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## Synthesis and characterization of oxygen-functionalised-NHC silver(i) complexes and NHC transmetallation to nickel(ii)†

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The new alcohol- and ether-functionalised-NHC silver(i) complexes bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)silver(i) chloride, [Ag{ImDiPP(C<sub>2</sub>OH)}<sub>2</sub>]Cl (**4**), bis(1-(2-hydroxyethyl)-3-mesityl-1*H*-imidazol-2(3*H*)-ylidene)silver(i) chloride, [Ag{ImMes(C<sub>2</sub>OH)}<sub>2</sub>]Cl (**5**), bis(1-(2-hydroxyethyl)-3-methyl-1*H*-imidazol-2(3*H*)-ylidene)silver(i) chloride, [Ag{ImMe(C<sub>2</sub>OH)}<sub>2</sub>]Cl (**6**), bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)silver(i) tetrafluoroborate, [Ag{ImDiPP(C<sub>2</sub>OH)}<sub>2</sub>]BF<sub>4</sub> (**9**), and bis(1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)silver(i) chloride, [Ag{ImDiPP(C<sub>2</sub>OMe)}<sub>2</sub>]Cl (**13**), were synthesized and fully characterized by NMR spectroscopy and single crystal X-ray diffraction. For some complexes, an uncommon heteronuclear coupling <sup>4</sup>J(<sup>107/109</sup>Ag–H) was unveiled. Their ability to transfer the NHC ligand to Ni(ii) was assessed in the presence of different nickel(ii) sources; the bis-NHC Ni(ii) complex bis(1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)nickel(ii) chloride, [NiCl<sub>2</sub>{ImDiPP(C<sub>2</sub>OMe)}<sub>2</sub>] (**15**), was obtained from **13** and shown by X-ray diffraction study to have a *trans*-arrangement of the two NHC ligands. However, in contrast to other Ag(i) NHC complexes the transmetallation reaction failed with the hydroxyl-functionalised silver complexes, possibly due to the acidity of the alcohol OH function, leading overall to reprotonation of the C<sub>NHC</sub> and isolation of the corresponding imidazolium salts.

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## Introduction

Since the isolation of the first stable, crystalline free carbene by Arduengo in 1991,<sup>1</sup> N-heterocyclic carbenes (NHCs) have been widely employed as ligands, in particular to prepare new metal-based catalysts.<sup>2</sup> One of the convenient synthetic methods to access NHC transition metal complexes consists of the use of the corresponding Ag(i)–NHC complexes as NHC transfer reagents, which avoids the cumbersome synthesis of free carbenes.<sup>3</sup> Generally, these silver complexes are readily synthesized, by reaction of the corresponding imidazolium salts with silver(i) oxide, without the need to work under an inert atmosphere.<sup>4</sup> In addition to their transmetallation ability, Ag(i)–NHC complexes are frequently used as

antimicrobial agents, where they promote a slow release of silver ions, thus suppressing infections over a long period of time, or as potential anti-cancer agents.<sup>5</sup>

Non-functionalised NHC ligands of the type bis-(alkyl/aryl)-imidazol(in)-ylidenes form either neutral [AgX(NHC)] or cationic [Ag(NHC)<sub>2</sub>]X (X = *e.g.* halide, BF<sub>4</sub>, PF<sub>6</sub>) complexes, which can coexist in solution, in equilibrium, depending on the nature of X. The silver(i) cation tends to adopt its preferred linear coordination geometry. Whenever X is a halide, the possible formation of [Ag<sub>n</sub>X<sub>m</sub>]<sup>m–n</sup> polynuclear complexes, through capping or bridging coordination modes of X, associated with coordination to [Ag(NHC)]<sup>+</sup> or [Ag(NHC)<sub>2</sub>]<sup>+</sup> moieties, can give rise to a large variety of silver(i) NHC polynuclear complexes or coordination clusters which benefit from favorable d<sup>10</sup>–d<sup>10</sup> attractive interactions between silver(i) cations.<sup>4a,6</sup> In these complexes, the coordination geometry of the silver cations can deviate substantially from linearity to become ultimately trigonal planar or tetrahedral. Furthermore, functionalised NHC ligands with certain pnictogen- and chalcogen-donor groups can easily provide access to interesting, structurally diverse NHC silver(i) complexes. Indeed, complexes with triangular [Ag<sub>3</sub>]-cores can often be obtained when N-functions such as pyridines, pyrazoles or imines are present.<sup>7</sup> [Ag<sub>4</sub>]-cores

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†Electronic supplementary information (ESI) available: All experimental and spectroscopic details and crystal data of **4–6**, **8**, **9** and **13–15** with ORTEP views. CCDC 963275–963282. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52773e

of rectangular or square geometry are frequently encountered when the NHC ligand is functionalised with N-heterocyclic ligands (pyridines, benzimidazoles, pyrazoles), thioethers, phosphines or is part of a pincer system.<sup>7g,8</sup> Linear or open chain arrays of  $[Ag_{\infty}]$ -cores are also widespread with heterocyclic functionalities (pyrimidines, triazoles, benzimidazoles, pyrazoles, pyridines, *etc.*) or with phosphines.<sup>9</sup> Less frequently, pseudo-cubane  $[Ag_4]$  substructures with phosphinites or phenolate functionalisations<sup>10</sup> or even higher nuclearity cores, from  $[Ag_6]$  to  $[Ag_{10}]$ , have been observed *e.g.* with amine or pyridine functionalisations.<sup>11</sup> These diverse structures and nuclearities result from both the geometric constraints of the chelating or bridging ligands and the ability of the silver(I) cations to aggregate through  $d^{10}$ – $d^{10}$  interactions.<sup>4a,6</sup>

