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NHC-based pincer ligands: carbenes with a bite†

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In this frontier article we overview the emergence and scope of NHC-based CCC and CNC pincer systems, *i.e.* complexes containing *mer*-tridentate ligands bearing two NHC donor groups, comment on their effectiveness in applications, and highlight areas for future development and exploitation.

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Introduction

Forming adducts with elements throughout the periodic table, the applications of N-heterocyclic carbenes (NHCs) pervade modern synthetic chemistry.[1,2] Rivalling more established phosphine ligands, these carbon-based donors have become ubiquitous in organometallic chemistry and, building on pioneering work by Herrmann in the late 90s, transformed homogeneous transition metal catalysis.[1–4] The evolution of ruthenium catalysts for olefin metathesis is the quintessential example (*e.g.* Grubbs II pre-catalysts), but the emergence of many other keystone organic transformations, such as palladium catalysed cross coupling reactions (*e.g.* PEPPSI pre-catalysts), 'click chemistry', and gold catalysed reactions of alkynes, are also associated with the ever increasing application of NHCs.[3,4] Most commonly employed imidazolylidene and imidazolinylidene NHCs are stronger sigma donors (and weaker pi-acceptors) in comparison to alkyl phosphines, although enhancing their appeal as ancillary ligands a wide range of donor properties can be accessed within the broader ligand class.[5,6] The steric characteristics of NHC ligands further distinguish them from their phosphine counterparts; the combination of shorter metal–ligand bonds and flanking substituents that are directed towards the bound metal, permit

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Rhiann, Adrian and Lucero (left – right) in customary Chaplin group poses

Rhiann graduated from the University of Liverpool in 2012 with a MChem with Research in industry, working at GlaxoSmithKline and in the research group of Prof. J. Xiao. Following award of a Chancellor's Scholarship in 2012, she has been a PhD student in the Chaplin group working on NHC-based macrocyclic pincers with a view to applications in supramolecular chemistry.

Lucero obtained BSc and MSc degrees from the National Autonomous University of Mexico (UNAM), remaining to work under the supervision of Prof. J. Garcia for her PhD (2013). Following postdoctoral work in the group of Prof. A. Paz at the Centre for Research and Advanced Studies of the National Polytechnic Institute (CINVESTAV) and award of a CONACYT postdoctoral stays abroad fellowship, she joined the Chaplin group in 2014 and has been working on the synthesis of imidazolinylidene-based pincers.

Born in New Zealand, Adrian obtained his undergraduate degree from Massey University (2003) before relocating to Switzerland, where he carried out his doctoral studies at the Ecole Polytechnique Fédérale de Lausanne (EPFL), graduating in 2007. He then spent four years as a postdoctoral researcher at the University of Oxford in the group of Prof. A. Weller, holding the R. J. P. Williams Junior Research Fellowship in Chemistry at Wadham College during the latter two years. Following award of a Royal Society University Research Fellowship, Adrian commenced his independent academic career at the University of Warwick in October 2011. Work in the Chaplin group involves synthetic organometallic chemistry of the late transition metals, focusing on the application of supramolecular inspired ligands (http://go.warwick.ac.uk/chaplingroup, @chaplinlab). For his contributions to organometallic chemistry, he was awarded a 2015 RSC Harrison-Meldola Memorial Prize.

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NHC ligands to encroach deep into the metal coordination sphere.[5] Underpinning these hallmarks, the ability to tune the electronic and steric environment of the metal coordination sphere using NHC ligands is facilitated by a wide range of straightforward synthetic protocols for the respective pro-ligands [NHC·H]$^+$.[7]

Alongside the meteoric rise in the use of NHC ligands, *mer*-tridentate "pincer" ligand architectures pervade contemporary homogeneous catalysis, conferring high thermal stability and supporting a broad range of metal-based reactivity.[8] Phosphine-based pincers with central pyridine or aryl donors in particular have been widely investigated, enabling excellent catalytic performance under forcing reaction conditions, such as those associated with alkane dehydrogenation,[9] and fine reaction control, for example, through cooperative metal–ligand reactivity mediated by pyridine dearomatisation.[10] Although significantly less developed, NHC-based CCC and CNC variants – combining the favorable characteristics of NHC donors with *mer*-tridentate ligand architectures – therefore represent a potentially powerful amalgamation of modern ligand design concepts. Supplementing earlier commentaries,[11] in this frontier article we overview the literature to gauge the emergence of NHC-based pincer systems, comment on their effectiveness in applications, and highlight areas for future development and exploitation.

