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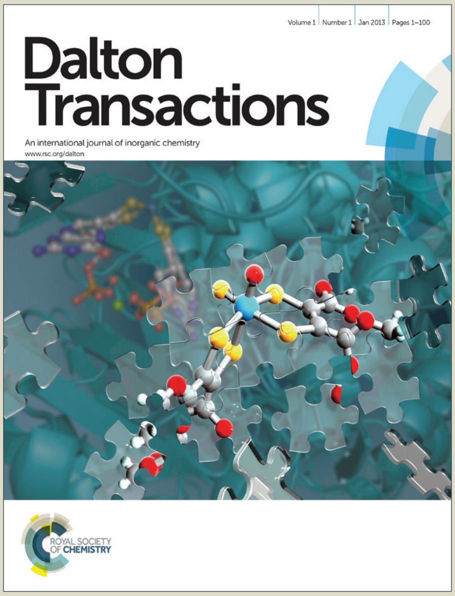

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Synthesis and characterization of oxygen-functionalised-NHC silver(I) complexes and NHC transmetallation to nickel(II) †

Sophie Hameury,[a] Pierre de Frémont,[a] Pierre-Alain Breuil,[b] Hélène Olivier-Bourbigou,[b]
Pierre Braunstein [a] *

ABSTRACT

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_2OH)}$_2$]Cl (**4**), bis(1-(2-hydroxyethyl)-3-mesityl-1*H*-imidazol-2(3*H*)-ylidene)silver(I) chloride, [Ag{ImMes(C_2OH)}$_2$]Cl (**5**), bis(1-(2-hydroxyethyl)-3-methyl-1*H*-imidazol-2(3*H*)-ylidene)silver(I) chloride, [Ag{ImMe(C_2OH)}$_2$]Cl (**6**), bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)silver(I) tetrafluoroborate, [Ag{ImDiPP(C_2OH)}$_2$]BF_4 (**9**), and bis(1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)silver(I) chloride, [Ag{ImDiPP(C_2OMe)}$_2$]Cl (**13**), were synthesized and fully characterized by NMR spectroscopy and single crystal X-ray diffraction. For some complexes, an uncommon heteronuclear coupling $^4J(^{107/109}\text{Ag-H})$ was unveiled. Their ability to transfer the NHC ligand to Ni(II) was assessed in 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, [$NiCl_2${ImDiPP(C_2OMe)}$_2$] (**15**), was obtained from **13** and shown by X-ray diffraction study to have a *trans*- arrangement of the two NHC ligands. However, and 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_{NHC} and isolation of the corresponding imidazolium salts.

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[a] Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, CS 90032, 67081 Strasbourg, France

[b] IFP Energies Nouvelles, Rond Point de l'Echangeur de Solaize, 69360 Solaize, France

† Electronic Supplementary Information (ESI) available: all experimental and spectroscopic details and crystal data of **4-6**, **8**, **9** and **13-15** with ORTEP views. The Crystallographic information files (CIF) 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 963275–963282. This material is also available free of charge via the Internet at http://pubs.rsc.org.

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, in particular to prepare new metal-based catalysts.[2] One of the convenient synthetic methods to access NHC transition metals complexes consists of the use of the corresponding Ag(I)-NHC complexes as NHC transfer reagents, which avoids the cumbersome synthesis of free carbenes.[3] Generally, these silver complexes are readily synthesized, by reaction of the corresponding imidazolium salts with silver(I) oxide, without the need to work under inert atmosphere.[4] 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.[5]

Non-functionalised NHC ligands of the type bis-(alkyl/aryl)-imidazol(in)-ylidenes form either neutral [AgX(NHC)], or cationic $[Ag(NHC)_2]X$ (X = e.g. halide, BF_4, PF_6) 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 $[Ag_nX_m]^{m-n}$ polynuclear complexes, through capping or bridging coordination modes of X, associated with coordination to $[Ag(NHC)]^+$ or $[Ag(NHC)_2]^+$ moieties, can give rise to a large variety of silver(I) NHC polynuclear complexes or coordination clusters which benefit from favorable d^{10}-d^{10} attractive interactions between silver(I) cations.[4a,6] 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 $[Ag_3]$-cores can often be obtained when N-functions such as pyridines, pyrazoles or imines are present.[7] $[Ag_4]$-cores 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.[7g,8] Linear or open chain arrays of $[Ag_\infty]$-cores are also widespread with heterocyclic functionalities (pyrimidines, triazoles, benzimidazoles, pyrazoles, pyridines etc.) or with phosphines.[9] Less frequently, pseudo-cubane $[Ag_4]$ substructures with phosphinites or phenolate functionalisations[10] or even higher nuclearity cores, from $[Ag_6]$ to $[Ag_{10}]$, have been observed e.g. with amine or pyridine functionalisations.[11] 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.[4a,6]