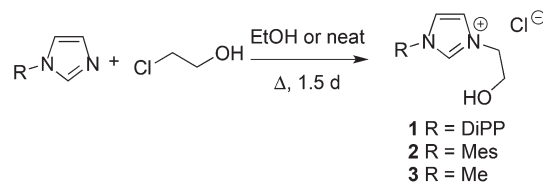
We have recently observed this structural diversity with phosphinite<sup>10a,c</sup> or thioether<sup>8c,j</sup>-functionalised NHCs, which led to the formation of cubane- or rectangle-type  $[Ag_4]$  clusters, respectively. As an extension of these studies, we decided to study the reactivity of hydroxy-functionalised NHC ligands with two main objectives: (i) explore their coordination behaviour, including the possibility of an intramolecular coordination of the weak hydroxy donor function and the stability of the ensuing silver(I) complexes, and (ii) use these functionalised silver(I) NHC complexes as transmetallating reagents, in particular toward Ni(II) centres in view of potential applications in catalytic ethylene oligomerization.<sup>12</sup> Indeed, numerous non-functionalised-NHC nickel(II) complexes have already been synthesized and shown to be active pre-catalysts toward ethylene oligomerization.<sup>12b,c,13</sup> Furthermore, an enolate-functionalised NHC nickel(II) complex synthesized by Waymouth *et al.* efficiently oligomerizes ethylene upon activation with  $ZnEt_2$ , and alcoholate- or aryloxide-functionalised NHC nickel(II) complexes catalyze norbornene polymerization upon activation with MAO.<sup>14</sup> Upon activation with  $NaBPh_4$ , a salicylaldiminato-functionalised NHC Ni(II) complex catalyzes the polymerization of styrene with an activity higher than that of its analogous non-functionalised-NHC or even of  $PPh_3$  Ni(II) halide complexes.<sup>15</sup>

In this paper, we describe the synthesis and characterization of a series of hydroxyethyl-functionalised NHC silver(I) complexes, attempts to transfer the NHC ligands to different nickel(II) precursors and the synthesis and characterization of ether-functionalised NHC silver(I) and nickel(II) complexes.

## Results and discussion

### Alcohol-functionalised NHC complexes

The salt 3-(2-hydroxyethyl)-1-methyl-1H-imidazol-3-ium chloride ( $[ImMe(C_2OH)]Cl$ , **3**) was prepared by the quaternization of N-substituted imidazoles following a published procedure.<sup>16</sup> This procedure was modified for the synthesis of 1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1H-imidazol-3-ium chloride,  $[ImDiPP(C_2OH)]Cl$  (**1**), and 1-mesityl-3-(2-hydroxyethyl)-1H-imidazol-3-ium chloride,  $[ImMes(C_2OH)]Cl$  (**2**), to reduce the reaction times (Scheme 1). (All experimental details for this paper



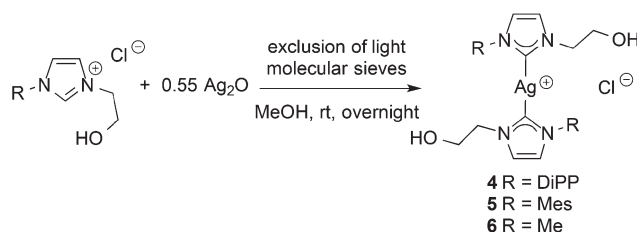
Scheme 1 Synthesis of the imidazolium salts 1–3.

are given in the ESI†.) A procedure avoiding the use of a solvent and thus allowing access to higher reaction temperatures was initially reported for the synthesis of aryl- and bis-(arylimidazolium)-pyridines<sup>7h,17a</sup> and applied on many other occasions, *e.g.* to the synthesis of precursors to amine-tethered NHC rhodium complexes.<sup>17b</sup> The  $^1H$  NMR spectra in  $CD_2Cl_2$  of **1–3** display the characteristic resonances of the NCHN protons around 9–10 ppm, in agreement with the formation of the imidazolium salts.

A dry methanol solution of the imidazolium salts **1–3** was reacted with 0.55 equiv. of  $Ag_2O$  in the presence of molecular sieves at room temperature under exclusion of light to afford the complexes bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1H-imidazol-2(3H)-ylidene)silver(I) chloride,  $[Ag\{ImDiPP(C_2OH)\}_2]Cl$  (**4**), bis(1-(2-hydroxyethyl)-3-mesityl-1H-imidazol-2(3H)-ylidene)silver(I) chloride,  $[Ag\{ImMes(C_2OH)\}_2]Cl$  (**5**), and bis(1-(2-hydroxyethyl)-3-methyl-1H-imidazol-2(3H)-ylidene)silver(I) chloride,  $[Ag\{ImMe(C_2OH)\}_2]Cl$  (**6**), respectively, in good to excellent yields (77–93%) (Scheme 2). Complexes **4** and **5** are stable towards moisture in ambient daylight while **6** is not.

It was found that the use of methanol as the reaction medium for the synthesis of **4** was beneficial compared to other commonly used solvents (*e.g.* THF, MeCN,  $CH_2Cl_2$  or DMSO) resulting in shorter reaction times and high conversions. For example, the use of  $CH_2Cl_2$  as solvent resulted in a conversion of 80% after 12 h while in methanol complete conversion was observed within 4 h.

The formation of complexes **4–6** was confirmed by  $^1H$  NMR spectroscopy with the complete disappearance of the characteristic signals of the imidazolium salts. Thus the spectrum of **4** displays two apparent triplets for the imidazole backbone protons at 7.27 and 6.92 ppm. Since two doublets were initially expected for these non-equivalents protons, experiments were carried out to rationalise the appearance of the observed spectrum. Since both silver isotopes  $^{107}Ag$  and  $^{109}Ag$  are NMR active ( $S = 1/2$ ), a heteronuclear  $^1H$ – $^{109}Ag$  HMQC experiment was carried out and revealed a  $^4J(H-^{109}Ag)$  coupling between the backbone



Scheme 2 Synthesis of the Ag(I) complexes 4–6.

