Coordination features of bis(*N*-heterocyclic carbenes) and bis(oxazolines) with 1,3-alkylidene-2,4,6-trimethylbenzene spacers. Synthesis of the ligands and silver and palladium complexes†‡

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The synthesis of simple imidazolium-based ligand precursors containing a 1,3-alkylidene-2,4,6-trimethylbenzene spacer was examined and different synthetic protocols were applied depending on the nature of the alkylidene arm. For a methylene arm, simple dications **5a,b·2Cl** were obtained directly. The higher homologue counterparts were conveniently prepared by general multistep routes following a five-step sequence for ethylene dications **6a,b·2Br** or a six-step sequence for propylene dications **7a,b·2Br** in ≥ 52% overall yield. Imidazolium salts based on the shorter methylene spacer were used to prepare palladium complexes (**17–20**) with *N*-heterocyclic carbenes *via* transmetallation from well-defined silver compounds or directly in basic conditions. In order to facilitate spectroscopic characterisation of the palladium species two [Pd(allyl)(bis-oxazoline)]$^+$ (**25–26**) complexes with the same ligand bridge were synthesized. [PdX_2bisL] complexes appeared in solution as mixtures of species, mononuclear with *cis*- or *trans*-geometry or oligomeric compounds. The reaction of $[PdCl(allyl)]_2$ and μ-bis(carbene)$(AgX)_2$ complexes in 1 : 1 or in 0.5 : 1 ratio leads to binuclear compounds $[Pd_2Cl_2(allyl)_2$(μ-bis-carbene)] (**19a,19b**) and to very labile monomeric [Pd(allyl)(bis-carbene)]$^+$ (**20a,20b**) compounds, respectively. The preparation of analogous [Pd(allyl)(bis-oxazoline)]$^+$ complexes showed the formation of one of the four possible isomers. [Pd(allyl)(bis-oxazoline)]PF_6 complexes were inactive as catalytic precursors in the allylic substitution reaction.

1. Introduction

Transition metal complexes bearing *N*-heterocyclic carbene (NHC) ligands have been known for many years. The first complexes were obtained by deprotonation of imidazolium salts[1,2] and by double bond splitting of electron-rich olefins of the 1,3-substituted imidazol-2-ylidene moiety.[3] In the last few years, after the isolation of stable free carbenes,[4] the number of NHC ligands described has regularly increased with the emergence of different applications.[5] In particular, transition metal complexes containing the new NHC ligands showed excellent performance in a large number of catalytic processes.[6,7] The nature of the metal–carbon bond in the NHC carbenes has been discussed recently.[8] Between the valuable properties of the complexes are the higher thermal stability and the lower sensitivity towards oxygen and moisture. The relatively easy preparation of the carbene ligands starting from imidazolium salts allowed their systematic study either as monodentate, polydentate or mixed donor systems.[9,10,11]

Imidazolium salts are frequently used as direct precursors for metal *N*-heterocyclic carbene complexes. Deprotonation of the imidazolium salt is performed by the use of a suitable base. However, a widely employed synthetic strategy introduced by Wang and Lin[12] involves the use of silver–NHC complexes as air stable reagents for carbene transfer reactions in mild conditions.[13]

So, the preparation of bis(imidazolium) salts as intermediates to obtain polydentate NHC ligands is an attractive field of research. One of the main features of these salts is the nature of the bridging moiety. The use of a substituted aromatic ring generates different coordination possibilities depending on the ring substitution, 1,2-1, 3- or 1,4-.

The study of the coordination features of 1,2-xylyl or similar 1,2-cyclohexyl bis(carbene) ligands has been reported, and *cis*-[14,15,16] and *trans*-[17]geometry of the dihalo palladium complexes has been observed. The *meta*-xylyl bis(imidazolium) salts could lead to a coordination in a bidentate or arene-tethered fashion depending on the overall chain length. Metallation of the central C–H proton has also been observed giving a pincer ligand, similar to those obtained when 2,6-substituted pyridine is used as the aromatic ring.[17,18]

In this paper we report the synthesis of a group of bis(imidazolium) salts containing 1,3-alkylidene-2,4,6-trimethylbenzene linkers, where the alkyl arm could be a methylene (**5a,b·2Cl**), ethylene (**6a,b·2Br**) or propylene (**7a,b·2Br**) fragment and the preparation of the silver carbene complexes of the shorter and longer arms, methylene (**15a,b**) and propylene (**16a,b**) fragments. We also discuss the coordination features of the potentially bidentate 1,3-$(CH_2ImR)_2$-2,4,6-trimethylbenzene bis(carbene) ligand with palladium, since the use of the trimethylbenzene unit

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† The HTML version of this article has been enhanced with colour images.

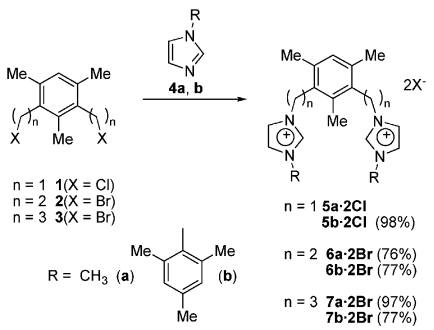
‡ Electronic supplementary information (ESI) available: Fig. S1–S16 (ESI mass spectra and NMR spectra of selected compounds). See DOI: 10.1039/b703656f

in the bridge could make metallation processes difficult. As the geometry and nuclearity of the palladium carbene complexes obtained was not evident, analogous bis(oxazoline) and carbene-oxazoline ligands[19] were coordinated to support our conclusions. Well-defined [bis(oxazoline)(allyl)palladium] complexes were inactive as catalytic precursors in the allylic substitution reaction.

2. Results and discussion

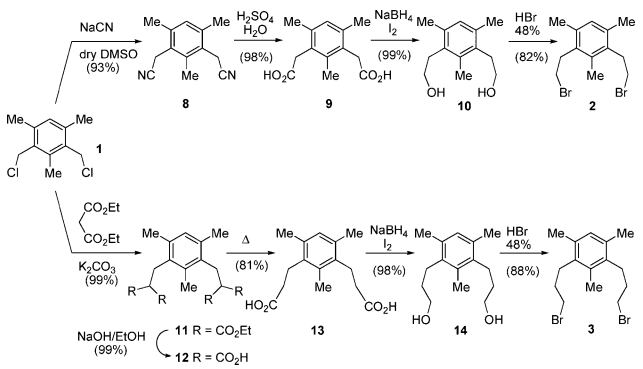
2.1 Preparation of the imidazolium precursors

Dicationic ligand precursors **5b·2Cl**, **6a,b·2Br** and **7a,b·2Br** were prepared following standard protocols for quaternizing *N*-substituted imidazoles.[19] Dications **5a·2Cl** and **5b·2Cl** have been described by Cristau *et al.*[20] and Trudell,[21] respectively. Reaction of bis(haloalkyl)-1,3,5-trimethylbenzenes **1**, **2** or **3** with *N*-substituted imidazoles **4a** or **4b** under neutral conditions produced the targeted dications **5b·2Cl**, **6a,b·2Br** and **7a,b·2Br** in yields ranging from 76% to 98% (Scheme 1).



Scheme 1

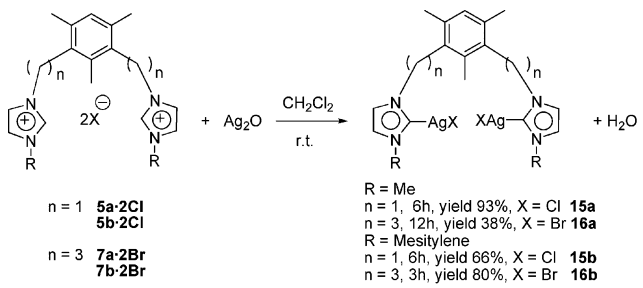
From 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene **1**, both dications **5a·2Cl**[20] and **5b·2Cl**[21] were prepared directly, whereas multistep routes were necessary to obtain the bis(bromoalkyl) intermediates **2** and **3** (Scheme 2). The synthesis of the key intermediate **2** proceeded in four-steps starting from compound **1** in 74% overall yield, by transformations to known compound **8**[19] and hydrolysis to the corresponding diacetic acid **9**, followed by reduction of this with $NaBH_4/I_2$ to bis(hydroxyethyl) derivative **10** in excellent yield. Using conc. HBr, the desired bis(bromoethyl) key compound **2** was obtained. Following a five-step sequence, preparation of bis(bromopropyl) key compound **3** was carried out from bis(chloromethyl)arene **1** in 68% overall yield. An efficient malonic-ester acid synthesis protocol applied to bis(chlorobenzylic) derivative **1** afforded dimalonate **11**, and subsequent hydrolysis gave dimalonic acid **12**, which underwent decarboxylation to give diacetic acid **13**. This was subsequently reduced to dipropan-1-ol **14** which was converted to the key bis(3-bromopropyl) intermediate **3**.



