Anionic tethered *N*-heterocyclic carbene chemistry

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Since the discovery of a stable "bottleable" *N*-heterocyclic carbene (NHC), there has been a spectacular explosion of interest in this ligand class. This interest stems from a desire to understand the fundamentals of the structure and bonding of these systems, but also because of their numerous and emerging applications in small molecule activation, homogeneous catalysis and Lewis acid-catalysed reactions. In this *Tutorial Review*, we introduce the reader to NHCs, cover general synthetic methods to prepare anionic tethered NHCs and their metal complexes, and discuss emerging applications in reactivity and catalytic studies.

1. Introduction

A carbene is a 6-electron, divalent carbon centre which may be linear or bent.[1] The linear, sp-hybridised form implies a triplet state, whereby two electrons each singly occupy two degenerate, mutually orthogonal p-orbitals (**A**, Fig. 1). In the bent form, the degeneracy of the two p-orbitals is broken, thus the carbene centre adopts a sp^2-hybridised form, which may be singlet or triplet in nature (**B–E**, Fig. 1). The multiplicity of these bent systems is heavily dependent on the carbene α-substituents. In *N*-Heterocyclic Carbenes (NHCs, **F**, Fig. 1), the carbene centre is bent by virtue of its incorporation into a (usually) five-membered ring. The two α-amino substituents play two electronic roles. Firstly, they stabilise the formally sp^2-hybridised non-bonding lone pair by a σ-inductive withdrawing effect. Secondly, the vacant p-orbital is destabilised by a mesomeric effect, *viz* donation of the α-amino lone pairs into the vacant p-orbital. This push–push (mesomeric) pull–pull (inductive) arrangement ensures the preservation of electroneutrality at the carbene centre and renders the singlet state dominant.

Although NHCs are very different to phosphines both electronically and in terms of their spatial arrangement of

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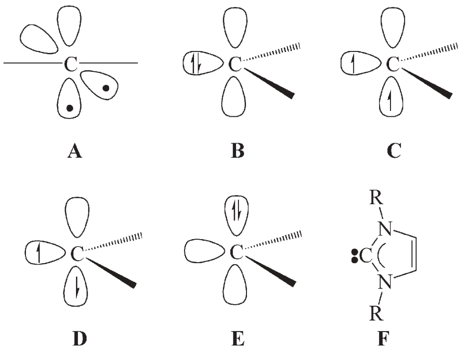


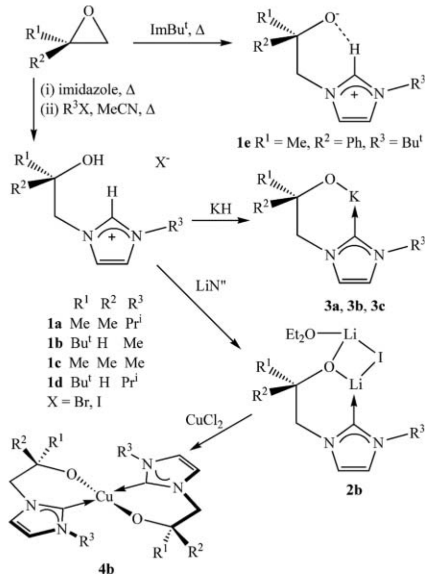
Fig. 1 Electronic structures of NHCs.

substituents (and thus their steric properties), they both possess a non-bonding singlet lone pair. Much has therefore been made of the phosphine–carbene analogy, in that both may act as Lewis base donors to metal centres. Consequently, NHCs are increasingly finding use as phosphine ligand replacements in transition metal complexes for homogeneous catalysis.[2–4] There is, therefore, an ever increasing volume of research directed at mid- and late-transition metal–NHC complexes for homogeneous catalysis, and the reader is directed to several excellent reviews on these areas.[5–9] However, whereas phosphines are better suited to mid- and late-transition metals due to their soft nature and involvement in backbonding, NHCs have no necessary requirement for backbonding, although the issue of backbonding to NHCs is still an area of controversy and discussion. As a consequence of the strongly nucleophilic NHC singlet lone pair, NHCs are suitable for a wide range of metals. That said, although strongly nucleophilic, NHCs are still softer than amides and alkoxides; for a significant expansion into early metal chemistry, functionalised NHCs are required. NHCs with pendant *neutral* donors were already known, and this area has recently been reviewed.[10] For early, electropositive metals, an *anionic* tether represents a method of covalently attaching the NHC to a hard, electropositive metal centre, such that the NHC will be more strongly bound, and even if displaced, will remain in close proximity to the metal centre.[11] For the purposes of this review, our definition of tethered is that at least one atom must separate the anionic centre from the NHC ring; therefore, any systems in which anionic charge resides only on the NHC ring, or is directly bonded to it, are excluded from it. A number of research groups are now beginning to realise the potential of anionic tethered NHCs in early metal chemistry, and their use is rapidly expanding across the d-block of the periodic table. Herein, we review the synthesis of pro-ligands and their NHC–metal complex derivatives, and cover emerging reactivity and applications in catalysis.

2. Anionic tethered NHCs, metal complexes and reactivity

2.1. Alkoxide NHCs

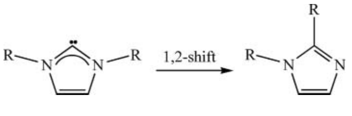
A particularly convenient and flexible entry point to alkoxide-tethered NHCs is through the use of epoxides, which are cheap and can be bought in a chiral, non-racemic form, enabling the synthesis of a library of chiral alkoxy NHCs. The reaction between an epoxide and imidazole affords the ring-opened product, which can then be quaternised with an alkyl halide to afford the corresponding imidazolium pro-ligand (**1a–1d**, Scheme 1).[12] The use of 2,2-substituted epoxides results in highly regiospecific ring openings and essentially quantitative yields. Alternatively, zwitterionic, halide-free pro-ligands are obtainable by the reaction of alkyl imidazoles with epoxides (**1e**, Scheme 1).[12] Conversion of the imidazolium or zwitterionic pro-ligands to lithium (**2b**) or potassium (**3a–3c**) alkoxy NHCs is readily accomplished by sequential deprotonation using two or one equivalents, respectively, of bases such as LiBu^n, KH, LiN″ or KN″ [N″ = N(SiMe$_3$)$_2$]. These potassium alkoxy NHCs are particularly noteworthy because heavier alkali metal NHCs are usually unstable with respect to a 1,2-alkyl migration reaction (Scheme 2). However, the alkoxy-tethered NHCs reported by Arnold *et al.* are highly resistant to this decomposition reaction. One potassium salt (**3a**) was characterised by X-ray crystallography and shown to be based around K$_4$O$_4$ cubane units, with numerous interactions between the olefinic NHC backbone and potassium centres.[13]



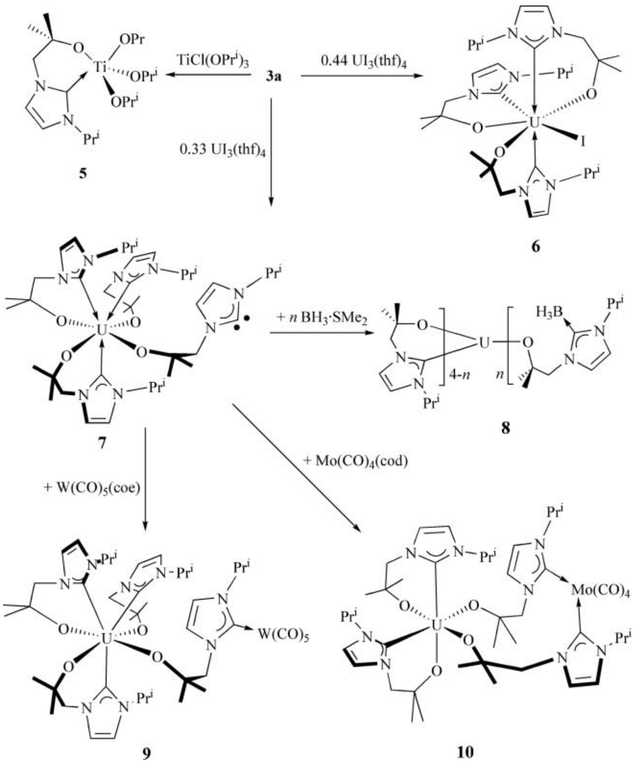
Scheme 1 Synthesis of alkoxy NHCs.

Alkali metal alkoxy NHCs are excellent ligand transfer reagents. For example, **2b** can be used to cleanly prepare copper(II) *bis*-alkoxy NHCs, such as **4b** (Scheme 1).[12] Compound **4b** was found be active for the enantioselective conjugate addition of diethyl zinc to cyclohexenone, catalysing rapid (2 h) and high yielding (up to 100%) reactions with a moderate ee of 51% at −30 °C.[12]

Potassium alkoxy NHC **3a** has proven to be especially effective for the preparation of early metal–NHC complexes. The reaction between **3a** and [Ti(Cl)(OPr^i)$_3$] cleanly affords



Scheme 2 1,2-Alkyl migration of NHCs.