imidazole protons and silver (1.5 Hz). Careful inspection shows that these apparent triplets are actually doublets of doublets ( $^3J(\text{H-H}) = 1.5$  Hz and  $^4J(^{107/109}\text{Ag-H}) = 1.5$  Hz). The observation of the  $^4J(\text{H-}^{109}\text{Ag})$  coupling highlights the lack of lability of the C-Ag bond on the NMR time-scale.<sup>4a,b</sup> In the  $^{13}\text{C}$  NMR spectra, the carbene signals appear at 182.6 ppm for **4** and **5** and at 181.2 ppm for **6**. For **4** and **5**,  $^1J$  and  $^3J$  couplings with both  $^{107/109}\text{Ag}$  isotopes are observable for the carbene and the imidazole backbone carbon atoms, respectively. They give rise to two sets of two doublets having the following coupling constants:  $^1J(^{107}\text{Ag-}^{13}\text{C}) = 184$  and  $182$  Hz,  $^1J(^{109}\text{Ag-}^{13}\text{C}) = 212$  and  $210$  Hz and  $^3J(^{107/109}\text{Ag-}^{13}\text{C}) = 5.5$  and  $5.0$  Hz, respectively. For all three complexes,  $^1\text{H}$  NMR spectroscopy indicates the presence of both  $[\text{AgCl}(\text{NHC})]$  and  $[\text{Ag}(\text{NHC})_2]^+$  in solution,<sup>7h</sup> which are known to be in equilibrium when the counterion associated with the latter is  $[\text{AgCl}_2]^-$  (its progressive decomposition in  $\text{Ag}(0)$  or  $\text{AgCl}$  liberates  $\text{Cl}^-$  anions and affects the equilibrium).<sup>18</sup> Preliminary studies performed in  $\text{CDCl}_3$  indicated a slow decomposition of the complexes that could be avoided by filtering the chloroform solution through a plug of alumina (thus removing traces of  $\text{HCl}$ ). To confirm the instability of **4-6** toward acidic media, they were dissolved in dry  $\text{CD}_2\text{Cl}_2$  in the presence of a small amount of an ether solution of  $\text{HCl}$ . Gratifyingly, the same decomposition pathway was recorded by NMR as in  $\text{HCl}$ -contaminated  $\text{CDCl}_3$ . The ESI mass spectra of complexes **4** and **5** display only two signals for  $m/z = [\text{Ag}(\text{NHC})_2]^+$  and  $[(\text{NHC})\text{H}]^+$ . For **6**, the fragment  $m/z = [(\text{NHC})\text{H}]^+$  was not detected due to a too small window chosen for the analysis, but numerous unidentifiable signals are visible. It is reasonable to assume that **4-6** are unstable under the mass spectral analysis conditions and mainly reconverted to some imidazolium salts. There is no signal accounting for the formation of  $[\text{AgCl}(\text{NHC})]$  or for any silver-containing species with  $m/z$  higher than  $[\text{Ag}(\text{NHC})_2]^+$ . X-Ray quality crystals of **4-6** were grown by slow diffusion or evaporation of solutions of  $\text{CH}_2\text{Cl}_2$ -pentane,  $\text{CH}_2\text{Cl}_2$ -hexane, and ether, respectively (Fig. 1 and 2) (the ORTEP views of all complexes are given in the ESI†). The formation of complexes of the type  $[\text{Ag}(\text{NHC})_2]\text{X}$  with  $\text{X} = \text{Cl}$  was thus confirmed, ruling out the formation of higher nuclearity silver complexes.

Complexes **4** and **6** crystallize in the monoclinic system with the  $C2/c$  space group. Complex **5** crystallizes in the triclinic system with the  $P\bar{1}$  space group. The unit cell of **4** contains 4 motifs including slightly disordered  $\text{CH}_2\text{Cl}_2$  molecules around twofold axes passing through chloride anions. The silver centres are positioned on inversion centres. The unit cell of **5** contains two motifs. The Ag-C distances fall in the range between 2.039(4) and 2.086(3) Å, in good agreement with other reported distances for homoleptic cationic bis-(NHC) silver(I) complexes.<sup>4a,19</sup> The C-Ag-C angles are in the range  $174.8(3)^\circ$ – $180.0^\circ$  and correspond to a nearly linear coordination environment. No interaction between the silver centres and the hydroxyl groups is noticeable in the solid state. The unit cell of **6** contains also 4 motifs without any co-crystallized solvent. The silver and chloride ions are located on twofold axes. In contrast to **4** and **5**, the structure of **6** reveals a weak

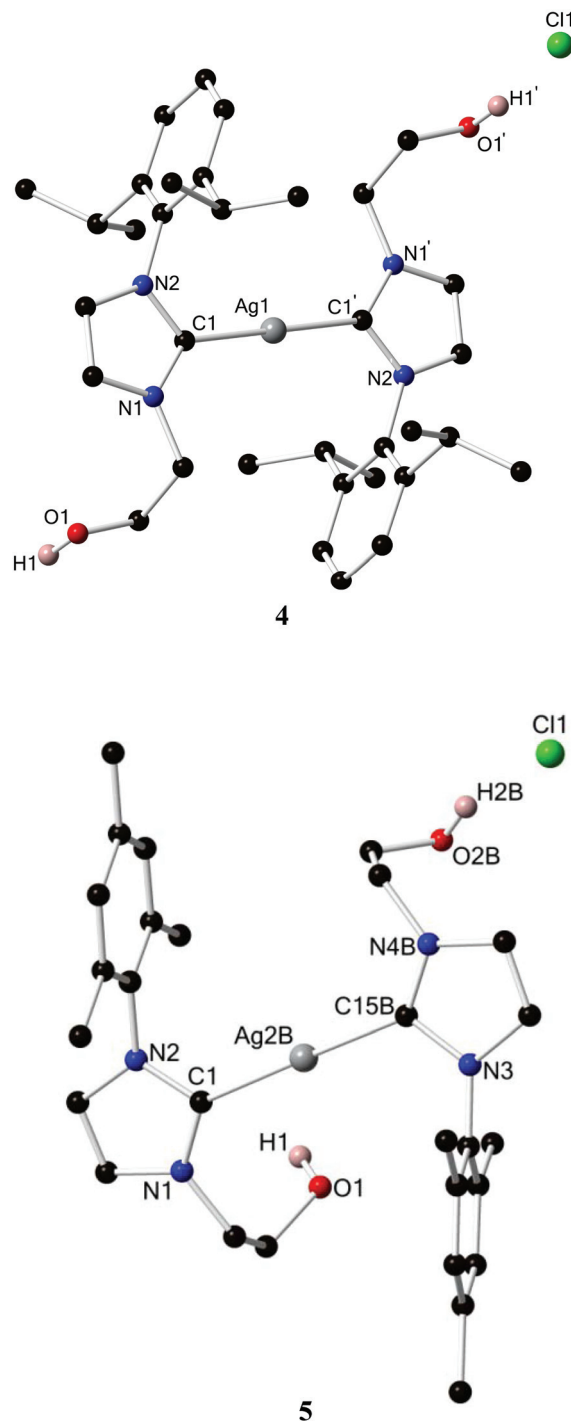


Fig. 1 Ball and stick representation of the structures of  $[\text{Ag}(\text{ImDiPP}-(\text{C}_2\text{OH})_2)\text{Cl}]$  (**4**) (top) and  $[\text{Ag}(\text{ImMes}(\text{C}_2\text{OH})_2)\text{Cl}]$  (**5**) (bottom). Hydrogen atoms have been omitted for clarity, except the OH protons (ORTEP views are provided in Fig. S3 and S4 of the ESI†).

