Recent developments in amino acid-derived imidazole-, imidazolium- and *N*-heterocyclic carbene-carboxylate complexes

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ARTICLE INFO

ABSTRACT

Compounds based on imidazole or imidazolium moieties are excellent building blocks for the preparation of a plethora of ligand precursors. The introduction of chirality in these compounds is relatively easy through the Debus-Radziszewski reaction, in which the chiral pools are natural or non-natural amino acids. Using this synthetic route, enantiopure imidazole-carboxylate, imidazolium-carboxylate, and imidazolium-dicarboxylate ligand precursors can be prepared, from which *N*-heterocyclic carbenes (NHC) with one or two carboxylate groups can also be obtained. This review is a personal account that summarizes our recent results regarding the use of all these compounds as chiral ligands coordinated to several transition metals (Cu, Zn, Ag and Mo). The structural features of the new synthesized coordination polymers with novel bonding modes will be described, and the bonding capabilities of these ligands rationalized on the basis of theoretical calculations. The efficiency of homochiral imidazolium-dicarboxylate compounds as chiral inductors in asymmetric catalysis will also be discussed. Finally, the antimicrobial and antitumoral activities of imidazolium- and NHC-carboxylate silver complexes and the found chirality-activity and structure–activity relationships will be highlighted.

1. Introduction

The importance of imidazole- and imidazolium-based carboxylic acids has recently increased because of the diversity of their applications. Their use as acid–base bifunctional catalysts [1], precursors of ionic liquids [2,3], of *N*-doped porous carbon materials [4] and of *N*-heterocyclic carbenes (NHC) [5,6], and also as bridging ligands for the construction of coordination polymers [7–10] or metal–organic frameworks [11–13] has been reported in recent years. Our contribution to this area started about a decade ago with the incorporation of chirality into these derivatives [14–16]. The use of enantiopure amino acids (natural or non-proteinogenic) can be employed as efficient chiral pools through the Debus–Radziszewski (DR) reaction (Scheme 1) [17,18]. This is a multicomponent reaction [19] that allows, under relatively mild conditions, straightforward syntheses of imidazole and imidazolium compounds that can be conveniently substituted (R_1 to R_3 in Scheme 1). The use of pure amino acids, instead of ammonia or amines, allows the obtention of several chiral derivatives constituted by the imidazole or imidazolium ring with one or two carboxylic or carboxylate

functionalities (Scheme 2). These compounds behave as efficient ligands in coordination polymers and metal–organic frameworks with interesting structural [20,21], magnetic [10,22], and optical properties [23] and are convenient precursors of NHC ligands [24–26] (Scheme 2).

Here, we report a brief account of our recent personal research on the use of chiral imidazole- [27] or imidazolium-carboxylate compounds [28,29] as ligands and as NHC precursors [24] and the applications of the resulting complexes in catalysis [30,31] and bioinorganic areas [32–34].

2. Structural and theoretical characteristics

2.1. Imidazole-carboxylate compounds

When aqueous ammonia was used in the DR reaction with an equivalent of the appropriate amino acid, formaldehyde, glyoxal, and NaOH, the imidazole-carboxylate compounds Na[(*S*)–L^R] and Na[(*R*)–L^R] can be obtained (Scheme 3) [35]. By reaction with acids, imidazole-carboxylic compounds (*S*)–HL^R and (*R*)–HL^R are obtained (Scheme 2)

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[36]. The lack of structural data for the chiral Na[(*S*)–L^R] compounds led us to characterize by X-ray diffraction the derivatives of R = Me and CH$_2^i$Pr [27], which were isolated as homochiral 2D coordination polymers, {Na(H$_2$O)[(*S*)-L^{Me}]}$_n$ and {Na[(*S*)-L^{CH2iPr}]}$_n$, displaying unprecedented coordination modes: μ_3-$\kappa^2 O \kappa O'$ and μ_4-$\kappa N, \kappa^2 O \kappa^2 O'$, respectively (Fig. 1). Specifically, {Na(H$_2$O)[(*S*)-L^{Me}]}$_n$ was the first reported example in which the [(*S*)-L^{Me}]$^-$ anion is bonded only through oxygen atoms without the participation of the N atom of imidazole. This situation contrasts with those of all of the reported compounds, where these types of ligands always behave as ditopic linkers because of the presence of one nitrogen atom of imidazole plus one carboxylate group as potential donor functionalities. In fact, we analyzed the coordination capabilities of [L^R]$^-$ anions as ligands using density functional theory (DFT) calculations, and the two σ O lone pairs of the carboxylate group are centered on HOMO and HOMO–1 (*in-phase* and *out-of-phase*, respectively), while the σ N lone pair on the nitrogen atom of imidazole is identified as HOMO–5 [27]. For example, Fig. 2 shows the results for the optimized [(*R*)-L^{Me}]$^-$ anion. In particular, the accessibility of the compound Na[(*R*)-L^{Me}] (Scheme 3) allowed us to synthesize the first examples of homochiral coordination polymers with imidazole–monocarboxylate ligands based on non-natural amino acids, namely {Ag[(*R*)–L^{Me}]}$_n$, {Cu[(*R*)-L^{Me}]}$_n$ and {Zn[(*R*)-*L^{Me}*]$_2$}$_n$ by reaction of Na[(*R*)-L^{Me}] with the appropriate metal salt [27]. The silver complex showed an experimental powder diffractogram (XRPD) identical to the simulated one of {Ag[(*S*)-L^{Me}]}$_n$, from single-crystal X-ray studies, in agreement with a 2D coordination polymer and a μ_4-$\kappa N, \kappa^2 O, \kappa O'$ bonding mode for the [L^{Me}]$^-$ anion. Similarly, the XRPD of the complex {Zn[(*R*)-*L^{Me}*]$_2$}$_n$ was identical to that of the previously reported {Zn[(*S*)-*L^{Me}*]$_2$}$_n$ [37].