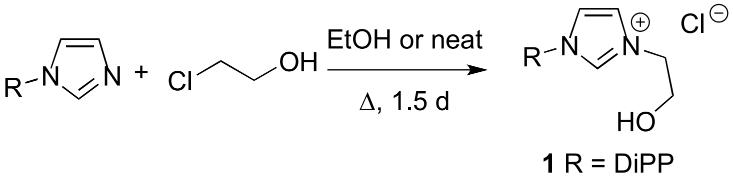
We have recently observed this structural diversity with phosphinite-[10a,10c] or thioether-[8c,j] functionalised NHCs which led to the formation of cubane- or rectangle-type $[Ag_4]$ clusters, respectively. As an extension of these studies, we decided to study the reactivity of hydroxy-functionalised 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 the potential of the resulting complexes in catalytic ethylene oligomerization.[12] Indeed, numerous non-functionalised-NHC nickel(II) complexes have already been synthesized and shown to be active pre-catalysts toward ethylene oligomerization.[12b,c,13] 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.[14] 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) halides complexes.[15]

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.

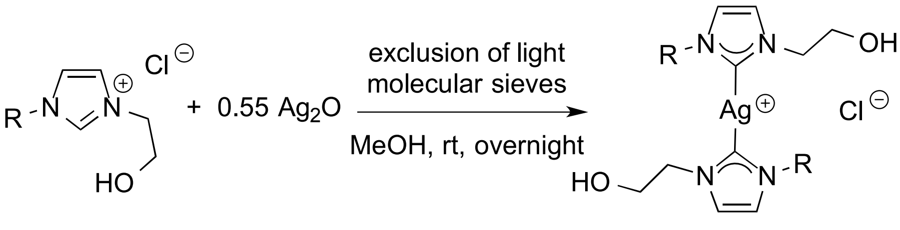
The salt 3-(2-hydroxyethyl)-1-methyl-1*H*-imidazol-3-ium chloride ([ImMe(C_2OH)]Cl, **3**) was prepared by the quaternization of N-substituted imidazoles following a published procedure.[16] This procedure was modified for the synthesis of 1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1*H*-imidazol-3-ium chloride, [ImDiPP(C_2OH)]Cl (**1**), and 1-mesityl-3-(2-hydroxyethyl)-1*H*-imidazol-3-ium chloride, [ImMes(C_2OH)]Cl (**2**), to reduce the reaction times (Scheme 1) (All experimental details for this paper are given in the Supporting Information). 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-(arylmidazolium)-pyridines[7h,17a] and applied on many other occasions e.g. to the synthesis of precursors to amine-tethered NHC rhodium complexes.[17b] The ^1H NMR spectra in CD_2Cl_2 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.



1 R = DiPP
2 R = Mes
3 R = Me

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_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)-1*H*-imidazol-2(3*H*)-ylidene)silver(I) chloride, [Ag{ImDiPP(C_2OH)}$_2$]Cl (**4**), bis(1-(2-hydroxyethyl)-3-mesityl-1*H*-imidazol-2(3*H*)-ylidene)silver(I) chloride, [Ag{ImMes(C_2OH)}$_2$]Cl (**5**), and bis(1-(2-hydroxyethyl)-3-methyl-1*H*-imidazol-2(3*H*)-ylidene)silver(I) chloride, [Ag{ImMe(C_2OH)}$_2$]Cl (**6**), respectively, in good to excellent yields (77-93%) (Scheme 2). The complexes **4** and **5** are stable towards moisture in ambient daylight while **6** is not.