interaction between the silver centre and the chloride anion. The C-Ag-Cl angle is equal to  $93.8(1)^\circ$ . Similarly to other structures,<sup>18b,20</sup> the Ag-Cl distance of 3.189(2) Å implies a weak electrostatic interaction, not strong enough to perturb the linear coordination geometry around the silver centre. Thus the chloride is considered as a counter-anion for the Ag

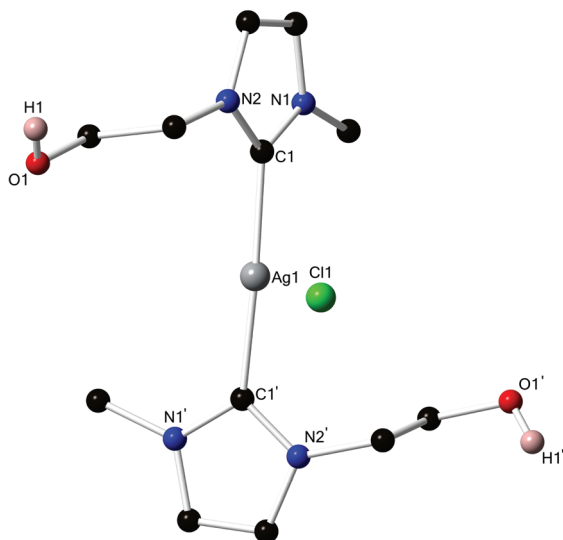


Fig. 2 Ball and stick representation of the structure of  $[\text{Ag}(\text{ImMe}-(\text{C}_2\text{OH}))_2]\text{Cl}$  (**6**). Hydrogen atoms have been omitted for clarity, except the OH protons (an ORTEP view is provided in Fig. S5 of the ESI†).

$(\text{NHC})_2^+$  moiety. For all three complexes, the cohesion in the crystalline state is ensured by an extensive network of long distance hydrogen bonding interactions. The chloride anions interact with two hydroxyl groups belonging to two distinct motifs as well as with one proton from the unsaturated imidazole ring backbone. There is no noticeable interaction between the different hydroxyl groups present in the unit cells. Complexes **4–6** are similar to other alcohol-functionalised NHC silver(i) complexes;<sup>5d,21</sup> those characterized by X-ray diffraction did not reveal any interaction between the alcohol and the silver centre, ruling out the formation of NHC silver clusters supported by silver–oxygen bonds.<sup>22</sup>

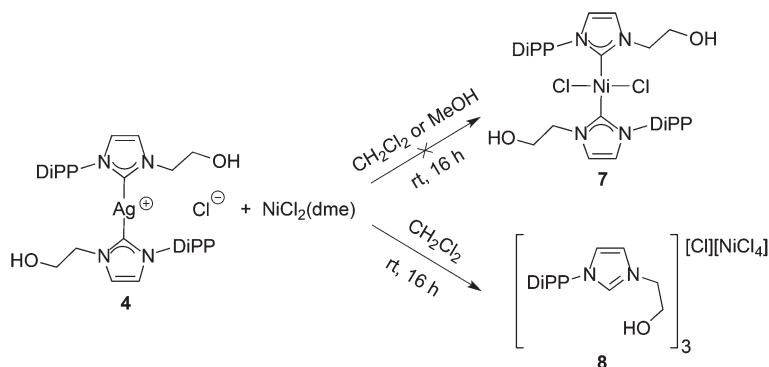
The synthesis of the complex bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)nickel(ii) chloride,  $[\text{NiCl}_2\{\text{ImDiPP}(\text{C}_2\text{OH})\}_2]$  (**7**), was attempted *via* transmetallation by reacting overnight **4** with  $[\text{NiCl}_2(\text{dme})]$  (Scheme 3). This classic method for the synthesis of Ni(ii)–NHC complexes<sup>9c,23</sup> was expected to yield a NHC nickel complex bearing a hydroxyethyl arm. The reaction was carried out in  $\text{CH}_2\text{Cl}_2$  or

MeOH and led to a deep green solution containing at least one paramagnetic product. Detailed NMR analyses were not possible, but confirmed the presence of imidazolium salts.

Blue crystals were grown from the crude reaction mixture, and their structure determination by X-ray diffraction established that reprotonation of the imidazolydene moieties bound to silver has occurred, instead of their transfer to nickel, with formation of a mixed tetrachloronickelate/chloride imidazolium salt **8** (Fig. 3). Although transmetallation leading to **7** would be accompanied by the precipitation of AgCl, formation of stable  $[\text{NiCl}_4]^{2-}$  appears to be kinetically favoured, thus preventing transmetallation. We were only able to isolate compound **8** (as hygroscopic crystals) even from carefully dried solvents. The salt **8** crystallizes in the orthorhombic system with the Sohncke space group  $P2_12_12_1$ . There are 4 motifs in the unit cell without any co-crystallized solvent. The nickel atoms are positioned along twofold axes and the  $[\text{NiCl}_4]^{2-}$  ions display the expected tetrahedral coordination geometry. The chloride anions interact with two hydroxyl groups and one proton from the unsaturated backbone of the imidazole ring. The azolium protons interact with two chlorides of  $[\text{NiCl}_4]^{2-}$ .

Attempts to use complex **6** for transmetallation of the functional NHC ligand **3** to Ni(ii) were inconclusive because of solubility reasons and only  $^1\text{H}$  NMR broad peaks were observed in DMSO- $d_6$ .

To avoid the formation of  $[\text{NiCl}_4]^{2-}$ , the counterion  $\text{Cl}^-$  present in the silver complex **4** was replaced by the less coordinating anion  $\text{BF}_4^-$  *via* a metathesis reaction carried out in acetone overnight (Scheme 4). The formation of the new complex bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)silver(i) tetrafluoroborate,  $[\text{Ag}\{\text{ImDiPP}(\text{C}_2\text{OH})\}_2]\text{BF}_4$  (**9**), was supported by the presence of a characteristic signal at  $-152.7$  ppm in  $^{19}\text{F}$  NMR spectroscopy. As for **4**, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra display  $^4J$  and  $^3J$  couplings between the  $^{107/109}\text{Ag}(\text{i})$  nuclei and the imidazole backbone hydrogen and carbon atoms, respectively. In the  $^1\text{H}$  NMR spectrum of **9**, the signals of the spacer  $\text{CH}_2$  protons are shifted upfield compared to **4** (by 0.18 and 0.10 ppm for the  $\text{CH}_2$  protons  $\alpha$  and  $\beta$  to N, respectively) and one of the imidazole backbone protons is shifted downfield by 0.06 ppm. The



Scheme 3 Attempted synthesis of  $[\text{NiCl}_2\{\text{ImDiPP}(\text{C}_2\text{OH})\}_2]$  (**7**) *via* transmetallation.