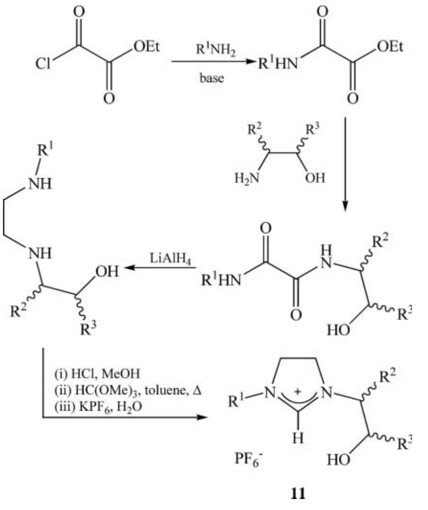


Scheme 3 Synthesis of uranium and titanium alkoxy NHCs, coe = cyclooctene, cod = cyclooctadiene.

complex **5** (Scheme 3), which was characterised by X-ray diffraction and shown to be trigonal bipyramidal at titanium.[14] Complex **5** was shown to be a good polymerisation catalyst for the ring opening polymerisation of D,L-lactide and superior to [Ti(Cl)(OPr^i)$_3$]; it appears that the titanium and NHC centres work together as a bifunctional catalyst.[14]

The utility of alkoxy NHCs in early metal chemistry is underscored by a series of uranium(IV) derivatives of **3a** (Scheme 3).[15] During salt elimination reactions of **3a** with UI$_3$(THF)$_4$, a disproportionation reaction, typical of uranium chemistry, occurs to give tri- or tetraalkoxy NHC uranium(IV) complexes (**6** and **7**, respectively), depending on the stoichiometry of the reaction. Complex **6** has much potential for subsequent salt elimination or reduction chemistry. Complex **7** is noteworthy for being the first NHC–metal complex with a pendant NHC; this was exploited to access borane adducts (**8**), and heterobimetallic tungsten (**9**) and molybdenum (**10**) carbonyl complexes, which underlines their potential use in bifunctional catalysis, such as that described for **5**.

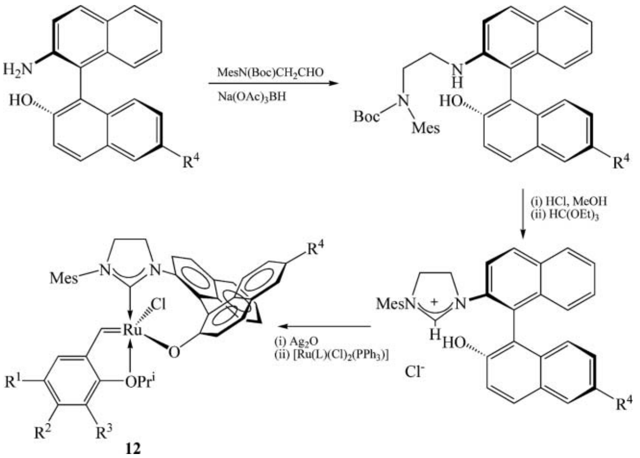
An alternative method of preparing alkoxy NHCs was reported by Mauduit *et al.* (Scheme 4).[16] Reaction between a primary amine and ethyloxalyl chloride affords the corresponding oxanilic ethylester. Subsequent treatment with an aminoalcohol (some chiral) gives the oxalamides in pure form, which may be reduced with lithium aluminium hydride and condensed with trimethylorthoformate to provide the desired imidazolinium chloride pro-ligand. Purification of these salts was achieved by anion exchange to give the corresponding PF$_6^-$ salts. A comprehensive library of twenty pro-ligands (**11** is a generic example) were assembled, some of which were characterised in the solid state. The corresponding alkoxy NHCs were generated *in situ* using LiBu^n in the presence of copper(II) triflate or copper(II) ethylacetylacetonate to afford the corresponding copper(II) alkoxy NHC complexes. These were tested as catalysts for the conjugate addition of diethyl zinc to a range of cyclic enones. Interestingly, for cyclohexenone, the best ee values were obtained for R^1 = Mes, R^2 = Me$_2$CHCH$_2$ (86%), Bu^t (87%) or Ph (86%), and R^3 = H (ee values in parentheses). Variation of the solvent had little affect on the observed ee values, although varying the copper(II) precursor and temperature did affect the reactions, which may reflect the fact that the copper alkoxy NHCs were formed *in situ* and not isolated beforehand.



Scheme 4 Synthesis of alcohol-tethered imidazolinium pro-ligands.

2.2. Aryloxide NHCs

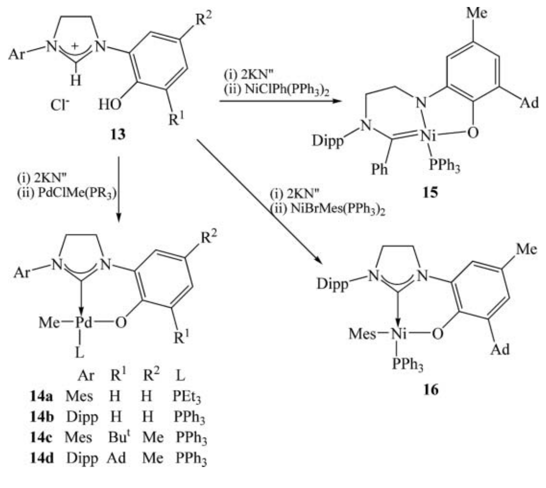
Hoveyda *et al.* have reported a range of ruthenium complexes supported by chiral aryloxide NHCs (of the generic form **12**, Scheme 5).[17,18] These complexes bear stereogenic ruthenium centres and can be obtained in >98% diastereo- and enantiomeric purity without resolution, and are air-stable and recyclable. The pro-ligands are prepared by reductive amination between an optically pure binaphthyl amine alcohol and an aldehyde, followed by a two step reaction to the



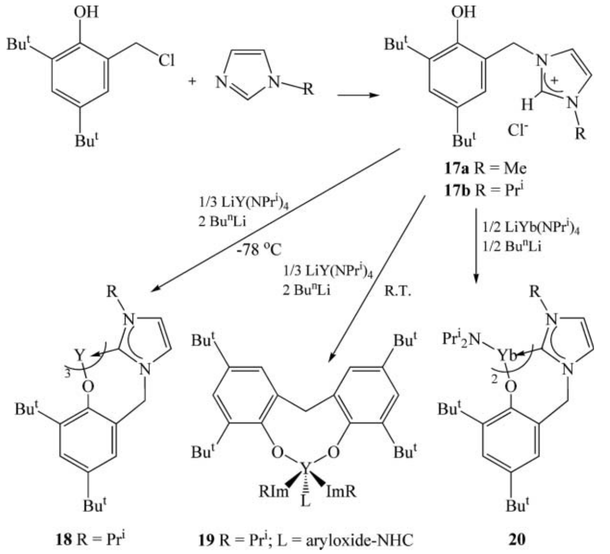
Scheme 5 Synthesis of chiral, ruthenium aryloxide NHC complexes.

corresponding imidazolinium salt. Conversion to the corresponding silver–NHC complex is achieved with silver oxide, which acts as a ligand transfer reagent to give **12**. This method of construction enabled a wide substitution pattern at R^1, R^2, R^3 and R^4. These complexes have been utilised in the asymmetric ring-opening/cross metathesis reactions of a range of tricyclic norbornenes and oxonorbornenes, and were found to be highly active (low catalyst loadings), with ee values obtained as high as 96%.[17]

Grubbs *et al.* have prepared a range of hydroxyaryl-imidazolinium pro-ligands (**13**) as precursors to aryloxide NHC complexes, in which the backbone of the NHC is saturated (Scheme 6, Dipp = 2,6-Pr^i_2-C_6H_3).[19,20] The synthetic routes employed to access the pro-ligands are predominantly analogous to that used by Mauduit *et al.* (see above),[16] but some modifications were required.[19] For example, for R^1 = R^2 = H, refluxing the oxanilic ester with 2-aminophenol in toluene at 120 °C afforded the corresponding oxalamide. However, for R^1 = Bu^t and R^2 = Me, it was necessary to employ a peptide coupling procedure of the oxanilic acid and 2-amino-4-methyl-6-*tert*-butyl-phenol in THF at 0 °C. Additionally, for R^1 = adamantyl (Ad) and R^2 = Me, it was necessary to firstly couple the oxanilic ester with 2-amino-4-methylphenol in toluene at 120 °C then secondly introduce adamantyl to the phenol *ortho*-position by an acid-catalysed reaction of the oxalamide with 1-adamantol in dichloromethane at 25 °C. The palladium(II) complexes **14a–14d** were prepared by the straightforward, *in situ* treatment of the imidazolinium pro-ligands with two equivalents of KN″, followed by reaction with $[\{Pd(Me)(\mu\text{-}Cl)(PR_3)\}_2]$ (R = Et, Ph). **14a** and **14d** were characterised in the solid state and were shown to adopt typical square planar geometries at palladium with the two anionic donors *trans* to each other. However, the analogous nickel(II) syntheses proved to be more problematic; reaction of the *in situ*-generated aryloxide NHC with $[Ni(Ph)(Cl)(PPh_3)_2]$ resulted in the nickelacycle **15**, in which cleavage and expansion of the NHC had occurred to give a nickel centre bound to a tridentate Fischer carbene, amide and phenoxide ligand, where the nickel centre retained a distorted square planar geometry. The mechanism of this ring opening/expansion was proposed to be the result of aryl attack into the vacant carbene-based p-orbital. Accordingly, the use of a nickel precursor with a bulkier aryl group, Mes (Mes = mesityl, 2,4,6-$Me_3C_6H_2$), $[Ni(Mes)(Br)(PPh_3)_2]$, afforded the desired complex **16**, analogous to complexes **14a–14d**.