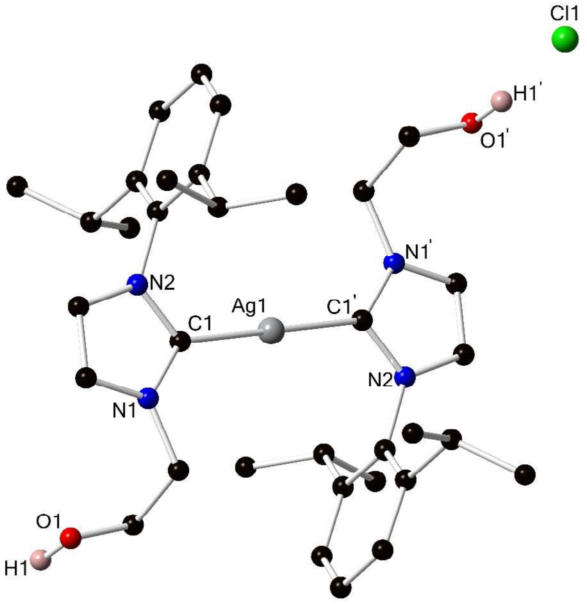


4 R = DiPP
5 R = Mes
6 R = Me

Scheme 2 Synthesis of the Ag(I) complexes **4-6**

It was found that the use of methanol as 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, 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 the complexes **4-6** was confirmed by ^{1}H 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 experiments were carried out in order to rationalise the appearance of the observed spectra. 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(H-^{109}Ag) coupling between the backbone imidazole protons and silver (1.5 Hz). Careful inspection shows that these apparent triplets are actually doublets of doublets (^3J(H-H) = 1.5 Hz and ^3J($^{107/109}$Ag-H) = 1.5 Hz). The observation of the ^4J(H-^{109}Ag) coupling highlights the lack of lability of the C-Ag bond on the NMR time-scale.[4a,b] In the ^{13}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 $^{107/109}$Ag isotopes are observable for the carbene and the imidazol backbone carbon atoms, respectively. They give rise to two sets of two doublets having the following coupling constants: ${}^{1}J({}^{107}\mathrm{Ag}\text{-}{}^{13}\mathrm{C})$ = 184 and 182 Hz, ${}^{1}J({}^{109}\mathrm{Ag}\text{-}{}^{13}\mathrm{C})$ = 212 and 210 Hz and ${}^{3}J({}^{107/109}\mathrm{Ag}\text{-}{}^{13}\mathrm{C})$ = 5.5 and 5.0 Hz, respectively. For all three complexes, ^{1}H NMR spectroscopy indicates the presence of both [AgCl(NHC)] and $[\mathrm{Ag(NHC)_2}]^+$ in solution,[7h] which are known to be in equilibrium when the counterion associated with the latter is $[\mathrm{AgCl_2}]^-$ (its progressive decomposition in Ag(0) or AgCl liberates Cl^- anions and affects the equilibrium).[18] Preliminary studies performed in $\mathrm{CDCl_3}$ 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 HCl). To confirm the instability of **4-6** toward acidic media, they were dissolved in dry $\mathrm{CD_2Cl_2}$ 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 $\mathrm{CDCl_3}$. The ESI mass spectra of complexes **4** and **5** display only two signals for m/z = $[\mathrm{Ag(NHC)_2}]^+$ and $[\mathrm{(NHC)H}]^+$. For **6**, the fragment m/z = $[\mathrm{(NHC)H^+}]$ 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 [AgCl(NHC)] or for any silver-containing species with m/z higher than $[\mathrm{Ag(NHC)_2}]^+$. X-Ray quality crystals of **4-6** were grown by slow diffusion or evaporation of solutions of $\mathrm{CH_2Cl_2}$/pentane, $\mathrm{CH_2Cl_2}$/hexane, and ether, respectively (Figure 1 and 2) (the ORTEP views of all complexes are given in the Supporting Information). The formation of complexes of the type $[\mathrm{Ag(NHC)_2}]$X with X = Cl was thus confirmed, ruling out the formation of higher nuclearity silver complexes.



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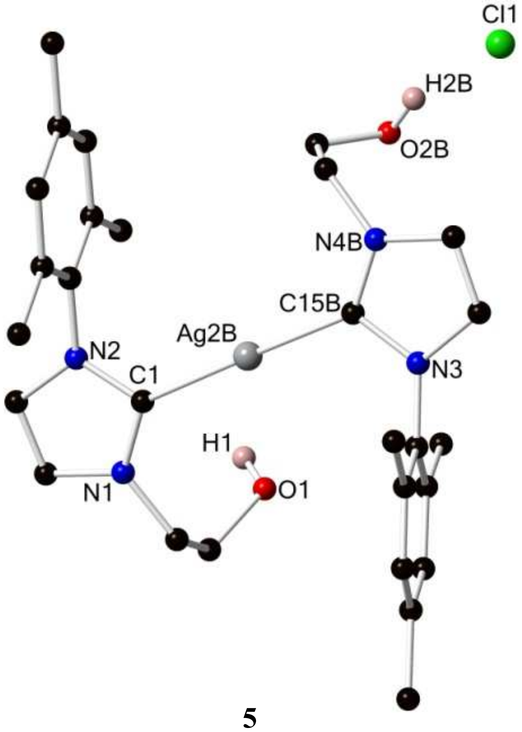

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Figure 1 Ball and stick representation of the structures of [Ag{ImDiPP(C_2OH)}$_2$]Cl (**4**) (top) and [Ag{ImMes(C_2OH)}$_2$]Cl (**5**) (bottom). Hydrogen atoms have been omitted for clarity, except the OH protons (ORTEP views are provided in Figures S3 and S4 of the ESI).

