.

[85] T. Chen, J. Gao, M. Shi, *Tetrahedron* **2006**, *62*, 6289–6294.

[86] H. Ren, P. Yao, S. Xu, H. Song, B. Wang, *J. Organomet. Chem.* **2007**, *692*, 2092–2098.

[87] R. A. Batey, M. Shen, A. J. Lough, *Org. Lett.* **2001**, *4*, 1411–1414.

[88] B. B. Toure, B. S. Lane, D. Sames, *Org. Lett.* **2006**, *8*, 1979–1982.

[89] C. Y. Liao, K. T. Chan, J. Y. Zeng, C. H. Hu, C. Y. Tu, H. M. Lee, *Organometallics* **2007**, *26*, 1692–1702.

[90] V. Cesar, S. Bellemin-Laponnaz, L. H. Gade, *Organometallics* **2002**, *21*, 5204–5208.

[91] M. C. Perry, X. Cui, K. Burgess, *Tetrahedron: Asymmetry* **2002**, *13*, 1969–1972.

[92] M. Shi, H.-x. Qian, *Tetrahedron* **2005**, *61*, 4949–4955.

[93] M. Shi, H.-x. Qian, *Appl. Organomet. Chem.* **2006**, *20*, 771–774.

[94] M. Frank, G. Maas, J. Schatz, *Eur. J. Inorg. Chem.* **2004**, 607–613.

[95] T. Brendgen, M. Frank, J. Schatz, *Eur. J. Org. Chem.* **2006**, 2378–2383.

[96] I. Dinares, C. GarciadeMiguel, M. Font-Bardia, X. Solans, E. Alcalde, *Organometallics* **2007**, *26*, 5125–5128.

[97] K. Inamoto, J. Kuroda, K. Hiroya, Y. Noda, M. Watanabe, T. Sakamoto, *Organometallics* **2006**, *25*, 3095–3098.

[98] J. Wolf, A. Labande, M. Natella, J.-C. Daran, R. Poli, *J. Mol. Catal. A* **2006**, *259*, 205–212.

[99] J. Wolf, A. Labande, J.-C. Daran, R. Poli, *J. Organomet. Chem.* **2006**, *691*, 433–443.

[100] C.-C. Lee, W.-C. Ke, K.-T. Chan, C.-L. Lai, C.-H. Hu, H. M. Lee, *Chem. Eur. J.* **2007**, *13*, 582–591.

[101] P. L. Chiu, C. L. Lai, C. F. Chang, C. H. Hu, H. M. Lee, *Organometallics* **2005**, *24*, 6169–6178.

[102] B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921–2944.

[103] A. Pfaltz, W. J. Drury III, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5723–5726.

[104] G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **2000**, *33*, 336–345.

[105] S. J. Roseblade, A. Ros, D. Monge, M. Alcarazo, E. Alvarez, J. M. Lassaletta, R. Fernandez, *Organometallics* **2007**, *26*, 2570–2578.

[106] F. Visentin, A. Togni, *Organometallics* **2007**, *26*, 3746–3754.

[107] Y. Canac, C. Duhayon, R. Chauvin, *Angew. Chem. Int. Ed.* **2007**, *46*, 6313–6315.

[108] L. G. Bonnet, R. E. Douthwaite, B. M. Kariuki, *Organometallics* **2003**, *22*, 4187–4189.

[109] N. Toselli, D. Martin, G. Buono, *Org. Lett.* **2008**, *10*, 1453–1456.

[110] S. Gischig, A. Togni, *Eur. J. Inorg. Chem.* **2005**, 4745–4754.

[111] T. Chen, J. J. Jiang, Q. Xu, M. Shi, *Org. Lett.* **2007**, *9*, 865–868.

[112] J. C. C. Chen, I. J. B. Lin, *Organometallics* **2000**, *19*, 5113–5121.

[113] X. Wang, S. Liu, G. X. Jin, *Organometallics* **2004**, *23*, 6002–6007.

[114] W. Li, H. Sun, M. Chen, Z. Wang, D. Hu, Q. Shen, Y. Zhang, *Organometallics* **2005**, *24*, 5925–5928.

[115] B. E. Ketz, X. G. Ottenwaelder, R. M. Waymouth, *Chem. Commun.* **2005**, 5693–5695.

[116] S. Benson, B. Payne, R. M. Waymouth, *J. Polym. Sci. A* **2007**, *45*, 3637–3647.

[117] H.-M. Sun, D.-M. Hu, Y.-S. Wang, Q. Shen, Y. Zhang, *J. Organomet. Chem.* **2007**, *692*, 903–907.