Scheme 6 Synthesis of nickel and palladium aryloxide NHC complexes.

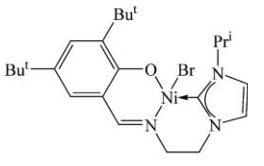


Scheme 7 Synthesis of yttrium and ytterbium aryloxide NHC complexes.

Shen *et al.* have reported the facile preparation of a hydroxyaryl-imidazolium pro-ligand by a straightforward nucleophilic substitution of an alkyl halide with an alkyl imidazole (**17a** and **17b**, Scheme 7).[21] A series of protonolysis reactions were attempted, with a variety of outcomes observed.[21,22] For example, the reaction of **17b** with $[LiY(NPr^i)_4]$ and $LiBu^n$ gave different results, depending on the temperature the reaction was conducted at. Conducting the reaction at −78 °C afforded the desired *tris*-ligand complex **18**. However, if the same reaction was carried out at room temperature, ligand fragmentation occurred to give **19** as the only isolated product. The surprising aspect of the formation of **19** was the presence of a methylene-bridged biaryl rather than the expected ethyl-bridged biaryl; a mechanism involving protonation of a carbene centre, ligand cleavage and methylene transfer to the amide was proposed.[22] Additionally, attempts to prepare mono-aryloxide NHC complexes of ytterbium were unsuccessful, and only the *bis*-aryloxide NHC complex **20** could be isolated from reaction mixtures.

The bromide congener of pro-ligand **17a** has been employed by Zhang and Kawaguchi to prepare mono-aryloxide NHC lithium, sodium and magnesium complexes, and a *bis*-aryloxide NHC nickel complex.[23] The sodium salt was structurally characterised and shown to be a THF-solvated dimer, constructed around a four-membered Na_2O_2 ring; the magnesium congener was of a similar structural type, except that the THF solvent was replaced by a mesityl group to maintain charge neutrality. Although not structurally characterised, the nickel complex was found to be active for the polymerisation of norbornene, with MAO (MAO = methylaluminoxane) as a co-catalyst (10^5 g PNBE mol Ni^{-1} h^{-1}).

Shen *et al.* have reported a modified aryloxide NHC that incorporates a salicylaldimine group.[24] Reaction between a salicylaldehyde and a β-bromoethylamine hydrobromide gives



21

Fig. 2 Nickel salicylaldimine NHC complex.

the condensation product, which readily quaternises an alkyl imidazole. Deprotonation with two equivalents of NaN″ and salt elimination with $NiBr_2(PPh_3)_2$ affords compound **21** (Fig. 2). Compound **21** was characterised by X-ray crystallography and shown to be square planar at nickel. Although inactive for the polymerisation of styrene on its own, compound **21** exhibited good activity in the presence of $NaBPh_4$. Under the conditions styrene : $NaBPh_4$: **21** = 500 : 7 : 1 in toluene at 80 °C, a 100% yield was obtained with M_w = 17600 and PDI = 1.97 (PDI = polydispersity index = M_w/M_n, M_W = weight average molecular weight, M_n = number average molecular weight). This is a more active and higher M_w-producing catalyst than nickel catalysts supported by PPh_3 or monodentate NHCs.

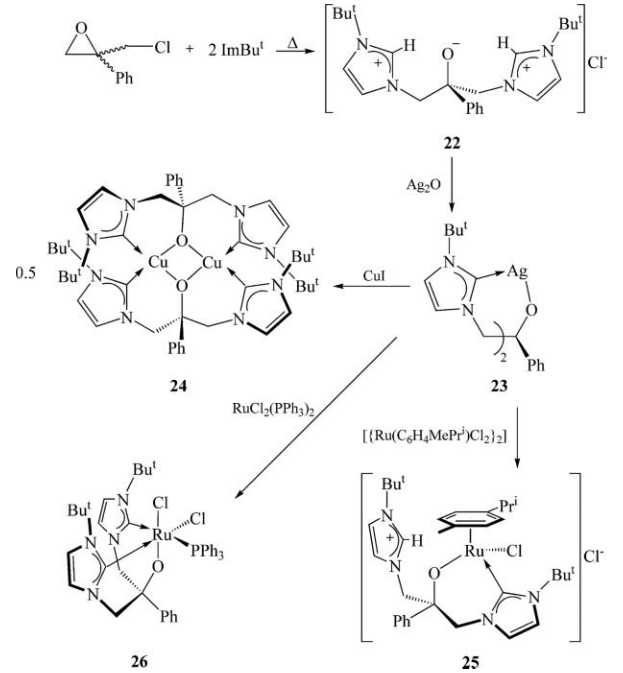
2.3. Alkoxide *bis*-NHCs

The first deliberate anionic NHC chelating ligand was reported by Arnold *et al.* (Scheme 8).[25] Pro-ligand **22** was prepared by the atom-efficient, one-pot reaction between two equivalents of *tert*-butyl imidazole (ImBu^t) and a functionalised epichlorohydrin. **22** was easily converted to the corresponding silver alkoxide *bis*-NHC complex **23** by treatment with excess silver oxide. Complex **23** is only moderately air- and light-sensitive, and is an excellent ligand transfer reagent. In particular, transmetallation with copper(I) halides affords the corresponding copper(I) complex **24**, of interest because copper carbenes are implicated in a number of catalytic processes, but remarkably few have been reported.[8] An X-ray diffraction experiment on **24** revealed the unusual feature of two almost square planar copper(I) centres.

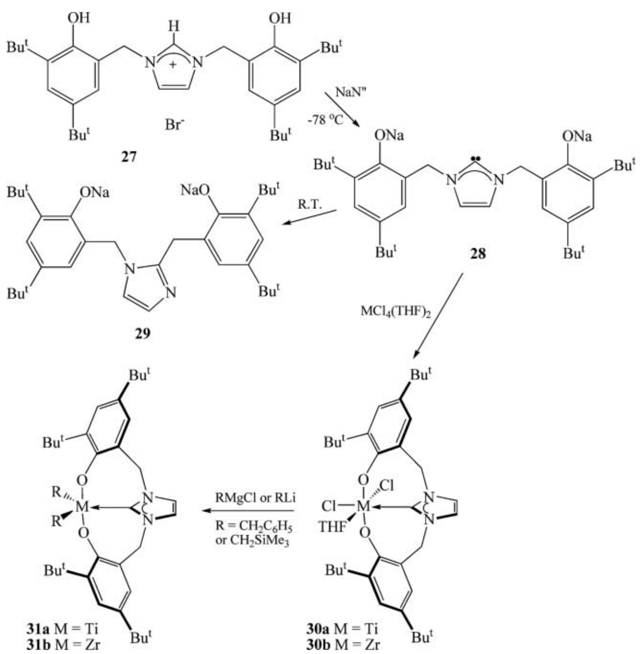
Complex **23** has also found utility in the preparation of ruthenium(II) and ruthenium(III) alkoxy *bis*-NHC complexes.[26] Treatment of **23** with $[\{Ru(C_6H_4MePr^i)Cl_2\}_2]$ or $RuCl_2(PPh_3)_2$ affords compounds **25** and **26**, respectively, after work up. Such complexes are of interest due to the involvement of the Ru(II)/Ru(III) couple in ruthenium-catalysed atom transfer radical polymerisation catalysis and the implicated Ru(III)–carbene in the catalytic oxidation of alkanes. The protonated NHC in **25** is derived from the basic pendant NHC picking up a proton from either the solvent or HCl during the reaction. Complex **26** is the first example of a Ru(III)–NHC complex, and shows how the incorporation of an alkoxide can stabilise high oxidation state metal–NHC complexes.

2.4. *Bis*-aryloxide NHCs

The only *bis*-aryloxide NHC ligand system reported thus far is that disclosed by Kawaguchi *et al.* (Scheme 9).[27,28] A stepwise alkylation of imidazole with 2-bromomethyl-4,6-di-*tert*-butylphenol affords the *bis*-phenol imidazolium salt **27**. Although **27** is readily deprotonated by NaN″ to form the disodium salt **28**, it is unstable and decomposes by a 1,2-benzyl migration reaction if allowed to warm to room temperature (see Scheme 2 above). However, **28** is stable at low temperature, thus, if generated and used *in situ*, titanium (**30a**) and zirconium (**30b**) complexes can be prepared that are stable and show no sign of decomposition, even at elevated temperatures in solution. The small size of titanium renders mono-ligand substitution quite straightforward. However, the larger size of zirconium results



Scheme 8 Synthesis of copper and ruthenium alkoxy *bis*-NHC complexes.



Scheme 9 Synthesis of titanium and zirconium *bis*-aryloxide NHC complexes.