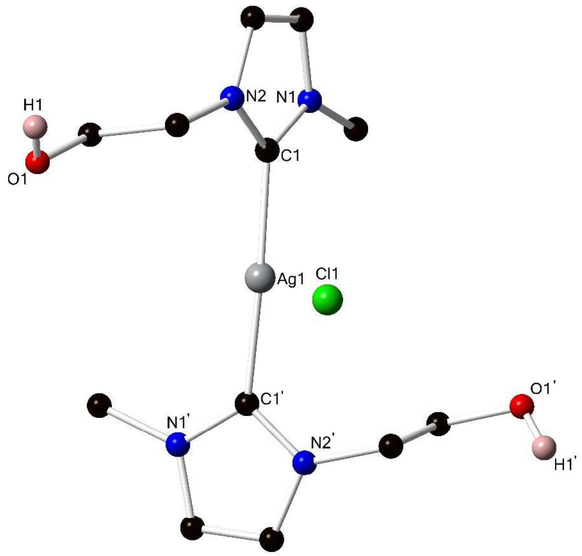
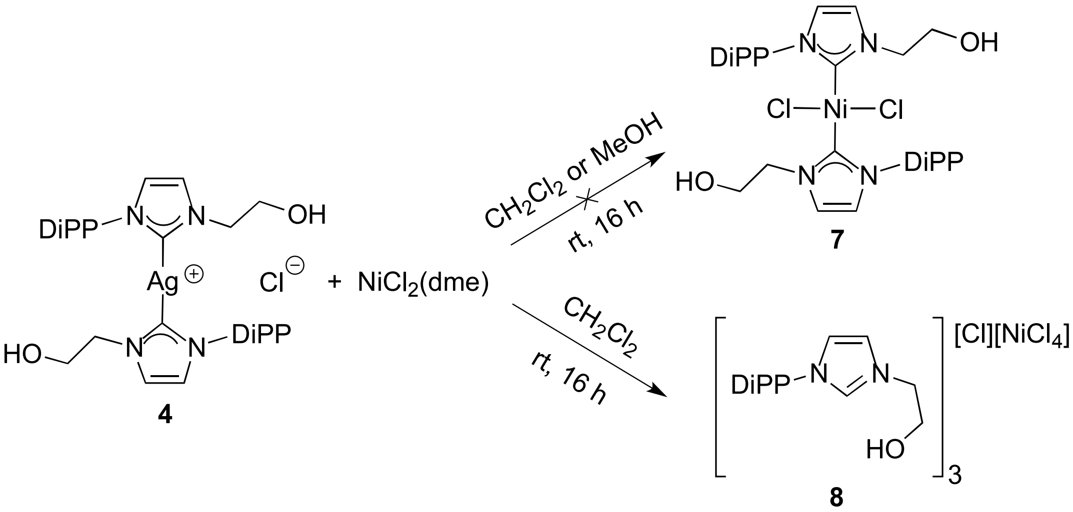


Figure 2 Ball and stick representation of the structure of $[Ag\{ImMe(C_2OH)\}_2]Cl$ (**6**). Hydrogen atoms have been omitted for clarity, except the OH protons (an ORTEP view is provided in Figure S5 of the ESI).

Complexes **4** and **6** crystallize in the monoclinic system with the *C*2/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 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.[4a,19] The C−Ag−C angles are in the range 174.8(3) - 180.0° 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 interaction between the silver centre and the chloride anion. The C−Ag−Cl angle is equal to 93.8(1)°. Similarly to other structures,[18b,20] the Ag−Cl distance of 3.189(2) Å implies a weak electrostatic interaction, not strong enough to perturb substantially the linear coordination geometry around the silver centre. Thus the chloride is considered as counter-anion for the $Ag(NHC)_2^+$ 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. The complexes **4-6** are similar to other alcohol-functionalised NHC silver(I) complexes;[5d,21] 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.[22]

The synthesis of the complex bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyethyl)-1*H*-imidazol-2(3*H*)-ylidene)nickel(II) chloride, [$NiCl_2${ImDiPP(C_2OH)}$_2$] (**7**), was attempted via transmetallation by reacting overnight **4** with [$NiCl_2$(dme)] (Scheme 3). This classic method for the synthesis of Ni(II)-NHC complexes[9c,23] was expected to yield a NHC nickel complex bearing a hydroxyethyl arm. The reaction was carried out in CH_2Cl_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(C_2OH)}$_2$] (**7**) via transmetallation

Blue crystals were grown from the crude reaction 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. The salt **8** crystallizes in the orthorhombic system with the Sohncke space group $P2_122_1$. 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 $[NiCl_4]^{2-}$.

