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Synthesis and characterization of oxygen-functionalized-NHC silver(I) complexes and transmetallation to nickel(II)

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ABSTRACT

The new oxygen-functionalized-NHC silver(I) complexes bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1H-imidazol-2(3H)-ylidene)silver(I) chloride ([Ag{ImDiPP(EtOH)}$_2$]Cl, 4), bis(1-(2-hydroxyethyl)-3-mesityl-1H-imidazol-2(3H)-ylidene)silver(I) chloride ([Ag{ImMes(EtOH)}$_2$]Cl, 5), bis(1-(2-hydroxyethyl)-3-methyl-1H-imidazol-2(3H)-ylidene)silver(I) chloride ([Ag{ImMe(EtOH)}$_2$]Cl, 6), bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1H-imidazol-2(3H)-ylidene)silver(I) tetrafluoroborate ([Ag{ImDiPP(EtOH)}$_2$]BF$_4$, 9) and bis(1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1H-imidazol-2(3H)-ylidene)silver(I) chloride ([Ag{ImDiPP(EtOMe)}$_2$]Cl, 13), have been synthesized and fully characterized by NMR spectroscopy and single crystal X-ray diffraction. For some complexes, an uncommon heteronuclear coupling of $^4J(^{107/109}\text{Ag}-^1\text{H})$ was unveiled. Their transmetallation ability was assessed in presence of different nickel(II) sources and the bis-NHC Ni(II) complex bis(1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1H-imidazol-2(3H)-ylidene)nickel(II) chloride ([NiCl$_2${ImDiPP(EtOMe)}$_2$], 15) was obtained from 13 and shown by X-ray diffraction to have a *trans*-arrangement of the two NHC ligands. In contrast, it was found with the other Ag(I) NHC complexes that the acidity of the alcohol OH proton was detrimental for the transmetallation process, and reprotonation of the C$_{\text{NHC}}$ carbon to give the corresponding imidazolium salt was observed.

INTRODUCTION

Since the isolation of the first stable, crystalline free carbene by Arduengo in 1991,[1] N-heterocyclic carbenes (NHCs) have been widely employed as ligands to prepare new metal-based catalysts.[2] One of the convenient synthetic methods to access NHC transition metals complexes is to use the corresponding silver(I)-NHC complexes as transfer reagents to avoid the cumbersome synthesis of free carbenes.[3] Generally, these silver complexes are readily synthesized, without the need to work under inert atmosphere, by reaction of the corresponding imidazolium salts with silver(I) oxide.[4] In addition to their transmetallation ability, Ag(I) NHC complexes are frequently used as antimicrobial agents. They promote a slow release of silver ions thus preventing infections over a large period of time.[5]

Non-functionalized NHC ligands of the type bis-(alkyl/aryl)-imidazol(in)ylidenes form either neutral [AgX(NHC)], or cationic [Ag(NHC)$_2$]X complexes which can coexist, in equilibrium, in solution depending on the nature of X. The silver(I) cation tends to be linearly two-coordinated through favored sp / sd hybridization in presence of NHCs. Whenever X is a halide, the possible formation of [Ag$_n$X$_m$]$^{m-n}$ cluster-type anions, though capping or bridging coordination modes of X, and subsequent coordination to [Ag(NHC)]$^+$ or [Ag (NHC)$_2$]$^+$ moieties, can give rise to a broad variety of self-assembled silver(I) NHC polynuclear complexes and clusters which benefit from favorable d^{10}-d^{10} attractive interactions between silver(I) cations.[4a] In these complexes, the coordination geometry of the silver cations can deviate substantially from linearity to become ultimately trigonal or tetrahedral. By contrast, functionalized NHC ligands with donor pnictogen- and chalcogen-donor groups easily yield a broad structural diversity of NHC silver(I) clusters. Indeed, triangular [Ag$_3$]-cores complexes are often obtained with N-functionalizations such as pyridines, pyrazoles or imines.[6] [Ag$_4$]-cores of rectangular or square geometry are also frequent with N-heterocycles (pyridines, benzimidazoles, pyrazoles), thioethers, phosphines or pincers.[6g,7] Linear or open chain array of [Ag]$_\infty$-cores are also widespread with heterocyclic functionalities (pyrimidines, triazoles, benzimidazoles, pyrazoles, pyridines...) or even with phosphines.[8] Less frequently, pseudo-cubane [Ag$_4$] substructures with phosphinites or phenolate functionalizations[9] or even higher nuclearity cores, from [Ag$_6$]- to [Ag$_{10}$]-, can for example be observed with amine or pyridine functionalizations.[10] These diverse structures and nuclearities are both induced by the geometric constrain of the chelating or bridging ligands, and the ability of the silver(I) cations to aggregate through d^{10}-d^{10} interactions.