2.2. Imidazolium-dicarboxylate compounds

In the DR reaction with amino acids, symmetric imidazolium-dicarboxylate compounds can be readily obtained with the appropriate (*S,S*)- or (*R,R*)- configuration, depending on the nature of the amino acids, and without significant racemization (Scheme 4) [14,15,16]. These chiral compounds usually exist as zwitterions, HL^R, but two other known forms are the acid species [H$_2$L^R]$^+$ and the basic species [L^R]$^-$ [3]. From a structural point of view, several zwitterionic compounds, HL^R, have been described [14,15,38], and an example of acid form, [H$_2$L^R]$^+$, is also known [39]. However, structural data for the basic form, [L^R]$^-$, were not reported and we decided to investigate their preparation and characterization. Compounds M[(L^{iPr})] (M = Na, NH$_4$, and Li) were prepared by treating (*S,S*)- or (*R,R*)-HL^{iPr} with the appropriate base [29]. In the solid state, {M[(*S,S*)-L^{iPr}]}$_n$ and {M[(*R,R*)-L^{iPr}]}$_n$ (M = Na, NH$_4$) are 1D homochiral coordination polymers, in which the cations are placed in an approximate linear array. The [L^{iPr}]$^-$ anion acts as bridging linker and showed for the sodium derivative a novel μ_4-$\kappa^2 O^1, \kappa^2 O^3, \kappa^1 O^4$ coordination mode (Fig. 3). The enantiomeric relationship between {Na[(*S,S*)-L^{iPr}]}$_n$ and {Na[(*R,R*)-L^{iPr}]}$_n$ is evidently observed when the 1D polymer is viewed along the four-fold screw symmetry axis. The specific coordination mode of the chiral [L^{iPr}]$^-$ anion creates an opposite helical sense growing along the *c* axis, as shown in Fig. 4. The use of (*R,R*)-HL^{iPr}, obtained from a non–natural amino acid, allowed us to describe the first examples of compounds containing this type of [(*R,R*)-L^{iPr}]$^-$ anions [29].

In solution, the NMR spectra of M[(L^{iPr})] agree with the dissociation of the M$^+$ and [L^{iPr}]$^-$ ions and this was corroborated by the good agreement found between the experimental and calculated NMR chemical shifts of the [L^{iPr}]$^-$ anion. NMR showed an H-D exchange at the C^2-H atom of the imidazolium ring, which is a process that was not detected for the HL^{iPr} form. The presence of the M$^+$ cation favors this process through an intramolecular nucleophilic attack of one of the carboxylate groups towards the hydrogen atom at the C^2-H position of imidazolium, according to DFT calculations [29]. In the mechanism, a transient carbene intermediate was proposed to explain the H-D exchange, as illustrated in Scheme 5. This fact prompted us to investigate the possible formation of NHC ligands coordinated to silver ions (see below).
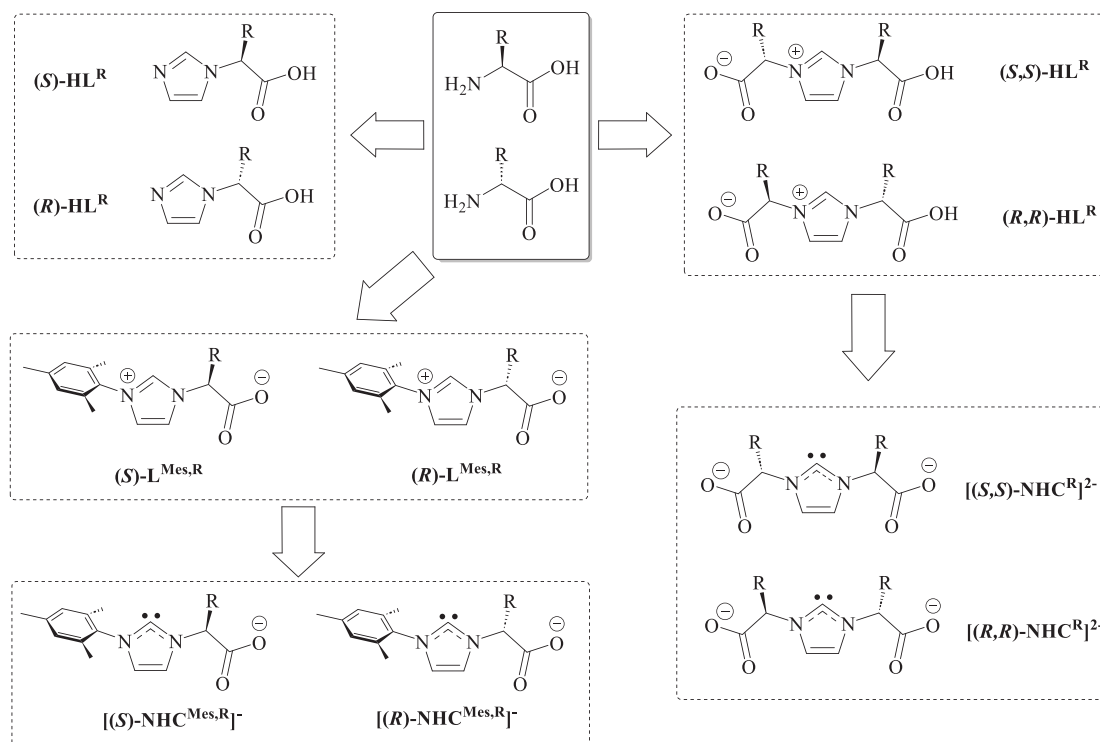
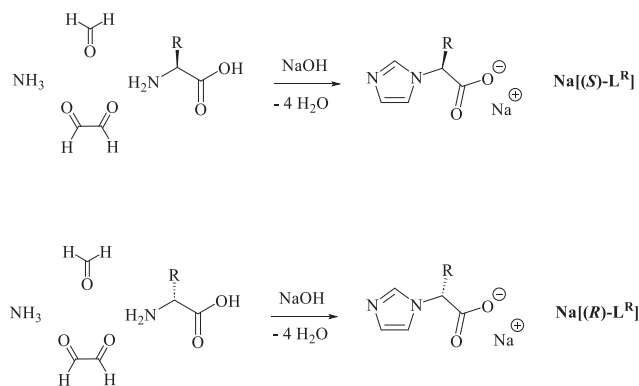The compounds (*S,S*)-HL^R and (*R,R*)-HL^R were used by us as efficient
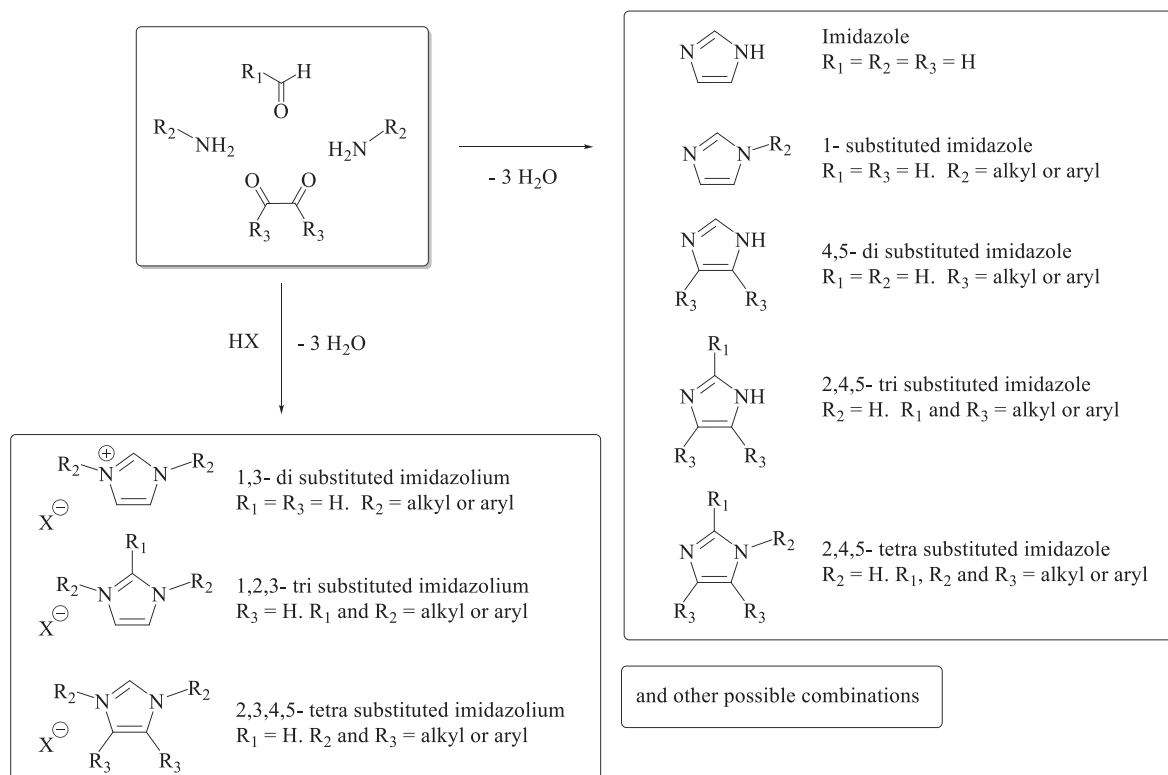
Scheme 1. Imidazole and imidazolium compounds obtained from the Debus–Radziszewski reactions.