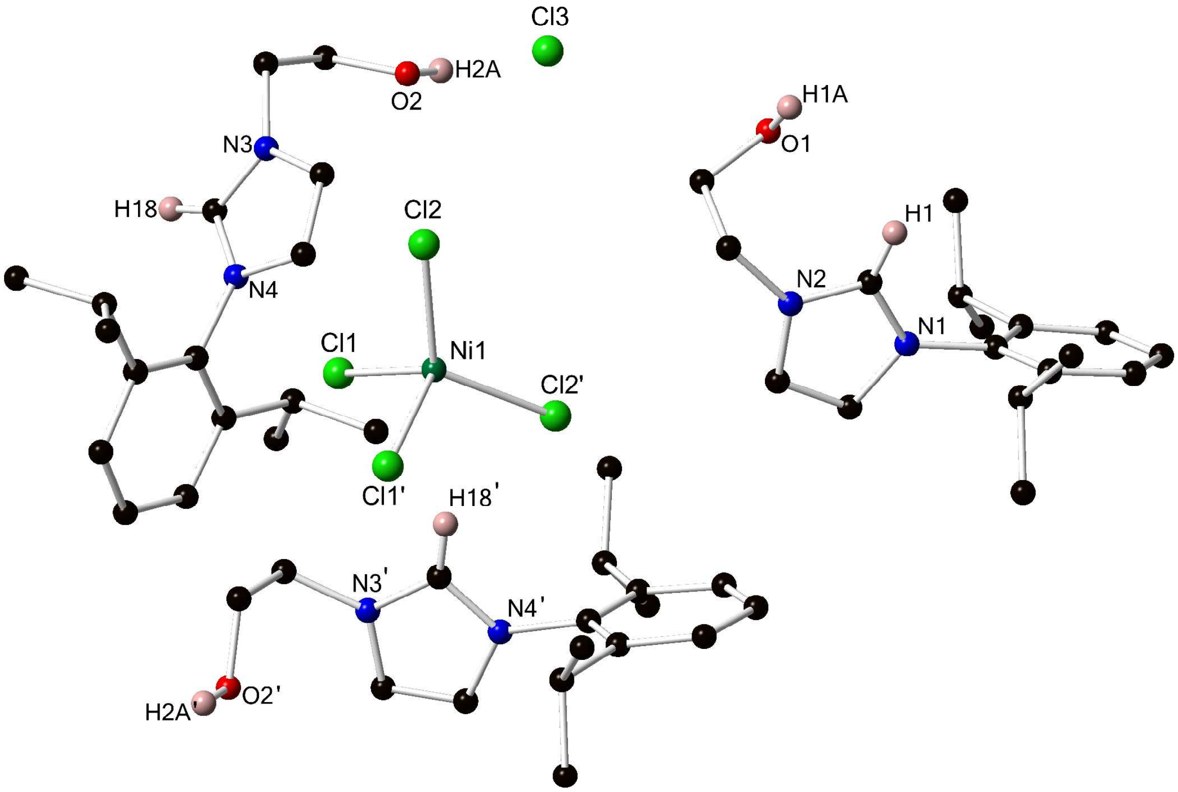
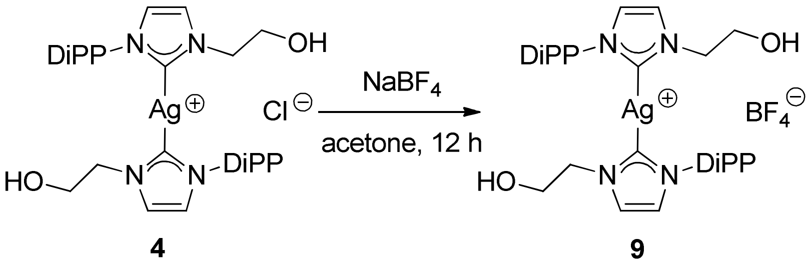


Figure 3 Ball and stick representation of **8**. Hydrogen atoms have been omitted for clarity, except the OH and the NCHN protons (an ORTEP view is provided in Figure S6 of the ESI).

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}H NMR broad peaks were observed in DMSO-d_6.

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)-1*H*-imidazol-2(3*H*)-ylidene)silver(I) tetrafluoroborate, $[Ag\{ImDiPP(C_2OH)\}_2]BF_4$ (**9**), was supported by the presence of a characteristic signal at -152.7 ppm in ^{19}F NMR spectroscopy. As for **4**, the ^{1}H and ^{13}C NMR spectra display ^{4}J and ^{3}J couplings between the $^{107/109}$Ag(I) nuclei and the imidazole backbone hydrogen and carbon atoms, respectively. In the ^{1}H NMR spectrum of **9**, the signals of the spacer CH_2 protons are shifted upfield compared to **4** (by 0.18 and 0.10 ppm for the CH_2 protons α and β to N, respectively) and one of the imidazole backbone proton is shifted downfield by 0.06 ppm. The $CH^{m\text{-}Ar}$ is shifted downfield in contrast to the $CH^{p\text{-}Ar}$ 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 a ^{3}J coupling (^{3}J = 2.2 Hz) between the N-C carbon atoms of the alcohol side chain and $^{107/109}$Ag(I).



Scheme 4 Synthesis of [Ag{ImDiPP(C_2OH)}$_2$]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_2Cl_2 solution (Figure 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 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 Figure S1 in the ESI).

