EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201901064

Link to VoR: http://dx.doi.org/10.1002/ejic.201901064

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Silver(I) and Nickel(II) Complexes with Oxygen- or Nitrogen-Functionalized NHC Ditopic Ligands and Catalytic Ethylene Oligomerisation

Xiaoyu Ren,[a] Marcel Wesolek*,[a] Corinne Bailly,[b] Lydia Karmazin,[b] and Pierre Braunstein*,[a]

Dedicated to Professor Charles U. Pittmann, Jr., Mississippi State University (USA), on the occasion of his 80th birthday, and to Professor F. Ekkehardt Hahn, University of Münster (Germany), on the occasion of his 65th birthday, with our warmest congratulations and best wishes.

Abstract. Potentially bidentate ditopic ligands containing a N-heterocyclic carbene (NHC) donor associated with an ether or an amine have been prepared and coordinated to Ni(II) centres. The influence of the length of the alkyl chain, -(CH$_2$)$_2$- or –(CH$_2$)$_3$- connecting the ether or the amine group to the heterocycle was examined. In the analogous Ag(I) complexes [Ag{Im(Dipp)(C$_3$OMe)-κ^{1}C^{NHC}}$_2$]Cl (**8**), **9** and **10**, in the neutral Ni(II) complexes with a C$_3$ spacer *trans*-[NiCl$_2${Im(Dipp)(C$_3$OMe)-κ^{1}C^{NHC}}$_2$] (**5a**), **6**, and **7**, and in the cationic *cis*-[Ni{Im(Dipp)(C$_3$OMe)-κ^{1}C^{NHC}}$_2$(NCMe)$_2$](PF$_6$)$_2$ (**15**) and *cis*-[Ni{Im(Mes)(C$_3$OMe)-κ^{1}C^{NHC}}$_2$(NCMe)$_2$](PF$_6$)$_2$ (**16**), the ligand is monodentate. [(ImH)(Dipp)(C$_3$OMe)][NiX$_3${Im(Dipp)(C$_3$OMe)-κ^{1}C^{NHC}}] (**14a**, X = Cl) and (**14b**, X = Br) are rare examples of complexes of the type [NiX$_3$(NHC)]$^-$. For comparison, [NiBr$_2${(Im)(Dipp)(C$_2$NMe$_2$)-κ^2,C^{NHC},N^{amine}}] (**24**) and [NiBr$_2${Im)(Dipp)(C$_3$NMe$_2$)-κ^2,C^{NHC},N^{amine}}] (**25**) contain a six- or a seven-membered κ^{2}C^{NHC},N^{amine} chelate, respectively. Various Ni(II) complexes were evaluated as precatalysts for ethylene oligomerisation. The structures of the carbene (Dipp)(C$_3$OMe)imidazole-ylidene (**4**) and of the complexes **5a**, **7**, **8**, [(ImH)(Dipp)(C$_3$OMe)]$_2$[NiCl$_4$] (**11a**), [(ImH)(Dipp)(C$_3$OMe)]$_2$[NiBr$_4$] (**11b**), [(ImH)(Me)(C$_3$OMe)]$_2$[NiCl$_4$] (**13**), **14b**, **16**·NCMe, [Im(H){C(Me)(=NDipp)}(C$_3$OMe)]$_2$ [NiCl$_4$] (**18**), [AgCl{Im[C(Me)=NDipp](C$_3$OMe)}-κ^{1}C^{NHC}] (**19**), [AgCl{Im(Dipp)(C$_3$NMe$_2$)-κ^{1}C^{NHC}}] (**23**), **24, 25** and *trans*-[NiCl$_2${Dipp[CH$_2$CH$_2$C(O)OEt]}$_2$] were analysed by X-ray diffraction.

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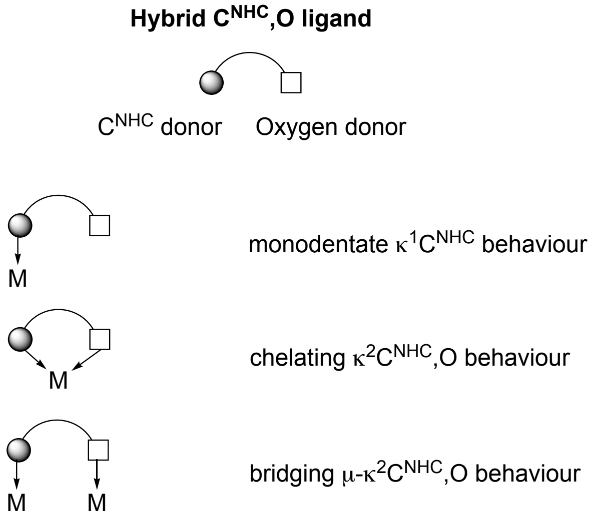
Introduction

Following the report of the first complexes containing *N*-heterocyclic carbene (NHC) ligands[1] and the isolation of the first stable NHC ligands,[2] a fast growing interest developed for this class of ligands and their metal complexes, largely triggered by their often unique properties and wide range of applications.[3] Hundreds of ligands have been synthesized in which the NHC functionality is part of multidentate, homofunctional ligands[4] or of *hybrid* ligands, which associate at least two different donor groups (e.g. NHC with nitrogen, phosphorus, oxygen or sulphur) within the same molecule.[5] Combining one (or more) NHC(s) with a neutral or an anionic donor group has been shown to be beneficial for stabilizing reactive species, providing structural diversity and leading to the formation of novel polynuclear motifs.[6] One such family of hybrid ligands, which is investigated in this paper, combines NHC and oxygen-donor groups and, depending on their stereoelectronic properties and on the type and length of the spacer connecting a NHC nitrogen atom to the oxygen-donor, monodentate, chelating and bridging behaviour have been observed in their metal complexes, as documented in a recent review article (Scheme 1).[7]



Scheme 1. Bonding modes of a C^{NHC},O ditopic ligand

In the course of our studies on the synthesis of bis(ether-functionalized NHC) Ni(II) complexes aimed at examining the impact of the presence of an oxygen donor group on the structure and properties of the corresponding NHC metal complexes,[8] we found that only monodentate behaviour through the NHC function (κ^1C^{NHC}) was observed in the case of the C^{NHC},O^{ether} ditopic ligands studied. In contrast, alcoholate-functionalized NHC ligands with a similar –CH_2CH_2– (C_2) spacer connecting a NHC nitrogen atom with the oxygen-donor led to mononuclear, chelated complexes (κ^2C^{NHC},O bonding type) or to oxygen-bridged dinuclear NHC complexes (μ-

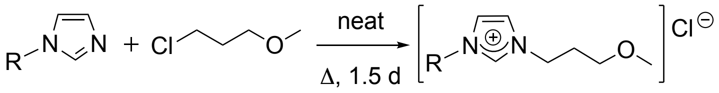
κ^2C^{NHC},O bonding type).[9] Interestingly, the chelating κ^2C^{NHC},O bonding mode of an anionic ligand, where the oxygen donor belongs e.g. to an alcoholate or an enolate function, is reminiscent of the κ^2P,O bonding mode of functional phosphine ligands endowed with a very rich chemistry,[10] in particular in relation to SHOP-type ethylene oligomerization catalysts,[11] and this has certainly provided an incentive for their study.[9,12] We thus wondered whether in C^{NHC},O^{ether} systems, formation of ($\kappa^2C^{NHC},O^{ether}$) chelates could be favoured by an increase in the length of the spacer from C_2 to C_3. For comparison, C^{NHC},N^{amine} hybrid ligands containing an amino group and a C_3 spacer are also reported here.

Furthermore, we recently showed that binding of the amine group present in $N^{imine},C^{NHC},N^{amine}$ pincer-type ligands depends on a number of parameters, in addition to the length of the spacer connecting a NHC nitrogen atom with the amine.[13] Considering the impressive developments of the research on transition metal complexes with pincer ligands[14] and capitalizing on our own recent studies on N,C^{NHC},N-based pincer ligands,[13,15] we investigated for comparison the bonding behaviour of potentially tridentate $N^{imine},C^{NHC},O^{ether}$ pincer ligands to nickel in order to examine whether the desired chelation of the O^{ether} donor could be promoted by the binding of the better N^{imine} donor. Interestingly, palladium complexes stabilized by $N^{pyr},C^{NHC},O^{aryloxide}$ pincer ligands were recently found to display better catalytic activities than the corresponding bidentate bis(aryloxide-NHC) palladium complexes in norbornene polymerization.[16] In addition to our interest for NHC-type hybrid ligands and the selectivity of the interactions between their donor groups and metal centres in their complexes, we also evaluated the catalytic properties of the new nickel complexes obtained in ethylene oligomerization. Triggered by industrial market requirements, in particular the rapid growth of the demand for short-chain α-olefins, catalytic ethylene oligomerization remains of considerable academic and industrial interest,[17] and nickel complexes have a long and very successful history in this field.

Results and Discussion

Syntheses and Structures.

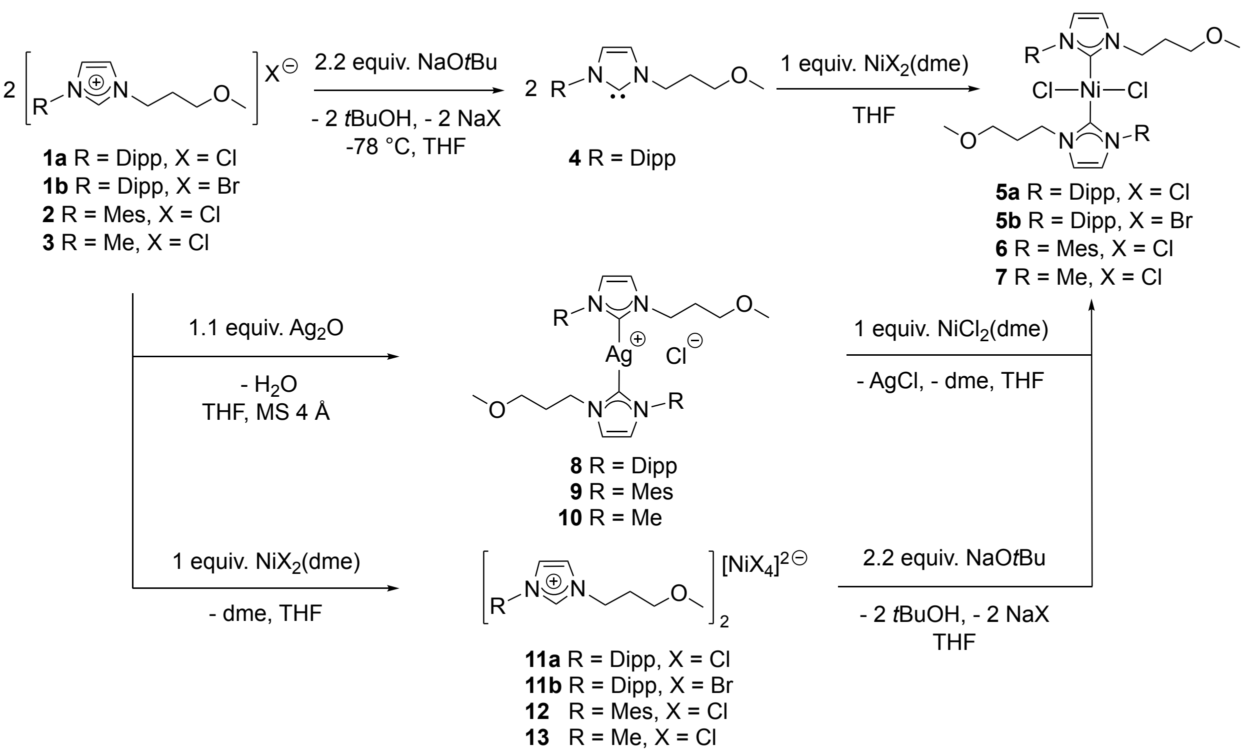
Extending a protocol previously established to access C^{NHC},O^{ether} ditopic ligands containing a –CH_2CH_2– (C_2) spacer between a NHC nitrogen atom and the ether oxygen[8] to analogous ligands containing a –$(CH_2)_3$– (C_3) spacer, we prepared 1-(2,6-diisopropylphenyl)-3-(3-methoxypropyl)-1*H*-imidazol-3-ium chloride, [(ImH)(Dipp)(C_3OMe)]Cl (**1a**), 1-mesityl-3-(3-methoxypropyl)-1*H*-imidazol-3-ium chloride, [(ImH)(Mes)(C_3OMe)]Cl (**2**), and 1-methyl-3-(3-methoxypropyl)-1*H*-imidazol-3-ium chloride, [(ImH)(Me)(C_3OMe)]Cl (**3**) in good yields according to the reactions of eq. 1.



(1)

1a R = Dipp
2 R = Mes
3 R = Me

As detailed below, the corresponding bis(ether-functionalized NHC) nickel complexes were typically obtained by deprotonation of these imidazolium salts followed by direct addition of the resulting free carbene to $[NiCl_2(dme)]$ (dme = 1,2-dimethoxyethane), by ligand transmetallation from a NHC silver complex, or by an indirect pathway consisting firstly in the formation of a bis-imidazolium salt of $[NiX_4]^{2-}$ followed by its deprotonation (Scheme 2). In the latter case, using a slight excess of NaO*t*Bu (2.2 equiv.) as a base led to improved yields.



Scheme 2. Various synthetic approaches to *trans*-coordinated bis-ether-functionalized NHC Ni(II) complexes.

The free carbene 1-(2,6-diisopropylphenyl)-3-(3-methoxypropyl)-1*H*-imidazol-2(3*H*)-ylidene (**4**) was prepared by dropwise addition of a THF solution of NaO*t*Bu to a THF suspension of the corresponding imidazolium salt at –78 °C and colourless crystals were isolated. An X-ray diffraction analysis, performed on single crystals grown from a saturated Et_2O solution at –30 °C (Scheme 2, Figure 1), confirmed the nature of the ligand. Compound **4** crystallizes in the monoclinic system (space group $P2_1/c$, Table S1). The lengths of the C1-N1 and C1-N2 bonds of 1.367(2) and 1.363(2) Å, respectively, are perfectly consistent with their partial double bond character and with literature values.[2]

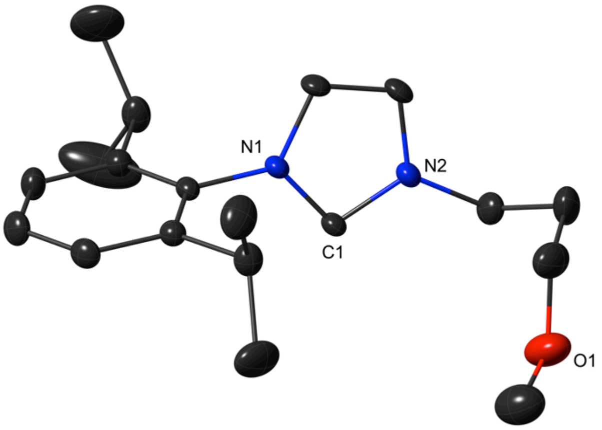


Figure 1. View of the structure of the C^{NHC},O^{ether} free carbene **4** with H atoms omitted for clarity. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): C1−N1 1.367(2), C1−N2 1.363(2), N1−C1−N2 101.7(1).