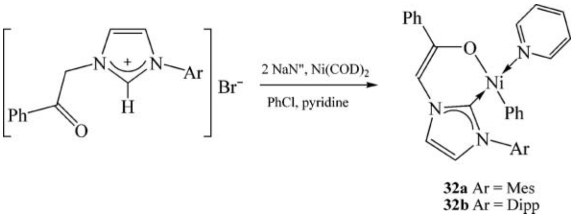
in reactions affording **30b** being contaminated with quantities of the corresponding *bis*-ligand complex, although the two complexes are easily separated by fractional crystallisation.[28] Complexes **30a** and **30b** can be alkylated with Grignard or group 1 alkyl reagents to give complexes **31a** and **31b**. Complex **30a** has been tested in the polymerisation of ethylene in the presence of MMAO (MMAO = modified methylaluminoxane). Under the conditions reported (Al : Ti = 1000 : 1, 0.5 h, 1 L toluene, 30 °C, 9 bar), an activity of 290 kg $\mathrm{mol_{Ti}}^{-1}$ h^{-1} bar^{-1} was observed, producing polyethylene with $M_n = 3.98 \times 10^4$, PDI = 4.65 and T_m = 135 °C (T_m = crystalline melting temperature).

2.5. Enolate NHCs

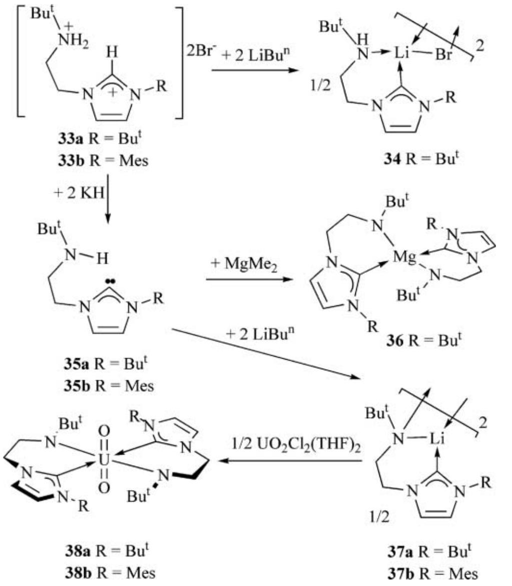
Waymouth *et al.* reported two enolate–NHC complexes of nickel, which are analogous to the nickel enolate–phosphine complexes used in the Shell Higher Olefin Process (SHOP) (Scheme 10).[29] A reaction between ketone-tethered imidazolium pro-ligands,[10,29] NaN″ and nickel(0) *bis*-COD (COD = cyclooctadiene) in a pyridine/phenyl chloride mix afforded complexes **32a** and **32b** in high yields (76 and 91%, respectively). Solutions of **32a** and **32b** in toluene are active in the polymerisation of ethylene (E) in the absence of co-catalysts, producing linear polyethylenes (PEs) of modest molecular weights (M_n = 1000–7100 g mol^{-1}, T_m = 123–132 °C), with productivities under the conditions 1–15 bar ethylene, 20–60 °C, ranging from 0.8–56.0 $\mathrm{kg_{PE}}$ $\mathrm{mol_{Ni}}^{-1}$ h^{-1} (TOF = 28–2000 $\mathrm{mol_E}$ $\mathrm{mol_{Ni}}^{-1}$ h^{-1}), which is comparable to nickel enolate–phosphine SHOP-type catalysts. Increasing the temperature and pressure was found to increase activity, but the addition of MAO gave lower activities and low M_n branched polymers. However, in contrast to nickel enolate–phosphine SHOP-type catalysts, no extended induction period for ethylene polymerisation was observed. Studies showed that the catalysts decomposed rapidly under polymerisation conditions, which was attributed to chain transfer by β-H elimination, followed by reductive elimination of nickel(0) from the resulting nickel hydride, with concomitant formation of an imidazolium salt. Reductive elimination from nickel alkyls was ruled out due to the lack of imidazolium-terminated end groups and the high percentage of phenyl-terminated end groups.

2.6. Amido NHCs

The first amide NHCs were reported by Arnold *et al.* (Scheme 11).[30] Pro-ligands **33a** and **33b** were prepared by the straightforward alkylation of an alkyl or aryl imidazole with $\mathrm{Bu^tNHCH_2CH_2Br{\cdot}HBr}$. Compounds **33a** and **33b** can be deprotonated with a variety of bases with different outcomes.



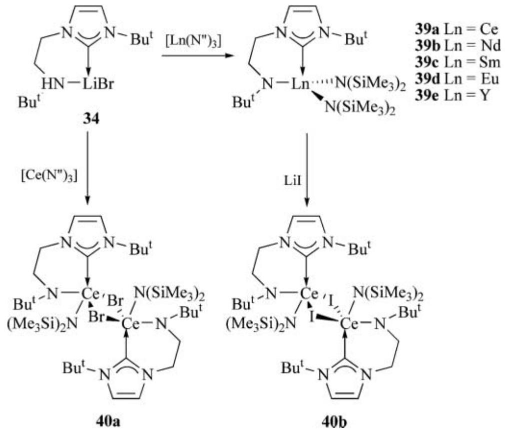
Scheme 10 Synthesis of nickel enolate NHC complexes.



Scheme 11 Synthesis of lithium, magnesium, and uranyl amido NHC complexes.

For example, the reaction of **33a** with two equivalents of $\mathrm{LiBu^n}$ or LiN″ results in formation of the corresponding amine–NHC as its lithium bromide adduct (**34**). Reactions to give salt-included complexes are common when the alkali metal is lithium; using KH or KN″ instead affords **35a**, the free amine–NHC, since potassium is too large to be incorporated. Compounds **35a** and **35b** may be deprotonated to afford amide–NHC complexes. For example, the reaction of **35a** with $\mathrm{MgMe_2}$ or a further equivalent of $\mathrm{LiBu^n}$ yields complexes **36** and **37a**, respectively.[31] Both **36** and **37a** were characterised in the solid state, and, surprisingly, **37a** was found to exhibit a strongly bent NHC–lithium interaction. This deviation from the anticipated trigonal planar geometry at the carbene centre was also observed in the solid state structure of the uranyl complex **38a**, which was prepared from **37a** and $\mathrm{UO_2Cl_2(THF)_2}$.[31] The deviation from trigonal planar geometry at the carbene centres in **38a** contrasts with the solid state structure of **38b**, which exhibits very little deviation. Such distortions were unknown in late-metal NHC chemistry, and subsequent studies have demonstrated that in early metal systems, distortions do not apparently affect the binding strength, suggesting a dominance of electrostatic character in closed shell electropositive metal–carbene bonds.

Arnold *et al.* have shown that complex **34** has considerable utility for the preparation of lanthanide-amido NHCs (Scheme 12).[30,32] Entry is achieved by transamination between **34** and homoleptic [Ln(N″)$_3$] amides. Reactions typically proceed in quantitative yield overnight to afford complexes **39a–39e**, which may be isolated in a crystalline form in high yield (~85%). However, whilst this chemistry is very reliable, the preparation of **39a** is not so straightforward. Occasionally, complex **40a**, the product of ligand exchange with the LiBr incorporated in **34**, is isolated from attempted preparations of **39a**. Compound **39a** is synthetically more desirable due to its utility in salt elimination chemistry. Unfortunately, the ligand exchange reaction is somewhat capricious, although

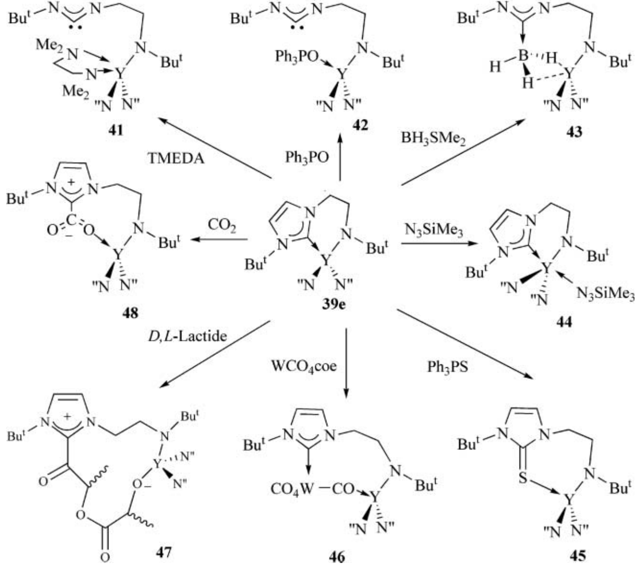


Scheme 12 Synthesis of lanthanide amido NHC complexes.