reagents to create homochiral coordination complexes with copper, zinc [28], molybdenum [31] and silver [32] transition metals, in which the corresponding anion [L^R]$^-$ behaves as bridging ligand according to X-ray diffraction studies. For copper and zinc, imidazolium-dicarboxylate ligands provide 2D homochiral coordination polymers, {M[(*S,S*)-L^R]$_2$}$_n$ and {M[(*R,R*)-L^R]$_2$}$_n$ (five X–ray structures), in which Cu(II) and Zn(II) ions are coordinated by the two carboxylate groups of [L^R]$^-$ anions in the typical bridging monodentate μ_2-$\kappa^1 O^1$,$\kappa^1 O^3$ bonding mode. This coordination afforded tetrahedral or square-planar metal environments for Zn and Cu complexes, respectively. Although the coordination mode μ_2-$\kappa^1 O^1$,$\kappa^1 O^3$ is common in these five complexes, the resulting crystal packing is not the same and two factors control the 3D arrangement. The first is the wide range of torsion angles C$_{carboxy}$–C$_{chiral}$–C'$_{chiral}$–C'$_{carboxy}$, which goes from 20° in {Zn[(*S,S*)-L^{CH2Ph}]$_2$}$_n$ to 117° in {Cu[(*S,S*)-L^{iPr})]$_2$}$_n$, and the second is the alternative κ^1-*syn*,κ^1-*syn* or κ^1-*anti*,κ^1-*anti* for monodentate coordination. Both factors are responsible for the different directionality of the growing chain in the coordination polymer [28].

To confirm the conformational flexibility as ditopic linkers and the possible formation of different coordination polymers for four-coordinated metal centers, DFT calculations on anions [L^R]$^-$ were performed. At least three conformers were optimized for each [L^R]$^-$ anion in which the 1,3-substituted arms show different orientations with respect to the imidazolium ring. Data for [(*S,S*)-L^R]$^-$ (R = Me, ^{i}Pr and CH$_2$Ph) anions were published [28], and here Fig. 5 shows the optimized structures of the three conformers located for the anion [(*R,R*)-L^{iPr}]$^-$. In all cases, the maximum energy difference between the conformers was <1 kcal mol^{-1} (relative ΔG) and this agreed with the various orientations of these arms found in the X-ray structures of Zn and Cu complexes and confirmed the conformational flexibility as ditopic linkers of the [L^R]$^-$ ligands. Additionally, the coordination capabilities of the [L^R]$^-$ anions were analyzed by DFT calculations. For the [(*S,S*)-L^{iPr}]$^-$ anion, the HOMO to HOMO–3 orbitals display principally the *in-phase* and *out-of-phase* combinations of σ O lone pairs responsible for the ligand bridging coordination [28]. Fig. 6 shows similar MOs for the enantiomer [(*R,R*)-L^{iPr}]$^-$ anion.