This structural diversity has recently been observed with phosphinite-[9a,9c] or thioether-[7c] functionalized NHCs which have allowed the formation of cubane- or rectangle-type [Ag$_4$] clusters, respectively. As an extension of these studies, we decided to study the reactivity of alcohol-functionalized NHC ligands with two main objectives: (*i*) explore their coordination behaviour toward silver(I) centres and the possibility of an intramolecular coordination of the weaker alcohol donor function, (*ii*) use these functionalized silver(I) NHC complexes as transmetallating reagents, in particular toward Ni(II) centres because of the potential of the latter complexes in catalytic ethylene oligomerization.[11]

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

RESULTS AND DISCUSSION
Alcohol functionalization

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The salt 3-(2-hydroxyethyl)-1-methyl-1*H*-imidazol-3-ium chloride ([ImMe(EtOH)]Cl, **3**) was prepared using a published procedure based on the quaternization of N-substituted imidazoles.[12] This procedure was modified for 1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1*H*-imidazol-3-ium chloride ([ImDiPP(EtOH)]Cl, **1**) and 1-mesityl-3-(2-hydroxyethyl)-1*H*-imidazol-3-ium chloride ([ImMes(EtOH)]Cl, **2**) to reduce the reaction times (Scheme 1). Avoiding the use of a solvent allowed access to higher reaction temperatures. The ^{1}H NMR spectra of **1-3** display the characteristic resonances of the NC*H*N protons around 9-10 ppm, in agreement with the formation of the imidazolium salts.
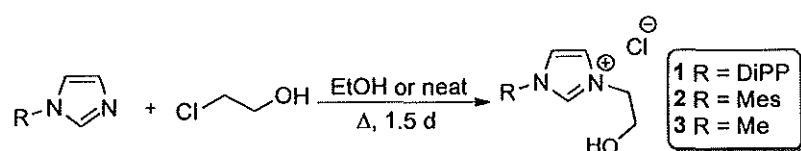
Scheme 1 Synthesis of the imidazolium salts **1-3**

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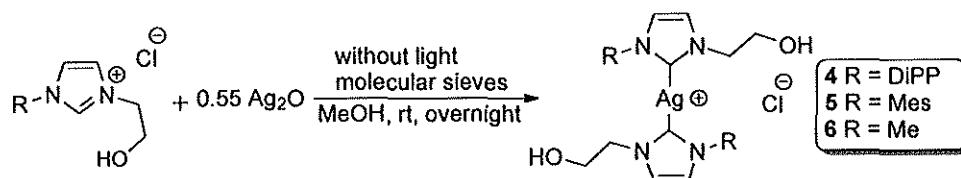
Scheme 2 Synthesis of the Ag(I) complexes **4-6**

Initially, the synthesis of **4** was carried out in CH$_2$Cl$_2$ with a conversion of 80% after 12 h. To reduce the reaction time, different solvents such as THF, MeOH, MeCN and DMSO were used and the best results were obtained with MeOH for which the reaction time was reduced to 4 h with 100% conversion.

The formation of the complexes **4-6** was confirmed by ^{1}H NMR spectroscopy with the complete disappearance of the characteristic signals of the imidazolium salts. The spectrum of **4** displays two apparent triplets for the imidazolium backbone proton signals at 7.27 and 6.92 ppm. Two doublets were initially expected for these magnetically non-equivalents and mutually coupled protons. Since both silver isotopes ^{107}Ag and ^{109}Ag are NMR active (S = ½), a heteronuclear ^{1}H-^{109}Ag HMQC experiment was carried out and revealed a $^4J(^1$H-^{109}Ag) coupling between the imidazolium protons and the silver (1.5 Hz).

In fact, these apparent triplets are doublets of doublets ($^3J(^1H\text{-}^1H)$ = 1.5 Hz and $^3J(^{107/109}Ag\text{-}^1H)$ = 1.5 Hz). This coupling highlights the lack of lability of the C-Ag bond on the NMR time-scale.[4a,b] ENREF_6 In the ^{13}C NMR spectra, the carbenic signals appear at 182.6 ppm for **4** and **5** and 181.2 ppm for **6**. For **4** and **5**, first and third order couplings with both $^{107/109}Ag$ isotopes are observable for the carbene and the backbone carbon atoms. They give rise to two sets of two doublets having the following coupling constants: $^1J(^{107}Ag\text{-}^{13}C)$ = 184 Hz, $^1J(^{109}Ag\text{-}^{13}C)$ = 212 Hz and $^3J(^{107/109}Ag\text{-}^{13}C)$ = 5.5 Hz and 5.9 Hz, respectively.