Scheme 2

2.2 Synthesis of silver–carbene complexes

Silver carbene complexes display a wide variety of structures depending on several factors.[13] In solid state they tend to dimerize–oligomerize *via* silver–silver interactions or bridging ligands like halide or polycarbenes.[22,23,24] Since the discovery of the transmetallation reaction,[12] they have regularly been used as intermediate species to generate transition-metal–carbene bonds because the reactions proceed under mild conditions and without the use of strong bases. So, silver dinuclear complexes, $[1,3((CH_2)_nImMeAgCl)_2]$-2,4,6-$Me_3C_6H$] (**15–16**) were obtained by reacting the corresponding imidazolium salt and Ag_2O in CH_2Cl_2 (Scheme 3). The white complexes are stable in the solid state in the dark, but on standing in solution, the formation of insoluble oligomeric species was observed and was faster with the complexes containing the *N*-mesitylene substituent. The analytical data and NMR spectra of the complexes are compatible with the expected simple halide and carbene coordination to silver. Crystal structure determination for analogous *meta*-xylyl complexes, where R = Me, has been reported.[25]



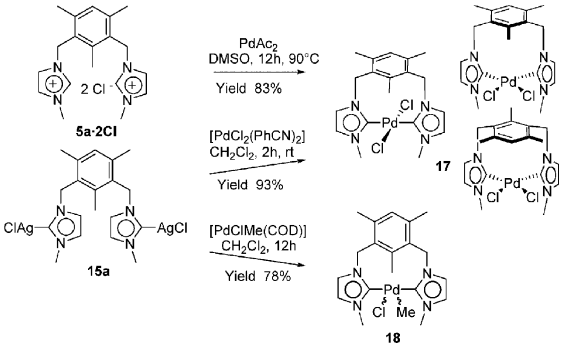
Scheme 3

The proton NMR spectra of the complexes at room temperature showed well-defined signals. The main differences with the spectrum of the corresponding bis(imidazolium) salts are the absence of the 2*H*-imidazolium proton and the high field shift of the 4*H* and 5*H*-imidazolium hydrogens. The protons of each of the methylene groups of the alkyl bridge appeared as single signals coupled between them as expected. The $^{13}C\{^1H\}$ NMR spectrum of complex **15a** was recorded to compare with published results, the carbene resonance appeared at 179.4 ppm in $CDCl_3$ and in pincer silver complexes at 179.8 or 181.1 ppm.[5,22]

2.3 Synthesis and characterisation of the palladium(II) carbene complexes

To explore the coordination features of the 1,3-$(CH_2ImR)_2$-2,4,6-trimethylbenzene moiety as a potential bidentate ligand we tried to obtain the $[PdCl_2$(bis-carbene)] complex. Using either the direct reaction of palladium acetate with the imidazolium salt **5** or the carbene transfer from the silver complex **15a** to a palladium

dichloro complex with a labile ligand the same white precipitate **17** was obtained (Scheme 4).



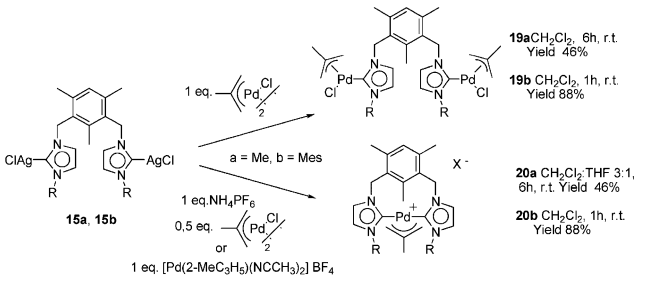
Scheme 4

As reported for similar complexes[14,15,17] compound **17** has limited solubility in several common solvents and unfortunately the ^{1}H-NMR spectrum obtained showed a single group of very broad signals, although they were in the positions expected for the coordinated carbene. The analytical data was disappointing but the mass spectra showed the correct mass distribution for the $[PdCl(bis\text{-}carbene)]^{+}$ fragment and a major signal pertaining to the "Pd-bis(carbene)" cation. Ions with a ratio palladium : bidentate ligand different to 1 : 1 were not observed. The $^{13}C\{^{1}H\}$ spectrum showed the expected group of signals but duplicated, the minor set sharp and the major set broad signals suggesting the presence of at least two different species in solution. The carbenic carbon appeared at 170.18 (sharp) and 169.60 (broad) ppm.

Therefore, since metallation products were not detected, all data point towards mononuclear species, probably mixtures of *trans*- and the two conformations of the *cis*-complexes (Scheme 4). The assignment of a *trans*- or *cis*-geometry is not evident, central *ortho*-xylyl groups, *cis*-,[15] *trans*- or dinuclear species[17] were determined by X-ray crystallography. With central *meta*-xylyl groups it is even less evident. Furthermore, in a rigid environment the proton signals of the methylene linkers would be different in both geometries, so it is unhelpful in supporting geometric assignations.

To obtain additional information about the coordination fashion of the bis(carbene) ligand, the transmetallation reaction between **15a** and [PdClMe(COD)] was performed. The white product obtained (**18**), scarcely soluble in common organic solvents, showed analogous erratic analytical data and very broad proton NMR signals. A signal at 0.55 ppm could be associated to the methyl group bonded to palladium and the mass spectrum (ESI+) presents the fragment $[PdMe(bis\text{-}carbene)]^{+}$ at 419.12 uma. No new information about the geometry of the compounds can be deduced.

Allyl complexes [{PdCl(η^3-2-$CH_3C_3H_4$)}$_2$(μ-carbene)] (19) and [Pd(η^3-2-$CH_3C_3H_4$)(carbene)]PF_6 (20). The methodology of transmetallation using the silver carbene complex proposed by Lin *et al.*[12] was used to obtain allyl palladium complexes. This methodology has previously been used successfully.[26–28] Changing the stoichiometry of the allyl palladium precursor it was possible to obtain well-defined neutral complexes (**19**) where the carbene operates in a monodentate fashion, or cationic allyl carbene complexes that can be *cis*-mononuclear species or oligomers (**20**) (see Scheme 5). Compounds **19a** and **19b** were obtained



Scheme 5

in mild conditions as white solids sparingly soluble in common organic solvents but soluble enough to obtain acceptable proton and $^{13}C\{^{1}H\}$ spectra. Analytical data were disappointing but mass spectra (ESI+) gave the expected pattern for the $[M–Cl]^{+}$ and $[M–2Cl]^{2+}$ fragments of both compounds without significant contamination (see ESI‡).

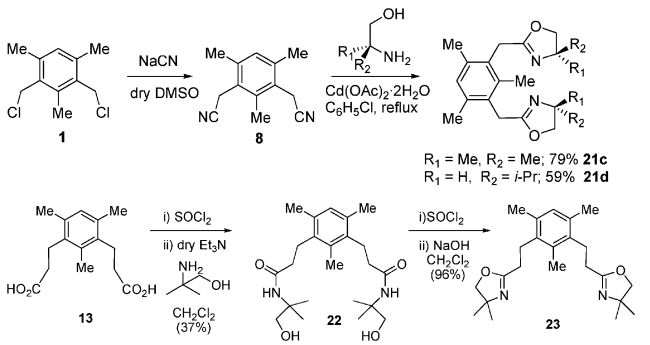
The signals at 181.18 and 182.6 ppm of the $^{13}C\{^{1}H\}$ spectrum of **19a** and **19b** could be assigned to the carbenic carbon in good agreement with published results which were 175–215 or 173–177 ppm.[26,27] The difference of chemical shifts between the terminal allylic carbons was high, and the signals appear at 71.76 and 48.5 ppm for **19a** and at 70.87 and 49.23 ppm for **19b**. The proton 1D NMR spectrum of **19a** showed one set of singlets for the different types of hydrogen atoms. The allyl ligand gives rise to the expected two *syn*- and two-*anti*-protons in agreement with the asymmetric structure of the complex. Since the plane defined by the carbene ligand adopts a perpendicular disposition with respect to the coordination plane,[26] two isomers of the allyl complex depending on the position of the central allylic methyl with respect to the different *N*-substituents could be obtained. The 2D NOESY experiment showed a fast interchange of the *syn* and *anti* allylic protons with the second isomer present in an almost undetectable amount in the 1D spectrum (see ESI‡), where the exchange mechanisms involved are the pseudorotation of the whole allyl ligand and the η^3–η^1–η^3 isomerization process. The exchange between *syn*/*anti* allyl methylene proton pairs was selectively observed with one pair that could be considered *cis* to the carbene atom according to the strong *trans*-influence of the carbene ligand.[26] The proton NMR spectrum of **19b** showed some interesting features: the signals of the *para*-methyl group and the methine proton of the mesitylene ligand appeared duplicated, and four signals could be assigned to the *ortho*-methyl groups of the same ligand. Furthermore, one *syn* and one *anti* proton of the set of four signals of the allylic ligand of each isomer appeared duplicated. So, in the compound **19b** the rotation around the *N*-mesitylene bond was restricted at room temperature and the two allylic isomers present in the same amount were observed. The proton signals of the spacer group appeared as singlets, as did the methine hydrogens of the imidazole skeleton.

Slightly coloured solids **20** were obtained when the preparation of cationic mononuclear allyl complexes with a bidentate coordination mode of the bis(carbene) ligand (Scheme 5) was attempted using the same preparative method that led to compounds **19**. However, proton NMR spectra of the complexes in acetone showed very broad signals where it was not possible to observe the allylic protons. Only the analytical data of compound **20b**, which was obtained using a preformed allyl cationic complex, gave

reasonable results but when the dinuclear compound $[PdCl(allyl)]_2$ in the presence of NH_4PF_6 was used to prepare **20b**, a signal at 8.6 ppm was observed in the ^1H NMR spectrum in the range of the 2*H*-imidazolium proton in the imidazolium salts. Furthermore, in the MS (ESI+) spectrum a fragment was observed at 339.14 uma corresponding to a $[M + H]^{2+}$ stoichiometry, coherent with a dicationic allyl palladium compound with one arm of the former bis(carbene) coordinated and the second arm converted into the original imidazolium cation (see ESI‡). Metallation reactions cannot be discarded but no clear evidence suggests that kind of process. The dynamic behaviour of this kind of bis(carbene) ligand bridge, even when the unit is fixed with a Pd–carbon bond in pincer systems,[14,15,17,29,30] makes it difficult to conclude clearly about the real capacity to act as a bidentate ligand in a *cis*-coordination mode. It was not possible to obtain suitable crystals to perform X-ray diffraction studies. For this reason we used the analogous available bis(oxazoline) ligands in order to obtain a clear confirmation of the coordination admitted by the 1,3-dimethylene-2,4,6-trimethylbenzene bridge.

2.4 Synthesis and characterisation of the allylic palladium(II) bis(oxazoline) complexes (25c, 25d)

In order to compare the suitability of the 1,3-dimethylene-2,4,6-trimethylbenzene bridge in bis(oxazoline) ligands analogous to the bis(carbene) described previously, we used two bis[(oxazolinyl)methyl]-2,4,6-trimethylbenzene compounds (**21c**, (*S*,*S*)-**21d**) already reported by us (Scheme 6).[19] These ligands could be useful to confirm the coordination in a bidentate fashion giving either *cis*- or *trans*-mononuclear complexes.