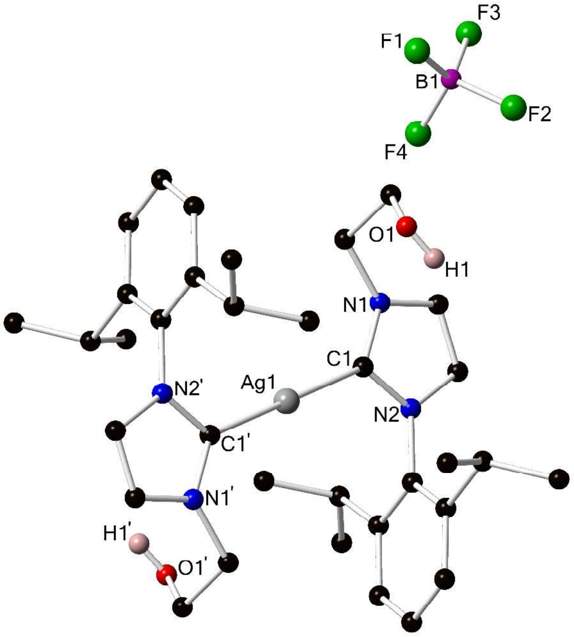
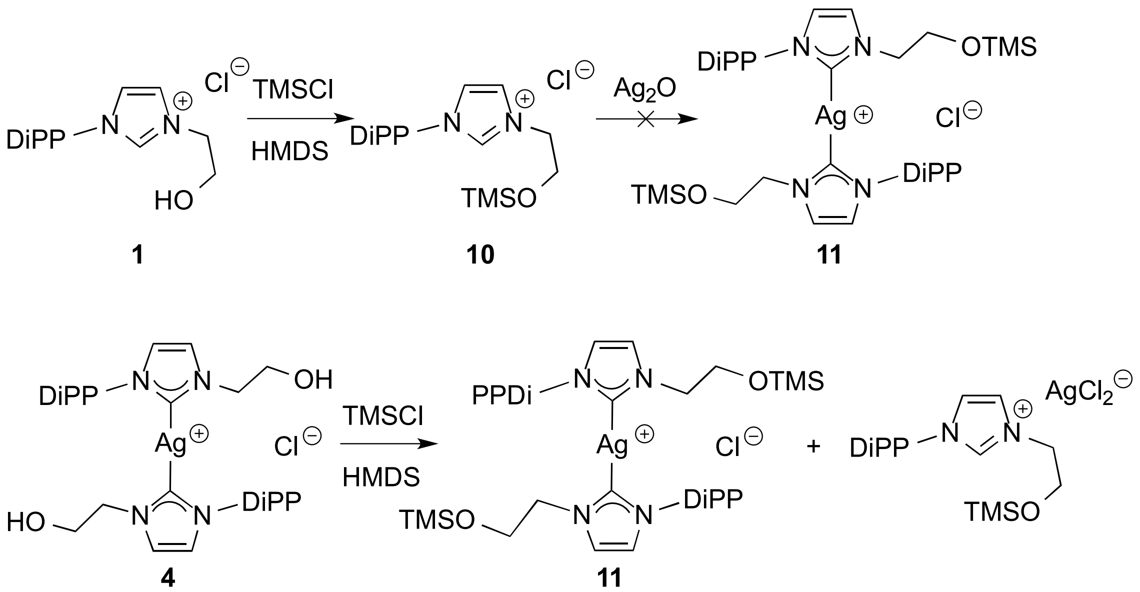


Figure 4 Ball and stick representation of [Ag{ImDiPP(C_2OH)}$_2$]BF_4 (**9**). Hydrogen atoms have been omitted for clarity, except the OH protons (an ORTEP view is provided in Figure S7 of the ESI).

Complex **9** was reacted in dry MeCN or THF with different nickel precursors generally known to lead to NHC nickel(II) complexes by transmetallation, such as [$NiBr_2(PPh_3)_2$], [$NiCl_2$(dme)], [$Ni(NCMe)_4](BF_4)_2$ 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.

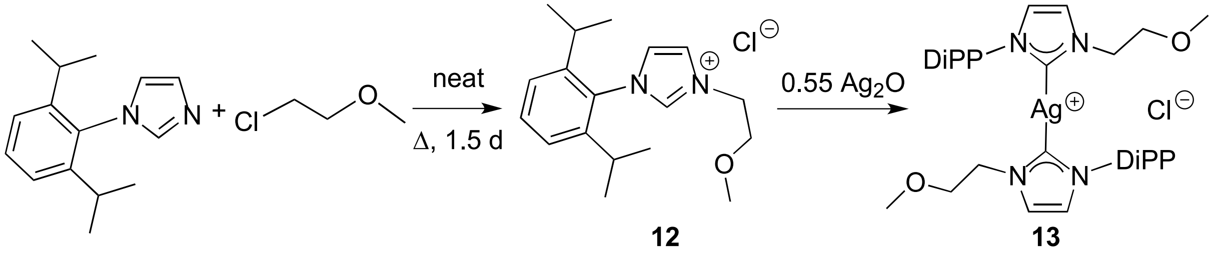
Silylether- and ether-functionalised NHC complexes

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_2OTMS)]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_2OTMS)}$_2$]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_3) were used. Both compounds **10** and **11** were identified by ^{1}H and ^{13}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 revealed to be stable. During the formation of the silylether, the HCl released might be trapped by HMDS or NEt_3 or react with **11**, thus explaining the formation of imidazolium salt (Scheme 5).