Discussion

Current ligand scope and synthetic procedures

Imidazolylidene-based systems of the type **A** (C–E–C) and **B** (C^E^C) were the first examples of NHC-based pincers and remain heavily investigated.[12] Indeed, from a survey of the literature, these systems account for 84% of publications and 78% of solid-state structures associated with this bourgeoning ligand class (as of 09/2015; Fig. 1).[13] As a consequence of the change in backbone composition, **A** and **B** display significantly different ligand characteristics: the presence of bridging

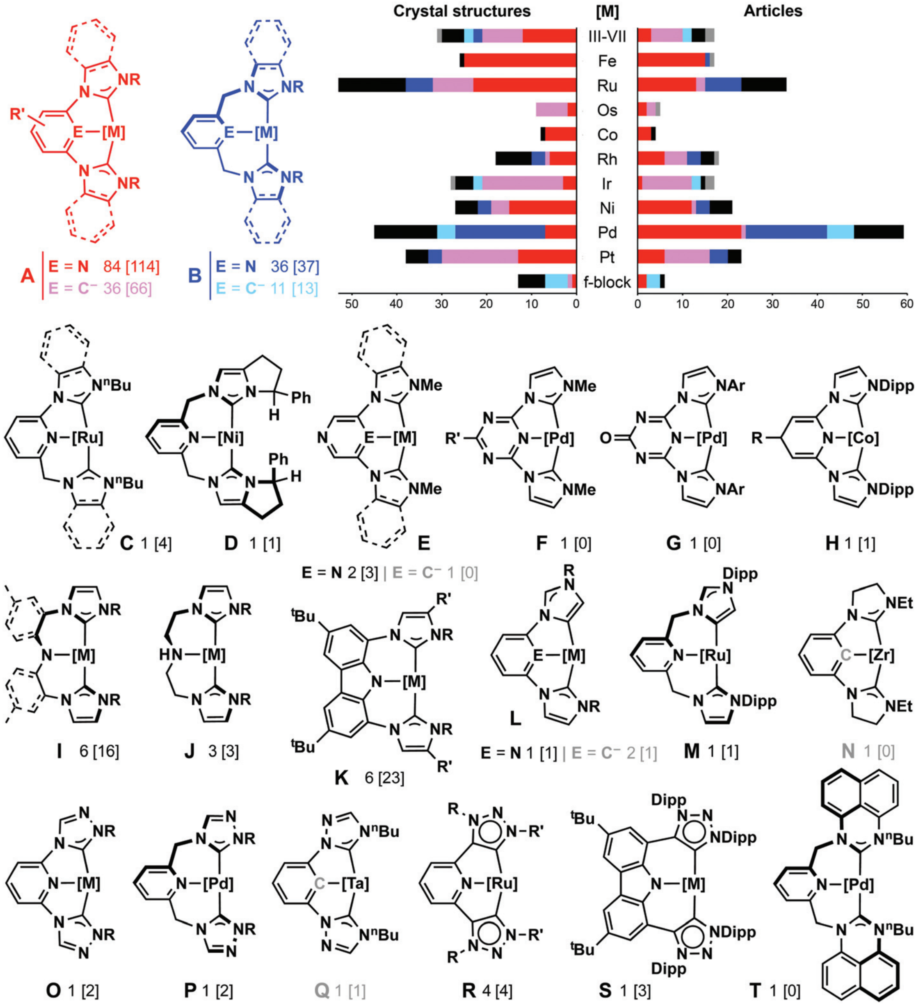
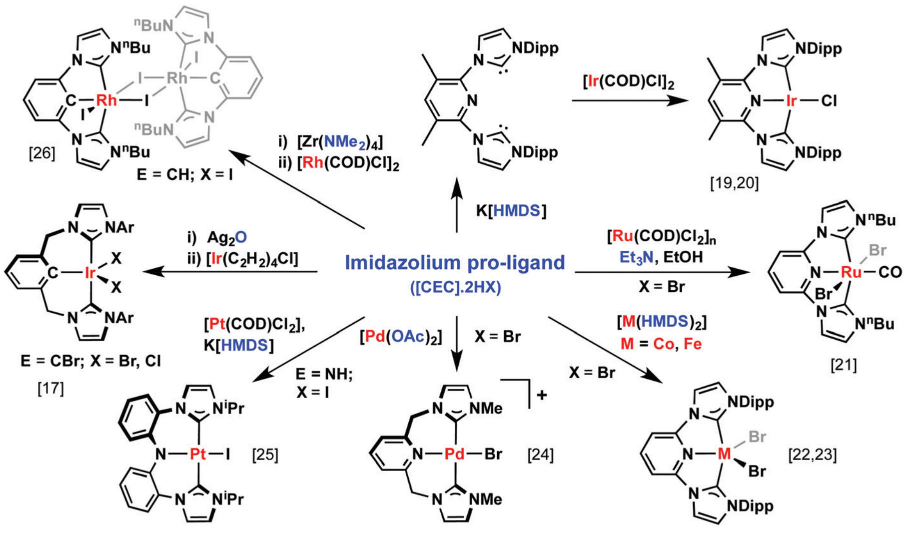