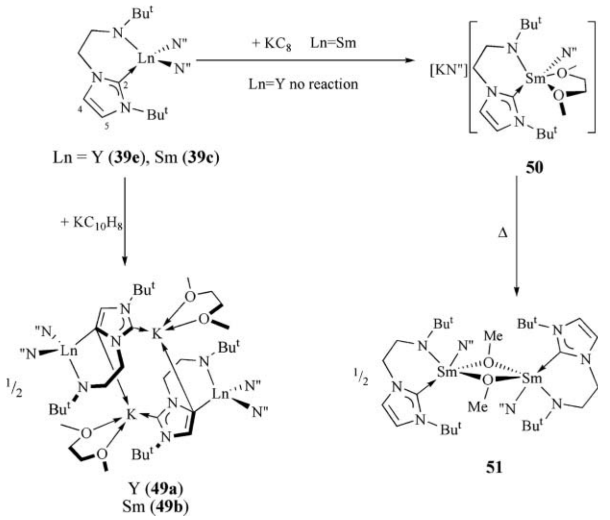
scrupulously removing THF shuts down the amide–halide exchange. However, the reaction of **39a** with LiI affords the iodide congener of **40a**, **40b**. Complexes **40a** and **40b** are noteworthy because heteroleptic complexes of the form [LnLL$'$L$''$] are far rarer than complexes of the type [LnLL$'_2$], and such examples are usually limited to the heavier and smaller members of the lanthanide series.

The strength of the metal amide–NHC bond in complexes such as **39a–39e** makes a controlled study of the reactivity of the electropositive metal–NHC fragment possible, precluding ligand redistribution processes that can complicate lanthanide coordination chemistry, allowing the fate of the metal cation and the NHC to be monitored. A series of competition reactions of **39e** with potential donor ligands was assessed, exemplified by the reactions shown in Scheme 13.[11]

The reduction of complexes **39e** and **39c** by alkali metal reagents has also been reported (Scheme 14),[33] since lanthanide complexes can exhibit rich small-molecule activation chemistry when activated with alkali metal reductants and exist in unusual formal oxidation states when supported by 6π-electron heterocycles.



Scheme 13 Reactivity of a yttrium amido NHC complex.



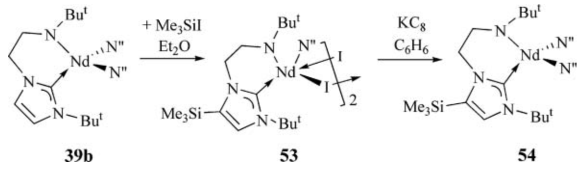
Scheme 14 Reduction chemistry of lanthanide amido NHC complexes.

Neither small molecule activation nor low oxidation state compounds were observed or isolated. However, unprecedented C4-regioselective C–H activation of the NHC backbone was observed to give **49a** when **39e** was treated with potassium naphthalenide. Compound **49a** exhibits the largest $^1J_{\mathrm{Y-C}}$ (C4) coupling constant yet recorded (62 Hz). Complex **49a** may be quenched with a range of electrophiles; for example, the reaction with Me$_3$SiCl proceeds quantitatively to furnish the C4-silylated congener of **39e**.

Analogously to **49a**, compound **49b** is isolated when **39c** is treated with potassium naphthalenide, although in much lower yield. This is because reduction of the Sm(III) centre competes with reduction at the NHC. The reduction of **39c** with KC$_8$ gives the putative, DME-stabilised Sm(II)–NHC complex [Sm(L)(N″)(DME)] (**50**). However, **50** could not itself be isolated without ligand scrambling and disproportionation reactions occurring to give **39c** and reduced quantities of **50**, which is a purple oil. Briefly heating **50** in a non-polar solvent affords **51**, which results from C–O bond activation and DME cleavage, which is characteristic of traditional metal-based reduction chemistry.

Evidence supporting the assertion that the NHC group is reduced *en route* to **49a** and **49b** was provided by the reduction of **35a** with potassium, which afforded the first stable, chemically-generated, radical anion of an NHC (**51**, Scheme 15). The X-band EPR spectrum of **52** is clearly resolved in fluid toluene at 298 K and exhibits a 15-line spectrum with g_{iso} = 2.004719.[33]

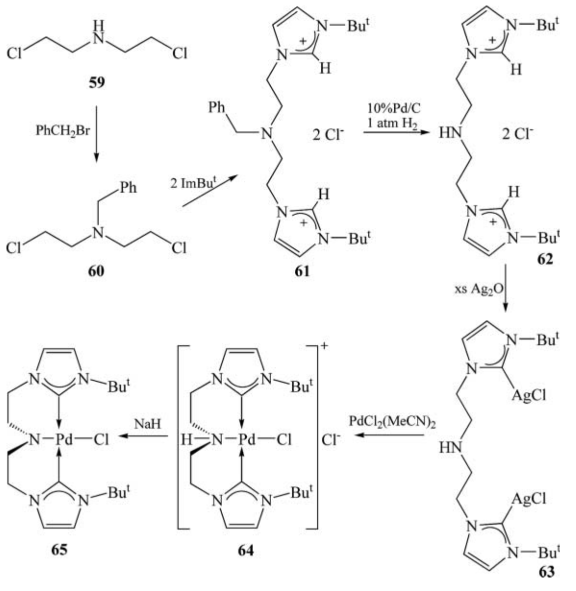
Scheme 15 Synthesis of a stable, chemically generated radical anion of an NHC.



Scheme 16 Regiospecific silylation chemistry of lanthanide amido NHC complexes.

In an effort to extend the reduction chemistry described above, Arnold and Liddle reported a facile, one-pot reaction that furnished C4-regioselective silylation of the NHC ring (Scheme 16).[34] As has been observed in group 4 chemistry previously, it was anticipated that the reaction of Me_3SiI with **39b** should proceed to eliminate $N'''[N(SiMe_3)_3]$ and afford $[Nd(L)(N'')(\mu\text{-}I)]_2$, analogously to the way group 4 *bis*-dimethylamide compounds are smoothly converted to the corresponding dichlorides by treatment with Me_3SiCl, along with concomitant elimination of Me_3SiNMe_2. However, although amide/iodide exchange did indeed occur, simultaneous and regioselective silylation of the backbone of the NHC at the C4 position occurred (with elimination of HN'' rather than N''') to give **53**. This is the first functionalisation of an NHC backbone that does not need to proceed *via* a refunctionalisation of the basic C2 atom, or 1,3-proton or -alkyl migration. It is proposed that silylation occurs as follows: nucleophilic substitution of N'' by I^- generates free N''^-, which deprotonates the NHC at the C4 position. Subsequently, the newly formed carbanion centre (*cf.* **49a**) is then readily quenched by the trimethylsilyl cation, which is a long-lived species stabilised by the ether solvent of the reaction. The synthesis of **53** enabled reduction reactions to be tested; however, although reduction occurred, all that could be isolated from reaction mixtures was the disproportionated ligand redistribution product **54**.

Taken together, the C4-deprotonation and -silylation reactions are important because they clearly demonstrate that the NHC group is not an innocent group in organometallic chemistry. Furthermore, these observations indicate that care should be taken when using catalysts containing NHCs under reducing conditions.



Scheme 17 Synthesis of palladium amido *bis*-NHC complexes.

Arnold *et al.* have also demonstrated the utility of complex **37a** and its mono and dilithium bromide salts as ligand transfer agents with other electropositive metals. For example, titanium complexes **55–58** were prepared from $TiCl(OPr^i)_3$ (Fig. 3).[35] Two aspects of complexes **55–58** are of principal interest. Firstly, three complexes incorporate bromide, which derives from the lithium bromide present in some of the NHC precursor complexes employed, as a consequence of an alkoxide-halide exchange reaction which is analogous to the amide-halide exchange chemistry observed with cerium (**40a** and **40b**).[32] Secondly, distortions at the titanium centre indicated possible '*cis*-ligand backbonding' of the NHC with the bromide and alkoxide π-donor ligands. However, density functional theory calculations showed negligible interactions between the NHC and the π-donor ligands, and it was concluded the distortions are a result of lone pair repulsions between the π-donor ligands.

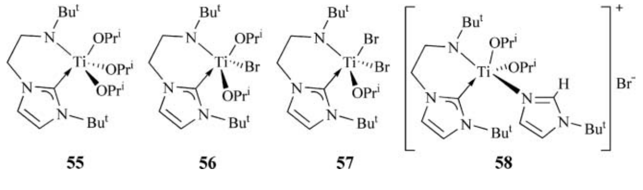
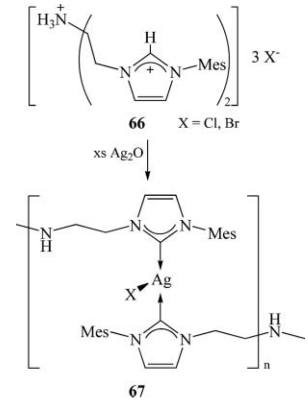


Fig. 3 Titanium amido NHC complexes.