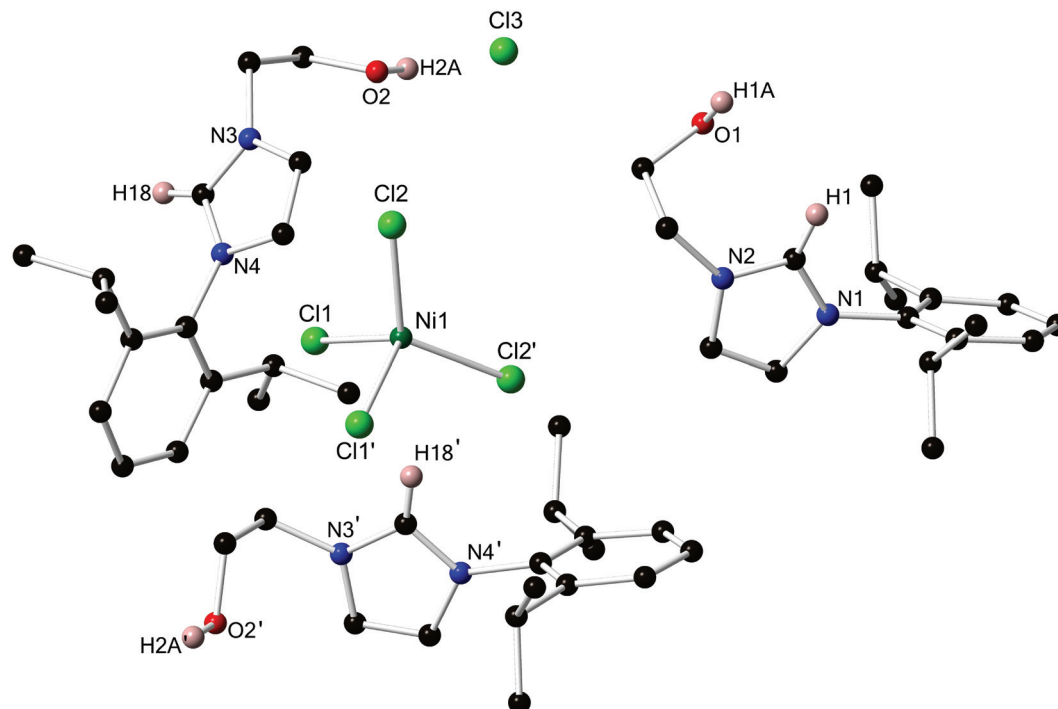
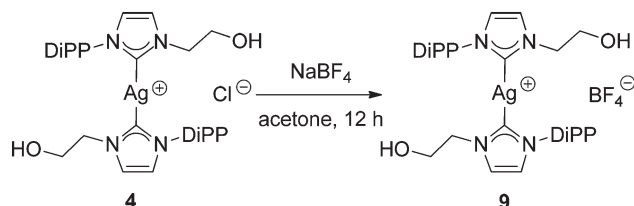


Fig. 3 Ball and stick representation of **8**. Hydrogen atoms have been omitted for clarity, except the OH and the NCHN protons (an ORTEP view is provided in Fig. S6 of the ESI†).



Scheme 4 Synthesis of  $[\text{Ag}\{\text{ImDiPP}(\text{C}_2\text{OH})\}_2]\text{BF}_4$  (**9**).

$\text{CH}^{m\text{-Ar}}$  is shifted downfield in contrast to the  $\text{CH}^{p\text{-Ar}}$  which is shifted upfield (both by 0.06 ppm). The  $\text{CH}_3^{\text{iPr}}$  are shifted downfield by 0.07 and 0.03 ppm whereas the  $\text{CH}^{\text{iPr}}$  is not affected. The anion exchange has no significant influence on the chemical shifts measured on the  $^{13}\text{C}$  NMR spectra of both complexes, except for the appearance in the spectrum of **9** of a  $^3J$  coupling ( $^3J = 2.2$  Hz) between the N–C carbon atoms of the alcohol side chain and  $^{107/109}\text{Ag}(\text{I})$ .

The structure of **9** was confirmed by X-ray diffraction on single crystals obtained by slow diffusion of pentane into a saturated  $\text{CH}_2\text{Cl}_2$  solution (Fig. 4). This complex crystallizes in the triclinic system with two motifs per unit cell including slightly disordered diethyl ether molecules. The silver atoms are positioned on inversion centres and the Ag–C distances are equal to 2.090(5) and 2.065(5) Å. The  $\text{BF}_4^-$  anions interact with the two protons from the same imidazole backbones. They also interact with one hydroxyl group from another molecule, which interacts itself with another hydroxyl group. The hydrogen bonding interactions between hydroxyl groups being not reciprocal, polymeric zigzag chains are built (see Fig. S1 in the ESI†).

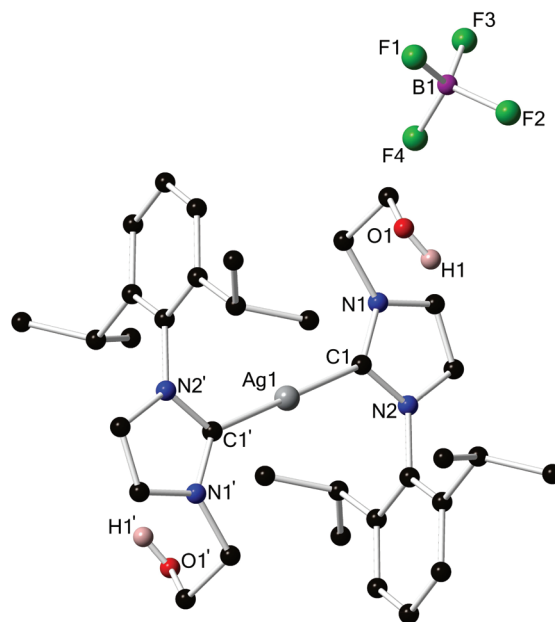


Fig. 4 Ball and stick representation of  $[\text{Ag}\{\text{ImDiPP}(\text{C}_2\text{OH})\}_2]\text{BF}_4$  (**9**). Hydrogen atoms have been omitted for clarity, except the OH protons (an ORTEP view is provided in Fig. S7 of the ESI†).