The Ni(II) complexes dichlorobis[1-(2,6-diisopropylphenyl)-3-(3-methoxypropyl)-1*H*-imidazol-2(3*H*)-ylidene]nickel, [$NiCl_2${Im(Dipp)(C_3OMe)-κ^1C^{NHC}}$_2$] (**5a**), dichlorobis[1-mesityl-3-(3-methoxypropyl)-1*H*-imidazol-2(3*H*)-ylidene]nickel, [$NiCl_2${Im(Mes)(C_3OMe)−κ^1C^{NHC}}$_2$] (**6**), and dichlorobis[1-methyl-3-(3-methoxypropyl)-1*H*-imidazol-2(3*H*)-ylidene]nickel, [$NiCl_2${Im(Me)(C_3OMe)-κ^1C^{NHC}}$_2$] (**7**), were obtained as orange, diamagnetic, air-stable powders in good yield by reaction of the free carbene with [$NiCl_2$(dme)] (Scheme 2). Complexes **5a** and **7** were characterized by X-ray diffraction (Figure 2), they crystallize in the monoclinic system (space group *P*2_1/c, Table S1). The nickel centre displays a square-planar coordination environment with two trans chlorides and two trans NHC ligands. The Ni1−C1 distances of 1.918(3) and 1.923(2) Å, respectively, are typical for Ni-C^{NHC} bonds in such complexes.[3n,8] The ether groups remain dangling, as previously observed with the shorter spacer –CH_2CH_2–between the N and O atoms, which demonstrates that ether chelation was not hampered by steric considerations.[8] Moreover, a minor isomer present in solution, as indicated by ^{1}H NMR spectroscopy, could not be unambiguously identified, but we suggest that it corresponds to mutual *syn*- and *anti*-orientations of the NHC ligands in complex **5a** (see Experimental section).[8]

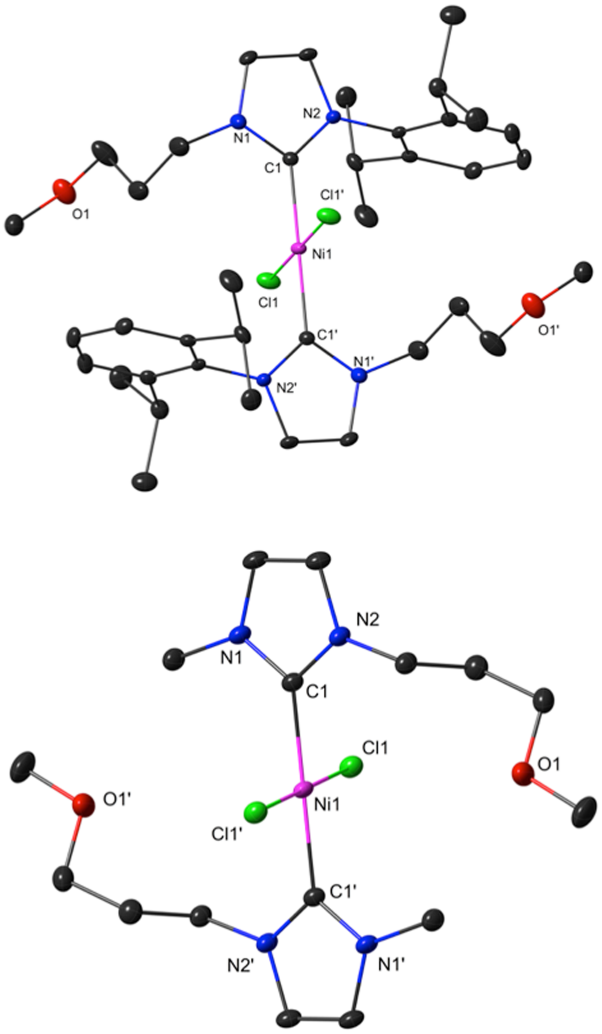


Figure 2. Views of the structures of the *trans*-Ni(II) complexes **5a** (top) and **7** (bottom) with H atoms omitted for clarity. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): in **5a** Ni1−C1 1.918(3), Ni1−Cl1 2.190(7), C1−N1 1.355(3), C1−N2 1.352(3), C1−Ni1−Cl1 87.5(8), C1−Ni1−Cl1’ 92.5(8), N1−C1−Ni1 131.1(2), N2−C1−Ni1 124.4(2), N1−C1−N2 104.3(2); in **7** Ni1−C1 1.923(2), Ni1−Cl1 2.199(4), C1−N1 1.350(2), C1−N2 1.351(2), C1−Ni1−Cl1 90.0(5), C1−Ni1−Cl1’ 90.0(5), N1−C1−Ni1 127.8(1), N2−C1−Ni1 127.2(1), N1−C1−N2 104.8(1).

To examine the possibility to synthesize these Ni(II) complexes by transmetallation reaction, the corresponding Ag(I) complexes **8-10** were prepared according to Scheme 2. X-ray quality crystals of the complex [Ag{ImDipp(C$_3$OMe)-κ^{1}C$^{\text{NHC}}$}$_2$]Cl (**8**) were obtained by slow diffusion of pentane into a THF solution of the complex, which crystallizes in the monoclinic system (*C*2/c space group, Table S1) (Figure 3). As expected, the coordination geometry about the silver cation is nearly linear (C$^{\text{NHC}}$−Ag−C$^{\text{NHC}}$ angle = 174.4(7)°) and the mean planes of the two NHC ligands make an angle of 40.51(4)°, most likely for steric reasons. The Ag−C$^{\text{NHC}}$ distance of 2.094(1) Å is in good agreement with data reported for related homoleptic cationic bis-(NHC) Ag(I) complexes.[8a,18] In the crystal, the Ag−Cl separation of 2.8777(6) Å is similar to that observed in related complexes,[8a, 19] but is much longer than in dicoordinated complexes of the type [AgCl(NHC)][13c] (see below the Ag-Cl distances of 2.332(4) Å in **19** and 2.314(1) Å in **23**, ESI). Consistent with an almost linear C1−Ag1−C1' array (angle =174.4(7)°), this Ag−Cl separation reflects the electrostatic interaction between the silver cation and the halide anion.

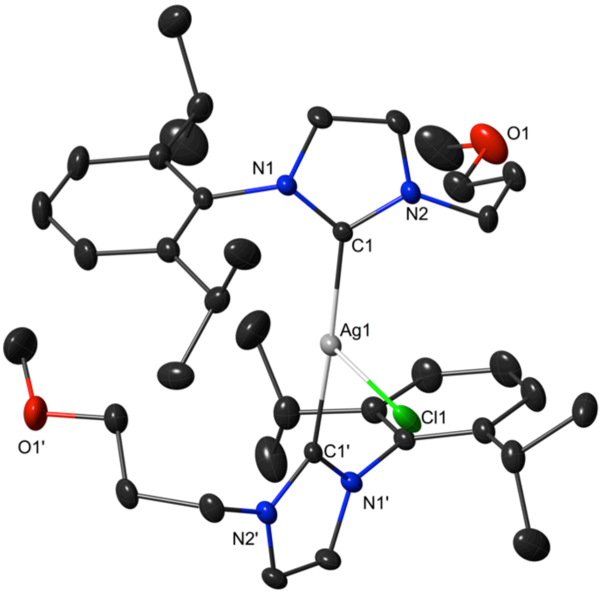


Figure 3. Structure of the Ag(I) complex **8** with H atoms omitted for clarity. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ag1−C1 2.094(1), Ag1−Cl1 2.877(6), C1−N1 1.358(2), C1−N2 1.352(2), C1−Ag1−Cl1 92.8(3), C1−Ag1−C1' 174.4(7), N1−C1−Ag1 128.9(9), N2−C1−Ag1 127.0(9), N1−C1−N2 103.8(1). The electrostatic Ag···Cl interaction is materialized in order to better visualize the coordination geometry around the metal centre.

A third synthetic method was explored to access the bis-NHCs nickel complexes **5a-7** (Scheme 2), which involved first formation of the bis-imidazolium salts of $[NiCl_4]^{2-}$ followed by their deprotonation with a slight excess of NaO*t*Bu. This method presented the clear advantages of requiring shorter reaction times and of not involving air-sensitive, free carbenes. The salts $[(ImH)(Dipp)(C_3OMe)]_2[NiCl_4]$ (**11a**), $[(ImH)(Dipp)(C_3OMe)]_2[NiBr_4]$ (**11b**), $[(ImH)(Mes)(C_3OMe)]_2[NiCl_4]$ (**12**) and $[(ImH)(Me)(C_3OMe)]_2[NiCl_4]$ (**13**) were obtained in high yield by reaction of 2 equiv. of the corresponding imidazolium chloride with 1 equiv. of $[NiX_2(dme)]$. Blue (X = Cl) or purple (X = Br) powders were isolated which are soluble in MeCN or CH_2Cl_2, but insoluble in THF. Crystallographic analyses of **11a** and **13** confirmed the presence of $[NiCl_4]^{2-}$ dianions associated with two imidazolium cations (Figure 4, Table S1). The nickel centre is in a tetrahedral environment constituted by four chlorides at a typical distance of 2.245(1) and 2.250(1) Å, respectively.[20] Complex **11a** crystallizes in the orthorhombic system (space group $P2_12_12_1$), and the H1···Cl2 and H1···Cl4 distances of 2.673 Å and 2.952 Å, respectively, reveal weak hydrogen-bonding interactions. Complex **13** crystallizes in the monoclinic system (space group *C*2/c) and the asymmetric unit contains one organic cation and half a $[NiCl_4]^{2-}$ dianion, with the nickel atom occupying a special position (population 50%).

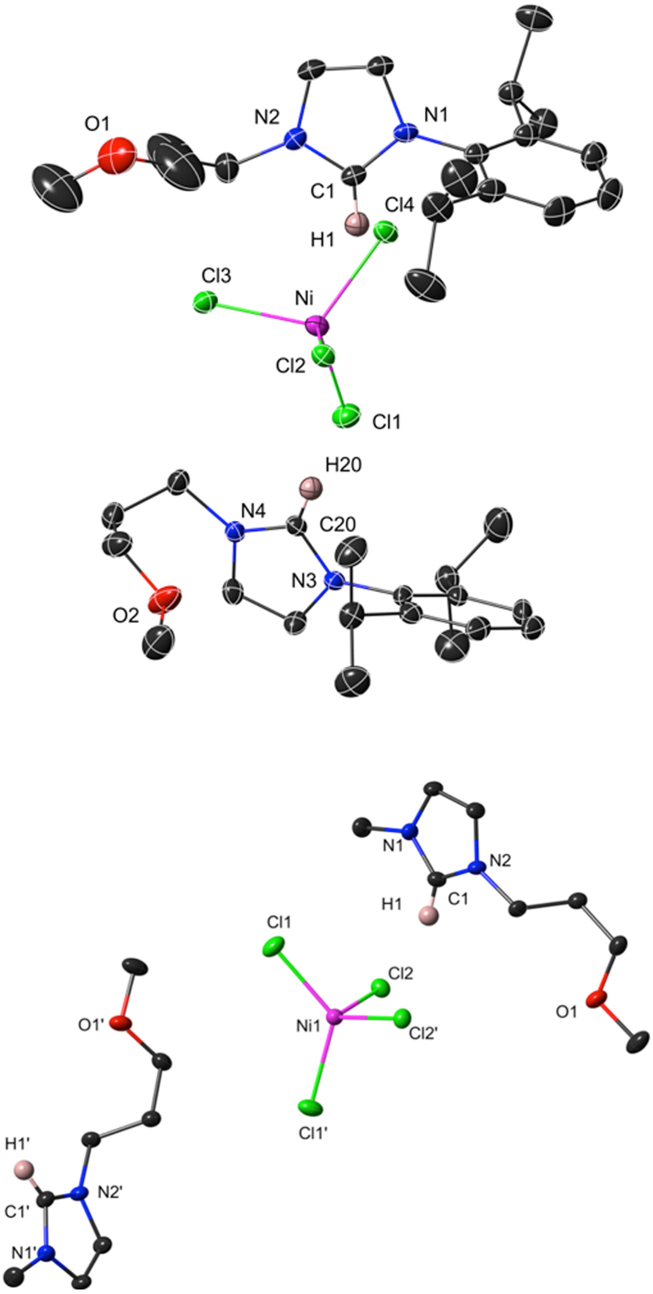
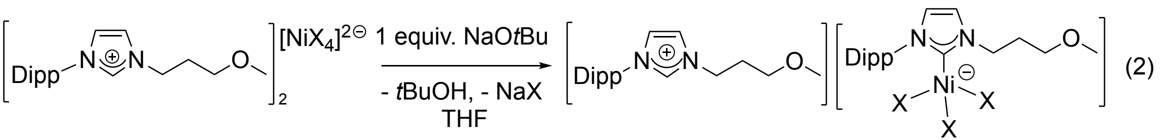


Figure 4. Structures of the complexes **11a** (top) and **13** (bottom) with H atoms omitted for clarity, except the NC*H*N hydrogen atoms. Thermal ellipsoids at the 40% (**11a**) and 30% (**13**) probability level. Selected bond lengths (Å) and angles (deg): in **11a** Ni1−Cl1 2.245(1), Ni1−Cl2 2.282(9), Ni1−Cl3 2.275(9), Ni1−Cl4 2.266(9), C1−N1 1.331(4), C1−N2 1.331(4), C20−N3 1.334(4), C20−N4 1.317(4); N1−C1−N2

109.2(3), N3−C20−N4 109.0(3); in **13** Ni1−Cl1 2.250(1), Ni1−Cl2 2.277(1), C1−N1 1.332(4), C1−N2 1.322(5); N1−C1−N2 108.8(3).

When the salt **11a** was used for the synthesis of the corresponding bis(NHC) Ni(II) complex, few dark blue crystals of the Ni(II) complex [(ImH)(Dipp)(C_3OMe)][$NiCl_3${Im(Dipp)(C_3OMe)-κ^{1}C^{NHC}}] (**14a**) were unexpectedly obtained. Similar blue crystals, previously isolated in a irreproducible manner, were shown by X-ray diffraction analysis to contain the first example of anionic Ni(II) complex where three chlorides and one NHC ligand coordinate the metal, associated with an imidazolium cation.[8b] The isolation of the mono-NHC nickel complex **14a** suggested that it may be more rationally prepared by decreasing the quantity of base from 2 to 1 equiv. (eq. 2).



11a X = Cl
11b X = Br

14a X = Cl
14b X = Br

Addition of diethyl ether to a toluene solution of the reaction mixture afforded dark blue, paramagnetic, air-stable crystals, but these were not suitable for crystallographic analysis. We then turned to the bromide analogue and isolated in good yield [(ImH)(Dipp)(C_3OMe)][$NiBr_3${Im(Dipp)(C_3OMe)-κ^{1}C^{NHC}}] (**14b**) from the imidazolium salt [(ImH)(Dipp)(C_3OMe)]$_2$[$NiBr_4$] (**11b**) under similar reaction conditions. Single crystals of complexes **11b** (monoclinic system, space group *C*c) and **14b** (monoclinic system, space group P2$_1$/c) were analysed by X-ray diffraction (Figure 5, Table S1). These complexes are similar to their chloride analogues[8b] and the structure of **11b** displays weak hydrogen-bonding interactions (H20···Br1 = 2.943 Å and H20···Br2 = 2.876 Å). In complex **14b**, the nickel centre is surrounded by three bromides and one NHC ligand which form a tetrahedral coordination environment. To the best of our knowledge, such an arrangement has only been characterized once before by X-ray diffraction.[21] The first structurally characterized example of a [NiX_3(NHC)]$^-$ anion was reported only recently.[8b] The Ni−Br bond lengths, in the range 2.376(9) - 2.404(8) Å and 2.402(5) - 2.424(5) Å, in **11b** and **14b**, respectively, compare well with literature values.[22] The distances H20···Br1 (2.738 Å), H20···Br2 (3.043 Å), H16B···Br2 (2.914 Å) and H35A···Br2 (3.128 Å) are indicative of weak hydrogen-bonding interactions in **14b**.