2.7. Amido *bis*-NHCs

Douthwaite *et al.* reported the synthesis of the first amine-*bis*-imidazolium pro-ligand and its conversion to a silver complex, which was utilised to prepare palladium complexes (Scheme 17).[36] It was found that the reaction between **59** and $ImBu^t$ was thwarted by a competitive oligomerisation of **59**. In order to circumvent this, benzylated derivative **60** was prepared, which afforded **61** after treatment with $ImBu^t$. Removal of the benzyl protecting group was achieved by palladium-catalysed hydrogenation to give the amine-*bis*-imidazolium pro-ligand **62**. Compound **62** was smoothly converted to the corresponding amine *bis*-NHC silver



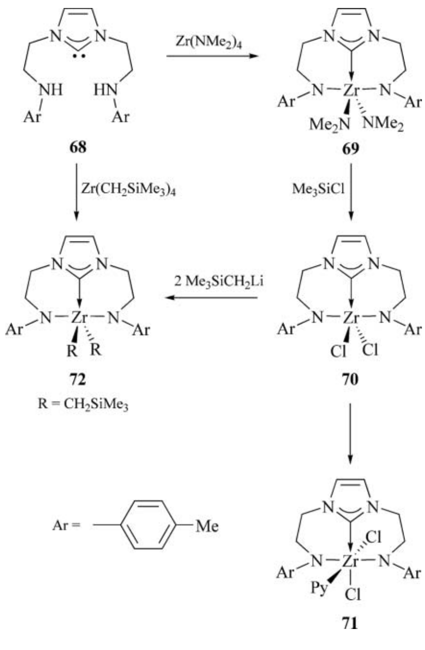
Scheme 18 Synthesis of silver amine *bis*-NHC complexes.

complex, **63**, by treatment with excess silver oxide, which was shown to be an efficient ligand transfer reagent for the preparation of amine *bis*-NHC palladium complex **64**. This complex was characterised in the solid state and shown to be square planar at palladium. Complex **64** was smoothly converted to the corresponding amido *bis*-NHC palladium complex, **65**, by treatment with sodium hydride.

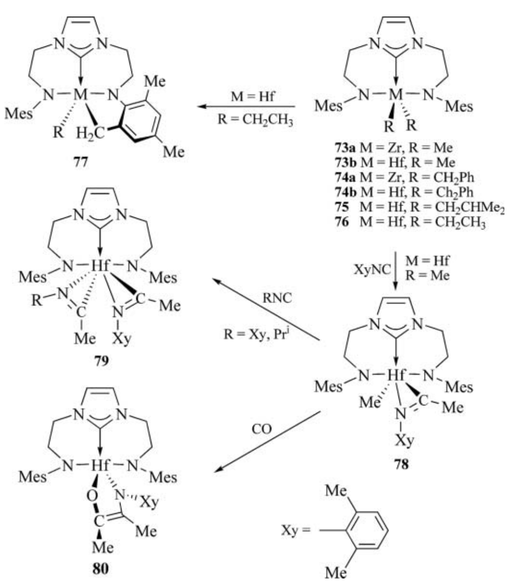
The only other example of an amine *bis*-NHC was reported by Arnold *et al.* (Scheme 18).[37] In contrast to the synthesis of **62**, pro-ligand **66** was prepared in a straightforward, one-pot reaction between mesityl imidazole and di(chloroethyl)ammonium chloride or di(bromoethyl)ammonium bromide. Treatment of **66** with excess silver oxide generated the corresponding amine *bis*-NHC silver halide complex **67**, which was shown by X-ray crystallography to adopt a one-dimensional zig–zag chain in the solid state, in which the silver centres adopt a conventional T-shape geometry.

2.8. *Bis*-amido NHCs

The first *bis*-amine NHC ligand **68** was reported by Fryzuk *et al.* (Scheme 19).[38] The potentially tridentate *bis*-amine NHC ligand **68** was prepared from a borane–dimethylsulfide-mediated reduction of a *bis*-amide-imidazolium chloride, followed by deprotonation with KN″ to yield *bis*-amine NHC **68**. Compound **68** reacted cleanly with $Zr(NEt_2)_4$ to give complex **69**. Treatment of **69** with excess Me_3SiCl gave dichloride **70** in quantitative yield. Complex **70** is extremely insoluble in common organic solvents, but the addition of pyridine afforded the benzene-soluble complex **71**; this was characterised by X-ray diffraction, which showed the zirconium to be octahedral and the NHC ligand to be bound in a *mer* fashion. The reaction of **70** with two equivalents of Me_3SiCH_2Li, or treatment of **68** with $Zr(CH_2SiMe_3)_4$, afforded zirconium dialkyl complex **72**, which is the first zirconium dialkyl with a NHC-based ancillary ligand. Complex **72** was also crystallographically characterised and shown to adopt a distorted trigonal bipyramidal geometry at zirconium. In common with other zirconium alkyls, **72** was found to be light sensitive. A series of competition reactions between the bound NHC in **71** and pyridine, and tetramethylethylenediamine demonstrated that the NHC is firmly bound as a consequence of the two flanking amide groups.



Scheme 19 Synthesis of zirconium *bis*-amido NHC complexes.



Scheme 20 Synthesis and reactivity of zirconium and hafnium *bis*-amido NHC complexes.

Fryzuk *et al.* subsequently reported the synthesis of a closely related ligand to **68** (Ar = Mes) and, by following analogous chemistry to the preparation of **69–72**, prepared a series of zirconium and hafnium dialkyls **73–76** (Scheme 20).[39] In contrast to the zirconium dialkyls, which decompose in solution to unidentified products over 24 hours, the hafnium dialkyls were found to possess excellent thermal stability in all but one case; complex **76** undergoes decomposition to give the C–H-activated, cyclometallated complex **77**. A deuterium labelling study revealed that **76** eliminates d_6-ethane by β-hydrogen transfer, and the resulting η^2-ethylene intermediate readily undergoes C–H bond activation to afford **77**. The dialkyls displayed some interesting small molecule activation chemistry. For example, complex **73b** was found to undergo facile insertion chemistry with isonitriles to afford complexes **78** and **79**, although thermolysis of complex **79** did not give the corresponding enediamido metallocycle, this being attributed to the difficulty of the two aminoacyl groups achieving a coplanar arrangement. Since facile insertion with isonitriles occurs stepwise, it is possible to prepare and isolate **78** and then react it with carbon monoxide to give the eneamidolate complex **80**. The reactions of **73b** and **75** with carbon monoxide were also investigated. For **73b**, insertion of CO into one Hf–C bond occurred to give the anticipated η^2-acyl complex. However, the η^2-acyl complex unexpectedly rearranged to give a vinyl enolate, which suggests that the oxycarbene-methyl resonance form of the acyl group undergoes a hydrogen atom shift from the methyl substituent to the carbene to give the vinyl enolate. For **75**, insertion of CO into both Hf–C bonds and coupling of the putative acyl groups

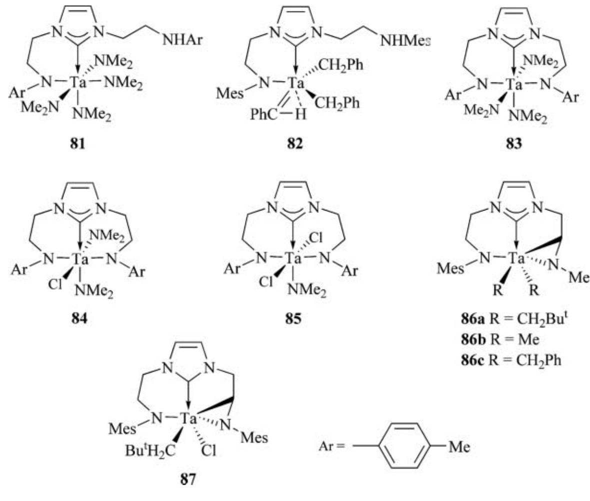


Fig. 4 Tantalum *bis*-amido NHC complexes.

occurs to give an enediolate complex, which is presumed to be monomeric, but which rearranges to give a dimeric, bridged dihafnium *bis*(enediolate) complex, as confirmed by X-ray crystallography.

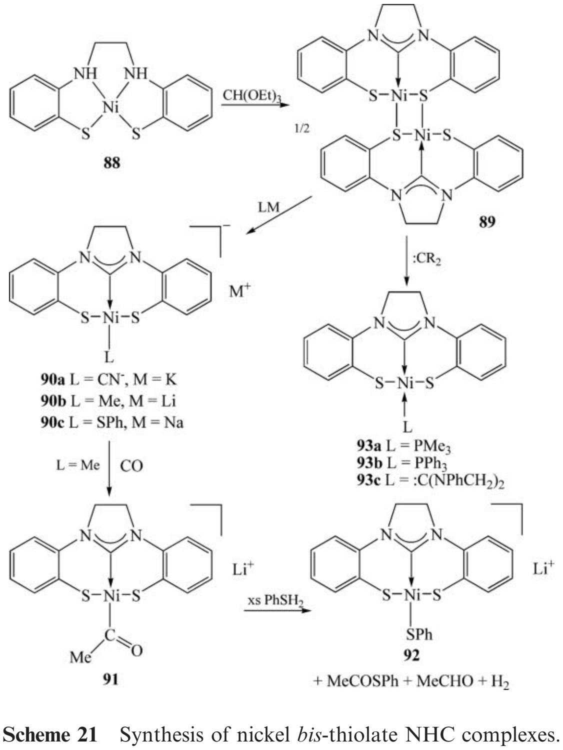
Utilising ligand **68** and the *N*-Mes variant, Fryzuk *et al.* have very recently reported a range of tantalum *bis*-amido NHC complexes (Fig. 4).[40] Complex **81** was prepared by a reaction between **68** and $Ta(NMe_2)_5$; despite all attempts to the contrary, only the mono-deprotonated complex with a pendant amine arm could be obtained, and no reaction occurred between $Ta(NMe_2)_5$ and the *N*-Mes ligand variant, even at an elevated temperature. Similarly, reaction of the *N*-Mes derivative of **68** with $Ta(CH_2Ph)_5$ afforded complex **82**, which features a tantalum alkylidene and a pendant amine arm. All attempts to promote deprotonation of the pendant amine arm resulted in decomposition. In light of these difficulties, a salt elimination strategy was pursued. The dilithium *bis*-amido NHC derivative of **68** was prepared and reacted with $TaCl_2(NMe_2)_3$, $TaCl_3(NMe_2)_2$ and $TaCl_4(NMe_2)$ to cleanly afford complexes **83**, **84** and **85**, respectively. In contrast, reactions with alkyl precursors proved to be more complicated. The reaction of the dilithium salt of the *N*-Mes derivative of **68** with $TaCl_2R_3$ ($R = CH_2Bu^t$, Me, CH_2Ph) and $TaCl_3(=CHBu^t)(THF)_2$ afforded complexes **86a–c** and **87**, respectively. These complexes are notable because, surprisingly, they all exhibit a cyclometallated arm of the ligand, giving rise to metallaaziridines, as a consequence of an endocyclic C–H activation reaction. A detailed investigation using density functional theory showed that the formation of the metallaaziridine rings enabled a more favourable Ta–NHC interaction. Assuming the first step is formation of a trialkyl complex, the calculations indicate the lowest energy pathway to complexes **86a–c** and **87** involves a tantalum alkylidene intermediate (formed by an α-H abstraction reaction), which undergoes C–H bond activation α to the amido centre to afford the metallaaziridine (as opposed to a possible concerted σ-bond metathesis from the trialkyl directly to the cyclometallated complex). The proposed tantalum alkylidene mechanism was confirmed by an experimental deuterium labelling experiment.