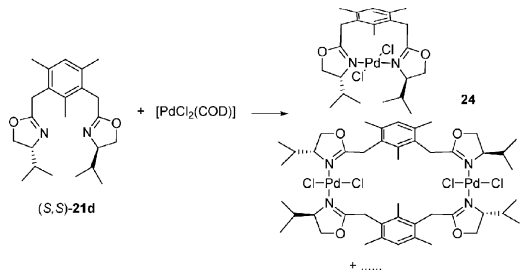


Scheme 6

The preparation of the bis(oxazoline) ligands was performed starting from the diacetonitrile intermediate. After mixing with the proper aminoalcohol, the condensation and ring closing took place in one step. Similar methodology can be used to prepare the analogous ligands but with longer spacers. As shown in Scheme 6, bis[(oxazolyl)ethyl]-2,4,6-trimethylbenzene **23** was prepared from dipropanoic acid **13**, *via N*-acylation giving compound **22**, and this was subsequently converted to bis(oxazoline) **23** in 36% overall yield.

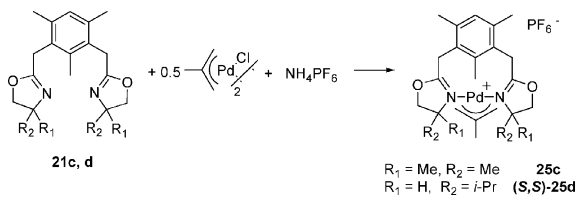
Similar bis[(oxazolyl)methyl]-4,6-dimethylbenzene pincer ligands obtained in the same way have been previously described. The reaction with $RhCl_3$ led to cyclometallated mononuclear pentacoordinated rhodium(III) complexes and in some cases to *trans*-[Rh(II)Cl_2(bisox)] compounds.[31]

The mixture of the bis(oxazoline) (*S*,*S*)-**21d** with $[PdCl_2(COD)]$ in $CHCl_3$ led to the substitution of COD (Scheme 7). The proton NMR spectrum of the solid obtained (**24**) showed broad signals with the chemical shifts and with some of the splittings of the diastereotopic protons of the methylene linkers expected for the coordinated bis(oxazoline). The spectrum also showed the presence of at least two different products. The methyl protons of the isopropyl group appear as two doublets compatible with a mononuclear *trans*-complex or polynuclear oligomers. Mass spectrometry (ESI+) points to the presence of fragments containing one or two bis(oxazoline) with one or two palladium centres. Similar results were observed by Danopoulos with 1,2-xylyl dicarbene ligands.[17]



Scheme 7

The reaction of $[Pd(\eta^3\text{-2-Me-}C_3H_4)(\mu\text{-Cl})]_2$ with the appropriate bis(oxazoline) ligand (L = **21c**, (*S*,*S*)-**21d**) in the presence of ammonium hexafluorophosphate salt, afforded ionic allylic monometallic palladium square-planar complexes of general formula $[Pd(\eta^3\text{-2-Me-}C_3H_4)(L)]PF_6$ (**25c**,**d**) (Scheme 8), where the coordination of the bis(oxazoline) to the palladium is in a bidentate *cis*-fashion. Studies of the coordination chemistry of bis(oxazolinyl)benzene derivatives, which differ in the relative position of the two oxazoline moieties on the phenyl group, showed that the proximity of two nitrogen atoms in the *ortho*-bis(oxazoline) facilitates chelate coordination, while for *meta*- and *para*-bis(oxazoline) ligands only bridging coordination is observed.[32]



Scheme 8

The complexes were fully characterised by the usual techniques. The ^1H NMR spectrum of the allylic palladium complex **25c** showed a symmetrical structure in solution, with only one kind of oxazolinyl, mesityl and methylene protons. The *syn* and *anti* protons of the methylallyl group were also equivalent. The protons of both methylene groups, those associated with the mesityl group and with the oxazolinyl group are diastereotopic and appear as an AB pattern at room temperature in 400 MHz instruments. However, the methyl groups of the oxazoline appeared as a single signal. The 2D NOESY spectrum enables the allyl and the bis(oxazoline) protons to be correlated by NOE contacts. There are close contacts between the *syn* and *anti* protons and

between the *syn* and the methyl protons of the allyl ligand, and also between the *ortho* methyl and methylene groups of the mesitylene and between the methyl and methylene groups of the oxazolinyl fragment. But the most interesting interligand NOE interactions occur between the *anti* allyl protons and the *ortho* methyl protons of the mesitylene and between *syn* protons and the allyl methyl with the methyl groups of the oxazoline. All these data suggest the structure of the single isomer in which the plane containing the allylic group and that containing the mesityl group must be nearly perpendicular one with respect to each other with the *ortho* methyl of the mesityl and *anti* allyl protons in close contact, exactly like the conformer **A** (Fig. 1). Preliminary molecular mechanics calculations also point in this direction when the four possible conformations are compared. Fig. 1 depicts the two conformations coherent with the NMR data.

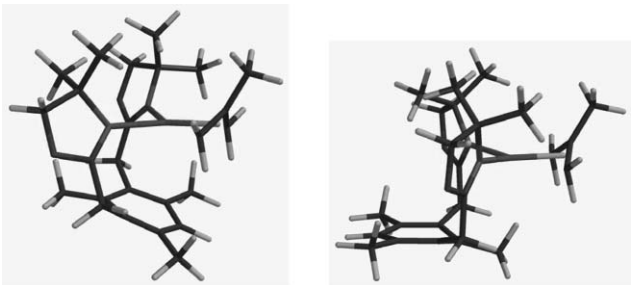
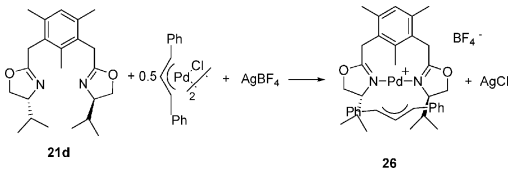


Fig. 1 Different bidentate coordination modes of the bis(oxazoline) ligands.

In the ^{1}H NMR spectrum of complex (*S*,*S*)-**25d** containing the (*S*,*S*)-**21d** oxazoline a single isomer was detected, contrasting with the results obtained with allylic palladium complexes containing bis(oxazolinyl)benzene.[33] Owing to the loss of C_2 symmetry of the ligand upon coordination, the two oxazoline fragments are not equivalent in a *cis*-environment and therefore each of the *anti* and *syn* allyl protons exhibit different chemical shifts. All four methylene protons of the oxazoline moiety appeared separately as triplets ($J_{gem} \sim {}^3J_{HH}$). Four signals were observed for the methyls of the isopropyl groups. In order to elucidate the solution structure of this complex, the NOESY experiment was especially useful because it allowed us a complete correlation between protons. One of the allyl *syn* protons was assigned on the basis of the NOESY experiment, since in the monodimensional ^{1}H NMR this proton is not distinguished because it is overlapped with the methylene signals of the bridge. The NOE contacts observed were similar to those described for complex **25c**. Furthermore, *anti* allyl protons interact with the aromatic CH proton and one *syn* proton showed a contact with one methyl of an isopropyl group. These data were also consistent with the same conformation **A** (Fig. 1) similar to that found in **25c**. The NOESY spectrum also reveals exchange signals of the *syn* and *anti* allyl protons of (*S*,*S*)-**25d** with a minor isomer which due to its low abundance cannot be characterised from the ^{1}H NMR spectrum. Both allyl complexes showed exchange signals between the pairs of methylene protons of the linkers and the oxazoline according to a complete interconversion of the coordination sphere with respect to the plane defined by the phenyl linker. Miecznikowski *et al.* studied similar interchanges in the methylene linkers of Pd pincer complexes, although here the mechanism could probably be different.[29] MS (ESI+ and FAB) data of both complexes gave the mass of the molecular allyl cation.

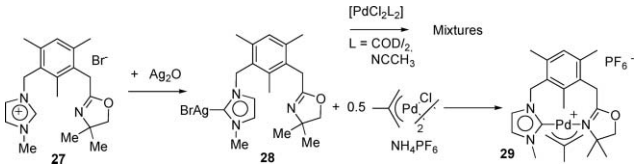
We tested the catalytic activity of complex (*S*,*S*)-**25d** in the allylic alkylation of the model substrates, *rac*-3-acetoxy-1,3-diphenyl-1-propene (cinammyl acetate) and (*E*)-3-acetoxy-1-phenyl-1-propene (1,3-diphenyl acetate) using dimethyl malonate as nucleophile, under basic conditions, in dichloromethane as a solvent and at room temperature, but the system was not active after 24 h. To understand these results, we synthesized the analogous complex [(1,3-Ph_2-C_3H_3)Pd((*S*,*S*)-**21d**)]$^+$, usually accepted as the Pd intermediate under catalytic conditions.[34] We prepared [(1,3-Ph_2-C_3H_3)Pd((*S*,*S*)-**21d**)]BF_4 by the reaction of [Pd(1,3-Ph_2-C_3H_3)(μ-Cl)]$_2$, with $AgBF_4$ and the oxazoline ligand (*S*,*S*)-**21d** in THF (eqn (1)). Purification by precipitation from an acetone solution with diethyl ether gave the desired complex as an orange solid (**26**). The insolubility of the complex avoided the obtainment of a useful ^{1}H NMR spectrum at room temperature. Evidence of the proposed monometallic complex in which the oxazoline ligand is bidentate comes from elemental analysis and the molecular ion ([(1,3-Ph_2-C_3H_3)Pd((*S*,*S*)-**21d**)]$^+$) in the MS (FAB positive spectrum). So, the steric hindrance of the more stable conformer of the bis(oxazoline) complexes (Fig. 1) could be responsible for the lack of activity in the catalytic reaction probably in the oxidative addition step.



(1)

2.5. Synthesis and characterisation of the silver and palladium(II) oxazoline–carbene complexes

Mixed bidentate carbene–oxazoline ligands have been reported,[35] and since we recently obtained oxazolinyl-imidazolium salts containing the same mesityl bridge[19] it was possible to check the behaviour of the ligand precursor **27**. To obtain analogous palladium complexes (**20**) we used the same strategy based on the carbene transfer from the silver *N*-heterocyclic carbene complex (Scheme 9). Stirring the imidazolium salt **27** with Ag_2O in dichloromethane at room temperature for 3 h afforded the silver–NHC complex **28**. The proton NMR spectra at room temperature showed relatively sharp signals and the absence of the 2*H*-imidazolium hydrogen. The CH_2 protons of the two linkers appeared as singlets.