[118] G. Zassinovich, G. Mestroni, S. Gladiali, *Chem. Rev.* **1992**, *92*, 1051–1069.

[119] A. C. Hillier, H. M. Lee, E. D. Stevens, S. P. Nolan, *Organometallics* **2001**, *20*, 4246–4252.

[120] M. Albrecht, R. H. Crabtree, J. Mata, E. Peris, *Chem. Commun.* **2002**, 32–33.

[121] M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 3596–3604.

[122] J. R. Miecznikowski, R. H. Crabtree, *Organometallics* **2004**, *23*, 629–631.

[123] J. R. Miecznikowski, R. H. Crabtree, *Polyhedron* **2004**, *23*, 2857–2872.

[124] M. Poyatos, W. McNamara, C. Incarvito, E. Peris, R. H. Crabtree, *Chem. Commun.* **2007**, 2267–2269.

[125] E. Mas-Marza, M. Poyatos, M. Sanau, E. Peris, *Organometallics* **2004**, *23*, 323–325.

[126] P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699.

[127] B. Mauro, *Eur. J. Inorg. Chem.* **2006**, 4473–4482.

[128] Z. Weng, S. Teo, T. S. A. Hor, *Acc. Chem. Res.* **2007**, *40*, 676–684.

[129] F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L. A. Oro, *Organometallics* **2005**, *24*, 2203–2209.

[130] R. Corberan, M. Sanau, E. Peris, *Organometallics* **2007**, *26*, 3492–3498.

[131] E. Mas-Marza, M. Sanau, E. Peris, *Inorg. Chem.* **2005**, *44*, 9961–9967.

[132] C. Y. Wang, C. F. Fu, Y. H. Liu, S. M. Peng, S. T. Liu, *Inorg. Chem.* **2007**, *46*, 5779–5786.

[133] S. Díez-González, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 349–358.

[134] M. Sawamura, R. Kuwano, Y. Ito, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 111–113.

[135] B. Tao, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 3892–3894.