2.9. *Bis*-thiolate NHCs

Sellmann *et al.* reported the unexpected formation of a *bis*-thiolate NHC complex and its derivatives (Scheme 21).[41] Recrystallisation of complex **88** from DMF unexpectedly afforded, in low yield, complex **89**, which is the formal product of the insertion of CO into the Ni–N bonds followed by elimination of H_2O and subsequent dimerisation. Systematic experiments showed that **89** could be deliberately isolated in preparative yields by the reaction of **88** with $HC(OEt)_3$. Dimeric **89** can be broken up into anionic, monomeric complexes by its reaction with anionic ligand sources to afford, for example, complexes **90a–c**. Although **88** is unreactive towards carbon monoxide, **90b** inserts carbon monoxide to afford the acyl complex **91**, which reacts with thiophenol to give **92**, the thioester MeCOSPh, ethanal and hydrogen. Complex **89** can also be broken up into a neutral, monomeric form by reaction with Lewis bases such as phosphines and NHCs (**93a–c**).

2.10. Indenyl and fluorenyl NHCs

Despite the dominance of cyclopentadienide-substituted ligands (and annulated derivatives, *e.g.* indenyl, fluorenyl) in organometallic chemistry, it was not until very recently that the first indenyl- and fluorenyl-tethered NHC complexes were disclosed by Downing and Danopoulos (Fig. 5).[42] Quaternisation of β-bromoethylindene and β-bromoethylfluorene with Dipp-imidazole gave the corresponding imidazolium pro-ligand salts, which could be cleanly deprotonated, stepwise, to afford the corresponding potassium salts **94** and **95**. Potassium salt **95** was characterised by X-ray crystallography, showing a strong (short) NHC–K contact and various multi-hapto interactions between the potassium centre



Scheme 21 Synthesis of nickel *bis*-thiolate NHC complexes.

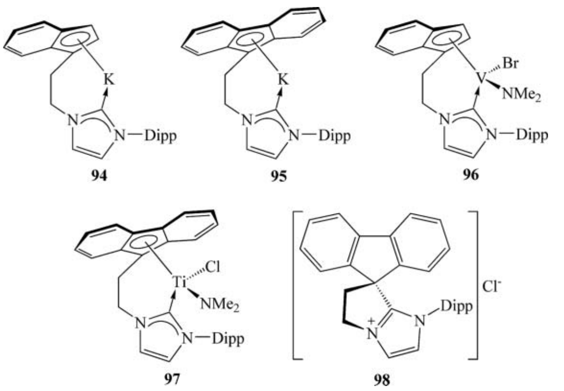
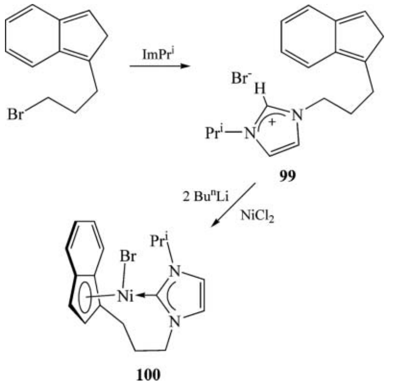


Fig. 5 Synthesis of potassium, titanium, and vanadium indenyl and fluorenyl NHC complexes.

and the phenyl rings. A reaction of the pro-ligands with silver oxide afforded the corresponding silver indenyl and fluorenyl NHC complexes. The indenyl-imidazolium and potassium fluorenyl NHC salts were shown to be effective reagents for the preparation of vanadium(III) (**96**) and titanium(III) (**97**) complexes from $V(NMe_2)_4$ and $TiCl_2(NMe_2)_2$, respectively. Interestingly, in both cases, reduction occurred during the preparation of **96** and **97**, which were both shown to be monomeric in the solid state with approximately tetrahedral metal(III) centres. As observed for **40a** and **40b**, amide–halide exchange occurred during the synthesis of **96**, which accounted for the presence of bromide. It is postulated that the ligands act as reducing agents in the course of the reaction, a proposition which is supported by the isolation and crystallographic characterisation of spiro-imidazolium salt **98**. No reactivity studies have yet been reported for these systems.

Subsequent to Downing and Danopoulos' report, Shen *et al.* reported a propyl-tethered indenyl NHC complex (Scheme 22).[43] Quaternisation of β-bromopropylindene with isopropyl-imidazole afforded imidazolium pro-ligand salt **99**. In direct contrast to the synthesis of **99**, Dipp-imidazole and Mes-imidazole did not react with β-bromopropylindene. The corresponding NHC-indenyl ligand was generated *in situ* by the treatment of **99** with $LiBu^n$, which was then used as a ligand transfer reagent to prepare the nickel bromide derivative **100**. This derivative was shown to be monomeric by an X-ray crystallographic study and found to be unreactive towards styrene. However, in the presence of $NaBPh_4$, considerable activity was observed; under the conditions styrene : $NaBPh_4$: **100** = 300 : 7 : 1 in toluene at 80 °C, a 75% yield was obtained after 24 h to give a polymer with M_n = 27000 and PDI = 1.89. This is better than for the closely-related system indenyl nickel(II) bromide, co-supported by a non-tethered 1,3-diisopropyl NHC. Clearly, the tether is of benefit with regard to stabilising the catalytically-active species.



Scheme 22 Synthesis of a nickel indenyl NHC complex.

2.11. Aryl-cyclometallated NHCs

Lappert *et al.* reported a comprehensive series of aryl-cyclometallated NHC complexes, two of which were crystallographically characterised (**101** and **102**, Fig. 6).[44] The complexes were prepared by the reaction of ruthenium(II) dichloride bis-phosphine complexes with *N*,*N*′,*N*″,*N*‴-aryl-substituted enetetraamines (so-called electron-rich olefins) in xylene at 140 °C, with concomitant elimination of hydrogen chloride. The complexes were shown to be octahedral, or pseudo-octahedral with a vacant coordination site, with *trans*-phosphines and the NHC residing *trans* to the chloride ligand; the configurations being stereochemically rigid in solution.

Hollis *et al.* have reported a pincer-type NHC ligand that is anionic by virtue of metallation of the aryl spacer group (Scheme 23).[45] The copper-catalysed coupling of 1,3-dibromobenzene with imidazole gives the corresponding 1,3-imidazole benzene derivative, which is readily alkylated to afford **103**. Compound **103** is readily deprotonated by tetrakis-zirconium dimethyl amide, but facile amide/iodide ligand scrambling occurs to give complexes **104** and **105** in a 91 : 9 ratio, as determined by crystallographic modelling of the disorder. This mixture is easily converted to complex **106** by treatment with methyl iodide at room temperature. The crystal structure of **106** shows the expected *mer* coordination mode of the NHC ligand at the octahedral zirconium centre. Transmetallation of an *in situ*-generated mixture of **104** and **105** with $[\{Rh(COD)(Cl)\}_2]$, and addition of iodine, gives **107**, which is in equilibrium with **108**. During the reaction, the rhodium(I) centre is oxidised to rhodium(III), irrespective of whether iodine is added or not. If iodine is not added, a substantial proportion of zirconium starting material remains. During crystal growth, the dimethyl amine was lost, favouring the formation of **108**, which was characterised by X-ray crystallography, revealing the anticipated octahedral geometry at rhodium and the *mer* coordination of the NHC ligand.

3. Summary and outlook

It is clear that NHCs are better than trialkyl or triaryl phosphines as donor ligands in early metal chemistry.