Scheme 9

The silver complex **28** was reacted with [$PdCl_2$(NCPh)$_2$] and [(η^3-$CH_3C_3H_4$)PdCl]$_2$ to yield the corresponding palladium complexes. The solution of the reaction with the dichloropalladium complex

contains a mixture of different compounds similar to those observed with the bisoxazoline or biscarbene ligands. The solid obtained when CH_2Cl_2 solutions of the silver adduct and $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ were stirred for 6 h at room temperature gave the correct mass spectrum of **29** (ESI(+)-MS, *m*/*z* 486.3 uma), although no reproducible analytical data were obtained. The proton NMR spectrum in $CDCl_3$ showed very broad signals but in acetone it was possible to observe a group of well-defined signals where the two protons of the methylene linkers and the two methyl substituents of the oxazoline ring appeared separately. Therefore, it was assumed that the mononuclear complex **29** where the carbene–oxazoline ligand is coordinated in a bidentate fashion was present in the solution mixture.

4. Conclusions

In summary, new simple bis(imidazolium)-based ligand precursors containing a 1,3-alkylidene-2,4,6-trimethylbenzene spacer were prepared using efficient multi-step synthetic routes. Depending on the length of the alkylidene side chain, imidazolium-based substrates lead to different coordination possibilities, either bidentate fashion or through the tethering of the phenyl ring. The general synthetic protocols applied to these simple imidazolium-based frameworks should be adapted to a variety of chiral frameworks, thereby developing their catalytic performance in asymmetric reactions.

From these bis(imidazolium) salts it was possible to obtain silver carbene complexes which could be used in transmetallation reactions.

We also studied the coordination mode of the bis(carbene) ligand when the spacer is the shorter 1,3-methylene-2,4,6-trimethylbenzene moiety. In a square planar arrangement around simple palladium species, mixtures of mononuclear and binuclear compounds could be formed. When a *cis* geometry is imposed using allyl ligands, the preparation of neutral complexes where the bis(carbene) ligand coordinates in a monodentate fashion was achieved without any problem (**19**). However, when it was attempted to coordinate the bis(carbene) ligands in a bidentate fashion it was not possible to characterize clearly the species obtained in solution. No decomposition of the allyl compounds was observed and also no evidence of cyclometallation reactions was noted. The preparation of analogous well-defined bis(oxazoline) allyl complexes (**25**) showed that the 1,3-methylene-2,4,6-trimethylbenzene spacer is compatible with a *cis*-coordination, but this is subject to fast dynamic processes, probably due to the interchange between isomers as depicted in Fig. 1, and to the complete interconversion of the coordination sphere with respect to the plane defined by the phenyl linker.

The bis(oxazoline) complex (*S*,*S*)-**25d** was tested as catalytic precursor in the allylic substitution reaction carried out in mild conditions.[33] The result using *rac*-cinammyl acetate and (*E*)-3-acetoxy-1-phenyl-1-propene was negative, probably due to the crowding of the palladium centre. However, palladium complexes with similar bis(carbene) ligands showed activity in Heck or Suzuki coupling reactions although they were performed at high temperature.[14,15] Therefore the coordination of the bis(carbene) or bis(oxazoline) ligands containing the 1,3-methylene-2,4,6-trimethylbenzene spacer in a bidentate fashion in a square planar environment makes metallation reactions difficult although the steric crowding prevents easy access to the metallic centre.

5. Experimental

General methods

All compounds were prepared under a purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen. $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$,[36] $[Pd(\eta^3\text{-}1,3\text{-}Ph_2C_3H_3)(\mu\text{-}Cl)]_2$,[37] 1-mesityl-1*H*-imidazole **4b**,[38] 3,3′-[(2,4,6-trimethyl-1,3-phenylene)bis(methylene)]bis(1-methyl-1*H*-imidazol-3-ium) dichloride **5a**·**2Cl**,[20] 2,2′-(2,4,6-trimethyl-1,3-phenylene)diacetonitrile **8**,[19] 1,3-bis-[(4,4-dimethyl-4,5-dihydrooxazol-2-yl)methyl]-2,4,6-trimethylbenzene **21c**,[19] 1,3-bis{[(4*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl]methyl}-2,4,6-trimethylbenzene (*S*,*S*)-**21d**,[19] and 1-[3-(4,4-dimethyl-4,5-dihydro-2-oxazolyl)methyl-2,4,6-trimethylbenzyl]-3-methylimidazolium bromide **27**[19] was prepared as previously described. 2,4-Bis(chloromethyl)-1,3,5-trimethylbenzene **1**, 1-methyl-1*H*-imidazole **4a**, 2-amino-2-methyl-1-propanol were purchased from commercial sources. Melting point: CTP-MP 300 hot-plate apparatus with ASTM 2C thermometer. The ^1H and ^{13}C, NMR spectra were recorded on either a Varian XL-500 and Mercury-400 MHz or Varian Gemini 200 and 300 MHz, (standard $SiMe_4$) spectrometers in $CDCl_3$ unless otherwise cited. Chemical shifts in ppm were reported downfield from standards. The two-dimensional experiments were generally carried out with a Bruker DMX500 or a Varian XL-500 instrument. IR spectra were recorded on the following spectrometers: FT-IR Avatar 330 and FTIR Nicolet 5700. MS (ESI+ or FAB) spectra were obtained with a Fisons V6-Quattro or an Agilent LC/MSD-TOF spectrometer. Organometallic samples were introduced with 1% formic acid. Mass spectra (CI or EI at 70 eV) were obtained using a Hewlett-Packard spectrometer (HP-5989A model). TLC: Merck precoated silica gel 60 F254 plates or Merck neutral aluminium oxide 60 F254 plates using UV light (254 nm) as a visualizing agent and/or H_2PtCl_2 3% aq./KI 10% aq. (1 : 1) or $KMnO_4$ ethanolic solution. Column chromatography was performed on silica gel 60 ACC 35–70 μm Chromagel (SDS) or neutral aluminium oxide 90 activity II-III (Merck). The routine GC analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (50-m Ultra 2 capillary column) with a FID detector. Elemental analyses were carried out by the Serveis Cientificotècnics of the Universitat Rovira i Virgili in an Eager 1108 microanalyzer.

Synthesis of bis(imidazolium) salts

2,2′-(2,4,6-Trimethyl-1,3-phenylene)diacetic acid 9. To 40 mL of water was added concentrated sulfuric acid (35 mL). When the solution had cooled to about 50 °C, the diacetonitrile **8** (3.50 g, 17.65 mmol) was added and the mixture was refluxed for 12 h. The resulting mixture was cooled to room temperature and poured into ice-water (500 mL). The resulting suspension was filtered and dried under vacuum at 40 °C to give diacid **9** (4.10 g, 98% yield) as a white solid. Mp 232–234 °C. ^1H NMR (400 MHz, CD_3OD): δ = 2.33 (s, 3H, CH_3), 2.34 (s, 6H, CH_3), 3.77 (s, 4H, CH_2COOH), 6.96 (s, 1H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 16.5 (CH_3),

20.5 (CH_3), 36.3 (CH_2COOH), 130.8 (CH), 131.3, 136.8, 137.4, 175.6 (COOH) ppm. IR (KBr): ν = 1686 (C=O), 2950 (COO–H) cm^{-1}. EI-MS: m/z (%): 91(41), 145 (53) [$M^{+\bullet}$ −89], 191 (100) [$M^{+\bullet}$ −45], 236 (66) [$M^{+\bullet}$], 237 (9) [$M^{+\bullet}$ + 1].

2,2′-(2,4,6-Trimethyl-1,3-phenylene)diethanol 10. To a suspension of $NaBH_4$ (3.01 g, 79.57 mmol) in dry THF (85 mL) was added a solution of iodine (8.08 g, 31.84 mmol) in dry THF (20 mL), at 0 °C under an argon atmosphere. The resulting solution was heated at reflux temperature and then the acid **9** (3.76 g, 15.92 mmol) was added. The reaction mixture was stirred at reflux temperature for 21 h. The resulting mixture was cooled to room temperature and then methanol was added until an orange solution was formed. This solution was stirred for an additional 30 min and was concentrated under reduced pressure to give an orange residue, which was diluted in aqueous 20% KOH solution (450 mL) and stirred at room temperature for 12 h. The aqueous solution was extracted with CH_2Cl_2 (3 × 200 mL) and the organic layers were dried (anhydrous Na_2SO_4), filtered and concentrated to dryness to give alcohol **10** (3.27 g, 99% yield) as a white solid. Mp 92–94 °C. ^{1}H NMR (400 MHz, CD_3OD): δ = 2.33 (s, 6H, CH_3), 2.39 (s, 3H, CH_3), 2.98 (t, J = 7.4 Hz, 4H, CH_2), 3.64 (t, J = 7.4 Hz, 4H, CH_2OH), 6.87 (s, 1H) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 15.6 (CH_3), 20.2 (CH_3), 34.3 (CH_2), 62.0 (CH_2OH), 131.0 (CH), 133.7, 135.4, 136.1 ppm. IR (KBr): ν = 1043 (C–O), 3290 (O–H) cm^{-1}. EI-MS: m/z (%): 91 (22), 133 (39), 160 (37) [$M^{+\bullet}$ −48], 177 (100) [$M^{+\bullet}$ −31], 208 (37) [$M^{+\bullet}$], 209 (5) [$M^{+\bullet}$ + 1].