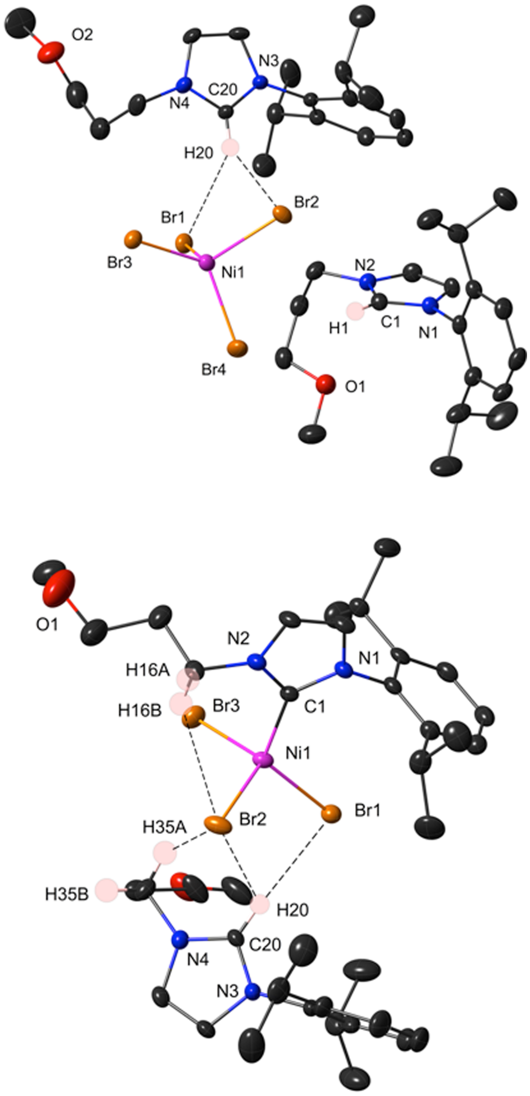


Figure 5. Views of the structures of complexes in **11b** (top) and **14b** (bottom), with H atoms omitted for clarity, except those involved in H-bonding interactions. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): in **11b** Ni1−Br1 2.394(8), Ni1−Br2 2.401(7), Ni1−Br3 2.404(8), Ni1−Br4 2.376(9), C1−N1 1.333(6), C1−N2 1.323(6), C20−N3 1.315(6), C20−N4 1.317(6); N1−C1−N2 108.6(4), N3−C20−N4 109.8(4); in **14b** Ni1−Br1 2.402(5), Ni1−Br2 2.424(5), Ni1−Br3 2.405(5), Ni1−C1 1.985(3), C1−N1 1.370(4), C1−N2 1.357(3), C20−N3 1.329(4), C20−N4 1.327(4); C1−Ni1−Br1 120.7(8), C1−Ni1−Br2 103.2(8), C1−Ni1−Br3 104.1(8), Br1−Ni1−Br2 109.0(2), Br1−Ni1−Br3 107.4(2), Br2−Ni1−Br3 112.5(2), N1−C1−Ni1 129.0(2), N2−C1−Ni1 127.0(2), N1−C1−N2 104.0(2), N3−C20−N4 108.6(2).

As shown in Figure 6, the paramagnetic nickel complex **14a** displays ^{1}H NMR peaks between 92 and -32 ppm in THF-d$_8$.

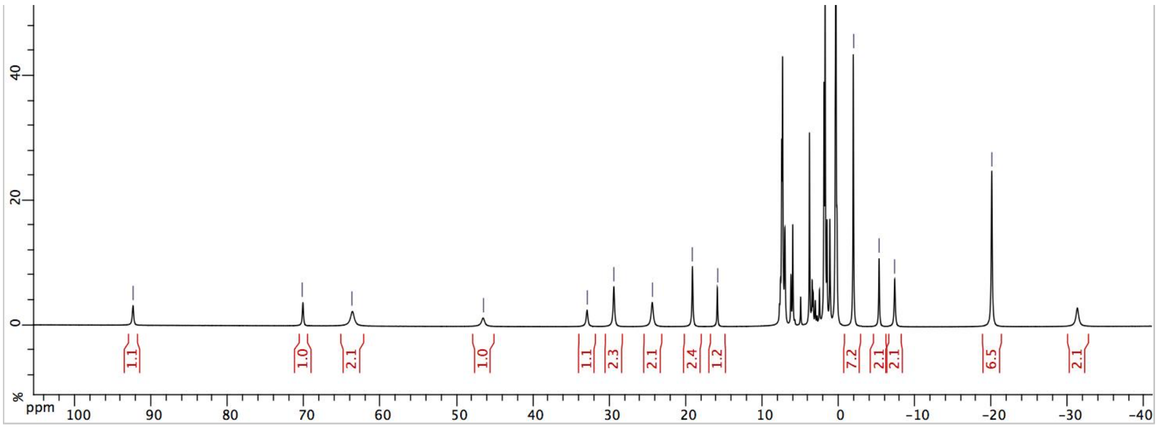


Figure 6. Paramagnetic ^{1}H NMR spectrum of **14a** in THF-d_8

Because of the presence of an ether-functionalized heterocycle in both the cationic and anionic moieties of this complex, further ^{1}H NMR investigations were performed in order to assign their signals. In Figure 7, the top spectrum (blue) is that of **14a** (**a**), and the three spectra below illustrate the shifts resulting from the addition of increasing amounts of imidazolium salt (**1a** = $\mathbf{b^+Cl^-}$) to **14a**. While some peaks ($\mathbf{a^-}$) remained unchanged, other ($\mathbf{a^+}$) were significantly shifted. Thus, the $\mathbf{a^-}$ peaks belong to the anionic part of the complex with the carbene ligand bound to the nickel centre whereas the $\mathbf{a^+}$ peaks belong to the imidazolium cation that interacts by hydrogen bonding with the paramagnetic nickel complex. In solution, the signals for $\mathbf{a^+}$ and $\mathbf{b^+}$ cannot be distinguished.

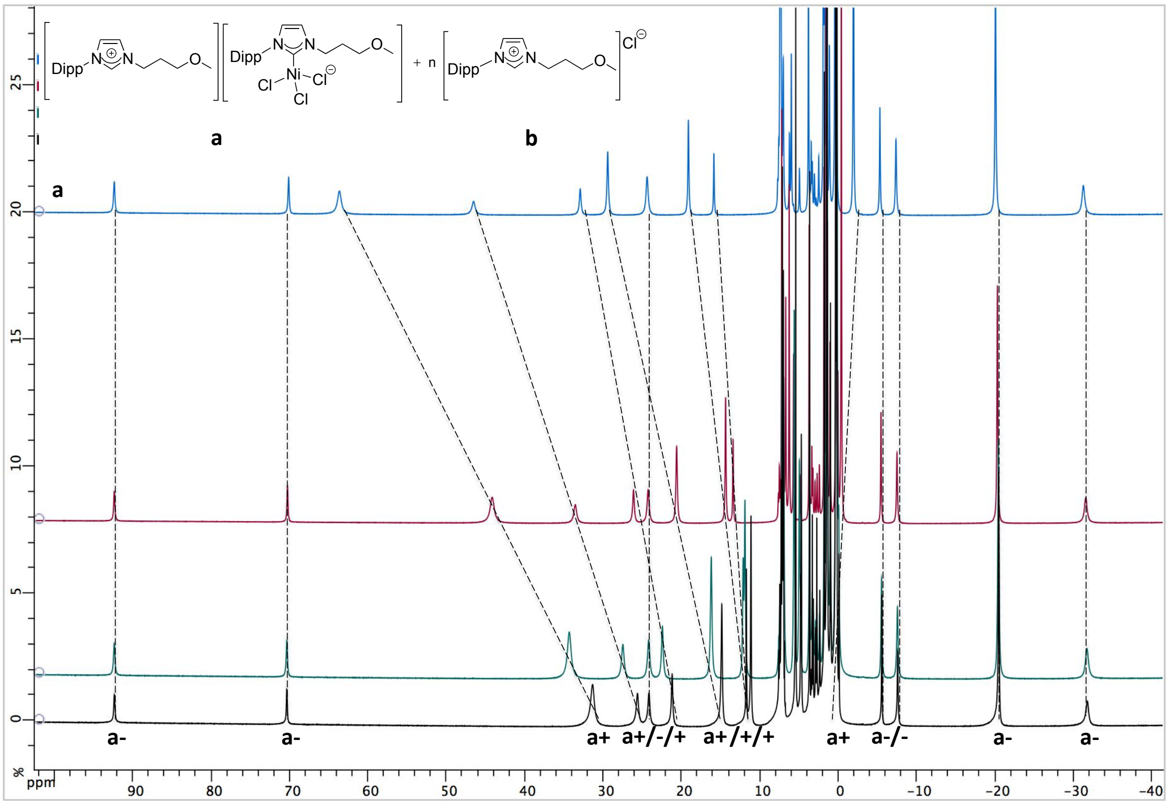
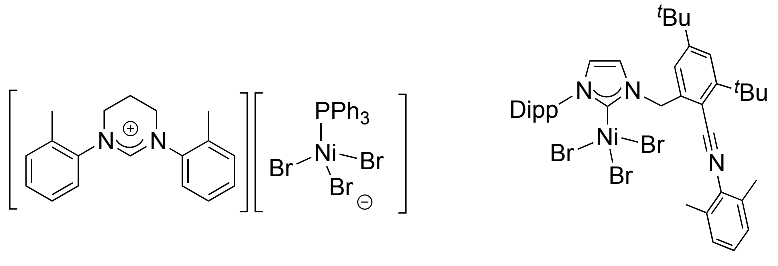


Figure 7. Changes in the ^{1}H NMR spectrum of **14** in THF-d$_8$ upon addition of increasing amounts of the corresponding imidazolium salt, [**a**+] represents the peaks assigned to [(ImH)(Dipp)(C$_3$OMe)]$^+$ and [**a**-] those assigned to the anion [NiCl$_3${Im(Dipp)(C$_3$OMe)-κ^{1}C^{NHC}}]$^-$.

For comparison of the ^{1}H NMR spectrum of **14a** with those of relevant complexes, we searched for other Ni(II) complexes possessing a [NiX$_3$]$^-$ moiety. In 2014, Whittlesey and co-workers obtained a complex containing the Ni(II) anion [NiBr$_3$(PPh$_3$)]$^-$ as a byproduct in the formation of a Ni(II) NHC complex by deprotonation of a N-aryl-substituted six-membered imidazolium ring followed by the addition of [NiBr$_2$(PPh$_3$)$_2$] (Figure 8).[23] The ^{1}H NMR resonances of the associated imidazolium cation were observed between 19.55 and -4.85 ppm. In 2017, Fout and co-workers[21] isolated a [NiBr$_3$(NHC)]$^-$ complex from the chemical oxidation of a bidentate NHC-η^2-iminoacyl Ni(II) complex by [Ph$_3$CBr] and its ^{1}H NMR signals ranged from 87.29 to -22.21 ppm (Figure 8). The latter range is more similar to that observed for **14a**, which is consistent with the structural similarity of the complexes.

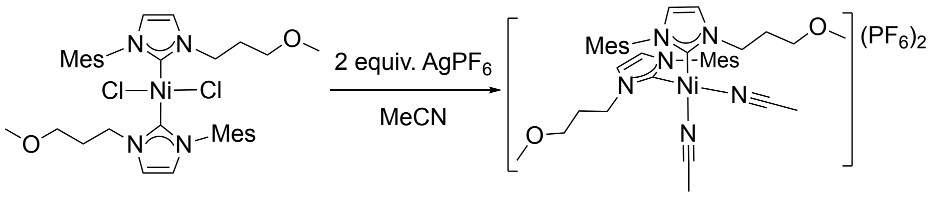


Whittlesey **Fout**

Figure 8. Ni(II) complexes containing a $[NiBr_3]^-$ moiety (see text)

In an attempt to promote chelation of the ether group, halogen abstraction was performed on complex **6**, using $AgPF_6$ or $TlPF_6$, the latter in order to prevent redox side reactions. With THF as a solvent, a yellow compound was formed that could not be fully identified. We then carried out the same reaction in the presence of very small amounts of water since previous work with a related Ni(II) complex has evidenced the stabilizing role of coordinated water molecules.[8b] However, we could not characterize such a species, but after dissolution of the solid in acetonitrile, the solvento complex *cis*-$[Ni\{Im(Mes)(C_3OMe)\text{-}\kappa^1C^{NHC}\}_2(NCMe)_2](PF_6)_2$ (**16**) was obtained. Pale yellow single crystals of **16**·NCMe were grown by slow diffusion of ether into an acetonitrile solution of the complex and characterized by X-ray diffraction (Figure 9). The complex crystallises in the triclinic system (space group *P*-1, Table S1). The structural analysis established that the nickel centre adopts a square planar coordination geometry, defined by two cis-NHC ligands and two cis-acetonitrile molecules. The trans to cis isomerisation observed on going from **6** to **16** is favoured by the solvent polarity. The Ni−C^{NHC} bond lengths of 1.884(2) Å are slightly shorter than in the *trans* complexes **5a** and **7** (see above), most likely because of the weaker trans-influence of acetonitrile compared with the NHC ligand **4**. The planes of the two carbene ligands in **16** are almost orthogonal to each other (88.74°) in order to minimize steric repulsions. The ^1H NMR spectra indicated that the *gem*-protons on the ether arms $\text{-NC}H_2\text{C}H_2\text{C}H_2\text{OMe}$ are diastereotopic because of the *cis*-coordination geometry of the two NHC ligands (Supporting information, Figures S1 and S2). When the crude product obtained from the halide abstraction reaction performed in dry THF on **6** was treated with acetonitrile, formation of the acetonitrile-coordinated complexes was not observed by NMR spectroscopy. However, when halide abstraction was directly carried out in dry acetonitrile, complex **16** was readily isolated (eq. 3). These reactions confirm the difficulty to coordinate the ether arm of the NHC ligand **4** to a Ni(II) centre. Clearly, acetonitrile is a better donor than an ether group.