Fig. 1 Reported NHC-based pincer systems: article count from Scifinder™ with deposits in CSD given in square brackets (up until 09/2015 and only for ligands shown to adopt *mer*-configurations).[13]



Scheme 1 Synthesis of NHC-based pincer complexes.

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methylene groups in the pincer backbone of **B** leads to characteristically twisted C_2 conformations, which project the NHC wingtips in opposite directions out of the coordination plane, and results in the adoption of more ideal metal coordination geometries in comparison to **A** (C–M–C = 172(2)° *vs.* 155(6)°).[14] This simple structural adaption of the ligand therefore results in systems with complementary steric profiles, and has significant implications for the nature of the constituent metal-NHC bonding.[15] Often dynamic in solution,[16,17] atropisomers of **B** can be resolved through incorporation of chiral substituents (*i.e.* **D**), and such species could be of future interest for applications in asymmetric catalysis.[18] Subsequent variations of **A** and **B** have included modification of the central donor group to produce ligands with different electronic profiles (**E**–**H**). Curiously, pincers that incorporate significantly different backbone geometries (**C**, **I**–**K**, **S**) or NHC donors (**L**–**T**) have received little attention, suggesting the full capacity of the wider ligand class is yet to be exploited. Amongst the reported CCC and CNC systems, the coordination chemistry of late transition metals, and particularly palladium and ruthenium, has been most frequently explored (Fig. 1). Helping to set them apart from their phosphine-based analogues, a significant body of work has also emerged based on NHC-based pincer complexes of both the early transition metals and f-block elements, and their applications (16 articles, 44 crystal structures, *vide infra*).[13]

Although preparation of the necessary pro-ligands is generally straightforward, the subsequent complexation is not always, providing a potential barrier to wider investigation. Scheme 1 gives representative methods that have been employed.[17,19–26] Direct coordination of the singlet carbene species, generated by pro-ligand deprotonation with a strong base, is conceptually the simplest means, although the high reactivity of these species often precludes their isolation. Indeed, well-defined free-carbenes of this type are limited to a handful of examples, primarily based on 2,6-functionalised pyridine and benzene backbones.[19,27–30] Avoiding issues associated with these highly reactive intermediates, 'accessible syntheses'[31] involving equilibrium reactions with weak (*e.g.* Et_3N, Cs_2CO_3) or coordinated bases ([M]OAc, [M]NR_2) can be used and account for approximately half of the reported pincer systems. Transmetallation is another common method; with silver transfer agents, generated by reaction of the respective pro-ligands with Ag_2O, the most popular. Coordination of anionic CCC-pincer ligands typically proceeds with concomitant C–H or C–Br bond cyclometalation of the backbone, although *in situ* preparation of anionic free-carbenes or use of zirconium transfer agents, generated by reaction with $Zr(NMe_2)_4$, have also proved to be valuable alternatives. Formation of multi-nuclear[20,32–35] or abnormal carbene complexes (*i.e.* **M**, **N**)[23,36–38] both represent potentially detrimental outcomes of the aforementioned methodology: metal precursors bearing non-chelating ligands and use of benzimidazolium-based pro-ligands, respectively, are possible means to avoid such outcomes.

Applications

Fuelled by the successful application of NHC ligands in palladium-catalysed transformations, the emergence of NHC-based pincer systems was closely associated with applications in C–C coupling reactions.[4,12] A variety of well-defined CCC- and CNC-Pd(II) pre-catalysts have been reported to promote the Suzuki–Miyaura and Heck–Mizoroki reactions with high efficiency using low metal loadings, however, increasingly reactions are being performed with pincer systems generated *in situ* from pro-ligand and $[Pd(OAc)_2]$.[39] Targeted for increased thermal stability under the forcing reactions conditions typically associated with such reactions, the exact role of the pincer remains unclear. For instance, although pre-catalysts **1** (Fig. 2) show high activity in Heck–Mizoroki reaction, as do