Scheme 3. Synthesis of the imidazole-carboxylate compounds Na[(*S*)–L^R] and Na[(*R*)–L^R].

Concerning silver, complexes [Ag(L^R)] were prepared by treatment of compounds HL^R with Ag$_2$O under the appropriate reaction conditions [32]. In the solid state, compounds {Ag[(*S,S*)-L^{iPr}]}$_n$, {Ag[(*R,R*)-L^{iPr}]}$_n$ and {Ag[(*S,S*)-L^{sBu}]}$_n$, were characterized as coordination polymers in which silver(I) cations are connected *via* the chiral [L^R]$^-$ anion with unprecedented coordination modes. The torsion angle C$_{carboxy}$–C$_{chiral}$–C'$_{chiral}$–C'$_{carboxy}$ of *ca.* 35° in the complex {Ag[(*S,S*)-L^{iPr}]}$_n$ allows the bonding of both carboxylate groups with up to four silver cations that affords the novel coordination mode, μ_4-$\kappa^2 O^1$,$\kappa^1 O^3$,$\kappa^1 O^4$ (Fig. 7). Both {Ag[(*S,S*)-L^{iPr}]}$_n$ and {Ag[(*R,R*)-L^{iPr}]}$_n$ are structurally organized as 1D coordination polymers and their enantiomeric relationship is clearly observed when the crystal structure is viewed along the *c* axis (Fig. 8). On the contrary, the coordination polymer {Ag[(*S,S*)-L^{sBu}]}$_n$ is 2D with a different bonding mode, μ_4-$\kappa^2 O^1$,$\kappa^1 O^2$,$\kappa^1 O^3$,$\kappa^1 O^4$ (Fig. 7). These facts are probably due to the higher torsion angle C$_{carboxy}$–C$_{chiral}$–C'$_{chiral}$–C'$_{carboxy}$ of 78° and the different steric pressure of the ^{s}Bu alkyl group.

Scheme 2. Typologies of chiral imidazole-, imidazolium- and NHC– carboxylate compounds considered in this review.
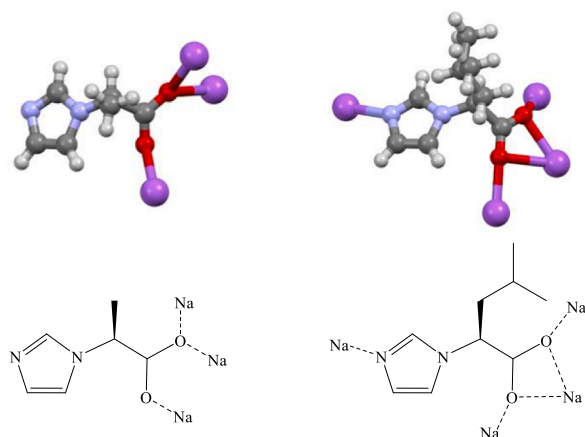
Fig. 1. New coordination modes of [(*S*)-L^R]$^-$ anions: μ_3-κ^2O,$\kappa O'$ in {Na(H$_2$O)[(*S*)-L^{Me}]}$_n$ (left) and μ_4-κN,κ^2O,κ^2O' in {Na[(*S*)-L^{CH2iPr}]}$_n$ (right). Colour codes: C, grey; H, white; O, red; N, blue; Na, violet. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. N-heterocyclic carbene compounds

As stated above, imidazolium carboxylate compounds are adequate precursors of NHC ligands (Scheme 2) [26,40–42]. The presence of one or two carboxylate groups makes it possible for additional coordination of this functionality to give potential bi- or tridentate ligands. This fact would prevent the rotation around the metal carbon bond that usually hampers efficient *enantio*-induction in monodentate chiral NHC ligands [43,44]. The introduction of a chiral NHC-carboxylate ligand coordinated to a transition-metal center usually occurs by transmetalation reactions with the appropriate silver complex. For example, complexes of type [Ag(NHC^{Mes,R})] were used by Mauduit, Baslé, and coworkers for this purpose [45–48]. These silver complexes were prepared with good yields by reacting imidazolium precursors with Ag$_2$O (Scheme 6). Their

complete characterization was poorly described, and binuclear or polymeric formulations have previously been proposed for these complexes. We have fully identified their nature in the solid state by X-ray determination of the complex [Ag(NHC^{Mes,H})]$_n$ [33]. The carbene ligand coordinates silver (2.046(8) Å), while the κ^1-O carboxylate group of NHC^{Mes,H} is bonded to a symmetry-related silver ion (2.100(6) Å), producing a coordination polymer that grows along the crystallographic *b* axis (Fig. 9). We have also investigated their behavior in solution. The presence of smaller units formed from the polymers was hypothesized and to confirm this, diffusion-ordered NMR spectroscopy (DOSY) was carried out. From the diffusion parameters obtained, a hydrodynamic radius of 8.8 Å was calculated for Ag(NHC^{Mes,H}). From the optimized structure of the dimer [Ag(NHC^{Mes,H})]$_2$, it is possible to estimate a value of 9.4 Å that compares well with the experimental data and strongly suggests a dimeric nature for the *in–solution* complex Ag(NHC^{Mes,H}) [33].