10.1002/ejic.201901064



6 **16** (3)

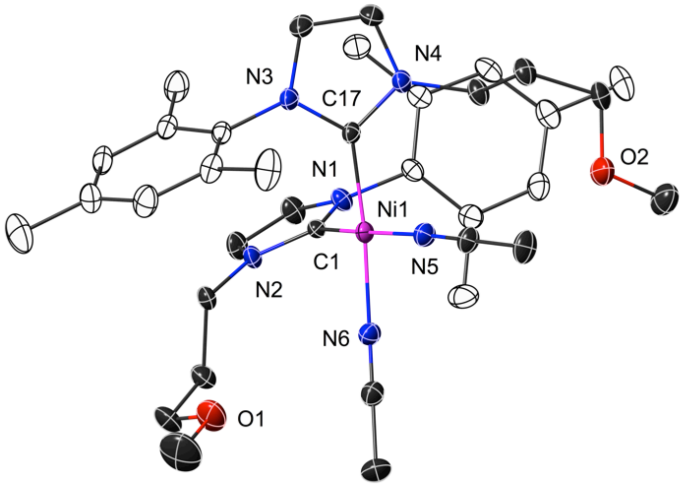
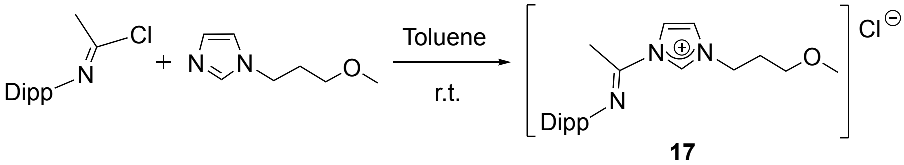


Figure 9. Structure of the Ni(II) complex **16** with H atoms and PF_6 anions omitted for clarity. Thermal ellipsoids at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ni1−C1 1.884(2), Ni1−C17 1.884(2), Ni1−N5 1.898(2), Ni1−N6 1.906(2), C1−N1 1.364(3), C1−N2 1.349(3), C17−N3 1.359(3), C17−N4 1.348(3); C1−Ni1−C17 89.8(9), C1−Ni1−N6 92.8(8), C17−Ni1−N5 91.0(8), N5−Ni1−N6 87.4(8), C1−Ni1−N5 172.4(9), C17−Ni1−N6 172.7(9), N1−C1−N2 105.2(2), N3−C17−N4 105.5(2).

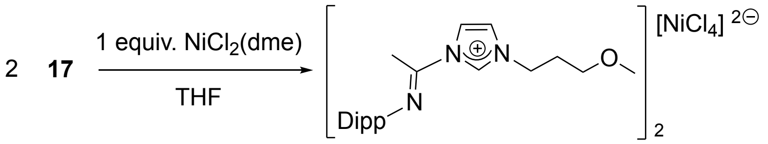
Pincer-type Ligands

Since potentially C^{NHC},O^{ether} bidentate ligands with a C2[8] or a C3 spacer (this work) connecting the heterocycle to the ether group were observed to only bind to Ni(II) in a monodentate κ^1C^{NHC} mode, the oxygen-function remaining dangling, we considered introducing an additional N^{imine} donor in the ligand system that could provide anchimeric assistance for ether coordination in a potentially N^{imine},C^{NHC},O^{ether} tridentate, pincer-type ligand. The imidazolium salt $[(ImH)\{C(Me)=NDipp\}(C_3OMe)]Cl$ (**17**) (eq. 4) was isolated as a white powder but its deprotonation followed by the addition of $[NiCl_2(dme)]$ afforded an intractable mixture. However, the indirect pathway mentioned above consisting in the formation of the bis-imidazolium salt $[(ImH)\{C(Me)=NDipp\}(C_3OMe)]_2[NiCl_4]$ (**18**) (eq. 5), followed by deprotonation with 1 or 2 equiv. of base, led to better results.



17

(4)



18

(5)

The salt **18** crystallizes in the monoclinic system (*C*2/c space group, Table S1) and the asymmetric unit contains one organic cation and half a dianion $[NiCl_4]^{2-}$, with the nickel atom occupying a special position (population 50%), as in compound **13** (see above) (Figure 10). A green, paramagnetic complex was obtained by deprotonation of **18** with 1 equiv. of NaO*t*Bu, but no crystals formed. From the ^{1}H NMR analysis, formation of a compound of the type $[NiCl_3(NHC)]^-$ could not be evidenced.

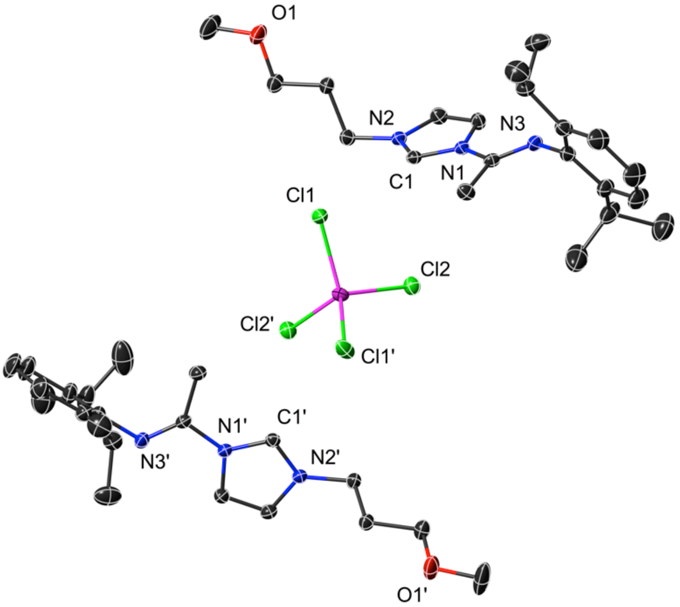
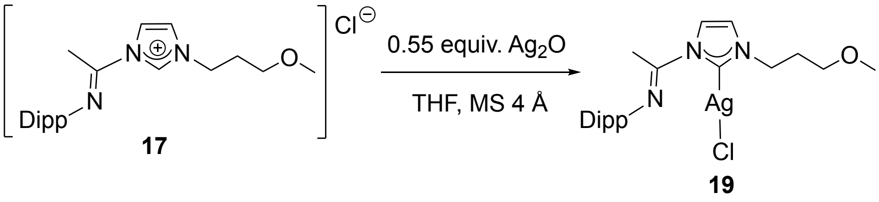


Figure 10. View of the structure of complex **18** with H atoms omitted for clarity, including the NC*H*N hydrogen atoms. Thermal ellipsoids at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ni1−Cl1 2.263(4), Ni1−Cl2 2.271(4), C1−N1 1.340(2), C1−N2 1.324(2), N1−C1−N2 108.3(1).

Considering the wide use of silver(I) complexes as transmetalating agents in the synthesis of transition metal NHC complexes,[24] the silver complex [AgCl{Im[C(Me)=NDipp](C_3OMe)}-κ^1C^{NHC}] (**19**) was prepared (eq. 6) and used for transmetallation reactions to Ni(II). Its crystallographic analysis (monoclinic system, space group *P*2_1/c, Table S1) (Figure 11) confirmed the expected nearly linear coordination geometry around the metal (C1−Ag1−Cl1 angle of 177.1(4) Å), and the presence of a monodentate NHC ligand with pendent N^{imine} and O^{ether} groups. The Ag-C^{NHC} bond length of 2.080(1) Å is slightly shorter than that in **8** (2.094(1) Å, see above) or in comparable complexes.[13c] The N and O atoms are directed toward the Ag atom although the Ag1···N3 (2.801 Å) and Ag1···O1 (3.334 Å) separations are too long to represent significant bonding interactions. Similar features were recently encountered with a potentially N^{imine},C^{NHC},N^{amine} tridentate ligand.[13c]



(6)

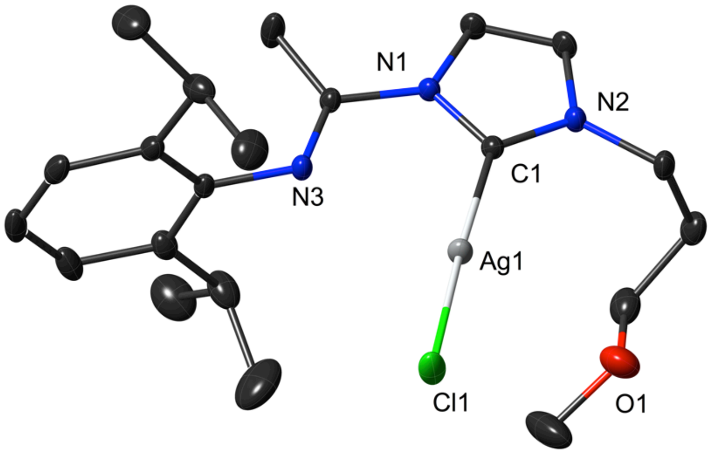
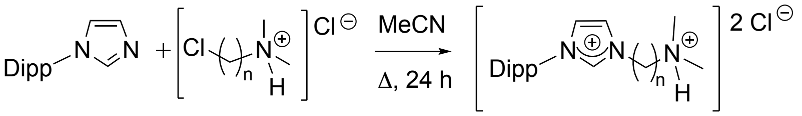


Figure 11. View of the structure of the Ag(I) complex **19** with H atoms omitted for clarity. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ag1−C1 2.080(1), Ag1−Cl1 2.332(4), C1−N1 1.366(2), C1−N2 1.346(2); C1−Ag1−Cl1 177.1(4), N1−C1−Ag1 125.1(1), N2−C1−Ag1 130.6(1), N1−C1−N2 104.3(1).

When [$NiCl_2$(dme)] was used for a transmetallation reaction from **19** in THF, a green oil was obtained that could not be analysed owing to its paramagnetic nature. The low solubility of [$NiCl_2$(dme)] that could favour formation of a bis-NHC complex prompted us to use a more soluble precursor. Therefore, [$Ni(NCMe)_6$](BF_4)$_2$ was employed in a Ni/Ag-NHC ratio of 1:1 or 2:1 but similar results were obtained in both cases, according to ^1H NMR spectroscopy. The product could not be crystallized. The additional imine donor introduced in the hybrid ligand has therefore not allowed the characterization of Ag(I) or Ni(II) complexes that would display coordination of the ether oxygen.

Introduction of an Amine Donor.

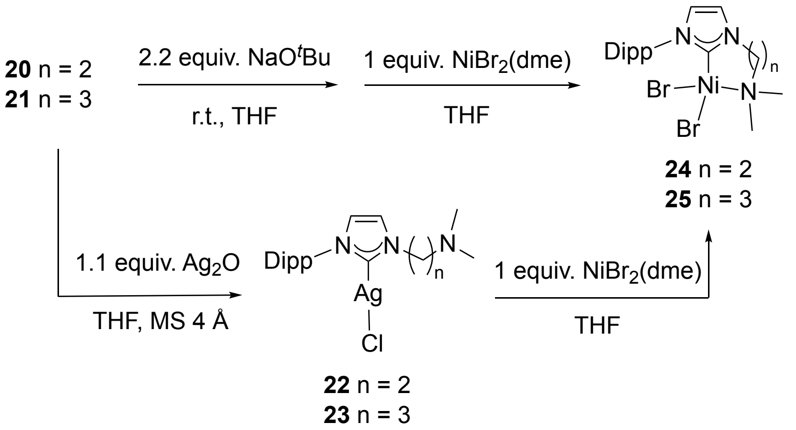
The results reported above and in the literature[7,8] clearly indicate that chelation of the ether group in C^{NHC},O^{ether} or in N^{imine},C^{NHC},O^{ether} systems is not favourable, whether the spacer connecting an imidazole nitrogen atom to the ether group is a -$(CH_2)_2$- or a $(-CH_2)_3$- unit. In contrast, chelation of the stronger alcoholate donor group to Ni(II) has been reported.[7,9] In view of this and for comparison, we introduced a stronger amine donor in place of the ether to investigate the possibility of forming a C^{NHC},N^{amine} chelate with either a C_2 or a C_3 spacer. The ammonium salts $[(ImH)(Dipp)(C_2NHMe_2)]Cl_2$ (**20**) and $[(ImH)(Dipp)(C_3NHMe_2)]Cl_2$ (**21**) were prepared according to eq. 7 and reacted with 2 equiv. of base and then with $[NiBr_2(dme)]$.



(7)

20 n = 2
21 n = 3

The purple Ni(II) complexes **24** and **25** thus isolated (Scheme 3) were also obtained by transmetallation from the Ag(I) complexes $[AgCl\{(Im)(Dipp)(C_2NMe_2)–\kappa^1C^{NHC}\}]$ (**22**) and $[AgCl\{(Im)(Dipp)(C_3NMe_2)\text{-}\kappa^1C^{NHC}\}]$ (**23**), respectively. The latter complex crystallizes in the monoclinic system ($P2_1/c$ space group, Table S1). As expected, its structure is similar to that of **19** (Figure 11), with a NMe_2 instead of OMe pending donor group and is shown in the Supporting Information (Figure S3). However, ligand chelation in the Ni(II) complexes was unambiguously established by an X-ray diffraction analysis of $[NiBr_2\{(Im)(Dipp)(C_2NMe_2)\text{-}\kappa^2N^{amine},C^{NHC}\}]$ (**24**) (Figure 12). This complex crystallizes in the monoclinic system ($P2_1/c$ space group, Table S1). The nickel centre is in a tetrahedral coordination environment consisting of two bromides, the NHC and the amine donor groups. Formation of a C^{NHC},N^{amine} chelated Ni complex is consistent with the stronger amine group coordinating more readily to Ni(II) than an ether. The purple Ni(II) complex $[NiBr_2\{(Im)Dipp(C_3NMe_2)\text{-}\kappa^2C^{NHC},N^{amine}\}]$ (**25**) has a similar structure (monoclinic system, space group $P2_1/c$, Table S1) but contains a seven-membered ring C^{NHC},N^{amine} chelate. Its bond distances and angles are similar to those in **24**, except for the much more open C1−Ni1−N3 angle (104.7(3)° in **25**, 94.8(2)° in **24**). In both complexes, the length of the Ni-N^{amine} dative bond, 2.042(5) and 2.056(8) Å, in **24** and **25**, respectively, compares well with those in recently reported Ni(II) complexes with κ^2C^{NHC},N^{amine} chelates[13b,c] and are typical for Ni(II)-tertiary amine bonds in tetracoordinated complexes (*aver.* 1.957 Å).[25]



Scheme 3. Synthesis of the amine-functionalized NHC Ag(I) and Ni(II) complexes **22-25**

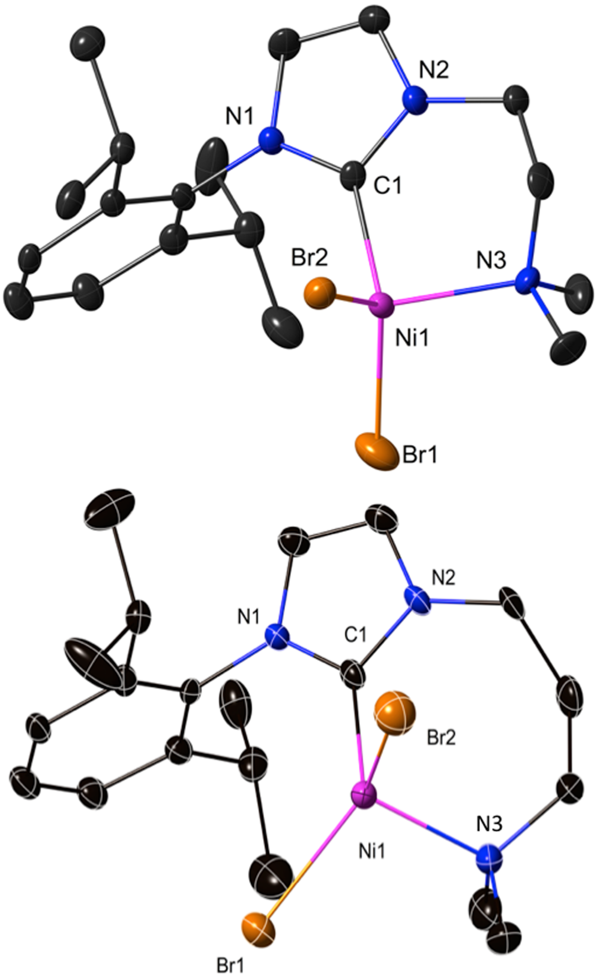


Figure 12. Views of the structures of complexes **24** (top) and **25** (bottom) with H atoms omitted for clarity. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): in **24** Ni1−Br1 2.342(1), Ni1−Br2 2.397(1), Ni1−C1 1.970(6), Ni1−N3 2.042(5), C1−N1 1.358(8), C1−N2 1.343(8); C1−Ni1−Br1 124.3(2), C1−Ni1−Br2 103.4(2), C1−Ni1−N3 94.8(2), Br1−Ni1−Br2 122.2(5), Br1−Ni1−N3 102.4(2), Br2−Ni1−N3 104.2(2), N1−C1−N2 104.5(5),

N1−C1−Ni1 130.9(5), N2−C1−Ni1 124.6(5); in **25** Ni1−Br1 2.353(2), Ni1−Br2 2.348(2), Ni1−C1 1.989(9), Ni1−N3 2.056(8), C1−N1 1.352(1), C1−N2 1.362(1); C1−Ni1−Br1 118.1(2), C1−Ni1−Br2 101.2(2), C1−Ni1−N3 104.7(3), Br1−Ni1−Br2 123.6(8), Br1−Ni1−N3 104.6(2), Br2−Ni1−N3 102.2(2), N1−C1−N2 104.5(7), N1−C1−Ni1 129.2(6), N2−C1−Ni1 125.3(6).