Scheme 5 Attempted syntheses of [Ag{ImDiPP(C_2OTMS)}$_2$]Cl (**11**) with TMSCl

The synthesis of silylether-functionalised NHC silver(I) complexes being unsuccessful, attempts were undertaken with an ether-functionalised NHC. The ligand 1-(2,6-diisopropylphenyl)-3-(2-methoxyethyl)-1*H*-imidazol-3-ium chloride, [ImDiPP(C_2OMe)]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_2OMe)}$_2$]Cl (**13**), was readily formed by reaction of **12** with 0.55 equiv. of Ag_2O (Scheme 6).

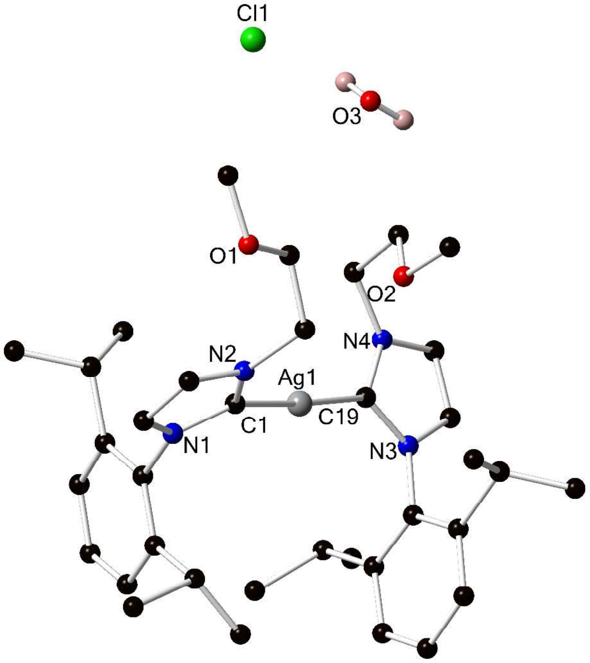


Scheme 6 Synthesis [ImDiPP(C_2OMe)]Cl (**12**) and [Ag{ImDiPP(C_2OMe)}$_2$]Cl (**13**)

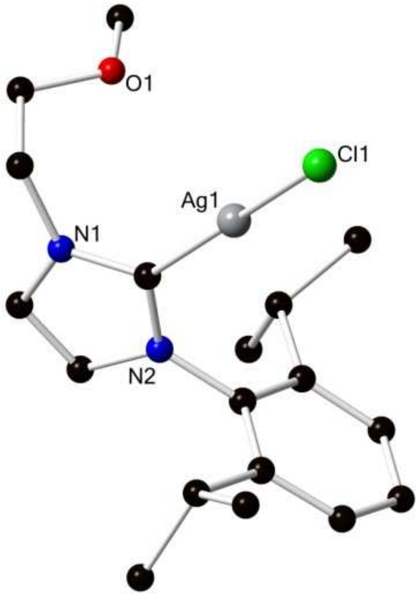
The disappearance of the imidazolium NC*H*N proton was observed in the ^{1}H NMR spectrum. As observed with **4**, a $^4J(^{107/109}$Ag-H) coupling of 1.5 Hz with the backbone imidazole hydrogen atoms is visible. The formation of **13** was also established by the characteristic downfield shift of the carbenic carbon at 182.4 ppm, which exhibits coupling with the $^{107/109}$Ag isotopes ($^1J(^{107/109}$Ag-^{13}C) = 183 and 212 Hz, respectively). A ^3J coupling between the imidazole backbone carbon atoms and the $^{107/109}$Ag isotopes

($^{3}J(^{107/109}$Ag-^{13}C) = 5.8 and 5.7 Hz) is visible as well as a $^{3}J(^{107/109}$Ag-^{13}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 $[Ag(NHC)_2]^+$, 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 **13** and of the less anticipated neutral mono-NHC complex [AgCl{ImDiPP(C_2OMe)}] (**14**)[18a] (Figure 5).