The bonding capabilities of the [(*S*)-NHC^{Mes,R}]$^-$ and [(*R*)-NHC^{Mes,}
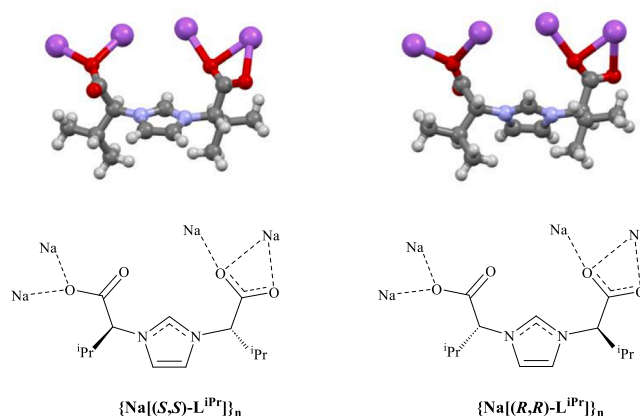
Fig. 3. New coordination mode μ_4-κ^2O^1,κ^2O^3,κ^1O^4 of the anion [L^R]$^-$ in {Na[(*S*,*S*)-L^{iPr}]}$_n$ and {Na[(*R*,*R*)-L^{iPr}]}$_n$ compounds. Colour codes as in Fig. 1.
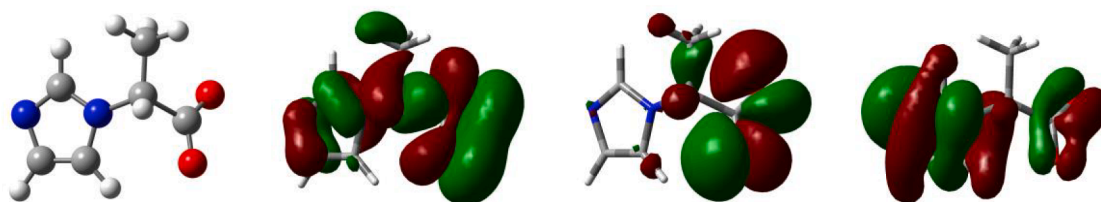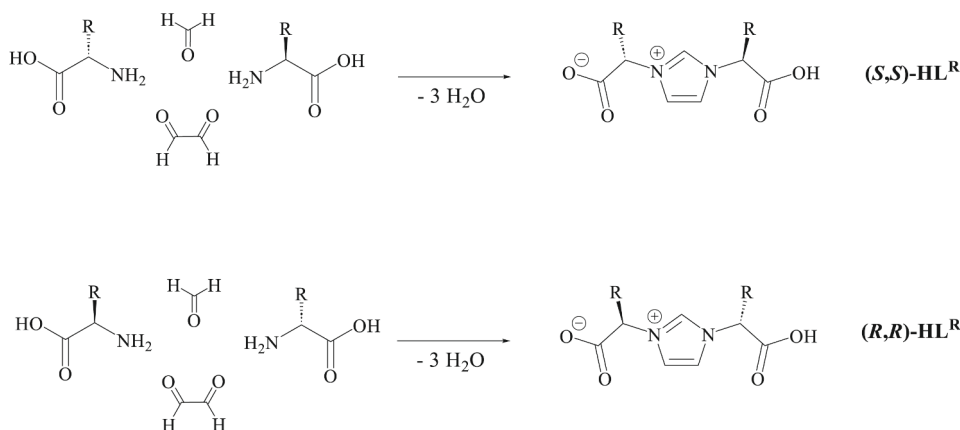

Fig. 2. Optimized structure of [(*R*)-L^{Me}]$^-$ anion and from the left to the right: HOMO, HOMO–1 and HOMO-5.

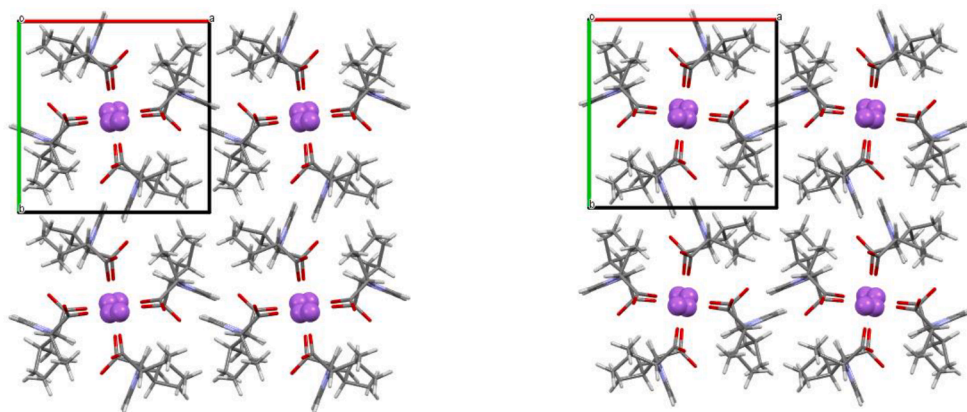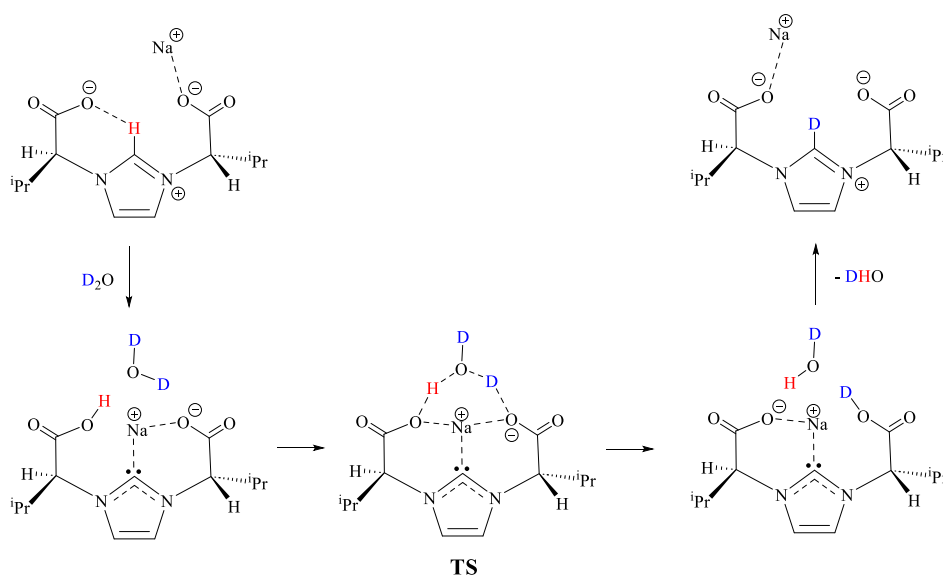**Scheme 4.** Synthesis of imidazolium-dicarboxylate compounds (*S*,*S*)–HL^R and (*R*,*R*)–HL^R.