These results confirm that both a C2 and a C3 spacer have a suitable length for allowing chelation of a functional NHC ligand to Ni(II) provided the affinity of the donor group associated with the C^{NHC} is sufficient.

Catalytic Ethylene Oligomerization

In view of the continuing interest in the catalytic ethylene oligomerization, in particular for the production of short-chain α-olefins,[17] and in continuation of previous investigations in our group on the use of Ni NHC complexes for this reaction, we examined the catalytic properties of the neutral complexes **5a**, **6**, **24** and **25**, of the monoanionic complex **14a** and of the dianionic complexes **11a** and **13** in toluene or in a mixture of toluene and chlorobenzene, in the presence of 10 equiv. ethylaluminum dichloride (EADC) as co-catalyst (Table 1). This diversity of precatalysts could allow an evaluation of the influence of the *N*-substituents (R = Dipp, Mes, Me), of the *N'*-bound functionality (C_3OMe, C_2NMe_2 and C_3NMe_2), and of the different cations present in the salts containing a $[NiCl_4]^{2-}$ dianion. A comparison will also be made with the data previously obtained with $[NiCl_2\{ImDipp(C_2OMe)\}_2]$, a complex analogous to **5a** but containing the shorter C_2OMe spacer.[8b]

The neutral bis-NHC Ni(II) complexes **5a** and **6** with the C_3OMe *N*-functionality displayed similar activities with R = Dipp or Mes (productivity: 3500 g C_2H_4/(g Ni·h) for **5a** and 3100 g C_2H_4/(g Ni·h) for **6**, Table 1, entries 2, 3). These values are slightly lower than that found under similar conditions with $[NiCl_2\{ImDipp(C_2OMe)\}_2]$, which contains the C_2OMe substituent in place of C_3OMe (4600 g C_2H_4/(g Ni·h) entry 1).[8b] However, with the neutral Ni(II) complexes bearing the C_2NMe_2 (**24**) or C_3NMe_2 (**25**) *N*-functionality, productivities under similar catalytic conditions were *ca*. 4 times higher than with **5a** (15600 g C_2H_4/(g Ni·h) for **24** and 13300 g C_2H_4/(g Ni·h) for **25**, Table 1, entries 4, 5). There is clearly a beneficial effect of amine chelation, possibly by stabilizing the active species and increasing its lifetime. To evaluate the influence of the quantity of cocatalyst on the catalytic activity of **25**, a lower amount (4 equiv.) of EADC was employed but this significantly reduced ethylene consumption and activity (productivity: 2000 g C_2H_4/(g Ni·h), entry 6). Butenes were the major products, with a selectivity ranging from 66% to 81%, and the formation of 1-butene being, as expected, more selective when the catalytic productivity is lower since re-insertion of the primary reaction product 1-butene, giving branched products, is less likely.

We used the same catalytic conditions with the monoanionic NHC Ni(II) complex [(ImH)Dipp(C_3OMe)][$NiBr_3${ImDipp(C_3OMe)-κ^1C^{NHC}}] (**14b**). Its productivity (12300 g C_2H_4/(g Ni·h), entry 7) was more than 3 times that of the neutral bis-NHC Ni(II) complexes (**5a** and **6**, entries 2, 3) but slightly lower than that of the neutral, κ^2C^{NHC},N^{amine} mono-NHC Ni(II) complexes (**24** and **25**, entries 4, 5). The selectivity of **14b** for the formation of butenes (80%) and hexenes (19%) is similar to that of the previous pre-catalysts (butenes: 66-81%, hexenes: 17-28%).

After examining the neutral and monoanionic complexes, the dianionic Ni(II) complexes were found to exhibit higher ethylene consumption and productivities (productivity: 16900 g C_2H_4/(g Ni·h) of **11a** and 18000 g C_2H_4/(g Ni·h) of **13**, entries 8, 9). For comparison, the well-known dianionic complex $[NEt_4]_2[NiBr_4]$ was tested under similar conditions and it showed the best productivity (19900 g C_2H_4/(g Ni·h), entry 10) among the dianionic nickel complexes. Butenes were the major products, as for the other nickel complexes discussed above. These results indicate that the presence of the imidazolium cation in **11a** and **13** has no positive impact on the catalytic properties of the metal complex.

Table 1. Catalytic performances of the Ni(II) complexes in ethylene oligomerization

					selectivity[c]					
entry		complex	ethylene consumed[a]	Productivity[b]	C_4	C_6	C_8+	1-butene[d]	1-hexene[d]	linear C_6[e]
1[8b]		[$NiCl_2${ImDipp(C_2OMe)}$_2$][8b]	6.3	4600	64	32	4	52	3	17
2	**5a**	[$NiCl_2${ImDipp(C_3OMe)}$_2$]	4.8	3500	73	23	3	51	5	
3	**6**	[$NiCl_2${ImMes(C_3OMe)}$_2$]	4.2	3100	81	17	2	48	6	
4	**24**	[$NiBr_2${ImDipp(C_2NMe_2)}]	21.3	15600	71	26	3	9	1	
5	**25**	[$NiBr_2${ImDipp(C_3NMe_2)}]	18.2	13300	74	24	2	8	1	
6	**25**[f]	[$NiBr_2${ImDipp(C_3NMe_2)}]	2.8	2000	66	28	6	32	2	
7	**14b**	[(ImH)Dipp(C_3OMe)] [$NiBr_3${ImDipp(C_3OMe)}]	15.3	12300	80	19	1	9	1	
8	**11a**	[(ImH)Dipp(C_3OMe)]$_2$ [$NiCl_4$]	23.2	16900	68	29	3	5	1	

9	**13**	$[(ImH)Me(C_3OMe)]_2[NiCl_4]$	24.7	18000	72	26	2	7	1
10		$[NEt_4]_2[NiBr_4]$	27.2	19900	67	30	3	7	1

Conditions: amount of catalyst: $4×10^{-5}$ mol, amount of cocatalyst (EADC): $4×10^{-4}$ mol (10 equiv.), *T* = 30–35 °C, solvent: toluene (except for **11a, 13** and $[NiCl_2\{(Im)(Dipp)(C_2OMe)\}_2]$ in chlorobenzene for solubility issues), total volume: 15 mL, 10 bar C_2H_4, reaction time 35 min., every test was repeated at least twice.

[a] equal to the quantity of ethylene introduced minus the unreacted ethylene collected at the end of the reaction (see experimental), expressed in g; [b] expressed in g C_2H_4/(g Ni·h); [c] expressed in %, calculated by GC analysis; [d] selectivity for a within the C_4 or C_6 fraction, expressed in % mol; [e] selectivity for linear olefins within the C_6 fraction; [f] amount of cocatalyst (EADC): $1.6×10^{-4}$ mol (4 equiv.).

Conclusions

A series of N-heterocyclic carbene-based hybrid ligands of the C^{NHC},O^{ether} type with different *N*-substituents (R = Dipp, Mes, Me) has been investigated and revealed a monodentate κ^1C^{NHC} coordination behaviour in both their silver and nickel complexes. Whereas the bis-NHC Ni(II) complex **5a** could be obtained from the isolated, free NHC ligand **4**, complexes **5a–7** were prepared by transmetallation reaction from the bis-NHC Ag(I) complexes **8-10** or via an indirect synthetic method (Scheme 1). The latter proceeds in two steps: formation of bis-imidazolium salts with a $[NiCl_4]^{2-}$ dianion, followed by deprotonation of this salt with a base. This procedure avoids the isolation of a sensitive free carbene and it is noteworthy that the formation of mono- or bis-NHC Ni(II) complexes **14** and **5a** – **7**, respectively, could be simply controlled by the quantity of base used. Interestingly, the rare examples of anionic, mono-NHC nickel complexes of the type $[NiX_3(NHC)]^-$, present in **14**, exhibit a paramagnetic ^1H NMR spectrum with well-defined peaks ranging from 92 to -32 ppm, probably associated with hydrogen bonding interactions between the imidazolium cation of the salt $[(ImH)(Dipp)(C_3OMe)]^+$ and the anionic moiety. Such interactions have been evidenced in the solid-state by an X-ray diffraction analysis of **14b**. Detailed ^1H NMR spectroscopic analyses allowed the assignment of the resonances of both the cationic and anionic fragments, by addition of increasing amounts of the corresponding imidazolium salt $[(ImH)(Dipp)(C_3OMe)]Cl$ (**1a**) to the nickel complex $[(ImH)(Dipp)(C_3OMe)][NiCl_3\{Im(Dipp)(C_3OMe)\text{-}\kappa^1C^{NHC}\}]$ (**14b**).

With either a C_2 or C_3 spacer between the heterocycle and the ether donor group, only κ^1C^{NHC} bonding of the C^{NHC},O^{ether} ditopic ligands was observed in the metal complexes reported in this work, which is fully consistent with previous findings,[7,8,26] For comparison, related C^{NHC},N^{amine} hybrid ligands with a C_2 or a C_3 spacer were evaluated and found to chelate the tetrahedral Ni(II) centre, demonstrating the ability of both spacers to allow chelation, provided the end donor group is strong enough. With the hope to promote anchimeric assistance to ether chelation, an additional imine donor function was introduced in the ligand to generate a new potential pincer system of the type N^{imine},C^{NHC},O^{ether}. Not surprisingly, its Ag(I) complex **19** only displayed κ^1C^{NHC} behaviour but we could not characterize the ligand bonding mode in its Ni(II) complexes owing to their paramagnetic nature.

Catalytic studies in ethylene oligomerization have shown an increased productivity for the neutral precatalysts with the chelating κ^2C^{NHC},N^{amine} ligand containing a C_2 spacer and with the mono- or dianionic Ni(II) complexes. However, in the case of the dianionic complexes, the functional imidazolium counter cation did not bring about any improvement of the catalytic performances, except a slight increase in selectivity for 1-butene.

This study has further demonstrated that with potentially bi- or tri-dentate hybrid ligands containing a NHC donor, coordination of the additional donor function(s) mostly depends on its chemical nature, as demonstrated by comparing ether and tertiary amine donors. A change in the length of the spacer used to connect it to a N atom of the heterocycle, from C2 to C3, was found not to be decisive. These results answer some key questions asked at the onset of our investigations. Identifying the key parameters allowing a better control of the coordination chemistry of polytopic ligands and the reactivity and catalytic properties of their metal complexes remains a topic of major importance.

Experimental Section

General methods

All manipulations involving organometallics were performed under nitrogen or argon in a Braun glovebox or using standard Schlenk techniques. Solvents were dried using standard methods and distilled under nitrogen prior use or passed through columns of activated alumina and subsequently purged with nitrogen or argon. The compounds 1-(2,6-diisopropylphenyl)-1*H*-imidazole, 1-mesityl-1*H*-imidazole, 1-metyl-1*H*-imidazole and $[NiCl_2(dme)]$ were synthesized according to published procedures.[27] NMR spectra were recorded on Bruker spectrometers (AVANCE I − 300 MHz, AVANCE III − 400 MHz or AVANCE I − 500 MHz equipped with a cryogenic probe). IR spectra were recorded in the region 4000-200 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the "Service de microanalyses", Université de Strasbourg. For the X-ray diffraction studies, suitable crystals were obtained as described below. Summary of the crystal data, data collection and refinement for compounds are given in Table S1 (see Supporting Information). The crystals were mounted on a glass fibre with grease, from Fomblin vacuum oil. For compounds **4**, **5a**, **8**, **11a, 11b**, **14b**, **16**·MeCN, **18**, **19**, **23** and **25**, data sets were collected at 173(2) K on a Bruker APEX-II CCD Duo diffractometer using Mo-Kα (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 Å). The cell parameters were determined (APEX2 software)[28a] from reflections taken from three sets of 12 frames, each at 10 s exposure. For compounds **7, 13 and 24**, data sets were collected at 173(2) K on a Nonius Kappa-CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The cell parameters were determined (Denzo software)[28b] from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20s exposure. The structures were solved by direct methods using the program SHELXS-2013.[29a] The refinement and all further calculations were carried out using SHELXL-2013[29b] or SHELXL-2014.[29c] The H-atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. Crystallographic information files (CIF) for the compounds **4**, **5a**, **7**, **8**, **11a, 11b**, **13**, **14b**, **16**·MeCN, **18**, **19**, **23**, **24** and **25** have been deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers CCDC 1955230-1955243 and 1956078. The catalytic reactions were performed in a magnetically stirred (1200 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to avoid corrosion of the autoclave walls. The procedures used have been previously detailed.[8b,13c]

Preparation of [(ImH)(Dipp)(C_3OMe)]Cl (1a).