For these three complexes, an equilibrium between the [AgCl(NHC)] and [Ag(NHC)$_2$]Cl forms was observed in solution. It appears to be strongly dependent from the solvents and the presence of traces of water. Similar results were recently obtained with sulfonate-functionalized NHC silver(I) complexes.[13] ENREF_44 Preliminary studies performed in CDCl$_3$ indicated a slow decomposition of the complexes which could be avoided by filtering the chloroform solution through a plug of alumina (thus removing any trace of HCl). To confirm the instability of **4-6** toward acidic media, they were dissolved in dry CD$_2$Cl$_2$ in the presence of a small amount of an ether solution of HCl. Gratifyingly, the same decomposition pathway was recorded by NMR as in HCl-contaminated CDCl$_3$. The mass spectra of complexes **4** and **5** display only two signals for m/z = [Ag(NHC)$_2$]$^+$ and [(NHC)H]$^+$. For **6**, the fragment m/z = [(NHC)H$^+$] is too light to be detected, but numerous unidentified signals are visible. It is reasonable to assume that **4-6** are unstable under the analysis conditions and mainly reconverted to some imidazolium entities. There is no signal accounting for the formation of [AgCl(NHC)] or for any silver-containing species with m/z higher than [Ag(NHC)$_2$]$^+$. X-Ray quality crystals of **4-6** were grown by slow diffusion or evaporation of solutions of CH$_2$Cl$_2$/pentane, CH$_2$Cl$_2$/hexane, and ether, respectively (Figure 1 and Figure 2). The formation of complexes of the type [Ag(NHC)$_2$]X with X = Cl was thus confirmed, ruling out the formation of higher nuclearity silver complexes.
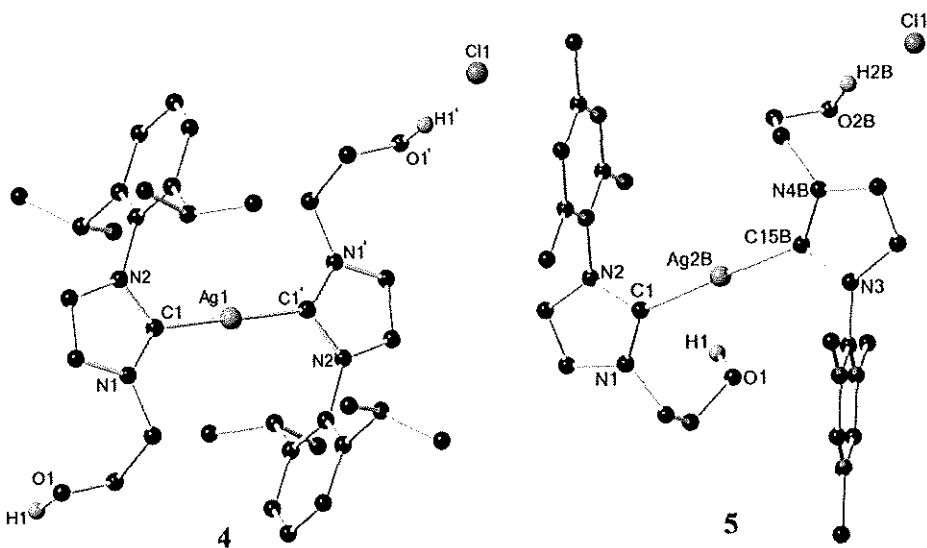
Figure 1 Ball and stick representation of the structure of [Ag{ImDiPP(EtOH)}₂]Cl, (4) and [Ag{ImMes(EtOH)}₂]Cl (5). Hydrogen atoms have been omitted for clarity, except the OH protons.
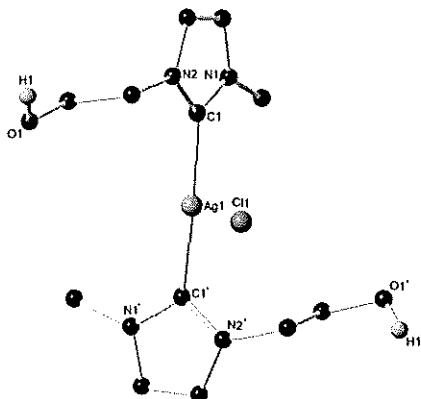

Figure 2 Ball and stick representation of the structure of [Ag{ImMe(EtOH)}₂]Cl (6). Hydrogen atoms have been omitted for clarity, except the OH protons.