Complex **9** was reacted in dry MeCN or THF with different nickel precursors generally known to lead to NHC nickel(II) complexes by transmetalation, such as  $[\text{NiBr}_2(\text{PPh}_3)_2]$ ,  $[\text{NiCl}_2(\text{dme})]$ ,  $[\text{Ni}(\text{NCMe})_4](\text{BF}_4)_2$  or  $[\text{NiBr}_2(\text{dme})]$ . The formation of  $[\text{NiX}_4]^{2-}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) was not observed. Due to the

paramagnetic nature of the products formed,  $^1\text{H}$  NMR signals were too broad to provide any valuable information with the exception of a broad signal around 9–10 ppm which could indicate that reprotonation of **9** has occurred. Unfortunately, X-ray quality crystals could not be grown. While reprotonation of **9** could be assumed, its pathway is not yet clear and might be due to the acidic proton of the alcohol which could trap the carbene during the transmetallation process.

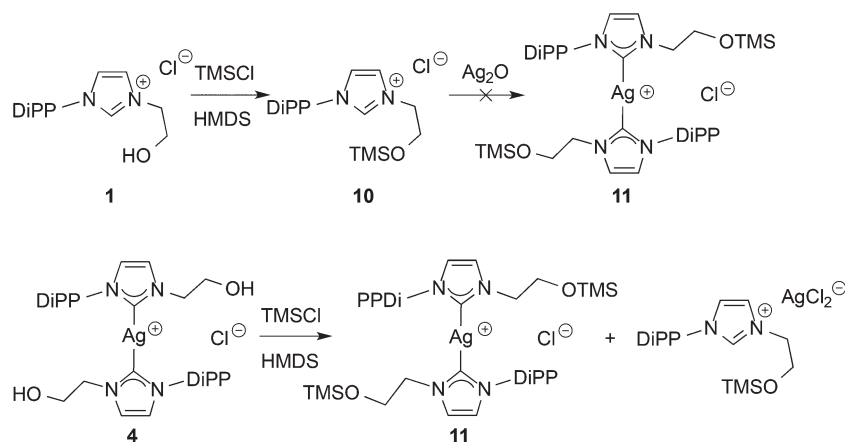
### Silylether- and ether-functionalised NHC complexes

In order to corroborate that reprotonation of the carbene ligand under transmetallation conditions is due to the OH proton of the alcohol, protection of the latter function with a trimethylsilyl group (TMS) was attempted. We first protected the imidazolium salt **1** before complexation to Ag(I), using trimethylsilyl chloride (TMSCl) and hexamethyldisilazane (HMDS) as a base in refluxing dioxane. The corresponding salt 1-(2,6-diisopropylphenyl)-3-(2-((trimethylsilyl)oxy)ethyl)-1*H*-imidazol-3-ium chloride, [ImDiPP(C<sub>2</sub>OTMS)]Cl (**10**), was isolated in 81% yield. To synthesize the complex bis(1-(2,6-diisopropylphenyl)-3-(2-((trimethylsilyl)oxy)ethyl)-1*H*-imidazol-2(3*H*)-ylidene)silver(i) chloride, [Ag{ImDiPP(C<sub>2</sub>OTMS)}<sub>2</sub>]Cl (**11**), the same procedure as that employed for the synthesis of **4** was applied but resulted in complete deprotection of the alcohol during metallation and formation of **4** instead. Therefore, we tried a direct protection of the silver complex **4**; the alcohol was properly protected but a major part (from 60 to 80%) of the carbene ligand was reprotonated during the reaction, even when distilled TMSCl and an excess of base (HMDS or NEt<sub>3</sub>) were used. Both compounds **10** and **11** were identified

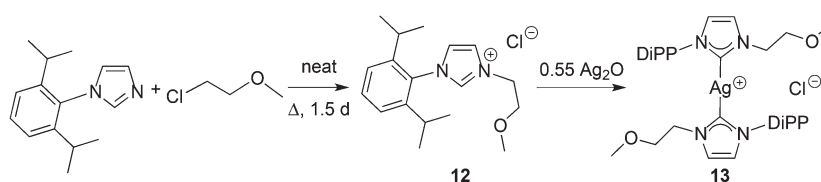
by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and ESI-MS. For the sake of comparison, the stability of the non-protected silver complex **4** was tested under similar reaction conditions (excess of base in refluxing dioxane) and was revealed to be stable. During the formation of the silylether, the HCl released might be trapped by HMDS or NEt<sub>3</sub> or reacts with **11**, thus explaining the formation of the imidazolium salt (Scheme 5).

The synthesis of silylether-functionalised NHC silver(i) complexes being unsuccessful, attempts were made with an ether-functionalised NHC. The ligand 1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1*H*-imidazol-3-ium chloride, [ImDiPP(C<sub>2</sub>OMe)]Cl (**12**), was prepared in high yield by applying a similar method to that used for ligands **1** and **2** (Scheme 6). The corresponding silver complex bis(1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)silver(i) chloride, [Ag{ImDiPP(C<sub>2</sub>OMe)}<sub>2</sub>]Cl (**13**), was readily formed by the reaction of **12** with 0.55 equiv. of Ag<sub>2</sub>O (Scheme 6).

The disappearance of the imidazolium NCHN proton was observed in the  $^1\text{H}$  NMR spectrum. As observed with **4**, a  $^4J(^{107/109}\text{Ag}-\text{H})$  coupling of 1.5 Hz with the backbone imidazole hydrogen atoms is visible. The formation of **13** was also established by the characteristic downfield shift of the carbenic carbon at 182.4 ppm, which exhibits coupling with the  $^{107/109}\text{Ag}$  isotopes ( $^1J(^{107/109}\text{Ag}-^{13}\text{C}) = 183$  and 212 Hz, respectively). A  $^3J$  coupling between the imidazole backbone carbon atoms and the  $^{107/109}\text{Ag}$  isotopes ( $^3J(^{107/109}\text{Ag}-^{13}\text{C}) = 5.8$  and 5.7 Hz) is visible as well as a  $^3J(^{107/109}\text{Ag}-^{13}\text{C})$  coupling of 2.2 Hz involving the N-C carbon atom from the ether side chain, as for **9**. In contrast to **4**–**6**, the mass spectrum of **13** only displays the characteristic signal at  $m/z = 681.31$  for



**Scheme 5** Attempted syntheses of [Ag{ImDiPP(C<sub>2</sub>OTMS)}<sub>2</sub>]Cl (**11**) with TMSCl.



**Scheme 6** Synthesis [ImDiPP(C<sub>2</sub>OMe)]Cl (**12**) and [Ag{ImDiPP(C<sub>2</sub>OMe)}<sub>2</sub>]Cl (**13**).

$[\text{Ag}(\text{NHC})_2]^+$ , without any trace of reprotonation/decomposition.