2,4-Bis(2-bromoethyl)-1,3,5-trimethylbenzene 2. To alcohol **10** (3 g, 13.60 mmol) was added 48% hydrobromic acid (11 mL, 206.02 mmol), at 0 °C. The resulting mixture was heated at reflux temperature for 3 h. The reaction mixture was cooled and water (100 mL) was added. The resulting solution was extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were dried (anhydrous Na_2SO_4), filtered and concentrated under reduced pressure to obtain bromide **2** (3.81 g, 82% yield) as a beige solid. Mp 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 6H, CH_3), 2.33 (s, 3H, CH_3), 3.22 (t, J = 7.4 Hz, 4H, CH_2), 3.37 (t, 4H, J = 7.4 Hz, CH_2Br), 6.90 (s, 1H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.5 (CH_3), 19.9 (CH_3), 29.7 (CH_2), 34.2 (CH_2Br), 130.6 (CH), 134.0, 134.9, 135.2 ppm. EI-MS: m/z (%): 91 (30), 115 (29), 129 (43), 145 (69), 159 (62), 239 (79) [$M^{+\bullet}$ −95], 241 (81) [$M^{+\bullet}$ −93], 253 (100) [$M^{+\bullet}$ −81], 255 (93) [$M^{+\bullet}$ −79], 334 (50) [$M^{+\bullet}$], 335 (8) [$M^{+\bullet}$ + 1], 336 (27) [$M^{+\bullet}$ + 2].

Tetraethyl 2, 2′-(2,4,6-trimethyl-1,3-phenylene)dimalonate 11. To a solution of diethyl malonate (13.9 mL, 92.10 mmol) and K_2CO_3 (31.82 g, 230.25 mmol) in dry acetonitrile (350 mL) was added under an argon atmosphere a solution of 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene **1** (10 g, 46 mmol) in dry acetonitrile (200 mL). The resulting mixture was refluxed for 48 h. The reaction mixture was cooled to room temperature, filtered and the solution was evaporated to dryness to yield dimalonate **11** (21.18 g, 99% yield) as a yellow solid. Mp. 58–60 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, J = 7.0 Hz, 12H, CH_3), 2.25 (s, 6H, CH_3), 2.26 (s, 3H, CH_3), 3.30 (d, J = 7.6 Hz, 4H, CH_2), 3.55 (t, J = 7.6 Hz, 2H, CH), 4.12 (q, J = 7.0 Hz, 8H, CH_2), 6.79 (s, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.9 (CH_3), 16.0 (CH_3), 20.1 (CH_3), 28.7 (CH_2), 51.6 (CH), 61.4 (OCH_2), 130.6 (CH), 132.9, 135.2, 135.5, 169.2 (C=O) ppm. IR (NaCl): ν = 1283 (C–O), 1733 (C=O) cm^{-1}. EI-MS: m/z (%): 157 (100), 185 (70), 213 (67), 287 (65), 305 (81), 418 (41) [$M^{+\bullet}$ −46], 446 (54) [$M^{+\bullet}$ −18], 464 (4) [$M^{+\bullet}$].

2,2′-(2,4,6-Trimethyl-1,3-phenylene)dimalonic acid 12. To a solution of ester **11** (21.39 g, 46.05 mmol) in ethanol (400 mL) was added a solution of NaOH (27.63 g, 690.75 mmol) in ethanol (200 mL) under an argon atmosphere. The reaction mixture was refluxed for 12 h. The resulting suspension was concentrated under reduced pressure to obtain a white solid, which was dissolved in water (200 mL). The resulting solution was acidified with 5N HCl and extracted with EtOAc (3 × 300 mL). The organic layers were dried (anhydrous Na_2SO_4), filtered and concentrated to dryness to obtain acid **12** (16.22 g, 99% yield) as a white solid. Mp 202–204 °C. ^{1}H NMR (300 MHz, CD_3OD): δ = 2.43 (s, 6H, CH_3), 2.47 (s, 3H, CH_3), 3.46 (d, J = 7.3 Hz, 4H, CH_2), 3.67 (t, J = 7.3 Hz, 2H, CH), 6.98 (s, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 16.3 (CH_3), 20.4 (CH_3), 30.0 (CH_2), 53.0 (CH), 131.6 (CH), 134.5, 136.1, 136.6, 173.0 (C=O) ppm. IR (KBr): ν = 1702 (C=O), 3008 (COO–H) cm^{-1}. EI-MS: m/z (%): 145 (65), 205 (100), 246 (31), 264 (49) [$M^{+\bullet}$ −88].

3,3′-(2,4,6-Trimethyl-1,3-phenylene)dipropanoic acid 13. Acid **12** (16.22 g, 46.04 mmol) was heated at melting temperature for 12 h. The resulting brown residue was basified with a saturated aqueous solution of K_2CO_3. The resulting solution was washed with ethyl acetate (3 × 250 mL). The aqueous layer was acidified with 5N HCl and extracted with EtOAc (3 × 300 mL). The organic layers were dried (anhydrous Na_2SO_4), filtered and concentrated under reduced pressure to give acid **13** (9.88 g, 81% yield) as a beige solid. Mp 158–160 °C. ^{1}H NMR (300 MHz, CD_3OD): δ = 2.39 (s, 6H, CH_3), 2.42 (s, 3H, CH_3), 2.50 (t, J = 7.3 Hz, 4H, CH_2COOH), 3.08 (t, J = 7.3 Hz, 4H, CH_2), 6.95 (s, 1H) ppm. ^{13}C NMR (75.4 MHz, CD_3OD): δ = 15.2 (CH_3), 19.9 (CH_3), 26.5 (CH_2), 36.6 (CH_2COOH), 131.2 (CH), 134.9, 136.4, 176.9 (C=O) ppm. IR (KBr): ν = 1739 (C=O), 2968 (COO–H) cm^{-1}. EI-MS: m/z (%): 145 (65), 205 (100) [$M^{+\bullet}$ −59], 246 (30) [$M^{+\bullet}$ −18], 264 (48) [$M^{+\bullet}$−48].

3,3′-(2,4,6-Trimethyl-1,3-phenylene)dipropan-1-ol 14. To a suspension of $NaBH_4$ (1.43 g, 37.85 mmol) in dry THF (40 mL) was added a solution of iodine (3.84 g, 15.14 mmol) in dry THF (10 mL), at 0 °C under an argon atmosphere. The resulting solution was heated at reflux temperature and then the acid **13** (2 g, 7.57 mmol) was added. The resulting mixture was refluxed for 21 h. The reaction mixture was cooled to room temperature and then methanol was added until an orange solution was formed. This solution was stirred for an additional 30 min and was concentrated under reduced pressure to give an orange residue, which was diluted in aqueous 20% KOH solution (200 mL) and stirred at room temperature for 12 h. The resulting solution was extracted with CH_2Cl_2 (3 × 150 mL). The organic layers were dried (anhydrous Na_2SO_4), filtered and evaporated to dryness to give alcohol **14** (1.76 g, 98% yield) as a white solid. Mp 128–130 °C. ^{1}H NMR (300 MHz, CD_3OD): δ = 1.70–1.76 (m, 4H, CH_2), 2.31 (s, 6H, CH_3), 2.35 (s, 3H, CH_3), 2.75 (t, J = 6.8 Hz, 4H, Ar–CH_2), 3.71 (t, J = 6.8 Hz, 4H, CH_2OH), 6.84 (s, 1H) ppm. ^{13}C NMR (75.4 MHz, CD_3OD): δ = 15.4 (CH_3), 20.0 (CH_3), 27.3 (Ar–CH_2), 33.6 (CH_2), 63.1 (CH_2OH), 130.9 (CH), 134.0, 134.6, 137.7 ppm. IR (KBr): ν = 1058 (C–O), 3376 (O–H) cm^{-1}. EI-MS: m/z (%): 71

(36), 133 (93), 147 (86) [$M^{+\bullet}$ −89], 191 (100) [$M^{+\bullet}$ −45], 236 (64) [$M^{+\bullet}$], 237 (12) [$M^{+\bullet}$ + 1].

2,4-Bis(3-bromopropyl)-1,3,5-trimethylbenzene 3. To alcohol **14** (6.34 g, 26.84 mmol) was added 48% hydrobromic acid (21.5 mL, 402.70 mmol), at 0 °C. The resulting mixture was heated at reflux temperature for 12 h. The reaction solution was cooled and then water (100 mL) was added. The resulting mixture was extracted with CH_2Cl_2 (3 × 250 mL). The organic layers were dried (anhydrous Na_2SO_4), filtered and concentrated under reduced pressure to obtain bromide **3** (8.56 g, 88% yield) as a brown oil. Mp 58–60 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97–2.05 (m, 4H, CH_2), 2.30 (s, 6H, CH_3), 2.31 (s, 3H, CH_3), 2.80 (t, J = 6.8 Hz, 4H, Ar–CH_2), 3.53 (t, J = 6.8 Hz, 4H, CH_2Br), 6.87 (s, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.3 (CH_3), 19.9 (CH_3), 28.8 (Ar–CH_2), 32.3 (CH_2), 34.0 (CH_2Br), 130.1 (CH), 133.8, 134.2, 135.7 ppm. EI-MS: m/z (%): 147 (29), 253 (100) [$M^{+\bullet}$ −109], 255 (98) [$M^{+\bullet}$ −107], 362 (25) [$M^{+\bullet}$], 363 (4) [$M^{+\bullet}$ + 1], 364 (12) [$M^{+\bullet}$ + 2].

General procedure for preparation of bis(imidazolium) dibromides 6a·2Br and 7a·2Br. Bromides **2** or **3** were dissolved in 1-methyl-1*H*-imidazole **4a** and heated at reflux temperature for 30 min, under argon atmosphere. After cooling to room temperature and reduction of the volume, the residue was ground several times with dry acetone. The resulting solid was filtered and used without further purification. The yields were not optimized.