13



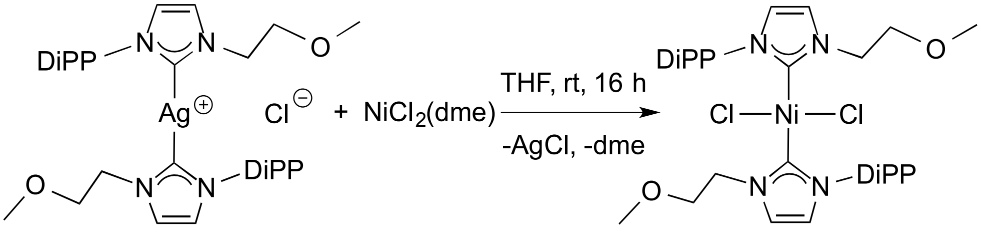
14

Figure 5 Ball and stick representation of [Ag{ImDiPP(C_2OMe)}$_2$]Cl (**13**) (top) and [AgCl{ImDiPP(C_2OMe)}] **(14)** (bottom). Hydrogen atoms have been omitted for clarity, except the OH protons (ORTEP views are provided in Figures S8 and S9 of the ESI).

Complexes **13** and **14** crystallize in the triclinic system with the *P*-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 on 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 [AgCl(NHC)] complexes.[4a,22c,24] 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 Figure 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 [$NiCl_2$(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 H_2O and redissolved in toluene, the solution was dried over Na_2SO_4 and 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 ([$NiCl_2${ImDiPP(C_2OMe)}$_2$], **15**) was confirmed by ^{13}C NMR spectroscopy with the displacement of the carbene chemical shift from 182.4 ppm to 171.7 ppm, a value which is in the range of those reported for other Ni(II) NHC complexes.[25]



13 **15**

Scheme 7 Synthesis of [$NiCl_2${ImDiPP(C_2OMe)}$_2$] (**15**) by transmetallation

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 (Figure 6).

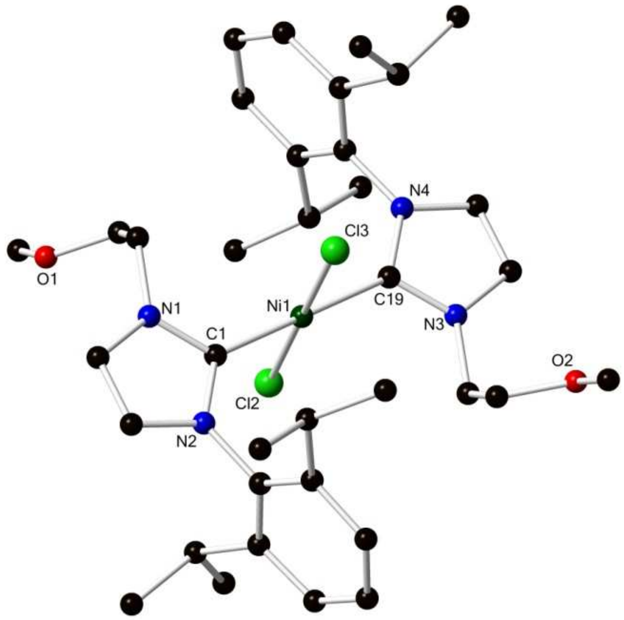


Figure 6 Ball and stick representation of [NiCl$_2${ImDiPP(C$_2$OMe)}$_2$] (**15**). Hydrogen atoms have been omitted for clarity (an ORTEP view is provided in Figure S10 of the ESI)..

This complex crystallizes in the orthorhombic system with the *P*ca2$_1$ space group. There are four motifs per unit cell without any solvent included and 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 2.1822(8), 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.[25]

Surprisingly, even though the ^{1}H NMR spectrum recorded when **15** was dissolved in deuterated solvents was consistent with the structural assignment in the solid state, it also 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 CH$_2^{imid}$ and CH$_2^{OMe}$ signals shifted downfield by 0.69 and 0.34 ppm and the CH^{iPr} and CH$_3^{iPr}$ signals shifted upfield by 0.21 and 0.32 ppm. Not any significant difference was noticeable in the corresponding ^{13}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.[26]

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 g C_2H_4/(g Ni·h) and a TOF of 9600 mol C_2H_4/(mol Ni·h). The selectivities for C_4 olefins and 1-butene 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 C_{NHC}-O chelates toward Ni(II) but the resulting complex was inactive toward ethylene.[27]

Conclusion

We have obtained a series of non-symmetric alcohol-, silylether- 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 transmetallation to Ni(II) since reprotonation of the carbene carbon was always observed. Consistent with these observations, we are not aware of any successful transmetallation 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,[28] we are currently using this approach to synthesize a series of ether-functionalised NHC Ni(II) complexes for this purpose.

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

Sophie Hameury, Pierre de Frémont, Pierre-Alain Breuil, Hélène Olivier-Bourbigou and Pierre Braunstein*

New silver complexes bearing alcohol- or ether-fonctionnalized NHCs were synthesized and characterized by X-ray diffraction. Their NHC transmetallation ability was assessed in presence of different nickel(II) sources and gave rise to a Ni(II) bis(NHC) complex in the case of the ether-fonctionalization.