A mixture of 1-(2,6-diisopropylphenyl)-1*H*-imidazole (5.000 g, 21.9 mmol) and 1-chloro-3-methoxypropane (12 mL, 109.5 mmol) was refluxed for 1.5 day. The unreacted 1-chloro-3-methoxypropane was removed under reduced pressure. The resulting sticky solid was triturated twice with Et_2O. It was then stirred in Et_2O for 16 h and the white solid **1a** was collected by filtration (7.260 g, 98%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 10.32 (br, 1H, $\mathrm{CH}^{\mathrm{imidazole}}$), 7.95 (br, 1H, $\mathrm{CH}^{\mathrm{imidazole}}$), 7.57 (t, ^3J = 7.8 Hz, 1H, $\mathrm{CH}^{p\text{-}\mathrm{Ar}}$), 7.34 (d, ^3J = 7.8 Hz, 2H, $\mathrm{CH}^{m\text{-}\mathrm{Ar}}$), 7.21 (br, 1H, $\mathrm{CH}^{\mathrm{imidazole}}$), 4.79 (t, ^3J = 6.7 Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_2OMe}$), 3.51 (t, ^3J = 5.6 Hz, 2H, $\mathrm{CH_2CH_2C}H_2\mathrm{OMe}$), 3.28 (s, 3H, $\mathrm{CH_2CH_2CH_2O}Me$), 2.33-2.26 (m, 4H, $\mathrm{CH_2C}H_2\mathrm{CH_2OMe}$ overlapped with $\mathrm{CH}^{i\mathrm{Pr}}$), 1.22 (d, ^3J = 6.7 Hz, 6H, $\mathrm{CH_3}^{i\mathrm{Pr}}$), 1.16 (d, ^3J = 6.7 Hz, 6H, $\mathrm{CH_3}^{i\mathrm{Pr}}$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ: 145.8 ($\mathrm{C}^{o\text{-}\mathrm{Ar}}$), 138.7($\mathrm{C}^{\mathrm{imidazole}}$), 132.1($\mathrm{C}^{p\text{-}\mathrm{Ar}}$), 130.6 ($\mathrm{C}^{ipso\text{-}\mathrm{Ar}}$), 125.0 ($\mathrm{C}^{m\text{-}\mathrm{Ar}}$), 124.2 ($\mathrm{C}^{\mathrm{imidazole}}$), 123.9 ($\mathrm{C}^{\mathrm{imidazole}}$), 69.5 ($C\mathrm{H_2CH_2CH_2OMe}$), 59.0 ($\mathrm{CH_2CH_2CH_2O}Me$), 48.6 ($\mathrm{CH_2CH_2}C\mathrm{H_2OMe}$), 30.7 ($\mathrm{CH_2}C\mathrm{H_2CH_2OMe}$), 29.0 ($\mathrm{CH}^{i\mathrm{Pr}}$), 24.5 ($\mathrm{CH_3}^{i\mathrm{Pr}}$), 24.3 ($\mathrm{CH_3}^{i\mathrm{Pr}}$). Anal. calcd for $C_{19}H_{29}ClN_2O$: C, 67.74; H, 8.68; N, 8.32%. Found: C, 67.35; H, 9.05; N, 7.95%.

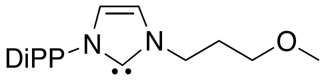
Preparation of [(ImH)(Mes)(C_3OMe)]Cl (2).

A procedure similar to that used for compound **1a** afforded **2** as a white solid (7.740 g, 98%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 10.79 (br, 1H, $CH^{imidazole}$), 7.79 (br, 1H, $CH^{imidazole}$), 7.20 (br, 1H, $CH^{imidazole}$), 7.04 (s, 2H, $CH^{m\text{-}Ar}$), 4.70 (t, ^3J = 6.7 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.48 (t, ^3J = 5.6 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.27 (s, 3H, $CH_2CH_2CH_2OMe$), 2.34 (s, 3H, Me^{para}), 2.08 (s, 6H, Me^{ortho}). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ: 141.5 ($C^{p\text{-}Ar}$), 139.4 ($C^{imidazole}$), 134.7 ($C^{o\text{-}Ar}$), 131.3 ($C^{ipso\text{-}Ar}$), 130.0 ($C^{m\text{-}Ar}$), 123.4 ($C^{imidazole}$), 123.1 ($C^{imidazole}$), 69.5 ($CH_2CH_2CH_2OMe$), 58.9 ($CH_2CH_2CH_2OMe$), 48.3 ($CH_2CH_2CH_2OMe$), 30.6 ($CH_2CH_2CH_2OMe$), 21.2 (Me $^{para\text{-}Mes}$), 17.7 (Me $^{ortho\text{-}Mes}$). Anal. calcd for $C_{16}H_{23}ClN_2O$: C, 65.18; H, 7.86; N, 9.50%. Found: C, 64.85; H, 8.10; N, 9.20%.

Preparation of [(ImH)(Me)(C_3OMe)]Cl (3)

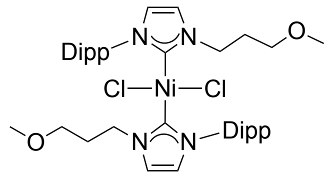
A procedure similar to that used for compound **1a** afforded **3** as a white solid (11.145 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.76 (br, 1H, $CH^{imidazole}$), 7.57 (t, ^3J = 1.7 Hz, 1H, $CH^{imidazole}$), 7.43 (t, ^3J = 1.7 Hz, 1H, $CH^{imidazole}$), 4.37 (t, ^3J = 7.0 Hz, 2H, $CH_2CH_2CH_2OMe$), 4.04 (s, 3H, $Me^{N\text{-}Me}$), 3.35 (t, ^3J = 5.8 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.24 (s, 3H, $CH_2CH_2CH_2OMe$), 2.17-2.12 (m, 2H, $CH_2CH_2CH_2OMe$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ: 138.6 ($C^{imidazole}$), 123.($C^{imidazole}$), 122.6 ($C^{imidazole}$), 68.6 ($CH_2CH_2CH_2OMe$), 58.8 ($Me^{N\text{-}Me}$), 47.4 ($CH_2CH_2CH_2OMe$), 36.6 ($CH_2CH_2CH_2OMe$), 30.42 ($CH_2CH_2CH_2OMe$).

Preparation of 1-(2,6-diisopropylphenyl)-3-(3-methoxypropyl)-1*H*-imidazol-2(3*H*)-ylidene (4)



To a suspension of the imidazolium salt [(ImH)(Dipp)(C_3OMe)]Cl (**1a**) (0.250 g, 0.74 mmol) in THF (5 ml) at -40 °C was added dropwise a solution of sodium hexamethyldisilazide (0.177 g, 0.96 mmol) in THF (8 ml). The reaction mixture was allowed to warm to room temperature and stirred for 30 min. Evaporation of the solvent under reduced pressure, extraction of the residue into pentane (3×20 ml), evaporation of the extracts to dryness and washing of the solid residue with pentane (5 ml) at -30 °C gave **4** as a colourless powder (0.102 g, 46%). X-ray quality crystals were obtained by slow cooling (-30 °C) of a dilute pentane solution for two days. ^{1}H NMR (300 MHz, C_6D_6) δ: 7.30-7.25 (m, 1H, $CH^{p\text{-}Ar}$), 7.17-7.15 (m, overlapped with C_6D_6, $CH^{m\text{-}Ar}$), 6.56 (AB spin system, J_{AB} = 1.5 Hz, 1H, $CH^{imidazole}$), 6.54 (AB spin system, J_{AB} = 1.5 Hz, 1H, $CH^{imidazole}$), 4.08 (t, ^3J = 6.8 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.21 (t, ^3J = 6.2 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.09 (s, 3H, $CH_2CH_2CH_2OMe$), 2.88 (sept, ^3J = 6.9 Hz, 2H, CH$^{i\text{Pr}}$), 1.98 (apparent quint, ^3J = 6.5 Hz, 2H, $CH_2CH_2CH_2OMe$), 1.24 (d, ^3J = 6.9 Hz, 6H, $CH_3^{i\text{Pr}}$), 1.13 (d, ^3J = 6.9 Hz, 6H, $CH_3^{i\text{Pr}}$). Anal. calcd for $C_{19}H_{28}N_2O$: C, 75.96; H, 9.39; N, 9.32%. Found: C, 75.65; H, 9.75; N, 9.05%.

Preparation of [NiCl$_2${(Im)(Dipp)(C$_3$OMe)-κ^{1}C$^{\text{NHC}}$}$_2$] (5a).

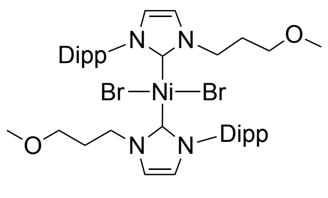


Method A: To a solution of the imidazolium salt [(ImH)Dipp(C$_3$OMe)]Cl (**1a**) (0.200 g, 0.59 mmol) in THF (8 mL) was added a solution of NaO*t*Bu (0.418 g, 0.60 mmol) in THF (5 mL). The reaction mixture was stirred for 1 h and to this solution was then added [NiCl$_2$(dme)] (0.065 g, 0.30 mmol). The reaction mixture was stirred for 3 h. The orange solution was then filtered through a Celite pad and the filtrate was evaporated under reduced pressure. The complex was precipitated from THF/Et$_2$O and washed with Et$_2$O to afford an orange powder. (0.164 g, 75%). X-ray quality crystals were obtained by slow diffusion of Et$_2$O into a THF solution of the complex.

Method B: To a solution of [(ImH)(Dipp)(C$_3$OMe)]$_2$[NiCl$_4$] (**11a**) (0.200 g, 0.25 mmol) in THF (8 mL) was added a solution of NaO*t*Bu (0.055 g, 0.57 mmol) in THF (5 mL). The reaction mixture was stirred for 3 h. The orange solution was then filtered through a Celite pad and the filtrate was evaporated under reduced pressure. The complex was precipitated from THF/Et$_2$O and washed with Et$_2$O to afford an orange powder (0.145 g, 80%). X-ray quality crystals were obtained by slow diffusion of Et$_2$O into a THF solution of the complex. *Anti*-form (82%): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.56 (t, ^3J = 7.8 Hz, 1H, CH$^{p\text{-Ar}}$), 7.40 (d, ^3J = 7.8 Hz, 2H, CH$^{m\text{-Ar}}$), 6.78 (d, ^3J = 1.5 Hz, 1H, CH$^{\text{imidazole}}$), 6.62 (d, ^3J = 1.5 Hz, 1H, CH$^{\text{imidazole}}$), 4.80 (t, ^3J = 7.2 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.32 (s, 3H, $CH_2CH_2CH_2OMe$), 3.17 (t, ^3J = 5.8 Hz, 2H, $CH_2CH_2CH_2OMe$), 2.71 (sept, ^3J = 6.9 Hz, 2H, CH$^{i\text{Pr}}$), 2.29 (apparent quint., ^3J = 7.2-5.8 Hz, 2H, $CH_2CH_2CH_2OMe$), 1.30 (d, ^3J = 6.9 Hz, 6H, $CH_3^{i\text{Pr}}$), 0.91 (d, ^3J = 6.9 Hz, 6H, $CH_3^{i\text{Pr}}$).^{13}C NMR (126 MHz, CDCl$_3$) δ: 168.9 (C$^{\text{carbene}}$), 148.0 (C$^{o\text{-Ar}}$), 136.0 (C$^{ipso\text{-Ar}}$), 129.9 (C$^{\text{imidazole}}$), 123.9 (C$^{p\text{-Ar}}$), 123.7 (C$^{m\text{-Ar}}$), 120.8 (C$^{\text{imidazole}}$), 69.5 ($CH_2CH_2CH_2OMe$), 58.7 ($CH_2CH_2CH_2OMe$), 47.8 ($CH_2CH_2CH_2OMe$), 30.3 ($CH_2CH_2CH_2OMe$), 28.4 (CH$^{i\text{Pr}}$), 26.7 ($CH_3^{i\text{Pr}}$), 22.8 ($CH_3^{i\text{Pr}}$). *Syn*-form (18%): ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.41 (overlapped with the *anti*-form) (t, ^3J = 7.8 Hz, 1H, CH$^{p\text{-Ar}}$), 7.14 (d, ^3J = 7.8 Hz, 2H, CH$^{m\text{-Ar}}$), 6.87 (d, ^3J = 1.8 Hz, 1H, CH$^{\text{imidazole}}$), 6.54 (d, ^3J = 1.8 Hz, 1H, CH$^{\text{imidazole}}$), 5.54 (t, ^3J = 7.2 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.62 (t, ^3J = 5.8 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.44 (s, 3H, $CH_2CH_2CH_2OMe$), 2.65 (partly overlapped with the *anti*-form) (apparent quint, ^3J = 7.2-5.8 Hz, 2H, $CH_2CH_2CH_2OMe$), 2.46 (sept, ^3J = 6.9 Hz, 2H, CH$^{i\text{Pr}}$), 0.92 (partly overlapped with the signals of the *anti*-form) (d, ^3J = 6.9 Hz, 6H, $CH_3^{i\text{Pr}}$), 0.84 (d, ^3J = 6.9 Hz, 6H, $CH_3^{i\text{Pr}}$). ^{13}C NMR (126 MHz,

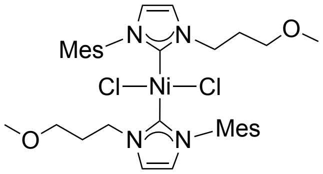
$\mathrm{CDCl_3}$) δ: not seen (C$^{\text{carbene}}$), 146.9 (C$^{o\text{-Ar}}$), 135.6 (C$^{ipso\text{-Ar}}$), 129.4 (C$^{\text{imidazole}}$), 124.4 (C$^{p\text{-Ar}}$), 123.9 (C$^{m\text{-Ar}}$), 120.2 (C$^{\text{imidazole}}$), 69.9 ($C\mathrm{H_2CH_2CH_2OMe}$), 58.9 ($\mathrm{CH_2CH_2CH_2O}Me$), 48.2 ($C\mathrm{H_2CH_2}C\mathrm{H_2OMe}$), 31.2 ($C\mathrm{H_2}C\mathrm{H_2CH_2OMe}$), 28.1 (CH$^{i\text{Pr}}$), 26.4 ($\mathrm{CH_3}^{i\text{Pr}}$), overlapped with the *anti*-form ($\mathrm{CH_3}^{i\text{Pr}}$). Anal. calcd. for $\mathrm{C_{38}H_{56}Cl_2N_4NiO_2}$: C, 62.48; H, 7.73; N, 7.67%. Found: C, 62.16; H, 7.67; N, 7.71%.

Preparation of [$\mathbf{NiBr_2\{(Im)(Dipp)(C_3OMe)–\kappa^1C^{NHC}\}_2}$] (5b).