Fig. 4. Comparison of crystal packing in {Na[(*S,S*)-L^{iPr}]}$_n$ (left) and {Na[(*R,R*)-L^{iPr}]}$_n$ (right), viewed along the *c* axis (four 1D coordination polymers). Colour codes as in Fig. 1.

Scheme 5. Concerted H-D exchange between D$_2$O and the *C*^{2}-H atom of the imidazolium ring through the proposed carbene intermediate.
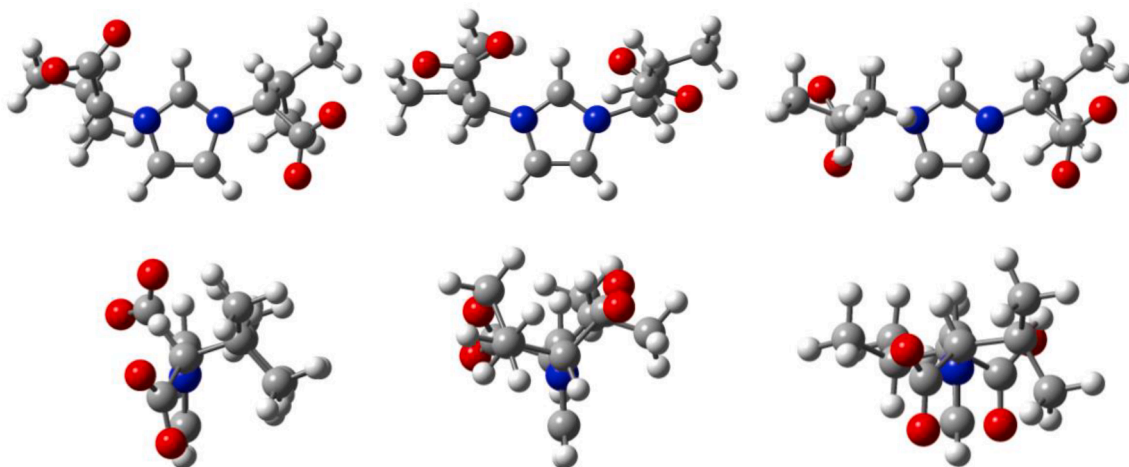

Fig. 5. Three conformers optimized for the [(*R,R*)-L^{iPr}]$^-$ anion: frontal (top) and lateral views (bottom).
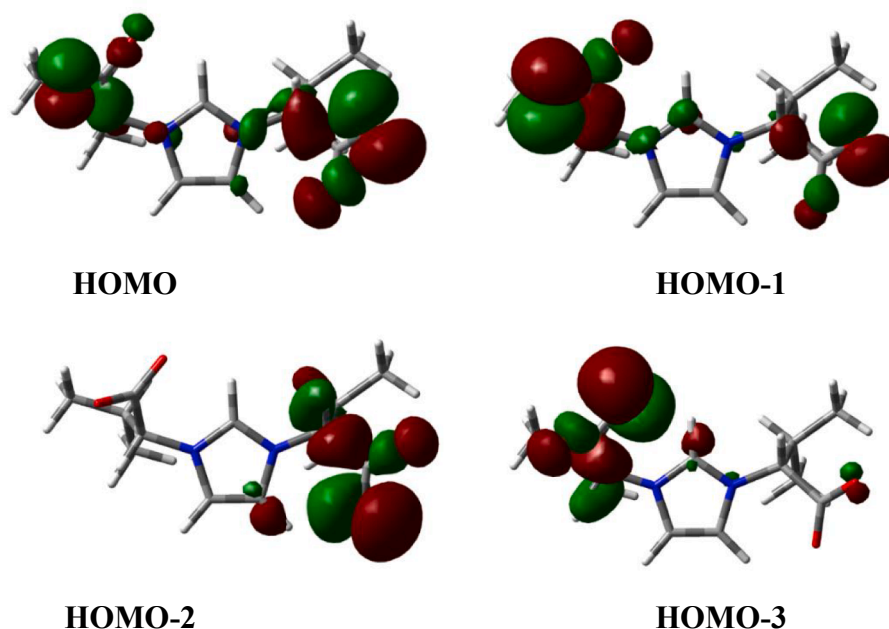
HOMO

HOMO-1

HOMO-2

HOMO-3

Fig. 6. Computed HOMO to HOMO-3 of the anion [(*R*,*R*)-L^{iPr}]$^-$.
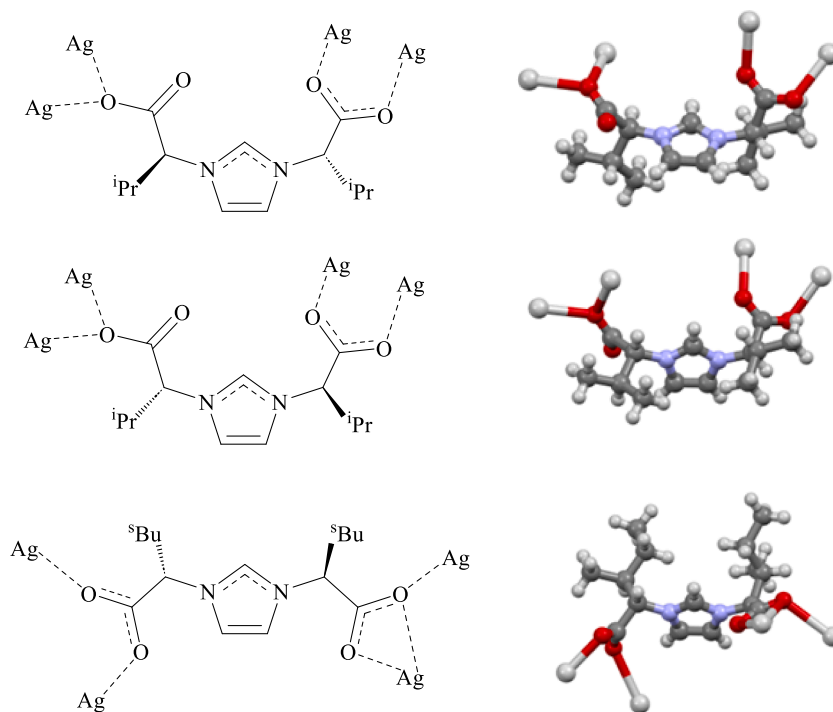
Fig. 7. Novel bonding modes of the anion [L^R]$^-$: μ_4-κ^2O^1,κ^1O^3,κ^1O^4 in {Ag[(*S*,*S*)-L^{iPr}]}$_n$ and {Ag[(*R*,*R*)-L^{iPr}]}$_n$ compounds and μ_4-κ^2O^1,κ^1O^2,κ^1O^3,κ^1O^4 in {Ag[(*S*,*S*)-L^{sBu}]}$_n$. Colour codes as in Fig. 1 and Ag, light grey.