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-1 space group. The unit cell of **4** contains 4 motifs including slightly disordered CH_2Cl_2 molecules around twofold axes commonly shared by the chloride anions. The silver centres are positioned on the intercept of glide mirrors and inversion centres. The unit cell of **6** contains also 4 motifs without any co-crystallized solvent. The silver and chloride ions are located on different twofold axes. The unit cell of **5** contains two motifs. There is no co-crystallized solvent, and no atom is located on special position. The Ag–C distances are comprised between 2.035(3) and 2.087(3) Å, in good agreement with other reported distances for homoleptic cationic bis-(NHC) silver(I) complexes.[4a,14] The C–Ag–C angles are in the range 172.3(1) -180.0(1)° and correspond to a nearly linear

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coordination environment. No interaction between the silver centres and the hydroxyl groups is noticeable in the solid state. By contrast with 4 and 5, the structure of 6 reveals an interaction between the silver centre and the chloride anion. The Ag–Cl distance of 3.189(2) Å suggests the existence of a weak electrostatic interaction. The C–Ag–Cl angle is equal to 93.86°. For all complexes, the crystal cohesion 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 cells. The complexes 4-6 are similar to other alcohol-functionalized NHC silver(I) complexes;[5d,15] 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.[16]

The synthesis of the complex bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1H-imidazol-2(3H)-ylidene)nickel(II) chloride ([NiCl$_2${ImDiPP(EtOH)}$_2$], 7) was attempted via transmetallation by reacting overnight 4 with [NiCl$_2$(dme)] (Scheme 3). The reaction was carried out in CH$_2$Cl$_2$ or MeOH and led to a deep green solution containing a mixture of paramagnetic product(s). Detailed NMR analyses were not possible, but confirmed the presence of imidazolium salts.
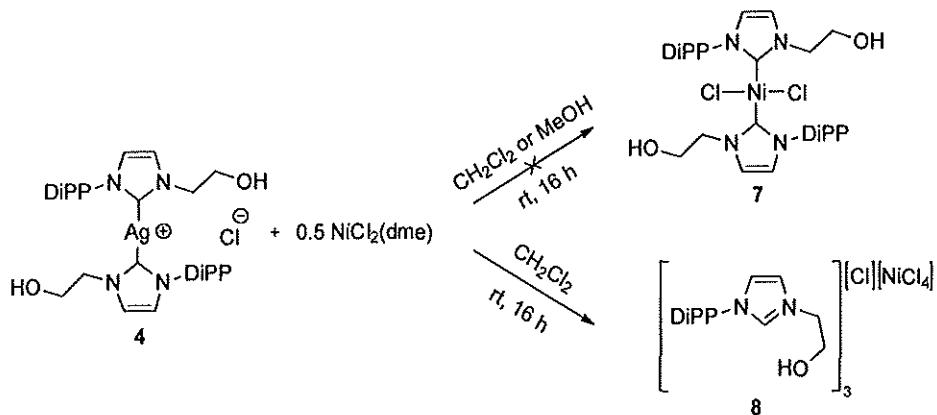
Scheme 3 Attempted synthesis of [NiCl$_2${ImDiPP(EtOH)}$_2$], 7 via transmetallation

Blue crystals were grown from the crude mixture, and their structure determination by X-ray diffraction established that reprotonation of the imidazolylidene moieties bound to silver has occurred, instead of their transfer to nickel, with formation of a mixed tetrachloronickelate / chloride imidazolium salt 8 (Figure 3). Although transmetallation leading to 7 would be accompanied by the precipitation of AgCl, formation of stable [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.
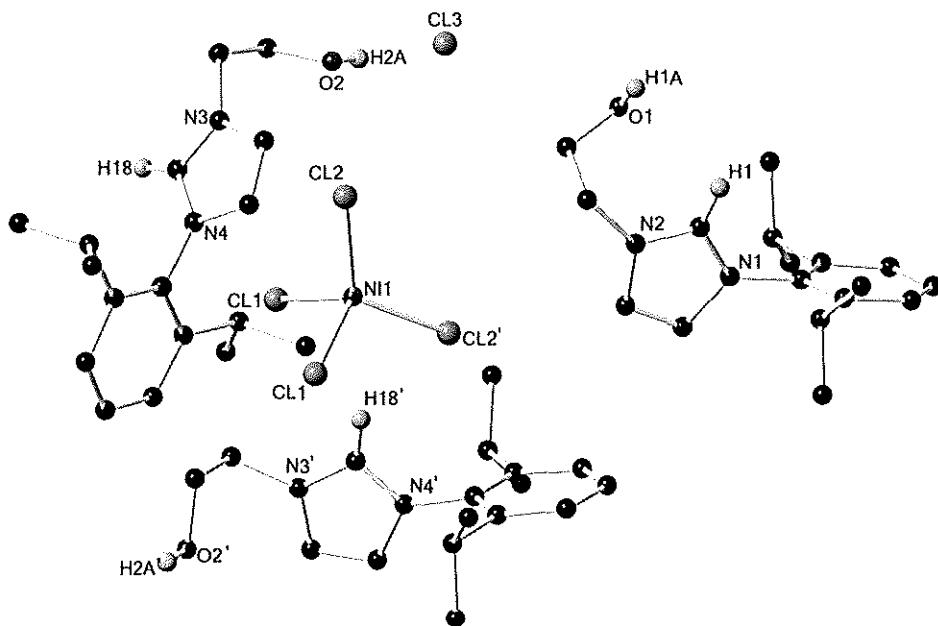
Figure 3 Ball and stick representation of **8**. Hydrogen atoms have been omitted for clarity, except the OH and the NCHN protons.