Colourless crystals were grown by dissolving **13** in pure  $\text{CH}_2\text{Cl}_2$  or in a mixture of THF and water, followed by slow diffusion of a layer of pentane. Crystals originating from the two corresponding batches displayed different cell parameters. Their structural investigation by X-ray diffraction ruled out any solvomorphism effect, but rather proved the formation of the expected complex **13** and of the less anticipated neutral mono-NHC complex  $[\text{AgCl}\{\text{ImDiPP}(\text{C}_2\text{OMe})\}]$  (**14**)<sup>18a</sup> (Fig. 5).

Complexes **13** and **14** crystallize in the triclinic system with the  $P\bar{1}$  space group, and the monoclinic system with the  $P2_1/c$  space group, respectively, with very similar cell parameters. The unit cell of **13** contains 2 motifs including slightly disordered water molecules close to inversion centres. The unit cell of **14** contains 4 motifs with no solvent or water included. For both cells, there is no atom in special positions. For **13** the Ag–C distances are equal to 2.075(4) and 2.077(4) Å and the C–Ag–C angle is equal to 176.6(1)°. These values are similar to those found for **4**–**6**. For **14**, the Ag–C and Ag–Cl distances of 2.084(5) and 2.323(2) Å, respectively, and the C–Ag–Cl angle of 173.7(1)° are in excellent agreement with those reported in the literature for similar  $[\text{AgCl}(\text{NHC})]$  complexes.<sup>4a,22c,24</sup> In both complexes, the ether functions do not interact with the silver centres. In **13**, two chloride anions interact strongly with two water molecules, forming a diamond arrangement *via* the 4 protons available (see Fig. S2 in the ESI†). They also participate in intermolecular interactions with a hydrogen atom from the imidazole rings. In **14**, the ether groups interact slightly with only one methyl proton per imidazolylidene moiety. The chloride ligand interacts with a hydrogen atom from the imidazole ring of an adjacent molecule.

The overnight reaction of **13** with  $[\text{NiCl}_2(\text{dme})]$  afforded an orange solution and white AgCl precipitate. The solution was filtered through Celite and the solvent was removed under reduced pressure. After the resulting orange solid residue was washed with  $\text{H}_2\text{O}$  and redissolved in toluene, the solution was dried over  $\text{Na}_2\text{SO}_4$  and the solvent evaporated to afford **15** in 50% yield (Scheme 7).

The formation of the complex bis(1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)nickel(II) chloride ( $[\text{NiCl}_2\{\text{ImDiPP}(\text{C}_2\text{OMe})\}_2]$ , **15**) was confirmed by  $^{13}\text{C}$  NMR spectroscopy with the displacement of the carbene chemical shift from 182.4 ppm to 171.7 ppm, a value which is in the range of those reported for other Ni(II) NHC complexes.<sup>25</sup>

The structure of **15** was unambiguously established by X-ray diffraction on single-crystals obtained by slow diffusion of hexane into a saturated THF solution (Fig. 6).

This complex crystallizes in the orthorhombic system with the  $Pca2_1$  space group. There are four motifs per unit cell without any solvent included and no atom in special positions. The structure exhibits two NHC ligands in *trans*-position to each other around a nickel centre in a square-planar coordination environment. There is no interaction between the ether groups and the nickel centre. The Ni–C and Ni–Cl distances are respectively equal to 1.902(2), 1.910(2) Å and 2.1822(8),

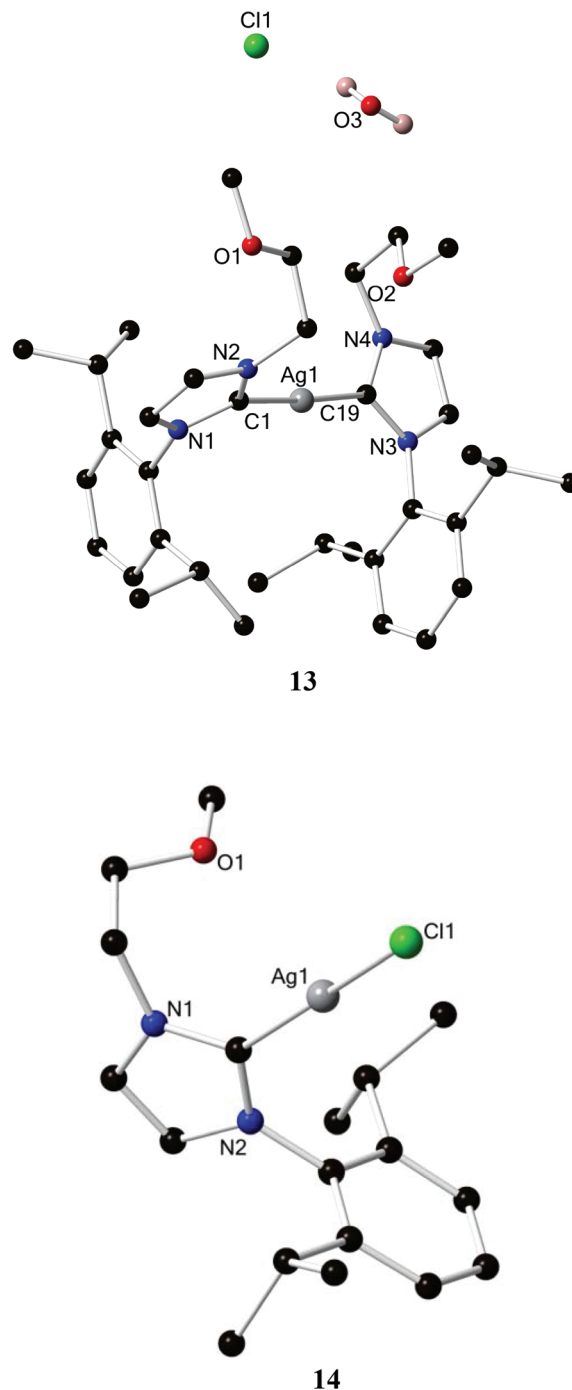
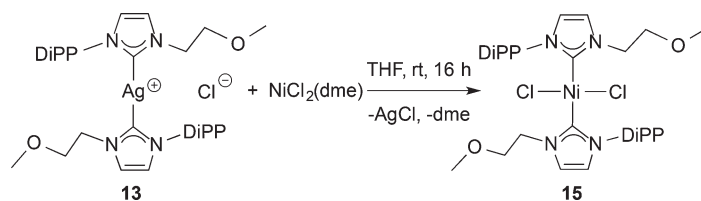


Fig. 5 Ball and stick representation of  $[\text{Ag}(\text{ImDiPP}(\text{C}_2\text{OMe}))_2]\text{Cl}$  (**13**) (top) and  $[\text{AgCl}(\text{ImDiPP}(\text{C}_2\text{OMe}))]$  (**14**) (bottom). Hydrogen atoms have been omitted for clarity, except the OH protons (ORTEP views are provided in Fig. S8 and S9 of the ESI†).