^{Me}]$^-$ anions were theoretically analyzed. These ligands were optimized and the MOs involved in the coordination to the metal were identified. For example, the [(*S*)-NHC^{Mes,Me}]$^-$ ligand showed HOMO and HOMO-1 that are composed of the *in-plane* lone pairs of the oxygen atoms of the carboxylate groups (Fig. 10). They are responsible for the σ-coordination through the oxygen atom to silver. The carbene-centered orbital, involved in the σ-coordination to silver, was HOMO-3 (Fig. 10) [33].

Complexes {Pd[(*S*)-NHC^{Mes,R}]$_2$} (R = Me, ^{i}Pr, ^{i}Bu) and {Pd[(*R*)-NHC^{Mes,Me}]$_2$} were prepared using imidazolium-carboxylate

compounds, (*S*)-2-*alkyl*(3-mesityl-1*H*-imidazol-3-ium-1-yl)acetate, or (*R*)-2-methyl(3-mesityl-1*H*-imidazol-3-ium-1-yl)acetate, as precursors of chiral NHC ligands. They can be prepared by a carbene transfer reaction from the silver complexes [Ag(NHC^{Mes,R})]$_n$ described above to palladium acetate or by the *in–situ* formation of the lithium salt of the corresponding carbene and subsequent reaction with palladium acetate (Scheme 7). The molecular structure of {Pd[(*S*)-NHC^{Mes,iBu}]$_2$} was determined by X–ray crystallography. The complex is square-planar and the C atoms of carbene and the O atoms of carboxylate ligands showed a
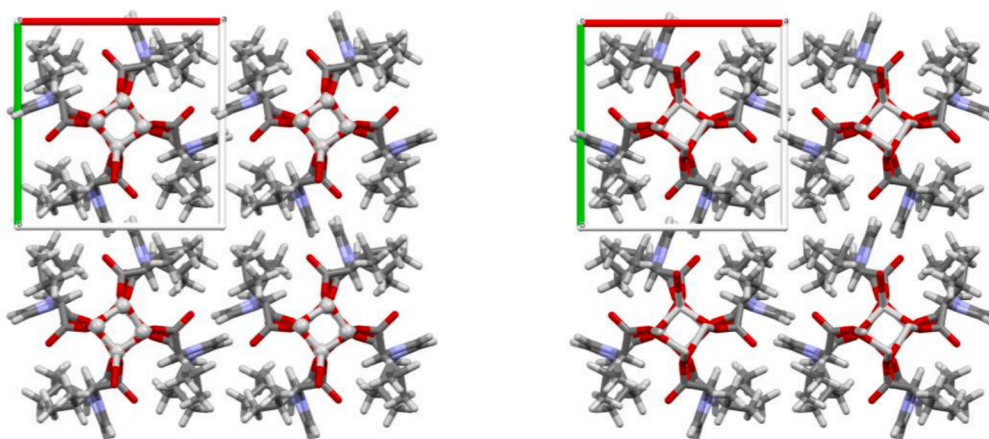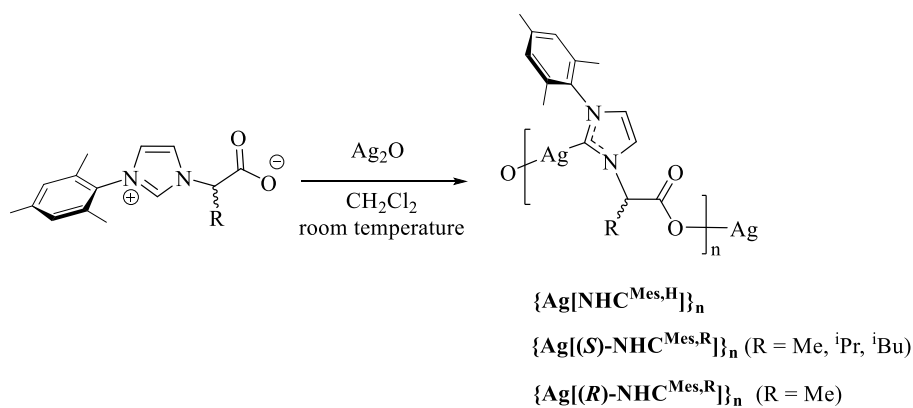
Fig. 8. Comparison of the crystal packing in {Ag[(S,S)-L^{iPr}]}$_n$ (left), and {Ag[(R,R)-L^{iPr}]}$_n$ (right), viewed along the c axis (four 1D coordination polymers). Colour codes as in Fig. 7.