[136] D. A. Evans, F. E. Michael, J. S. Tedrow, K. R. Campos, *J. Am. Chem. Soc.* **2003**, *125*, 3534–3543.
[137] V. César, S. Bellemin-Laponnaz, H. Wadepohl, L. H. Gade, *Chem. Eur. J.* **2005**, *11*, 2862–2873.
[138] L. H. Gade, V. César, S. Bellemin-Laponnaz, *Angew. Chem. Int. Ed.* **2004**, *43*, 1014–1017.
[139] W.-L. Duan, M. Shi, G.-B. Rong, *Chem. Commun.* **2003**, 2916–2917.
[140] Q. Xu, X. Gu, S. Liu, Q. Dou, M. Shi, *J. Org. Chem.* **2007**, *72*, 2240–2242.
[141] Y. Yuan, G. Raabe, C. Bolm, *J. Organomet. Chem.* **2005**, *690*, 5747–5752.
[142] A. R. Chianese, R. H. Crabtree, *Organometallics* **2005**, *24*, 4432–4436.
[143] A. Labande, J.-C. Daran, E. Manoury, R. Poli, *Eur. J. Inorg. Chem.* **2007**, 1205–1209.
[144] T. Chen, X.-G. Liu, M. Shi, *Tetrahedron* **2007**, *63*, 4874–4880.
[145] T. Fujihara, Y. Obora, M. Tokunaga, Y. Tsuji, *Dalton Trans.* **2007**, 1567–1569.
[146] A. J. Chalk, J. F. Harrod, *J. Am. Chem. Soc.* **1965**, *87*, 16–21.
[147] M. A. Schroeder, M. S. Wrighton, *J. Organomet. Chem.* **1977**, *128*, 345–358.
[148] C.-H. Jun, R. H. Crabtree, *J. Organomet. Chem.* **1993**, *447*, 177–187.
[149] E. Mas-Marza, M. Poyatos, M. Sanau, E. Peris, *Inorg. Chem.* **2004**, *43*, 2213–2219.
[150] M. Viciano, E. Mas-Marza, M. Sanau, E. Peris, *Organometallics* **2006**, *25*, 3063–3069.
[151] M. Poyatos, E. Mas-Marzá, J. A. Mata, M. Sanaú, E. Peris, *Eur. J. Inorg. Chem.* **2003**, 1215–1221.
[152] C. Vicent, M. Viciano, E. Mas-Marzá, M. Sanaú, E. Peris, *Organometallics* **2006**, *25*, 3713–3720.
[153] Electrospray-Ionisation Mass Spectrometry.
[154] J. Y. Zeng, M.-H. Hsieh, H. M. Lee, *J. Organomet. Chem.* **2005**, *690*, 5662–5671.
[155] Compound **13** was obtained from the reaction of $[RhCl(COD)]_2$ of CH_2Cl_2.
[156] H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972–975.
[157] see references so and so in this review.
[158] G. T. S. Andavan, E. B. Bauer, C. S. Letko, T. K. Hollis, F. S. Tham, *J. Organomet. Chem.* **2005**, *690*, 5938–5947.
[159] M. V. Jiménez, J. J. Pérez-Torrente, M. I. Bartolomé, V. Gierz, F. J. Lahoz, L. A. Oro, *Organometallics* **2008**, *27*, 224–234.
[160] Phenylacetylene was found to extensively polymerise.
[161] S. Ahrens, T. Strassner, *Inorg. Chim. Acta* **2006**, *359*, 4789–4796.
[162] M. Poyatos, A. Maisse-Francois, S. Bellemin-Laponnaz, L. H. Gade, *Organometallics* **2006**, *25*, 2634–2641.
[163] W. S. Knowles, R. Noyori, *Acc. Chem. Res.* **2007**, *40*, 1238–1239.
[164] R. Noyori, *Angew. Chem. Int. Ed.* **2002**, *41*, 2008–2022.
[165] W. S. Knowles, *Angew. Chem. Int. Ed.* **2002**, *41*, 1998–2007.
[166] S. J. Roseblade, A. Pfaltz, *Acc. Chem. Res.* **2007**, *40*, 1402–1411.
[167] E. Neumann, A. Pfaltz, M. G. Schrems, *Angew. Chem. Int. Ed.* **2007**, *46*, 8274–8276.
[168] M. C. Perry, X. Chi, M. Powell, D. R. Hou, J. H. Reibenspies, K. Burgess, *J. Am. Chem. Soc.* **2003**, *125*, 113–123.
[169] M. T. Powell, D. R. Hou, M. C. Perry, X. Cui, K. Burgess, *J. Am. Chem. Soc.* **2001**, *123*, 8878–8879.
[170] Y. Fan, X. Cui, K. Burgess, M. B. Hall, *J. Am. Chem. Soc.* **2004**, *126*, 16688–16689.
[171] J. Zhou, K. Burgess, *Angew. Chem. Int. Ed.* **2007**, *46*, 1129–1131.
[172] X. Cui, Y. Fan, M. B. Hall, K. Burgess, *Chem. Eur. J.* **2005**, *11*, 6859–6868.
[173] D. Chen, V. Banphavichit, J. Reibenspies, K. Burgess, *Organometallics* **2007**, *26*, 855–859.
[174] S. Nanchen, A. Pfaltz, *Chem. Eur. J.* **2006**, *12*, 4550–4558.
[175] C. Bolm, T. Focken, G. Raabe, *Tetrahedron: Asymmetry* **2003**, *14*, 1733–1746.
[176] B. A. Messerle, M. J. Page, P. Turner, *Dalton Trans.* **2006**, 3927–3933.
[177] K. Kallstrom, P. G. Andersson, *Tetrahedron Lett.* **2006**, *47*, 7477–7480.
[178] S. Nanchen, A. Pfaltz, *Helv. Chim. Acta* **2006**, *89*, 1559–1573.
[179] T. Focken, G. Raabe, C. Bolm, *Tetrahedron: Asymmetry* **2004**, *15*, 1693–1706.
[180] E. Bappert, G. Helmchen, *Synlett* **2004**, 1789–1793.
[181] J.-M. Becht, E. Bappert, G. Helmchen, *Adv. Synth. Catal.* **2005**, *347*, 1495–1498.
[182] M. Poyatos, P. Uriz, J. A. Mata, C. Claver, E. Fernandez, E. Peris, *Organometallics* **2003**, *22*, 440–444.
[183] R. Corberan, M. Sanau, E. Peris, *J. Am. Chem. Soc.* **2006**, *128*, 3974–3979.
[184] C. M. Yung, M. B. Skaddan, R. G. Bergman, *J. Am. Chem. Soc.* **2004**, *126*, 13033–13043.
[185] R. Corberan, V. Lillo, J. A. Mata, E. Fernandez, E. Peris, *Organometallics* **2007**, *26*, 4350–4353.
[186] E. Mas-Marza, E. Peris, I. Castro-Rodriguez, K. Meyer, *Organometallics* **2005**, *24*, 3158–3162.
[187] L. D. Field, B. A. Messerle, K. Q. Vuong, P. Turner, *Organometallics* **2005**, *24*, 4241–4250.
[188] S. Burling, L. D. Field, H. L. Li, B. A. Messerle, P. Turner, *Eur. J. Inorg. Chem.* **2003**, 3179–3184.

Received: March 31, 2008