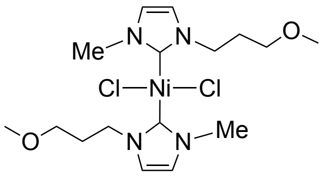
To a solution of the imidazolium bromide [(ImH)(Dipp)($\mathrm{C_3OMe}$)]Br (**1b**) (0.570 g, 1.49 mmol) in THF (8 mL) was added a solution of NaO*t*Bu (0.157 g, 1.64 mmol) in THF (5 mL). The reaction mixture was stirred for 1 h and [$\mathrm{NiBr_2(dme)}$] (0.230 g, 0.75 mmol) was then added to this solution. The reaction mixture was stirred for 3 h. The orange solution was then filtered through a Celite pad and the filtrate was evaporated under reduced pressure. The complex was precipitated from THF/ether and washed with $\mathrm{Et_2O}$ to afford a red powder (0.471 g, 76%). A crystalline product was obtained by slow diffusion of $\mathrm{Et_2O}$ into a THF solution. FTIR: ν_{max}(solid)/cm^{-1} : 3127w, 2926m, 2867m, 2819w, 1460m, 1417m, 1389m, 1382m, 1361m, 1321w, 1302w, 1285w, 1267w, 1223w, 1192w, 1118m, 1087w, 1068w, 1045w, 954m, 930m, 901w, 886w, 855w, 843w, 806m, 787w, 766m, 743m, 721w, 711m, 582w, 571m, 530m, 475m, 420w, 386w, 373w, 362w, 344w, 327w, 303w, 289w, 282w, 225w, 222w. *Anti*-form (87 %): ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.54 (t, ^3J = 7.8 Hz, 1H, CH$^{p\text{-Ar}}$), 7.38 (d, ^3J = 7.8 Hz, 2H, CH$^{m\text{-Ar}}$), 6.80 (d, ^3J = 1.4 Hz, 1H, CH$^{\text{imidazole}}$), 6.66 (d, ^3J = 1.4 Hz, 1H, CH$^{\text{imidazole}}$), 4.80 (t, ^3J = 7.2 Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_2OMe}$), 3.33 (s, 3H, $\mathrm{CH_2CH_2CH_2O}Me$), 3.18 (t, ^3J = 5.8 Hz, 2H, $\mathrm{CH_2CH_2C}H_2\mathrm{OMe}$), 2.87 (sept, ^3J = 6.9 Hz, 2H, CH$^{i\text{Pr}}$), 2.27 (apparent quint, ^3J = 7.2-5.8 Hz, 2H, $\mathrm{CH_2}CH_2\mathrm{CH_2OMe}$), 1.32 (d, ^3J = 6.9 Hz, 6H, $\mathrm{CH_3}^{i\text{Pr}}$), 0.91 (d, ^3J = 6.9 Hz, 6H, $\mathrm{CH_3}^{i\text{Pr}}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 126 MHz) δ: 170.5 (C$^{\text{carbene}}$), 148.0 (C$^{o\text{-Ar}}$), 135.9 (C$^{ipso\text{-Ar}}$), 130.0 (C$^{\text{imidazole}}$), 124.8 (C$^{p\text{-Ar}}$), 123.8 (C$^{m\text{-Ar}}$), 121.0 (C$^{\text{imidazole}}$), 69.5 ($C\mathrm{H_2CH_2CH_2OMe}$), 58.7 ($\mathrm{CH_2CH_2CH_2O}Me$), 48.2 ($C\mathrm{H_2CH_2}C\mathrm{H_2OMe}$), 29.9 ($C\mathrm{H_2}C\mathrm{H_2CH_2OMe}$), 28.7 (CH$^{i\text{Pr}}$), 26.8 ($\mathrm{CH_3}^{i\text{Pr}}$), 23.0 ($\mathrm{CH_3}^{i\text{Pr}}$). *Syn*-form (13 %): ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) δ: 7.40 (t, ^3J = 7.8 Hz, 1H, CH$^{p\text{-Ar}}$), 7.12 (d, ^3J = 7.8 Hz, 2H, CH$^{m\text{-Ar}}$), 6.89 (d, ^3J = 1.4 Hz, 1H, CH$^{\text{imidazole}}$), 6.58 (d, ^3J = 1.4 Hz, 1H, CH$^{\text{imidazole}}$), 5.50 (t, ^3J = 7.2 Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_2OMe}$), 3.63 (t, ^3J = 5.8 Hz, 2H, $\mathrm{CH_2CH_2C}H_2\mathrm{OMe}$), 3.44 (s, 3H, $\mathrm{CH_2CH_2CH_2O}Me$), 2.64 (apparent quit, ^3J = 7.2-5.8 Hz, 2H, $\mathrm{CH_2}CH_2\mathrm{CH_2OMe}$), 2.58 (sept, ^3J = 6.9 Hz, 2H, CH$^{i\text{Pr}}$), 0.94 (d, ^3J = 6.9 Hz, 6H, $\mathrm{CH_3}^{i\text{Pr}}$), 0.83 (d, ^3J = 6.9 Hz, 6H, $\mathrm{CH_3}^{i\text{Pr}}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 126 MHz) δ: 169.5 (C$^{\text{carbene}}$), 146.9 (C$^{o\text{-Ar}}$), 135.6 (C$^{ipso\text{-Ar}}$), 129.5 (C$^{\text{imidazole}}$), 125.1 (C$^{p\text{-Ar}}$), 124.0 (C$^{m\text{-Ar}}$), 120.5 (C$^{\text{imidazole}}$), 69.9 ($C\mathrm{H_2CH_2CH_2OMe}$), 58.9 ($\mathrm{CH_2CH_2CH_2O}Me$), 48.6 ($C\mathrm{H_2CH_2}C\mathrm{H_2OMe}$), 30.7 ($C\mathrm{H_2}C\mathrm{H_2CH_2OMe}$), 28.2 ($CH^{iPr}$), 26.5 ($CH_3^{iPr}$), 22.9 ($CH_3^{iPr}$). Anal. calcd. for $C_{38}H_{56}Br_2N_4NiO_2$: C, 55.70; H, 6.89; N, 6.84%. Found: C, 54.85; H, 6.55; N, 6.65%. Despite several attempts, no better elemental analysis data could be obtained.

Preparation of [NiCl$_2${(Im)(Mes)(C$_3$OMe)- κ^{1}C^{NHC}}$_2$] (6).



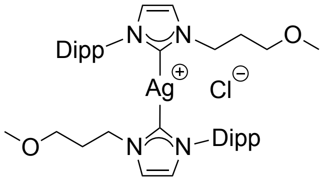
To a solution of the [(ImH)(Mes)(C$_3$OMe)]$_2$[NiCl$_4$] (**12**) (0.200 g, 0.28 mmol) in THF (8 mL) was added a solution of NaO*t*Bu (0.059 g, 0.61 mmol) in THF (5 mL). The reaction mixture was stirred for 3 h. The orange solution was then filtered through a Celite pad and the filtrate was evaporated under reduced pressure. The complex was precipitated from THF/Et$_2$O and washed with Et$_2$O to afford an orange powder. (0.145 g, 80%). Crystals were obtained by slow diffusion of Et$_2$O into a THF solution of the complex. Anal. Calcd for $C_{32}H_{44}Cl_2N_4NiO_2$: C, 59.47; H, 6.86; N, 8.67%. Found: C, 59.25; H, 6.75; N, 8.45%.

Preparation of [NiCl$_2${(Im)(Me)(C$_3$OMe)-κ^{1}C^{NHC}}$_2$] (7).



To a solution of [(ImH)Me(C$_3$OMe)]$_2$[NiCl$_4$] (**13**) (0.102 g, 0.20 mmol) in THF (8 mL) was added a solution of NaO*t*Bu (0.042 g, 0.44 mmol) in THF (5 mL). The reaction mixture was stirred for 3 h. The orange solution was then filtered through a Celite pad and the filtrate was evaporated under reduced pressure. The complex was precipitated from THF/ether and washed with Et$_2$O to afford an orange powder (0.055 g, 63%). X-ray quality crystals were obtained by slow diffusion of Et$_2$O into a THF solution of the complex. Anal. calcd. for $C_{16}H_{28}Cl_2N_4NiO_2$: C, 43.87; H, 6.44; N, 12.79%. Found: C, 43.65; H, 6.30; N, 12.55%.

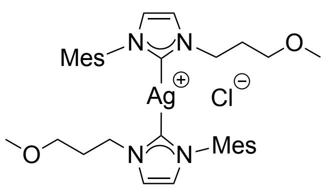
Preparation of [Ag{(Im)(Dipp)(C$_3$OMe)-κ^{1}C^{NHC}}$_2$]Cl (8).



A mixture of the imidazolium salt [(ImH)(Dipp)(C$_3$OMe)]Cl (**1a**) (0.420 g, 1.25 mmol), Ag$_2$O (0.159 g, 0.69 mmol) and molecular sieves in THF (10 mL) was stirred overnight under exclusion of light. The beige reaction mixture was then filtered through Celite and the filtrate was dried under reduced pressure. The resulting solid was washed with Et$_2$O to give a beige powder (0.359 g, 76%). X-ray quality crystals were obtained by slow diffusion of pentane into a THF solution of the complex. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 7.47 (t, ^3J = 7.8 Hz, 1H, $CH^{p\text{-}Ar}$), 7.44 (t, ^3J(H-H) = 1.5 Hz, ^4J(H-Ag) = 1.5 Hz, 1H, $CH^{imidazole}$), 7.23 (d, ^3J = 7.8 Hz, 1H, $CH^{m\text{-}Ar}$), 7.00 (t, ^3J(H-H) = 1.5 Hz, ^4J(H-Ag) = 1.5 Hz, 1H, $CH^{imidazole}$), 4.01 (t, ^3J = 7.0 Hz, 2H,

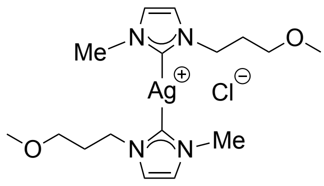
$C\mathit{H}_2CH_2CH_2OMe$), 3.26 (s, 3H, $CH_2CH_2CH_2O\mathit{Me}$), 3.21 (t, ^3J = 5.8 Hz, 2H, $CH_2CH_2C\mathit{H}_2OMe$), 2.25 (sept, ^3J = 6.9 Hz, 2H, $CH^{i\mathrm{Pr}}$), 1.85 (apparent quintet, ^3J = 7.0-5.8 Hz, 2H, $CH_2C\mathit{H}_2CH_2OMe$), 1.08 (d, ^3J = 6.9 Hz, 6H, $CH_3^{i\mathrm{Pr}}$), 0.98 (d, ^3J = 6.9 Hz, 6H, $CH_3^{i\mathrm{Pr}}$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ: 181.2 (d, $^1J(^{13}C\text{-}^{107}Ag)$ = 182 Hz, $^1J(^{13}C\text{-}^{109}Ag)$ = 210 Hz, C^{carbene}), 145.9 ($C^{o\text{-}\mathrm{Ar}}$), 134.9 ($C^{ipso\text{-}\mathrm{Ar}}$), 130.5 ($C^{p\text{-}\mathrm{Ar}}$), 124.1 ($C^{m\text{-}\mathrm{Ar}}$), 123.8 ($^3J$(C-Ag) = 5.6 Hz, $C^{\mathrm{imidazole}}$), 122.4 (^3J(C-Ag) = 5.6 Hz, $C^{\mathrm{imidazole}}$), 68.5 ($\mathit{C}H_2CH_2CH_2OMe$), 58.5 ($CH_2CH_2CH_2O\mathit{Me}$), 48.7 ($\mathit{C}H_2CH_2\mathit{C}H_2OMe$), 31.4 ($\mathit{C}H_2\mathit{C}H_2CH_2OMe$), 28.2 ($CH^{i\mathrm{Pr}}$), 24.4 ($CH_3^{i\mathrm{Pr}}$), 23.9 ($CH_3^{i\mathrm{Pr}}$). Anal. calcd. for $C_{38}H_{56}N_4O_2AgCl$: C, 61.33; H, 7.58; N, 7.53%. Found: C, 60.87; H, 7.67; N, 7.08%. Despite numerous attempts, no better elemental analysis data could be obtained.

Preparation of [Ag{(Im)(Mes)(C_3OMe)-κ$^1C^{\mathrm{NHC}}$}$_2$]Cl (9).



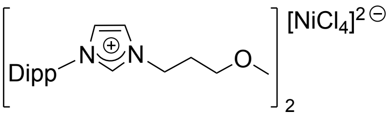
A mixture of the imidazolium salt [(ImH)(Mes)(C_3OMe)]Cl (**2**) (0.500 g, 1.70 mmol), Ag_2O (0.216 g, 0.94 mmol) and molecular sieves in THF (10 mL) was stirred overnight under the exclusion of light. The beige reaction mixture was then filtered through Celite and the filtrate was evaporated to dryness under reduced pressure. The resulting solid was washed with Et_2O to give a beige powder (0.454 g, 81%). Crystals were obtained by slow diffusion of pentane into a THF solution of the complex. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.21 (d, ^3J = 1.8 Hz, 1H, $CH^{\mathrm{imidazole}}$), 7.02 (br s, 2H, $CH^{m\text{-}\mathrm{Ar}}$), 6.98 (d, ^3J = 1.8 Hz, 1H, $CH^{\mathrm{imidazole}}$), 4.32 (t, ^3J = 6.8 Hz, 2H, $C\mathit{H}_2CH_2CH_2OMe$), 3.36 (t, ^3J = 5.8 Hz, 2H, $CH_2C\mathit{H}_2CH_2OMe$), 3.33 (s, 3H, $CH_2CH_2CH_2O\mathit{Me}$), 2.35 (s, 3H, $CH_3^{p\text{-}\mathrm{Ar}}$), 2.12 (apparent quintet, ^3J = 6.8-5.8 Hz, 2H, $CH_2C\mathit{H}_2CH_2OMe$), 1.99 (s, 6H, $CH_3^{o\text{-}\mathrm{Ar}}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz) δ: 181.1 (d, $^1J(^{13}C\text{-}^{107}Ag)$ = 182 Hz, $^1J(^{13}C\text{-}^{109}Ag)$ = 210 Hz, C^{carbene}), 145.9 ($C^{o\text{-}\mathrm{Ar}}$), 134.9 ($C^{ipso\text{-}\mathrm{Ar}}$), 130.5 ($C^{p\text{-}\mathrm{Ar}}$), 124.1 ($C^{m\text{-}\mathrm{Ar}}$), 123.8 ($^3J$(C-Ag) = 5.6 Hz, $C^{\mathrm{imidazole}}$), 122.4 (^3J(C-Ag) = 5.6 Hz, $C^{\mathrm{imidazole}}$), 68.5 ($\mathit{C}H_2CH_2CH_2OMe$), 58.5 ($CH_2CH_2CH_2O\mathit{Me}$), 48.7 ($\mathit{C}H_2CH_2\mathit{C}H_2OMe$), 31.4 ($\mathit{C}H_2\mathit{C}H_2CH_2OMe$), 28.2 ($CH^{i\mathrm{Pr}}$), 24.4 ($CH_3^{i\mathrm{Pr}}$), 23.9 ($CH_3^{i\mathrm{Pr}}$). Anal. calcd. for $C_{32}H_{44}AgClN_4O_2$: C, 58.23; H, 6.72; N, 8.49%. Found : C, 57.9; H, 6.80; N, 8.20%.

Preparation of [Ag{(Im)(Me)(C_3OMe)-κ$^1C^{\mathrm{NHC}}$}$_2$]Cl (10).



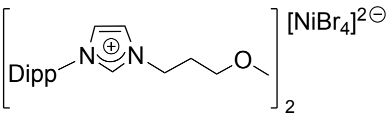
A mixture of the imidazolium salt [(ImH)(Me)(C_3OMe)]Cl (**3**) (0.500 g, 2.62 mmol), Ag_2O (0.334 g, 1.44 mmol) and molecular sieves in THF (10 mL) was stirred overnight under exclusion of light. The beige reaction mixture was then filtered through Celite and the filtrate was evaporated to dryness under reduced pressure. The resulting solid was washed with Et_2O to give a beige powder (0.462 g, 78%). The complex can be recrystallised by slow diffusion of pentane into a THF solution.

Preparation of [(ImH)(Dipp)(C_3OMe)]$_2$[$NiCl_4$] (11a).