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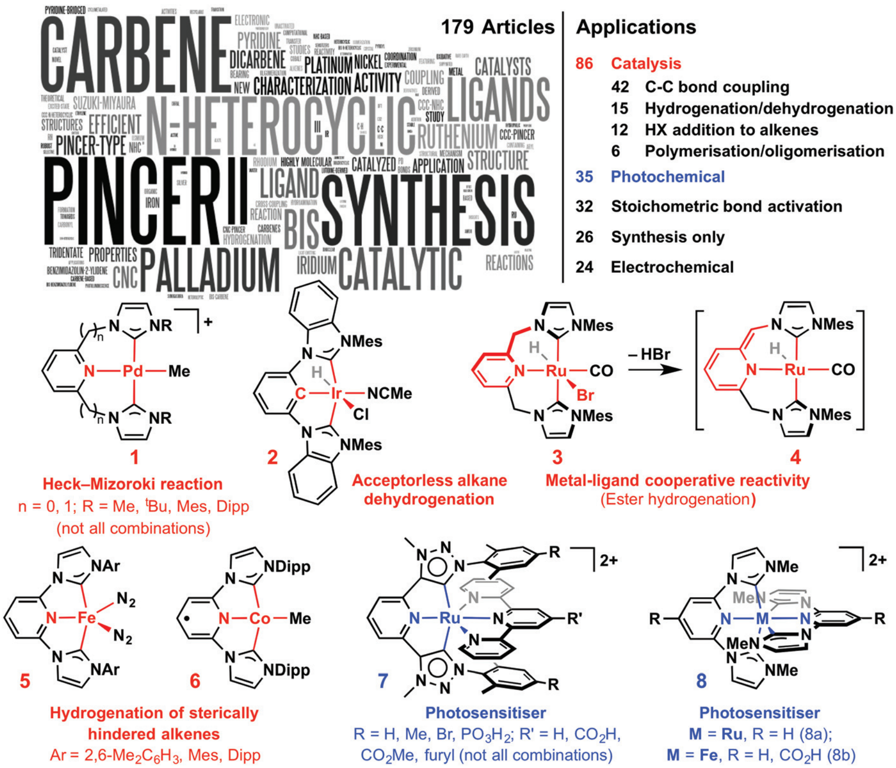

Fig. 2 Applications of NHC-based pincer systems (text cloud generated from article titles).[43]

mono-dentate NHC systems,[2] they were noted to thermally degrade *via* reductive methyl-NHC coupling.[40] A product of methyl group migration from palladium(II) to a coordinated NHC donor group of a CNC pincer has been crystallographically characterised and helps corroborate such reactivity.[41] A significant recent advance in this area is the development of active Ni(II) CNC pre-catalysts.[42]

Well defined platinum-metal-based CNC and CCC pincers have been used to promote a variety of other transformations, including hydrogenation (Ru, Rh),[14,20,30,33,44,45] hydrosilylation (Rh, Pd),[33,35] hydroamination (Rh, Ir, Pd, Pt),[28,46] hydrovinylation (Pt),[47] acceptorless alkane dehydrogenation (Ir, *e.g.* **2**),[48,49] and aryl C–H bond borylation (Ir).[49] As an interesting comparison to robust and highly active iridium phosphine-based PCP catalysis,[9] CCC-Ir analogues reported to date are notable for low activity in transfer dehydrogenation reactions performed at high temperature – typically achieving <20 catalytic turnovers (*cf.* >1000).[34,37,49,50] Interestingly though, **2** displays comparable activity to PCP analogues for the acceptorless dehydrogenation of cyclooctane, displaying a high initial activity (TOF 12 h^{-1} at 150 °C) and no product inhibition. These desirable characteristics could be a result of steric effects associated with the metal orientated *N*-aryl substituents, although ultimately the usefulness of **2** is limited by catalyst decomposition that prevents catalytic turnover greater than *ca.* 100 TON.[48] A particularly noteworthy development is the demonstration of metal–ligand cooperative reactivity within C^N^C ligand scaffolds.[36,44,51] For example, unlike a structurally analogous pyridine-based Ru-PNP pincer, **3** is an active pre-catalyst for the selective hydrogenation of esters.[36] Complex **4** could be characterised *in situ* and re-aromatises on reaction with hydrogen, carbon dioxide and nitriles.[36,51] Isolation of a structurally similar rhodium complex was recently demonstrated in our laboratories.[52]