3,3′-(2,4,6-Trimethyl-1,3-phenylenediethane-2,1-diyl)bis(1-methyl-1*H*-imidazol-3-ium) dibromide 6a·2Br. The above procedure was followed using 2,4-bis(2-bromoethyl)-1,3,5-trimethylbenzene **2** (1.00 g, 2.99 mmol) and 1-methyl-1*H*-imidazole **4a** (6.24 mL, 78.64 mmol). The product was obtained as a hygroscopic solid with 76% yield. Mp 137–139 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.22 (s, 6H, CH_3), 2.28 (s, 3H, CH_3), 3.12 (t, 4H, J = 6.8 Hz, CH_2), 3.88 (s, 6H, Imi-CH_3), 4.24 (t, 4H, J = 6.8 Hz, CH_2-Imi), 6.88 (s, 1H), 7.76 (s, 2H, Imi), 7.85 (s, 2H, Imi), 9.37 (s, 2H, Imi) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 15.5 (CH_3), 19.9 (CH_3), 30.6 (CH_2), 36.0 (Imi-CH_3), 47.6 (CH_2-Imi), 122.7 (Imi), 123.6 (Imi), 130.3, 131.5 (CH), 135.3, 135.8, 136.9 (Imi) ppm. IR (KBr): ν = 1565 (C=N) cm^{-1}. ESI(+)-MS: m/z (%): 169.3 (100) $[M]^{2+}$, 418.4 (2) $[M + Br]^+$. Anal. Calcd for $C_{21}H_{30}Br_2N_4 \cdot 2\ H_2O$: C, 47.21; H, 6.41; N, 10.49; found: C, 47.21; H, 6.16; N, 10.28.

3,3′-(2,4,6-Trimethyl-1,3-phenylenedipropane-3,1-diyl)bis(1-methyl-1*H*-imidazol-3-ium) dibromide 7a·2Br. The above procedure was followed using 2,4-bis(3-bromopropyl)-1,3,5-trimethylbenzene **3** (0.50 g, 1.38 mmol) and 1-methyl-1*H*-imidazole **4a** (0.30 mL, 3.80 mmol). The product was obtained as a hygroscopic foam with 97% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.81–1.88 (m, 4H, CH_2), 2.12 (s, 6H, CH_3), 2.13 (s, 3H, CH_3), 2.50 (bs, 4H, Ar–CH_2), 3.86 (s, 6H, Imi-CH_3), 4.28 (t, J = 7.0, 4H, CH_2-Imi), 6.77 (s, 1H), 7.74 (s, 2H, Imi), 7.88 (s, 2H, Imi), 9.25 (s, 2H, Imi) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 15.0 (CH_3), 19.6 (CH_3), 26.3 (Ar–CH_2), 29.3 (CH_2), 36.0 (Imi-CH_3), 49.0 (CH_2-Imi), 122.4 (Imi), 123.8 (Imi), 129.9 (CH), 133.2, 133.9, 135.3, 136.9 (Imi) ppm. ESI(+)-MS: m/z (%): 183.3 (100) $[M]^{2+}$, 446.5 (3) $[M + Br]^+$. Anal. Calcd for $C_{23}H_{34}Br_2N_4 \cdot 3.5\ H_2O$: C, 46.87; H, 7.01; N, 9.51; found: C, 47.27; H, 6.89; N, 9.15.

General procedure for preparation of bis(imidazolium) salts 5b·2Cl, 6b·2Br and 7b·2Br. Halides **1**, **2** or **3** (1 equiv) and 1-mesityl-1*H*-imidazole **4b** (1 equiv) were dissolved in dry DMF and heated to 100 °C under an argon atmosphere for 12 h and the solvent was then removed under vacuum. The solids obtained were washed several times with dry acetone and used without further purification. The yields were not optimized.

3,3′-[(2,4,6-Trimethyl-1,3-phenylene)bis(methylene)]bis[1-(2,4,6-trimethylphenyl)-1*H*-imidazol-3-ium] dichloride 5b·2Cl. The above procedure was followed using 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene **1** (1.08 g, 4.98 mmol) and 1-mesityl-1*H*-imidazole **4b** (1.85 g, 9.95 mmol) and dry DMF (10 mL). The product was obtained as a solid with 98% yield. Mp 94–96 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.95 (s, 12H, CH_3), 2.18 (s, 6H, CH_3), 2.31 (s, 6H, CH_3), 2.47 (s, 3H, CH_3), 3.26 (t, 4H, J = 7.4 Hz, CH_2), 4.46 (t, 4H, J = 7.4 Hz, CH_2-Imi), 7.12 (s, 4H), 7.24 (s, 1H), 7.93 (Imi), 8.20 (Imi), 9.50 (Imi) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 15.9 (CH_3), 17.0 (CH_3), 20.0 (CH_3), 20.7 (CH_3), 30.2 (CH_2), 48.3 (CH_2-Imi), 123.8 (Imi), 128.9 (Imi), 129.4 (CH), 130.3 (CH), 131.2, 131.5, 134.4, 135.4, 136.2, 137.6 (Imi), 140.4 ppm. ESI(+)-MS: m/z (%): 273.4 (100) $[M]^{2+}$, 626.7 (11) $[M + Br]^+$. Anal. Calcd for $C_{37}H_{46}Br_2N_4 \cdot H_2O$: C, 61.33; H, 6.68; N, 7.73; found: C, 61.41; H, 7.01; N, 7.49.

3,3′-(2,4,6-Trimethyl-1,3-phenylenediethane-2,1-diyl)bis[1-(2,4,6-trimethyl)-1*H*-imidazol-3-ium] dibromide 6b·2Br. The above procedure was followed using 2,4-bis(2-bromoethyl)-1,3,5-trimethylbenzene **2** (2.50 g, 7.48 mmol) and 1-mesityl-1*H*-imidazole **4b** (2.86 g, 15.33 mmol) and dry DMF (15 mL). The product was obtained as a hygroscopic foam with 97% yield. Mp 94–96 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.95 (s, 12H, CH_3), 2.18 (s, 6H, CH_3), 2.31 (s, 6H, CH_3), 2.47 (s, 3H, CH_3), 3.26 (t, 4H, J = 7.4 Hz, CH_2), 4.46 (t, 4H, J = 7.4 Hz, CH_2-Imi), 7.12 (s, 4H), 7.24 (s, 1H), 7.93 (Imi), 8.20 (Imi), 9.50 (Imi) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 15.9 (CH_3), 17.0 (CH_3), 20.0 (CH_3), 20.7 (CH_3), 30.2 (CH_2), 48.3 (CH_2-Imi), 123.8 (Imi), 128.9 (Imi), 129.4 (CH), 130.3 (CH), 131.2, 131.5, 134.4, 135.4, 136.2, 137.6 (Imi), 140.4 ppm. ESI(+)-MS: m/z (%): 273.4 (100) $[M]^{2+}$, 626.7 (11) $[M + Br]^+$. Anal. Calcd for $C_{37}H_{46}Br_2N_4 \cdot H_2O$: C, 61.33; H, 6.68; N, 7.73; found: C, 61.41; H, 7.01; N, 7.49.

3,3′-(2,4,6-Trimethyl-1,3-phenylenedipropane-3,1-diyl)bis[1-(2,4,6-trimethyl)-1*H*-imidazol-3-ium] dibromide 7b·2Br. The above procedure was followed using 2,4-bis(3-bromopropyl)-1,3,5-trimethylbenzene **3** (0.50 g, 7.48 mmol) and 1-mesityl-1*H*-imidazole **4b** (0.53 g, 2.83 mmol) and dry DMF (3 mL). The product was obtained as a white solid with 77% yield. Mp 218–220 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.93–1.98 (m, 4H, CH_2), 2.03 (s, 12H, CH_3), 2.14 (s, 9H, CH_3), 2.33 (s, 6H, CH_3), 2.49–2.55 (m, 4H, Ar–CH_2), 4.43 (t, J = 7.0 Hz, 4H, CH_2-Imi), 6.80 (s, 1H), 7.15 (s, 4H), 7.98 (s, 2H, Imi), 8.22 (s, 2H, Imi), 9.59 (s, 2H, Imi) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 14.9 (CH_3), 17.1 (CH_3), 19.6 (CH_3), 20.8 (CH_3), 26.3 (Ar–CH_2), 29.1 (CH_2), 49.8 (CH_2-Imi), 123.6 (Imi), 124.1 (Imi), 129.4 (CH), 130.0 (CH), 131.4, 133.3, 133.8, 134.5, 135.2, 137.7 (Imi), 140.5 ppm. IR (KBr): ν = 1547 (C=N) cm^{-1}. ESI(+)-MS: m/z (%): 287.4 (100) $[M]^{2+}$, 654.8 (8) $[M + Br]^+$. Anal. Calcd for $C_{39}H_{50}Br_2N_4 \cdot H_2O$: C, 62.77; H, 7.11; N, 6.81; found: C, 62.78; H, 7.01; N, 7.09.

Preparation of silver–NHC complexes

3,3′-[(2,4,6-Trimethyl-1,3-phenylene)bis(methylene)]bis(1-methylimidazol-2-ylidene)-[AgCl]$_2$ (15a). A CH_2Cl_2 (15 mL) solution containing bis(imidazolium) dichloride **5a·2Cl** (300 mg, 0.78 mmol) and Ag_2O (185 mg, 0.78 mmol) was stirred at room temperature for 5 h. The solution was filtered through Celite, and 30 mL of Et_2O were added to precipitate a white solid. Isolation by filtration yielded **15a**. Yield: 95% (443 mg, 0.75 mmol).

Anal. Calcd. for $C_{19}H_{24}Ag_2Br_2N_4$: C, 38.35%; H, 4.07%; N, 9.42%. Found: C, 38.89%; H, 4.58%; N, 8.95%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.18 (s, 3H, CH_3), 2.32 (s, 6H, CH_3), 3.81 (s, 6H, NCH_3), 5.29 (s, 4H, CH_2), 6.91 (d, 2H, J = 1.8 Hz, C(H)NCH_2), 6.98 (d, 2H, J = 1.8 Hz, MeNC(H)C, 7.11 (s, 1H aromatic) ppm.

3,3′-[(2,4,6-Trimethyl-1,3-phenylene)bis(methylene)]bis[1-(2,4,6-trimethylphenyl)imidazol-2-ylidene]-[AgCl]$_2$ (15b). A CH_2Cl_2 (5 mL) solution containing bis(imidazolium) dichloride **5b·2Cl** (101 mg, 0.17 mmol) and Ag_2O (44 mg, 0.19 mmol) was stirred at room temperature for 4 h. The solution was filtered through Celite, and Et_2O was added to precipitate a white solid. Isolation by filtration yielded **15b**. Yield: 66% (90 mg, 0.11 mmol).