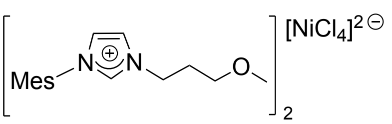
A mixture of the imidazolium salt [(ImH)(Dipp)(C_3OMe)]Cl (**1a**) (1.000 g, 2.97 mmol) and [$NiCl_2$(dme)] (0.327 g, 1.49 mmol) in THF was stirred overnight. The solvent was evaporated under reduced pressure. The blue slurry was then triturated with Et_2O until a blue powder was obtained (1.027 g, 86%). X-ray quality crystals were obtained by slow diffusion of Et_2O into a MeCN solution of the complex. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.58 (t, $^3J = 7.9$ Hz, 1H, $CH^{p\text{-Ar}}$), 7.35 (d, $^3J = 7.9$ Hz, 2H, $CH^{m\text{-Ar}}$), 7.08 (br s, 1H, $CH^{\text{imidazole}}$), 6.74 (br s, 1H, $CH^{\text{imidazole}}$), 4.32 (br s, 2H, $C\mathit{H}_2CH_2CH_2OMe$), 4.12 (br s, 2H, $CH_2CH_2C\mathit{H}_2OMe$), 3.62 (br s, 3H, $CH_2CH_2CH_2O\mathit{Me}$), 2.67 (br s, 2H, $CH_2C\mathit{H}_2CH_2OMe$), 2.09 (br sept, $^3J = 6.4$ Hz, 2H, $CH^{i\text{-Pr}}$), 1.94 (br d, $^3J = 6.4$ Hz, 6H, $CH_3^{i\text{Pr}}$), 1.24 (br d, $^3J = 6.4$ Hz, 6H, $CH_3^{i\text{Pr}}$) (no clear resonance for the NC*H*N proton was observed in the range δ =10-16).

Preparation of [(ImH)(Dipp)(C_3OMe)]$_2$[$NiBr_4$] (11b).



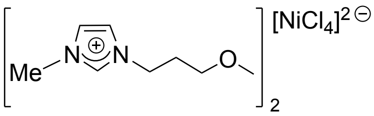
To a solution of the imidazolium bromide [(ImH)(Dipp)(C_3OMe)]Br (**1b**) (1.000 g, 2.62 mmol) in THF was added [$NiBr_2$(dme)] (0.405 g, 1.31 mmol). After the reaction mixture was stirred overnight, the solvent was evaporated under reduced pressure. The blue slurry was then triturated with Et_2O until a purple powder was obtained (1.073 g, 83%). X-ray quality crystals were obtained by slow diffusion of Et_2O into a MeCN solution of the complex.

Preparation of [(ImH)(Mes)(C_3OMe)]$_2$[$NiCl_4$] (12).



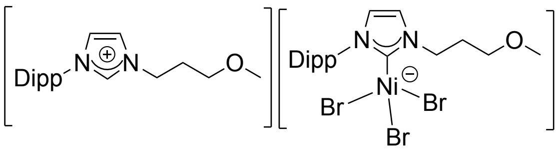
A mixture of the imidazolium salt [(ImH)(Mes)(C_3OMe)]Cl (**2**) (0.200 g, 0.68 mmol) and [$NiCl_2$(dme)] (0.075 g, 0.34 mmol) in THF was stirred overnight. The solvent was evaporated under reduced pressure. The blue slurry was then triturated with Et_2O until a blue powder was obtained (0.208 g, 85%). The complex can be recrystallised by slow diffusion of Et_2O into a MeCN solution.

Preparation of [(ImH)(Me)(C_3OMe)]$_2$[$NiCl_4$] (13).



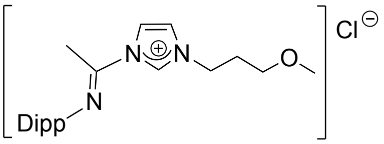
A mixture of the imidazolium salt [(ImH)(Me)(C_3OMe)]Cl (**3**) (0.200 g, 1.05 mmol) and [$NiCl_2$(dme)] (0.115 g, 0.52 mmol) in THF was stirred overnight. The solvent was evaporated under reduced pressure. The blue slurry was then triturated with Et_2O until a blue powder was obtained (0.227 g, 85%). The complex can be recrystallised by slow diffusion of Et_2O into a MeCN solution.

Preparation of [(ImH)(Dipp)(C_3OMe)][$NiBr_3${(Im)(Dipp)(C_3OMe)-κ^1C^{NHC}}] (14b).



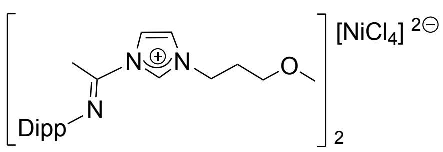
To a solution of the [(ImH)(Dipp)(C_3OMe)]$_2$[$NiBr_4$] (**11b**) (0.200 g, 0.20 mmol) in THF (8 mL) was added a solution of NaO*t*Bu (0.020 g, 0.21 mmol) in THF (5 mL). The reaction mixture was stirred for 3 h. The dark blue solution was then filtered through a Celite pad and the filtrate was evaporated under reduced pressure. The complex was precipitated from THF/Et_2O and washed with Et_2O to afford a blue powder (0.101 g, 56%). X-ray quality crystals were obtained by slow diffusion of a mixture of Et_2O and pentane into a THF solution of the complex. Anal. calcd. for $C_{38}H_{57}Br_3N_4NiO_2$: C, 50.70; H, 6.38; N, 6.22%. Found: C, 50.61; H, 6.44; N, 6.20%.

Preparation of [(ImH){C(Me)=NDipp}(C_3OMe)]Cl (17)



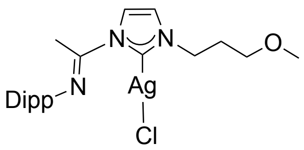
To a solution of 1-(3-methoxypropyl)-1*H*-imidazole (1.410 g, 10.1 mmol) in toluene (10 mL) was added dropwise (*E*)-*N*-(2,6-diisopropylphenyl)acetimidoyl chloride (2.39 g, 10.1 mmol). The reaction mixture was stirred overnight at room temperature. The resulting precipitate was then collected by filtration and washed with Et_2O to give the product as a white powder (3.17 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.23 (apparent l d, ^{4+5}J = 5.1 Hz, 1H, $CH^{imidazole}$), 8.28 (l s, 1H, $CH^{imidazole}$) 7.59 (l s, 1H, $CH^{imidazole}$), 7.48-7.23 (m, overlapped with $CDCl_3$, $CH^{m\text{-}Ar}$, $CH^{p\text{-}Ar}$), 4.80 (t, ^3J = 6.9 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.63 (t, ^3J = 5.4 Hz, 2H, $CH_2CH_2CH_2OMe$), 3.43 (s, 3H, $CH_2CH_2CH_2OMe$), 2.69 (sept, ^3J = 6.9 Hz, 2H, CH^{iPr}), 2.65 (s, 3H, CH_3^{imine}), 2.44 (apparent quint ^3J = 6.2 Hz, 2H, $CH_2CH_2CH_2OMe$), 1.24 (d, ^3J = 6.9 Hz, 6H, CH_3^{iPr}), 1.20 (d, ^3J = 6.9 Hz, 6H, CH_3^{iPr}).

Preparation of [(ImH){C(Me)=NDipp}(C_3OMe)]$_2$[$NiCl_4$] (18).



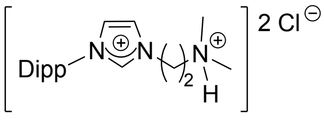
A mixture of the imidazolium salt [(ImH){C(Me)=NDipp}(C_3OMe)]Cl (**17**) (0.100 g, 0.26 mmol) and [$NiCl_2$(dme)] (0.029 g, 0.13 mmol) in THF was stirred overnight. The solvent was evaporated under reduced pressure. The blue slurry was then triturated with Et_2O until a blue powder was obtained (0.096 g, 83%). X-ray quality crystals were obtained by slow diffusion of Et_2O into a solution of the complex in MeCN.

Preparation of [AgCl{(Im)[C(Me)=NDipp](C_3OMe)}-κ^1C^{NHC}] (19).



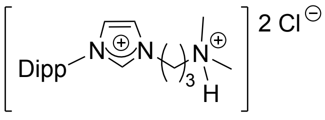
A mixture of the imidazolium salt [(ImH){C(Me)=NDipp}(C_3OMe)]Cl (**17**) (0.100 g, 0.26 mmol), Ag_2O (0.034 g, 0.15 mmol) and molecular sieves in THF (10 mL) was stirred overnight under exclusion of light. The beige reaction mixture was then filtered through Celite and the filtrate was dried under reduced pressure. The resulting solid was washed with Et_2O to give the product as a beige powder (0.101 g, 80%). X-ray quality crystals were obtained by slow diffusion of pentane into a THF solution of the complex. Anal. calcd. for $C_{21}H_{31}N_3AgClO$: C, 52.03; H, 6.45; N, 8.67%. Found: C, 52.37; H, 6.37; N, 9.20%. Despite several attempts, no better elemental analyses could be obtained.

Preparation of [(ImH)(Dipp)(C_2NHMe_2)]Cl_2 (20)



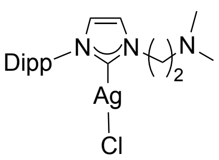
A mixture of 1-(2,6-diisopropylphenyl)-1*H*-imidazole (2.000 g, 8.8 mmol) and 2-chloro-*N*,*N*-dimethylethanamine hydrochloride (1.261 g, 8.8 mmol) in MeCN (30 mL) was refluxed overnight. After filtration of the reaction mixture, the solid was collected and washed with Et_2O, affording a white powder of **22** (2.064 g, 63%). This compound was directly used for the synthesis of **22**.

Preparation of [(ImH)(Dipp)(C_3NHMe_2)]Cl_2 (21)



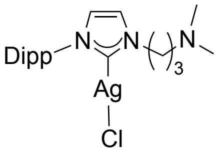
A mixture of 1-(2,6-diisopropylphenyl)-1*H*-imidazole (2.283 g, 10.0 mmol) and 3-dimethylamino-1-propyl chloride hydrochloride (1.580 g, 10.0 mmol) in MeCN (30 mL) was refluxed overnight. After filtration of the reaction mixture, the solid was collected and washed with Et_2O, affording a white powder of **21** (2.202 g, 57%). This compound was directly used for the synthesis of **23**.

Preparation of [AgCl{(Im)(Dipp)(C_2NMe_2)}] (22).



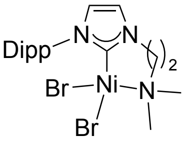
A mixture of the imidazolium salt [(ImH)(Dipp)(C_2NHMe_2)]Cl_2 (**20**) (0.300 g, 0.80 mmol), Ag_2O (0.131 g, 0.57 mmol) and molecular sieves in THF (10 mL) was stirred overnight under exclusion of light. The beige reaction mixture was then filtered through Celite and the filtrate evaporated under reduced pressure. The resulting solid was washed with Et_2O to give a beige powder (0.226 g, 58%). Crystalline **22** was obtained by slow diffusion of pentane into a THF solution.

Preparation of [AgCl{(Im)(Dipp)(C_3NMe_2)-κ^{1}C^{NHC}}] (23).



A mixture of the imidazolium salt [(ImH)(Dipp)(C_3NHMe_2)]Cl_2 (**21**) (0.300 g, 0.78 mmol), Ag_2O (0.126 g, 0.54 mmol) and molecular sieves in THF (10 mL) was stirred overnight under exclusion of light. The beige reaction mixture was then filtered through Celite and the filtrate was evaporated under reduced pressure. The resulting solid was washed with Et_2O to give a beige powder (0.242 g, 67%). X-ray quality crystals of **23** were obtained by slow diffusion of pentane into a THF solution.

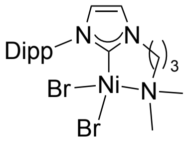
Preparation of [NiBr$_2${(Im)(Dipp)(C_2NMe_2)-κ^{2}C^{NHC},N^{amine}}] (24).



Method 1. To a solution of the imidazolium salt [(ImH)(Dipp)(C_2NHMe_2)]Cl_2 (**20**) (0.100 g, 0.27 mmol) in THF (8 mL) was added a solution of NaO*t*Bu (0.033 g, 0.34 mmol) in THF (5 mL). The reaction mixture was stirred for 1 h and then [NiBr$_2$(dme)] (0.089 g, 0.29 mmol) was added to this solution. The reaction mixture was stirred for 3 h. The orange solution was then filtered through a Celite pad and the filtrate was evaporated under reduced pressure. The complex was precipitated from THF/Et_2O and washed with Et_2O to afford a dark red powder (0.095 g, 68%). X-ray quality crystals of **24** were obtained by slow diffusion of Et_2O into THF solution. Anal. calcd. for $C_{19}H_{29}Br_2N_3Ni$: C, 44.06; H, 5.64; N, 8.11%. Found: C, 42.9; H, 5.40; N, 7.55%. Despite several attempts, no better elemental analyses could be obtained.

Method 2. To a solution of [AgCl{(Im)(Dipp)(C_2NMe_2)-κ^{1}C^{NHC}}] (**22**) (0.100 g, 0.226 mmol) in THF (10 mL) was added dropwise a THF solution of [NiBr$_2$(dme)] (0.070 g, 0.226 mmol). The reaction mixture was stirred overnight at room temperature. A purple solution and white precipitate were obtained. The dark red, purple solution was collected by filtration, and concentrated to 5 mL (0.088 g, 75%).

Preparation of [NiBr$_2${(Im)(Dipp)(C$_3$NMe$_2$)-κ^{2}C^{NHC},N^{amine}}] (25).



To a solution of [AgCl{(Im)(Dipp)(C$_3$NMe$_2$)-κ^{1}C^{NHC}}] (**23**) (0.100 g, 0.218 mmol) in THF (10 mL) was added dropwise a THF solution of [NiBr$_2$(dme)] (0.068 g, 0.220 mmol). The reaction mixture was stirred overnight at room temperature. A purple solution and a white precipitate were obtained. The solution was collected by filtration and concentrated to 5 mL. X-ray quality crystals were obtained by slow diffusion of pentane into a THF solution (0.094 g, 81%).

ACKNOWLEDGEMENTS

We are grateful to the China Scholarship Council for a PhD grant to X.R. We thank Marc Mermillon-Fournier for technical assistance, the CNRS and the MESR (Paris) for funding.

Keywords: N-Heterocyclic carbenes; Ditopic ligands; C,N ligands; C,O ligands; Catalytic ethylene oligomerisation; Crystal structures.

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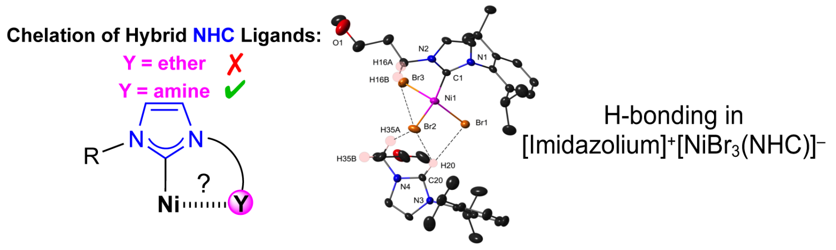

With potentially bi- or tri-dentate **hybrid NHC ligands**, the donor function Y coordinates to the metal under conditions that can be analysed by modular ligand design and chemical modifications of the donor groups (here ether or amine). Anionic [NiBr$_3$(NHC)]$^-$ undergoes H-bonding with its imidazolium cation.

Ditopic NHC ligands

Xiaoyu Ren Marcel Wesolek, Corinne Bailly, Lydia Karmazin, Pierre Braunstein**

Page No. – Page No.

Silver(I) and Nickel(II) Complexes with Oxygen- or Nitrogen-Functionalized NHC Ditopic Ligands and Catalytic Ethylene Oligomerisation.