The propensity for NHC ligands to form a wide range of metal adducts allows for unique opportunities for exploitation in catalysis and differentiates these pincer ligands from other donor-based variants. Indeed, complexes of first row and early transition metals have been showing promising activity in a range of organic transformations. For instance, Fe(0) and Co(II) complexes **5** and **6** bearing bulky C–N–C ligands are highly active catalysts for the hydrogenation of sterically hindered alkenes, such as *trans*-methylstilbene, 1-methyl-1-cyclohexene and 2,3-dimethyl-2-butene; substrates that typically can not be hydrogenated using platinum group metal catalysts.[53] Other notable examples include, C–C bond coupling reactions (Ni),[42] hydroamination (Ti, Zr, Hf),[54] ethylene dimerisation (Cr) and polymerization (Ti, V).[55] Investigation of f-block adducts also raises intriguing future prospects for the application of NHC-based pincer ligands.[29,56]

Other than applications in catalysis, NHC-pincer complexes, and in particular Ru(II) adducts, are increasingly being recognised for their useful photophysical properties. Ruthenium(II) complexes **7**, for example, are notable for microsecond

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^{3}MLCT excited-state lifetimes, four orders of magnitude higher than $[Ru(terpyridine)_2]^{2+}$ and, lending themselves towards practical implantation, the capacity for robust immobilisation on TiO_2 (*i.e.* R = PO_3H_2; R′ = CO_2H).[57] Interestingly, while both homoleptic C^N^C and terpyridine Ru(II) complexes are practically non luminescent at room temperature,[58] ruthenium(II) bis(C–N–C) complex **8a** displays long lifetime photoluminescence in solution.[59] Significantly the first row congener **8b** displays an exceptionally long ^{3}MLCT lifetime for Fe(II) (9 ps; R = H) – two orders longer than the related bis(terpyridine) complex – raising the exciting possibility for use of earth-abundant-metal-based photosensitisers.[60] Outside complexes of the group 8 transition metals, Pt(II) C–C–C complexes have been reported that exhibit blue light emission under ambient conditions, while analogous C–N–C complexes show aqua- and vapo-chromic behaviour.[61] Moreover, Ir(III) bis(C–C–C) complexes that emit in the near-UV have also been described recently.[62]

Outlook

The incorporation of NHC donors into pincer ligand topologies is a means for synergistically combining two of the most successful developments in contemporary ligand design. As a ligand class, NHC-based pincer ligands have vast scope for variation/tuning of donor characteristics and steric profiles. However, this potential is yet to be fully realised with the overwhelming majority of systems reported to date based on imidazolylidene donor groups. Systems bearing imidazolinylidene, pyrrolidinylidene, abnormal imidazolylidene and triazolylidene donor groups, widely employed as mono-dentate ligands in their own right, proffer further capacity for fruitful variation of the pincer donor properties. As a means to systematically quantify such variation, we suggest measurement of carbonyl stretching frequencies in $[Rh(CEC)(CO)]^+$ (*i.e.* in CH_2Cl_2 solution) or redox potentials of $[Ru(CEC)_2]^{2+}$ (E = N, C^-). Conveniently the respective pro-ligands should be readily accessed from established protocols from the respective mono-dentate analogues,[7] however, while a number of synthetic procedures are becoming established for the subsequent coordination to metal centers (free carbene, weak/coordinated bases, silver transmetallation reagents), further consolidation and evolution of this methodology is required. For instance, increased use of zirconium transmetallation reagents or implementation of decarboxylation reactions of CEC·2(CO_2) (E = N, CH, CBr).[2] Other potentially useful ligand variations could include incorporation of boryl or silyl donors in the pincer backbone.[63]

Increased structural variation would help support growing uses of NHC-based pincers as ancillary ligands in homogeneous catalysis. The ability of NHC donors to form adducts with metals outside of the platinum group is in particular an area for future exploration, especially using earth abundant metals such as Fe, Co and Ni. Under forcing reactions conditions, such as palladium catalysed C–C coupling reactions and alkane dehydrogenation, NHC-based pincer complexes show promising potential but also suffer from non-negligible decomposition; representing an important consideration in future ligand design. To this end some of us been have developing macrocyclic C–N–C and C^N^C ligands, which may enable not only more robust pincer ligand binding, but additional scope for reaction control.[16,52,64] With promising advances being made exploiting the photophysical properties of both CCC and CNC pincers, the ability to tune the absorption and emission characteristics of bound metals, through variation of the ligand composition, also makes for exciting future applications of NHC-based pincers in materials science.

Acknowledgements

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