The salt **8** crystallizes in the orthorhombic system with the Sohncke space group $P2_12_12$. There are 4 motifs in the unit cell without any co-crystallized solvent. The nickel atoms are positioned along twofold axes and the $[NiCl_4]^{2-}$ 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 $[NiCl_4]^{2-}$.

To avoid the formation of $[NiCl_4]^{2-}$, the counterion Cl⁻ present in the silver complex **4** was replaced by the less coordinating anion 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)-1H-imidazol-2(3H)-ylidene)silver(I) tetrafluoroborate ([Ag{ImDiPP(EtOH)}$_2$]BF$_4$, **9**) was supported by the presence of a characteristic signal at -152.7 ppm in ^{19}F NMR spectroscopy. As for **4**, the ^1H and ^{13}C NMR spectra display first, third and fourth order couplings between the $^{107/109}Ag(I)$ centres and the imidazole backbone carbon and hydrogen atoms. In the ^1H NMR spectrum, the CH$_2$ proton signals of the spacer are shifted upfield (by 0.07 and 0.14 ppm) compared to **4**, and one of the imidazole backbone proton is shifted downfield by 0.06 ppm. The CH^{m-Ar} is shifted downfield in contrast to the CH^{p-Ar} which is shifted upfield (both by 0.06 ppm). The CH$_3$^{iPr} are shifted downfield by 0.07 and 0.03 ppm whereas the CH^{iPr} is not affected. The anion exchange has no significant influence on the chemical shifts measured on the ^{13}C NMR spectra of both complexes, except for the appearance in the spectrum of **9** of an unexpected third order coupling between the $^{107/109}Ag(I)$ and the N-C carbon atoms of the alcohol side chain (^3J = 2.2 Hz).

7
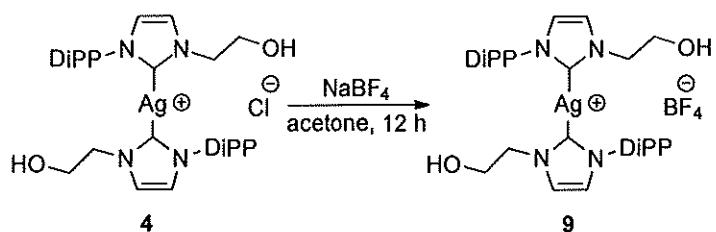
Scheme 4 Formation of [Ag{ImDiPP(EtOH)}$_2$]BF$_4$, 9

The structure of 9 was confirmed by X-ray diffraction on single crystals obtained by slow diffusion of pentane into a saturated CH$_2$Cl$_2$ solution (Figure 4).
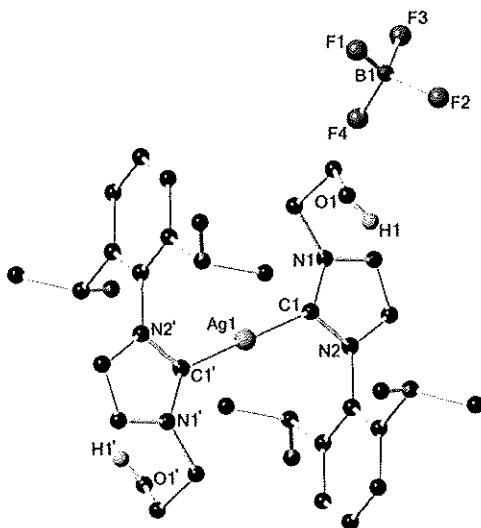

Figure 4 Ball and stick representation of [Ag{ImDiPP(EtOH)}$_2$]BF$_4$, 9. Hydrogen atoms have been omitted for clarity, except the OH protons.