Anal. Calcd. for $C_{35}H_{40}Ag_2Cl_2N_4$: C, 52.33%; H, 5.02%; N, 6.97%. Found: C, 52.16%; H, 5.65%; N.6.92%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.95 (s, 12H, *o*-CH_3 Mes), 2.26 (s, 3H, CH_3), 2.32 (s, 6H, *p*-CH_3 Mes), 2.39 (s, 6H, CH_3), 5.46 (s, 4H, CH_2), 6.94 (ov, 6H, NC(H)CH + aromatic Mes), 6.98 (2H, NC(H)CH), 7.15 (s, 1H, aromatic bridge) ppm.

3,3′-(2,4,6-Trimethyl-1,3-phenylenedipropane-3,1-diyl)bis(1-methylimidazol-2-ylidene)-[AgBr]$_2$ (16a). A CH_2Cl_2 (5 mL) solution containing bis(imidazolium) dibromide **7a·2Br** (50 mg, 0.14 mmol) and Ag_2O (35 mg, 0.15 mmol) was stirred at room temperature for 4 h. The solution was filtered through Celite, the solvent volume was reduced to 1 mL, and 9 mL of Et_2O were added to precipitate a white solid. Isolation by filtration yielded **16a**. Yield: 38% (40 mg, 0.06 mmol).

Anal. Calcd. for $C_{23}H_{32}Ag_2Br_2N_4$: C, 37.33%; H, 4.36%; N, 7.57%. Found: C, 38.26%; H, 4.65%; N.7.85%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.95 (m, 4H, CH_2), 2.12 (s, 3H, CH_3), 2.18 (s, 6H, CH_3), 2.63 (m, 4H, CH_2), 3.85 (s, 6H, NCH_3), 4.13 (m, 4H, CH_2), 6.78 (s, 1H, aromatic), 7.04 (d, 2H, J = 1.4 Hz, NC(H)CH), 7.10 (d, 2H, J = 1.4 Hz, NC(H)CH) ppm.

3,3′-(2,4,6-Trimethyl-1,3-phenylenedipropane-3,1-diyl)bis[1-(2,4,6-trimethyl)imidazol-2-ylidene]-[AgBr]$_2$ (16b). A CH_2Cl_2 (15 mL) solution containing bis(imidazolium) dibromide **7b·2Br** (100 mg, 0.13 mmol) and Ag_2O (32 mg, 0.13 mmol) was stirred at room temperature for 4 h. The solution was filtered through Celite, and 30 mL of Et_2O were added to precipitate a white solid. Isolation by filtration yielded **16b**. Yield: 80% (102 mg, 0.11 mmol).

Anal. Calcd. for $C_{39}H_{48}Ag_2Br_2N_4$: C, 49.39%; H, 5.10%; N, 5.91%. Found: C, 50.44%; H, 5.06%; N, 5.96%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.97 (bs, 16H, CH_3Mes + CH_2), 2.18 (s, 3H, CH_3), 2.22 (s, 6H, CH_3), 2.33 (s, 6H, CH_3), 2.64 (m, 4H, CH_2), 4.33 (m, 4H, CH_2), 6.84 (s, 1H, aromatic), 6.94 (m, 6H, NC(H)CH, CHMes), 7.30 (s, 2H, NC(H)CH) ppm.

Preparation of palladium–NHC complexes

(PdCl$_2${1,3-bis[(*N*-methylimidazol-2-ylidene)methylene]-2,4,6-trimethylbenzene}) (17). A CH_2Cl_2 (10 mL) solution of **15a** (100 mg, 0.17 mmol) and [$PdCl_2$(PhCN)$_2$] (65 mg, 0.17 mmol) was stirred at room temperature for 1 h. The solution was filtered through Celite, and hexane was added to precipitate a light yellow solid. Isolation by filtration yielded **17**. Yield: 93% (75 mg, 0.15 mmol). ESI(+)-MS: m/z 451.07 uma [Pd(ligand)Cl]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (b, 9H, CH_3), 4.16 (s, 6H, NCH_3), 5.87 (bs, 4H, CH_2), 6.29 (s, 2H, C(H)NCH_2), 6.73 (s, 2H, MeNC(H)), 7.03 (s, 1H aromatic) ppm.

(PdClMe{1,3-bis[(*N*-methylimidazol-2-ylidene)methylene)]-2,4,6-trimethylbenzene}) (18). A CH_2Cl_2 (10 mL) solution of **15a** (100 mg, 0.17 mmol) and [PdMeCl(COD)] (51 mg, 0.17 mmol) was stirred at room temperature overnight. The solution was filtered through Celite, and Et_2O was added to precipitate a white solid. Isolation by filtration yielded **18**. Yield: 78% (61 mg, 0.13 mmol). MS(ESI): m/z 429.12 uma [Pd(ligand)Me]$^+$.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.55 (bs, 3H, CH_3), 2.40 (vbs, 9H, CH_3), 4.04 (bm, 6H, NCH_3), 5.80 (vbs, 4H, CH_2), 6.30 (bs, 2H, C(H)NCH_2), 6.71 (bs, 2H, MeNC(H)), 7.00–7.20 (bs, 1H aromatic) ppm.

3,3′-[(2,4,6-trimethyl-1,3-phenylene)bis(methylene)]bis(1-methylimidazol-2-ylidene)]-[Pd(η^3-2-methylallyl)Cl]$_2$ (19a). A CH_2Cl_2 (10 mL) solution of **15a** (52 mg, 0.09 mmol) and bis[μ-Cl-(η^3-(2-methylallyl))palladium] (30 mg, 0.09 mmol) was stirred at room temperature for 6 h. The solution was filtered through Celite, the solvent volume was reduced to 1 mL, and 6 mL of Et_2O were added to precipitate a pale yellow solid. Isolation by filtration yielded **19a**. Yield: 46% (28 mg, 0.07 mmol). MS (ESI): m/z 667.08 uma [M–Cl]$^+$ and 316.05 uma [M–2Cl]$^{2+}$.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.02 (s, 6H, CH_3-allyl), 2.17 (s, 3H, CH_3), 2.33 (s, 6H, CH_3), 2.39 (s, 2H, H_{anti}allyl), 3.20 (s, 2H, H_{anti}allyl), 3.26 (s, 2H, H_{syn}allyl), 3.82 (s, 4H NCH_3), 4.11 (d, 2H, H_{syn}allyl), 5.43 (s, 4H, CH_2), 6.32 (d, 2H, J = 1.2 Hz, $CH_2NC(H)C$), 6.79 (d, 2H, J = 1.2 Hz, MeNC(*H*)C), 7.01 (s, 1H, aromatic) ppm.

3,3′-[(2,4,6-Trimethyl-1,3-phenylene)bis(methylene)]bis[1-(2,4,6-trimethylphenyl)imidazol-2-ylidene]-[Pd(η^3-(2-methylallyl))Cl]$_2$ (19b). A CH_2Cl_2 (10 mL) solution of **15b** (50 mg, 0.06 mmol) and bis[μ-Cl-(η^3-(2-methylallyl))palladium] (24 mg, 0.06 mmol) was stirred at room temperature for 4 h. The solution was filtered through Celite, and Et_2O was added to precipitate a white solid. Isolation by filtration yielded **19b**. Yield: 88% (49 mg, 0.11 mmol). MS (ESI): m/z 420.12 uma [M–Cl$_2$]$^{2+}$.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44 and 1.45 (s, 3H, *p*-CH_3Mes), 1.83 and 1.85 (s, 1H Hi), 2.07 and 2.08 (s, 6H, *o*-CH_3Mes), 2.28 (s, 6H, Me-allyl), 2.30 (s, 3H, CH_3bridge), 2.38 (s, 6H, CH_3 bridge), 2.82 (s, 2H, H_{syn}allyl), 2.90 (s, 2H, H_{anti}allyl), 3.86 and 3.87 (d, 1H, H_{syn}allyl), 5.72 (s, 4H, CH_2), 6.57 (d, 2H, J = 1.2 Hz, C(H)NCH_2), 6.79 (d, 2H, J = 1.2 Hz, MeNC(H)), 6.90 and 6.93 (s, 2H, aromatic-Mes), 7.03 (s, 1H, aromatic-bridge) ppm.

(Pd{[1,3-bis(*N*-mesitylimidazol-2-ylidene)methyl]-2,4,6-trimethylbenzene}-[η^3-(2-methylallyl)])[BF$_4$] (20b). A CH_2Cl_2 (10 mL) solution of **15b** (100 mg, 0.12 mmol) and [Pd(2-methylallyl)-(CH_3CN)$_2$][BF_4] (41 mg, 0.12 mmol) was stirred at room

temperature for 1 h. The solution was filtered through Celite, and Et_2O was added to precipitate a yellow solid. Isolation by filtration yielded **20b**. Yield: 61% (54 mg, 0.08 mmol).

Anal. Calcd. for $C_{39}H_{47}BF_4N_4Pd$: C, 61.23%; H, 6.19%; N, 7.23%. Found: C, 58.42%; H, 7.13%; N, 6.90%.