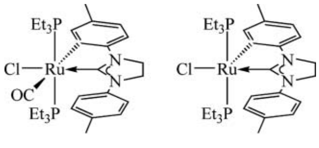
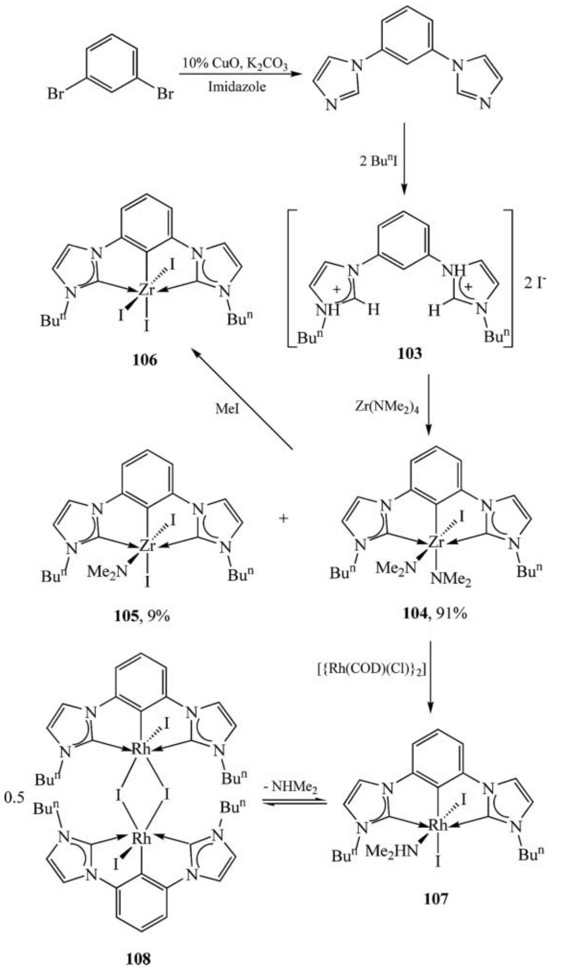


Fig. 6 Aryl-cyclometallated ruthenium NHC complexes.



Scheme 23 Synthesis of aryl-cyclometallated zirconium and rhodium NHC complexes.

However, the metal–carbene bond is significantly weaker and more reactive in these electropositive metal systems than it is in late metal systems. The use of bidentate and tridentate ligands containing NHC groups is still a relatively small area in early metal chemistry, but it is one which is clearly expanding rapidly. Those that combine an anionic group with the NHC can be particularly effective in stabilising early metal NHC complexes, generating systems with short metal–carbene bonds, but the anionic donor/NHC combination also renders them effective ligands across the periodic table, with a tolerance of a range of metal oxidation states.

Although the range of complexes reported to date is still relatively small, these electropositive metal-organometallics already display a range of chemistry as yet unseen in late metal NHC complexes, and are showing promise towards homogeneous catalysis and small molecule activation chemistry. Due to the strongly basic donor character of the carbene, the reactions that lead to NHC displacement can readily lead to other reaction chemistry, such as atom abstraction or polymerisation catalysis. However, the π-heterocycle of the carbene can also become involved in reaction chemistry. For example, the deprotonation of a backbone CH affords bimetallic complexes that bridge through the σ-framework of the carbene, and the metal coordinated carbene is readily silylated to generate asymmetric metal carbene complexes. Furthermore, other facile C–H bond activation reactions show that NHC ligands must not be regarded as innocent. This has implications for the wider context of organometallic chemistry as well as for NHC chemistry. Whilst this indicates that much remains to be achieved with anionic NHCs, the area shows much promise.

Acknowledgements

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References

1 D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.
2 W. A. Herrmann, K. Öfele, D. v. Preysing and S. K. Schneider, *J. Organomet. Chem.*, 2003, **687**, 229.
3 K. J. Cavell and D. S. McGuinness, *Coord. Chem. Rev.*, 2004, **248**, 671.
4 C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247.
5 W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162.
6 W. A. Herrmann, T. Weskamp and V. P. W. Böhm, *Adv. Organomet. Chem.*, 2001, **48**, 1.
7 W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290.
8 P. L. Arnold, *Heteroat. Chem.*, 2002, **13**, 534.
9 For a thematic review issue, see: *Coord. Chem. Rev.*, 2007, **251**, 595–896.
10 O. Kühl, *Chem. Soc. Rev.*, 2007, **36**, 592.
11 P. L. Arnold and S. T. Liddle, *Chem. Commun.*, 2006, 3959.
12 P. L. Arnold, M. Rodden, K. M. Davis, A. C. Scarisbrick, A. J. Blake and C. Wilson, *Chem. Commun.*, 2004, 1612.
13 P. L. Arnold, M. Rodden and C. Wilson, *Chem. Commun.*, 2005, 1743.
14 D. Patel, S. T. Liddle, S. A. Mungur, M. Rodden, A. J. Blake and P. L. Arnold, *Chem. Commun.*, 2006, 1124.
15 P. L. Arnold, A. J. Blake and C. Wilson, *Chem.–Eur. J.*, 2005, 6095.
16 H. Clavier, L. Coutable, L. Toupet, J.-C. Guillemin and M. Mauduit, *J. Organomet. Chem.*, 2005, **690**, 5237.
17 J. J. Van Veldhuizen, S. B. Garber, J. S. Kingsbury and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2002, **124**, 4954.
18 J. J. Van Veldhuizen, D. G. Gillingham, S. B. Garber, O. Kataoka and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2003, **125**, 12502.
19 A. W. Waltman and R. H. Grubbs, *Organometallics*, 2004, **23**, 3105.
20 A. W. Waltman, T. Ritter and R. H. Grubbs, *Organometallics*, 2006, **25**, 4238.
21 Z.-G. Wang, H.-M. Sun, H.-S. Yao, Y.-M. Yao, Q. Shen and Y. Zhang, *J. Organomet. Chem.*, 2006, **691**, 3383.
22 Z.-G. Wang, H.-M. Sun, H.-S. Yao, Q. Shen and Y. Zhang, *Organometallics*, 2006, **25**, 4436.
23 D. Zhang and H. Kawaguchi, *Organometallics*, 2006, **25**, 5506.
24 W. Li, H. Sun, M. Chen, Z. Wang, D. Hu, Q. Shen and Y. Zhang, *Organometallics*, 2005, **24**, 5925.
25 P. L. Arnold, A. C. Scarisbrick, A. J. Blake and C. Wilson, *Chem. Commun.*, 2001, 2340.
26 P. L. Arnold and A. C. Scarisbrick, *Organometallics*, 2004, **23**, 2519.
27 H. Aihara, T. Matsuo and H. Kawaguchi, *Chem. Commun.*, 2003, 2204.
28 D. Zhang, H. Aihara, T. Watanabe, T. Matsuo and H. Kawaguchi, *J. Organomet. Chem.*, 2007, **692**, 234.
29 B. E. Ketz, X. G. Ottenwaelder and R. M. Waymouth, *Chem. Commun.*, 2005, 5693.
30 P. L. Arnold, S. A. Mungur, A. J. Blake and C. Wilson, *Angew. Chem., Int. Ed.*, 2003, **42**, 5981.

31 S. A. Mungur, S. T. Liddle, C. Wilson, M. J. Sarsfield and P. L. Arnold, *Chem. Commun.*, 2004, 2738.

32 S. T. Liddle and P. L. Arnold, *Organometallics*, 2005, **24**, 2597.

33 P. L. Arnold and S. T. Liddle, *Organometallics*, 2006, **25**, 1485.

34 P. L. Arnold and S. T. Liddle, *Chem. Commun.*, 2005, 5638.

35 S. A. Mungur, A. J. Blake, C. Wilson, J. McMaster and P. L. Arnold, *Organometallics*, 2006, **25**, 1861.

36 R. E. Douthwaite, J. Houghton and B. M. Kariuki, *Chem. Commun.*, 2004, 698.

37 I. S. Edworthy, M. Rodden, S. A. Mungur, K. M. Davis, A. J. Blake, C. Wilson, M. Schröder and P. L. Arnold, *J. Organomet. Chem.*, 2005, **690**, 5710.

38 L. P. Spencer, S. Winston and M. D. Fryzuk, *Organometallics*, 2004, **23**, 3372.

39 L. P. Spencer and M. D. Fryzuk, *J. Organomet. Chem.*, 2005, **690**, 5788.

40 L. P. Spencer, C. Beddie, M. B. Hall and M. D. Fryzuk, *J. Am. Chem. Soc.*, 2006, **128**, 12531.

41 D. Sellmann, C. Allmann, F. Heinemann, F. Knoch and J. Sutter, *J. Organomet. Chem.*, 1997, **541**, 291 and references therein.

42 S. P. Downing and A. A. Danopoulos, *Organometallics*, 2006, **25**, 1337.

43 H.-M. Sun, D.-M. Hu, Y.-S. Wang, Q. Shen and Y. Zhang, *J. Organomet. Chem.*, 2007, **692**, 903.

44 P. B. Hitchcock, M. F. Lappert, P. L. Pye and S. Thomas, *J. Chem. Soc., Dalton Trans.*, 1979, 1929.

45 R. J. Rubio, G. T. S. Andavan, E. B. Bauer, T. K. Hollis, J. Cho, F. S. Tham and B. Donnadieu, *J. Organomet. Chem.*, 2005, **690**, 5353.