The complex 9 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(6) Å. The 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.

The complex 9 was reacted in dry MeCN or THF with different nickel precursors known to lead to (NHC) nickel(II) complexes by transmetallation, such as [NiBr$_2$(PPh$_3$)$_2$], [NiCl$_2$(dme)], [Ni(MeCN)$_4$](BF$_4$)$_2$ or [NiBr$_2$(dme)]. The formation of [NiX$_4$]$^{2-}$ (X = Cl or Br) was not observed. Due to the paramagnetic nature of the products formed, ^{1}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 functionalizations

In order to corroborate that reprotonation of the carbene ligand in transmetallation step conditions is due to the OH proton of the alcohol, protection of the latter 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(EtOTMS)]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(EtOTMS)}₂]Cl, **11**), the same procedure as 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 NEt₃) were used. Both compounds **10** and **11** were identified by ¹H NMR 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 revealed to be stable. During the formation of the silylether, the HCl released might be trapped by HMDS or NEt₃ or react with **11**, thus explaining the formation of imidazolium salt. (Scheme 5)
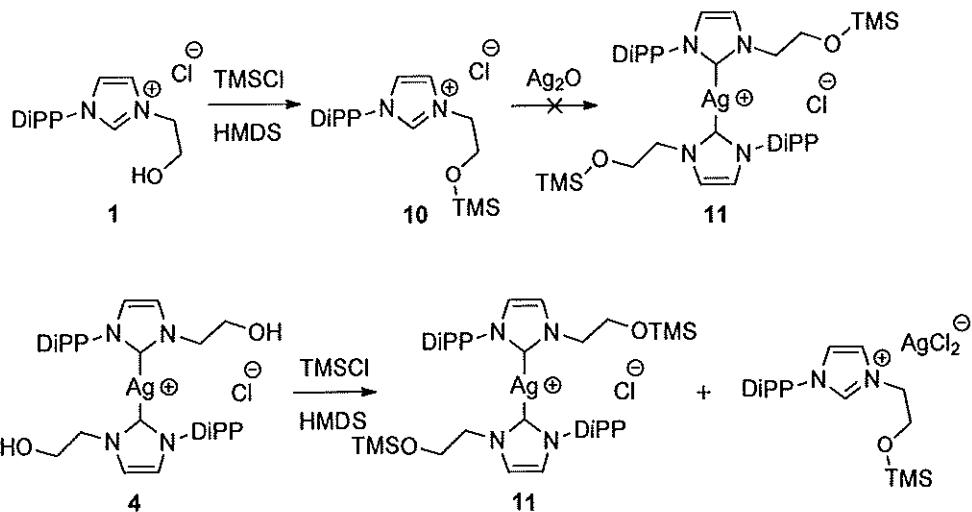
Scheme 5 Attempt to synthesize [Ag{ImDiPP(EtOTMS)}₂]Cl, 11 with TMSCl

The synthesis of functionalized silylether NHC silver(I) complexes being ineffective, attempts were undertaken with an ether-functionalized NHC. The ligand 1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1H-imidazol-3-ium chloride ([ImDiPP(EtOMe)]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)-1H-imidazol-2(3H)-ylidene)silver(I) chloride ([Ag{ImDiPP(EtOMe)}₂]Cl, **13**) was readily formed by reaction of **12** with 0.55 equiv. of Ag₂O (Scheme 6).
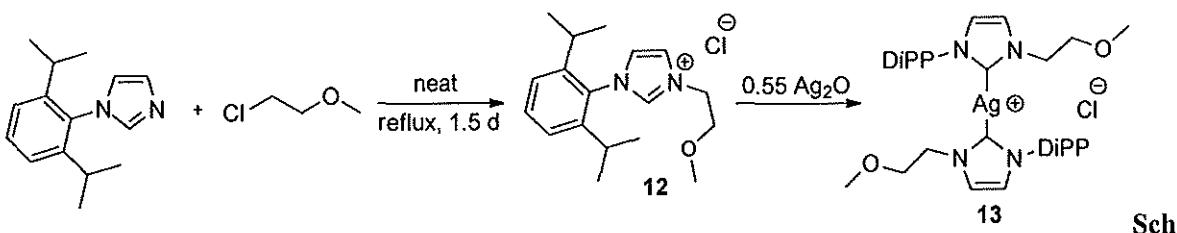
Sch eme 6 Synthesis [(EtOMe)DiPPIm]Cl (**12**) and [(EtOMe)DiPPIm]₂AgCl (**13**)