^{1}H NMR spectrum : see discussion

Synthesis of bis(oxazoline) ligands

1,3-Bis{*N*-[(2-hydroxy-1,1-dimethyl)ethyl]propanamide}-2,4,6-trimethylbenzene (22). A mixture of $SOCl_2$ (3.60 mL, 49.57 mmol) and diacid **13** (0.72 g, 2.71 mmol) was stirred at 60 °C for 4 h under an argon atmosphere. The reaction mixture was concentrated under reduced pressure. The resulting orange solid was taken into dry CH_2Cl_2 (7 mL), cooled to 0 °C added to a solution of 2-amino-2-methyl-1-propanol (1.03 mL, 10.84 mmol) and dry triethylamine (1.51 mL, 10.84 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. CH_2Cl_2 (10 mL) was added and the solution washed with a saturated aqueous solution of $NaHCO_3$ (2 × 25 mL) and a saturated aqueous solution of NaCl (25 mL). The organic layer was dried (anhydrous Na_2SO_4), filtered and concentrated to dryness to give an orange foam, which was purified by column chromatography (SiO_2) with hexanes, hexanes–ethyl acetate and ethyl acetate–methanol mixtures of increasing polarity as eluents to provide amide **22** (0.41 g, 37% yield) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (s, 12H, CH_3), 2.27 (s, 6H, CH_3), 2.29 (s, 3H, CH_3), 2.93–2.99 (m, 8H, CH_2, $CH_2C{=}O$), 3.55 (s, 4H, CH_2OH), 5.53 (bs, 2H, NH), 6.85 (s, 1H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): I = 15.5 (CH_3), 19.9 (CH_3), 24.7 (CH_3), 25.9 (CH_2), 36.6 ($CH_2C{=}O$), 56.2 ($C(CH_3)_2$), 70.7 (CH_2OH), 130.3 (CH), 134.2, 134.3, 135.4, 173.4 (C=O) ppm. IR (NaCl): ν = 1649 (C=O), 3310 (N-H) cm^{-1}. CI-MS: *m*/*z* (%): 407 (100) [M$^{+\bullet}$].

1,3-Bis[(4,4-dimethyl-4,5-dihydro-2-oxazolyl)ethyl]-2,4,6-trimethylbenzene (23). A mixture of amide **22** (0.35 g, 0.86 mmol) and $SOCl_2$ (10 mL, 137.85 mmol) was stirred at room temperature for 4 h, under an argon atmosphere. The reaction mixture was concentrated under reduced pressure. The resulting brown foam was dissolved in dry CH_2Cl_2 (25 mL), stirred with 10% NaOH (25 mL) overnight and the organic layers were separated. The organic layer was washed with an aqueous saturated solution of NaCl (3 × 50 mL), dried (anhydrous Na_2SO_4), filtered and evaporated to dryness to yield bis(oxazoline) **23** (0.31 g, 96% yield) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (s, 12H, CH_3), 2.25 (s, 6H, CH_3), 2.35 (s, 3H, CH_3), 2.95 (bs, 8H, CH_2), 3.52 (s, 4H, OCH_2), 6.81 (s, 1H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.4 (CH_3), 19.9 (CH_3), 24.5 (CH_3), 25.9 (CH_2), 36.4 (CH_2-oxazoline), 56.0 ($C(CH_3)_2$), 70.5 (OCH_2), 130.2 (CH), 134.0, 134.2, 135.5, 173.4. IR (NaCl): ν = 1647 (C=N) cm^{-1}. CI-MS: *m*/*z* (%): 371 (100) [M$^{+\bullet}$]. Anal. Calcd for $C_{23}H_{34}N_2O_2{\cdot}1.5\ CH_2Cl_2$: C, 59.10; H, 7.49; N, 5.63; found: C, 58.80; H, 7.30; N, 5.24.

Preparation of palladium–oxazoline complexes

(Pd{[1,3-bis(4,4-dimethyl-4,5-dihydro-2-oxazolyl)methyl]-2,4,6-trimethylbenzene}-[η^3-2-methylallyl])[PF$_6$] (25c). A solution of $[(\eta^3\text{-}CH_3C_3H_4)PdCl]_2$ (0.078 g, 0.2 mmol) and bis(oxazoline) **21c** (0.15g, 0.44 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 15 min and then NH_4PF_6 (0.097 g, 0.6 mmol) in tetrahydrofuran (4 cm^3) was added. The solution was stirred for 4 h and then 5 cm^3 of H_2O was added. After separation of the two layers, the organic phase was dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure. A white solid was obtained after addition of absolute EtOH. The product was separated by filtration and recrystallized from dichloromethane–ethanol giving **25c** in 60% yield. Data for **25c**: Anal. Found: C, 46.7; H, 6.3; N, 4.4%. Calcd for $C_{25}H_{37}F_6N_2O_2PPd$: C, 46.27; H, 5.75; N, 4.32%. MS/MALDI: *m*/*z* 503 [M$^+$].

^{1}H NMR (400 MHz, $CDCl_3$); δ 6.95 (s, 1H, H-aromatic), 4.25 (d, 2H, CHa oxa, *J* = 8 Hz),), 4.18(d, 2H, CHb oxa, *J* = 8 Hz), 3.82 (d, 2H, CHa linker), 3.76 (d, 2H, CHb linker), 3.53 (s, 2H, H_{syn}), 2.32 (s, 6H, *ortho*-Me), 2.16 (s, 6H, *para*-Me), 1.96 (s, H, CH_3-allyl), 1.31 (s, 2H, H_{anti}).

(Pd{[1,3-bis(4(*S*)-isopropyl-4,5-dihydro-2-oxazolyl)methyl]-2,4,6-trimethylbenzene}-[η^3-2-methylallyl])[PF$_6$] ((*S*,*S*)-25d). Compound (*S*,*S*)-**25d** was synthesized in a similar way as **25c** starting from: 0.078g (0.20mmol) of $[(\eta^3\text{-}MeC_3H_4)PdCl]_2$, 0.163 g (0.44 mmol) of the bis(oxazoline) (*S*,*S*)-**21d** and 0.097 g (0.6 mmol) of NH_4PF_6. A white–yellow solid was obtained which was recrystallized from dichloromethane–ethanol giving (*S*,*S*)-**25d** in 60% yield. Data for (*S*,*S*)-**25d**: Anal. Found: C, 48.7; H, 6.8; N, 4.1%. Calcd for $C_{27}H_{41}F_6N_2O_2PPd$: C, 47.90; H, 6.10; N, 4.14%. MS/MALDI: *m*/*z* 531 [M$^+$]. ^{1}H NMR (400 MHz, $CDCl_3$); δ 6.93 (s, 1H, H-aromatic), 4.62 (t, 1H, CHa oxa, *J* = 10 Hz), 4.43 (t, 1H, CHb oxa, *J* = 9.5 Hz), 4.35 (t, 1H, CHa oxa, *J* = 8 Hz), 4.19 (t, 1H, CHb oxa, *J* = 9 Hz), 3.93 (m, 1H, CH oxa), 3.87-3.84 (3H, CH oxa, 2 CH bridge), 3.77-3.68 (3H, H*syn*, 2 CH bridge), 3.33 (d, *J* = 2.5 Hz, 1H, H_{syn}), 2.30 (s, 3H) and 2.29 (s, 3H) *ortho*-Me, 2.06 (s, 3H, *para*-Me), 2.00 (bs, 2H, H-iPr), 1.92 (s, 3H, CH_3-allyl)], 1.36 (s, 1H, H_{anti}), 1.27 (s, 1H, H_{anti})

η^3-1,3-diphenylallyl((*S*,*S*)- 21d)-palladium(II) tetrafluoroborate (26)

(Pd{[1,3-bis(4(*S*)-isopropyl-4,5-dihydro-2-oxazolyl)methyl]-2,4,6-trimethylbenzene}-[η^3-1,3-diphenylallyl])[BF$_4$] (26). To a 0.130 g (0.20 mmol) sample of $[Pd(\eta^3\text{-}1,3\text{-}Ph_2C_3H_3)(\mu\text{-}Cl)]_2$ and 0.148 g (0.40 mmol) of the oxazoline ligand (*S*,*S*)-**21d** dissolved in 50 cm^3 of THF, 10 cm^3 of a 0.04 M solution of $AgBF_4$ in THF were added. The mixture was stirred at room temperature for 4 h. The precipitate was filtered and partially dissolved in acetone. From the acetone solution after adding diethyl ether a yellow–orange precipitate of **26** was obtained (40% yield). Anal. Calcd for $C_{38}H_{47}F_4N_2O_2BPd$: C, 60.29; H, 6.26; N, 3.70%. Found C, 58.9; H, 6.6; N, 3.31%. MS (FAB positive): *m*/*z* 669 [M$^+$], 476 [M$^+$–Ph_2allyl].

Synthesis of {1-[3-(4,4-dimethyl-4,5-dihydro-2-oxazolyl)methyl-2,4,6-trimethylbenzyl]-3-methylimidazol-2-ylidene}-[AgBr] (28)

A CH_2Cl_2 (6 mL) solution oxazolinyl-imidazolium bromide **27** (72 mg, 0.18 mmol) and Ag_2O (25 mg, 0.11 mmol) was stirred at room temperature for 1.5 h. The solution was filtered through Celite, and the yellow solution was immediately used to prepare the palladium complexes.

A small fraction of **28** was isolated as a white solid by precipitation in a CH_2Cl_2–Et_2O mixture. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.23 (s, 6H, CH_3), 2.26 (s, 6H, CH_3), 2.36 (s, 3H, CH_3), 3.60 (s, 2H, CH_2), 3.83 (s, 3H, NCH_3), 3.88 (s, 2H, CH_2-ox), 5.28 (s, 2H, CH_2), 6.57 (d, 1H, NCHC*H*, 2.4), 6.97 (d, 1H, NC*H*CH, 2.4), 6.90 (s, 1H, aromatic) ppm.

Synthesis of [Pd{1-[3-(4,4-dimethyl-4,5-dihydro-2-oxazolyl)methyl-2,4,6-trimethylbenzyl]-3-methylimidazol-2-ylidene}-(η^3-2-methylallyl)][PF_6] (29)

Bis[μ-Cl-(η^3-(2-methylallyl))palladium] (44 mg, 0.11 mmol) was added to a solution of freshly prepared **28** (considering a 100% conversion in the synthesis of **28**, 116 mg, 0.22 mmol) in THF (6 mL)–CH_2Cl_2 (6 mL), and then, NH_4PF_6 (37 mg, 0.22 mmol) was added and the solution was stirred overnight. It was filtered through Celite, and the solvent was removed under reduced pressure, affording 139 mg of **29** as a yellow solid. The product was extracted with a water/CH_2Cl_2 mixture (2 × 5 mL), the organic layers were washed with saturated NaCl, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure, affording **29** as a crystalline yellow solid. Yield: 39% (55 mg, 0.08 mmol). ESI (+)-MS *m*/*z*: 485 $[M]^+$.

The ^{1}H NMR spectrum was too broad and complex to make a feasible assignation, probably due to the dynamic behaviour of the complex.

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