2.1828(8) Å. The C–Ni–C and Cl–Ni–Cl angles are equal to 179.1(2) and 179.73(4)°. The metrical data of **15** are in excellent agreement with those reported for similar square-planar bis-NHC Ni(II) dichloride complexes.<sup>25</sup>

Surprisingly, even though the  $^1\text{H}$  NMR spectrum recorded when **15** was dissolved in deuterated solvents was consistent with the structural assignment in the solid state, it also



Scheme 7 Synthesis of  $[\text{NiCl}_2(\text{ImDiPP}(\text{C}_2\text{OMe}))_2]$  (**15**) by transmetalation.

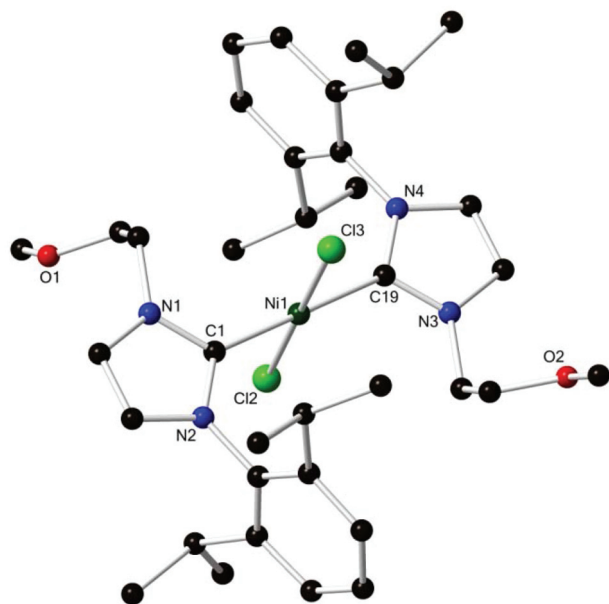


Fig. 6 Ball and stick representation of  $[\text{NiCl}_2(\text{ImDiPP}(\text{C}_2\text{OMe}))_2]$  (**15**). Hydrogen atoms have been omitted for clarity (an ORTEP view is provided in Fig. S10 of the ESI†).

demonstrated the presence of an additional minor species (*ca.* 10%), which displayed very similar spectral features: the signals due to the ligand framework were observable, with the  $\text{CH}_2^{\text{imid}}$  and  $\text{CH}_2^{\text{OMe}}$  signals shifted downfield by 0.69 and 0.34 ppm and the  $\text{CH}^{\text{iPr}}$  and  $\text{CH}_3^{\text{iPr}}$  signals shifted upfield by 0.21 and 0.32 ppm. No significant difference was noticeable in the corresponding  $^{13}\text{C}$  NMR spectra. Attempts to isolate the minor species by flash chromatography were unsuccessful. Re-dissolving of the authentic crystals of **15** in deuterated solvents resulted in the reformation of both species in the same ratio. The infrared spectra of the crystals and the bulk powder of **15** did not reveal any differences, in agreement with the existence of only one type of complex in the solid state. Consequently, the establishment of a dynamic equilibrium in solution involving two species was suspected and could be further confirmed by a ROESY NMR experiment. Plausible types of solution equilibria can be envisaged for such NHC nickel(II) complexes (*e.g.* *cis/trans*-isomerization at the metal or the presence of *syn/anti*-conformers through the Ni–C(NHC) rotation).<sup>26</sup>

Work currently in progress aims at investigating further these equilibria and at extending the family of ether-functionalised NHC nickel(II) complexes in order to thoroughly evaluate

their catalytic potential. Preliminary studies on catalytic ethylene oligomerization were performed with **15** in the presence of 10 equiv. of ethylaluminium dichloride (EADC) and indicated a low to moderate activity, with a productivity of  $4600 \text{ g C}_2\text{H}_4 (\text{g Ni} \cdot \text{h})^{-1}$  and a TOF of  $9600 \text{ mol C}_2\text{H}_4 (\text{mol Ni} \cdot \text{h})^{-1}$ . The selectivities for  $\text{C}_4$  olefins and 1-butene (in the  $\text{C}_4$  cut) were 64 mol%, and 52 mol%, respectively. Note that unsymmetrically substituted NHC ligands bearing a phenoxy group on one NHC N-atom were found to act as  $\text{C}_{\text{NHC}}\text{--O}$  chelates toward Ni (II) but the resulting complex was inactive toward ethylene.<sup>27</sup>

## Conclusion

We have obtained a series of non-symmetric alcohol-, silyl-ether- or ether-functionalised imidazolium salts and their corresponding bis-NHC silver(I) complexes. The cationic bis-NHC silver(I) complexes **4**, **5**, **6** and **9** and the neutral halide complex **13** were structurally characterized and were all mononuclear. No direct interaction was observed between the oxygen-containing groups and the Ag(I) centre in contrast to other functionalities mentioned in the introduction. Whereas this limits the stereoelectronic impact of the functional groups on the metal centre, access to alcohol-functionalised NHC silver complexes may have an interesting potential for the anchoring of moieties on surfaces and interesting biological or pharmaceutical properties *via* formation of *e.g.* ether or ester bonds. The presence of an OH group on the NHC ligand was found to be detrimental to the applicability of their silver(I) complexes in transmetalation to Ni(II) since reprotonation of the carbene carbon was always observed. Consistent with these observations, we are not aware of any successful transmetalation of an alcohol-functionalised NHC ligand to nickel. In contrast, the structurally characterized ether-functionalised NHC nickel(II) complex **15** was readily obtained from **13**, emphasizing the potential of ether-functionalised NHC silver(I) complexes as efficient transmetallating agents. In view of our continuing interest in catalytic ethylene oligomerization,<sup>28</sup> we are currently using this approach to synthesize a series of ether-functionalised NHC Ni(II) complexes for this purpose.

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