The disappearance of the imidazolium NCHN proton was observed in the ^{1}H NMR spectrum. As observed with **4**, a $^4J(^{107/109}$Ag-^{1}H) coupling of 1.5 Hz with the backbone imidazolium hydrogen atoms is visible. The formation of complex **13** was established also by the characteristic downfield shift of the carbenic carbon at 182.4 ppm, which exhibits a first order coupling with the $^{107/109}$Ag isotopes (^1J = 184 and 213 Hz, respectively). A third order coupling between the imidazole backbone carbon atoms and the $^{107/109}$Ag isotopes (^3J = 5.9 and 5.7 Hz) is visible as well as a third order coupling with the N-C carbon atom from the ether side chain (^3J =2.2 Hz), as for **9**. By contrast with **4-6**, the mass spectrum of **13**

displays only the characteristic signal at m/z = 681.31 for $[Ag(NHC)_2]^+$, without any trace of reprotonation/decomposition.

Colourless crystals were grown by dissolving **13** in pure CH_2Cl_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 [Ag{ImDiPP(EtOMe)}₂]Cl, **13** as well as the less anticipated neutral mono-NHC complex [AgCl{ImDiPP(EtOMe)}], **14**.[13] (Figure 5)
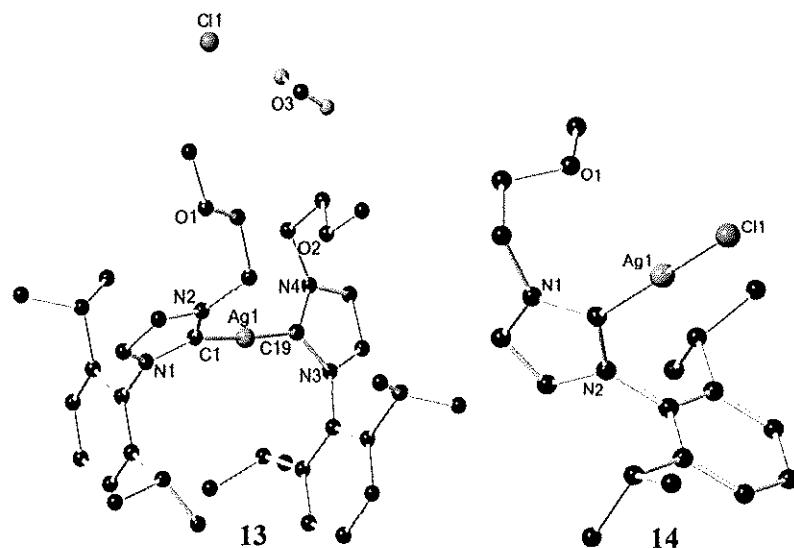
Figure 5 Ball and stick representation of [Ag{ImDiPP(EtOMe)}₂]Cl, **13** and [AgCl{ImDiPP(EtOMe)}], **14**. Hydrogen atoms have been omitted for clarity, except the OH protons.

Complexes **13** and **14** crystallize respectively in the triclinic system with the P-1 space group, and the monoclinic system with the $P2_1/c$ space group, 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 on special positions. For **13** the Ag–C distances are equal to 2.075(3) and 2.077(3) 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 are equal to 2.084(4) and 2.323(2) Å and the C–Ag–Cl angle is 173.7(1)°. These values are in excellent agreement with those reported in the literature for similar [AgCl(NHC)] complexes.[4a,16c,17] 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. 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 interact with a hydrogen atom from the imidazole ring of an adjacent molecule.

The reaction of **13** with [NiCl₂(dme)] overnight afforded an orange solution with a white precipitate of AgCl. The solution was filtered through Celite and the solvent was removed under reduced pressure. The resulting orange solid was washed with H_2O, redissolved in toluene and dried over Na_2SO_4, affording **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 ([NiCl₂{ImDiPP(EtOMe)}₂], **15**) was confirmed by ^{13}C NMR spectroscopy with the displacement of the carbene chemical shift from 182.4 ppm to 171.7 ppm, in the range of reported values for other Ni(II) NHC complexes.[18]
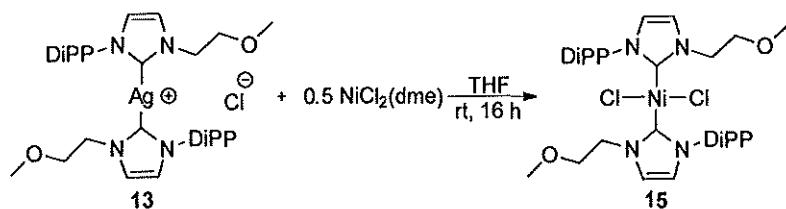
Scheme 7 Synthesis of [NiCl₂{ImDiPP(EtOMe)}₂], **15** by transmetallation

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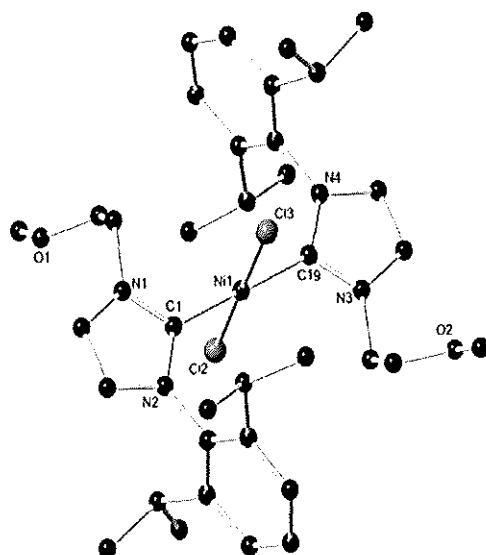

Figure 6 : Ball and stick representation of [NiCl₂{ImDiPP(EtOMe)}₂], **15**. Hydrogen atoms have been omitted for clarity.

This complex crystallizes in the orthorhombic system with four motifs per unit cell without any solvent included. There is no atom on 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 2.1823(8), 2.1828(8) Å. The C−Ni−C and Cl−Ni−Cl angles are equal to 179.1(2) and 179.73(3)°. The metrical data of **15** are in excellent agreement with those reported for similar square-planar bis-NHC Ni(II) dichloride complexes.[18]

Surprisingly, while ^{1}H NMR spectroscopy clearly indicated the presence of **15**, another, minor species (*ca.* 10%) was also present which displays very similar features: its CH_2 and CH_2^{OMe} signals are shifted downfield by 0.69 and 0.34 ppm while its CH^{iPr} and CH_3^{iPr} signals are shifted upfield by 0.21 and 0.32 ppm. No significant shift in the ^{13}C NMR spectrum was noticeable between the two species. Attempts to separate this species by flash chromatography were unsuccessful. Re-dissolution of authentic crystals of **15** in deuterated solvents resulted in the reformation of both species in the same ratio. Infrared spectra of crystals and bulk powder of **15** did not reveal any difference, in agreement with the existence of only one type of complex in the solid state. Consequently, a dynamic equilibrium in solution was suspected between the two species and it could be further confirmed by a ROESY NMR experiment. Different types of equilibrium for NHC nickel complexes, in solution, can be considered (e.g: modification of the complex geometry via *cis/trans*-isomers, or exchange between *syn/anti*-conformations).[19] Work currently in progress aims at investigating further these equilibriums and at extending the family of ether-functionalized NHC nickel(II) complexes in order to evaluate their catalytic properties.

Preliminary catalytic studies on ethylene oligomerization were performed with **15** in the presence of 10 equiv. of ethylaluminium dichloride (EADC) and indicate a low to moderate activity with a productivity of 4600 C_2H_4 (g Ni h)$^{-1}$ and a TOF of 9600 mol C_2H_4 (mol Ni h)$^{-1}$. C_4 olefins were mostly obtained (64 %) with a selectivity of 52 % mol for 1-butene.

Conclusion

We have obtained a series of non-symmetric alcohol, silylether or ether functionalized imidazolium salts and their corresponding bis-NHC silver(I) complexes. The cationic bis-NHC silver(I) complexes **4, 5, 6, 9** and **13** were structurally characterized. Access to functionalized alcohol-NHC silver complexes may have an interesting potential for the anchoring of moieties with interesting biological or pharmaceutical properties *via* formation of *e.g.* ether or ester bonds. Whereas no direct interaction was

observed between these oxygen-containing groups and the Ag(I) centre, the presence of an OH group on the NHC ligand was found to be detrimental to applications in transmetallation reactions involving Ni(II) centres since reprotonation of the carbene carbon was observed instead. In contrast, the ether-functionalized NHC nickel(II) complex **15** was readily obtained from **13**, emphasizing the potential of ether-functionalized NHC silver(I) complexes to act as efficient transmetallating agents. We are currently using this approach to synthesize a series of ether functionalized NHC Ni(II) complexes for ethylene oligomerization purposes.

Acknowledgments

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