{Ag[NHC^{Mes,H}]}$_n$

{Ag[(S)-NHC^{Mes,R}]}$_n$ (R = Me, ^{i}Pr, ^{i}Bu)

{Ag[(R)-NHC^{Mes,R}]}$_n$ (R = Me)

Scheme 6. Synthesis of NHC-carboxylate silver compounds [Ag(NHC^{Mes,R})]$_n$.
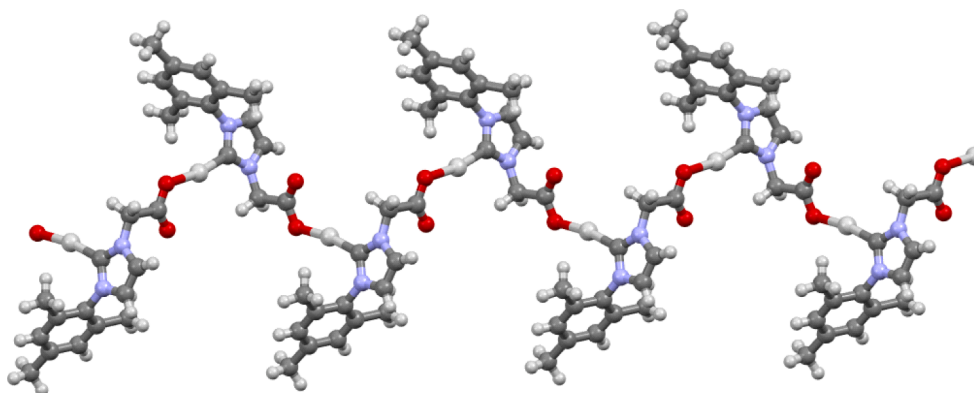
Fig. 9. Coordination 1D polymer formed by [Ag(NHC^{Mes,H})]$_n$ viewed along the c axis. Colour codes as in Fig. 7.
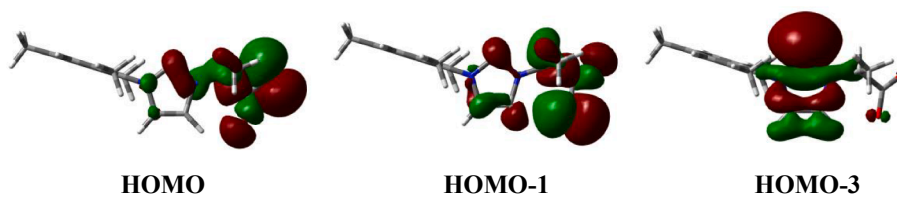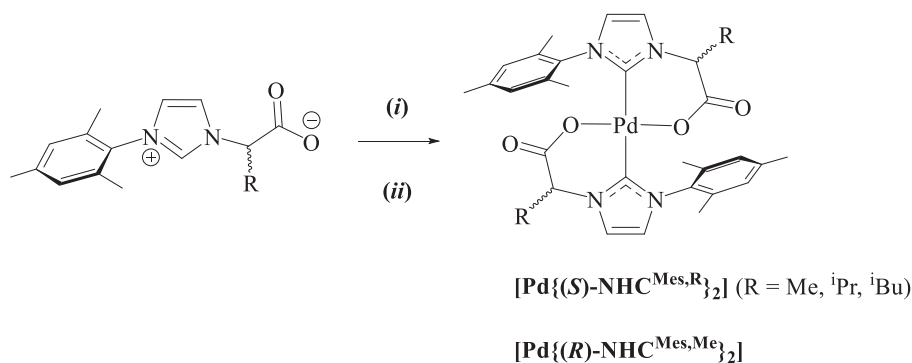

| HOMO | HOMO-1 | HOMO-3 |

Fig. 10. Selected MOs of the [(S)-NHC^{Mes,Me}]$^-$ ligand.

[Pd{(S)-NHC^{Mes,R}}_2] (R = Me, ^iPr, ^iBu)

[Pd{(R)-NHC^{Mes,Me}}_2]

**Scheme 7.** Synthesis of NHC-carboxylate palladium complexes [Pd(NHC^{Mes,R})_2] using two alternative procedures. Method A: (*i*) Ag_2O in CH_2Cl_2, and (*ii*) 0.5 equiv. of [Pd(OAc)_2] in CH_2Cl_2. Method B: (*i*) lithium diisopropylamide in THF, and (*ii*) 0.5 equiv. of [Pd(OAc)_2] in THF.

predictable *trans* disposition. The expected κ^2-*C,O* coordination mode was observed for each [(*S*)-NHC^{Mes,iBu}]⁻ ligand in agreement with the MO description of the NHC-carboxylate ligand discussed above. The imidazolium rings of both NHC ligands are essentially coplanar and the overall structure resembles that found for the complex [Pd(NHC^{Diip,H})_2] [49].

For the preparation of NHC ligands with two carboxylate functionalities, it is necessary to carry out the reaction in the presence of aqueous NaOH (Scheme 8). In the absence of this base, the interaction of the HL^R compounds with Ag_2O provided complexes [Ag(L^R)], as discussed above. Removal of the H atom of the imidazolium ring to give NHC ligands requires aqueous sodium hydroxide. In fact, the addition of NaOH to a solution of [Ag(L^R)] in an NMR tube caused the disappearance of the C^2-H signals indicating NHC formation [34]. They were obtained as colorless crystals or solids with the general formula Na_3[Ag(NHC^R)_2]. Their ^{13}C{^1H} NMR spectra showed the characteristic carbene resonance around 180 ppm, which is well resolved for Na_3[Ag{(*S,S*)-NHC^{iPr}}_2] showing two doublets with $^1J_{CAg}$ = 185 and 213 Hz. These $^1J_{CAg}$ values are typical of the homoleptic binding mode of NHC ligands. This formulation was confirmed by structural determination of the simplest derivative Na_3[Ag(NHC^H)_2]. The anionic part of the complex is composed of the silver center and two bonded NHC ligands (Ag-C bond length of 2.077(7) Å) with the classic linear arrangement (C_{carbene}-Ag-C_{carbene} angle of 173.1(3)°) and an eclipsed conformation (Fig. 11a). The NHC carboxylate groups are oriented to the same molecular side and this allows the formation of a hydrogen bonding network that controls the 3D crystal packing. Discrete [Na_5(H_2O)_{18}]^{5+} units are placed along *a* axis surrounded by the [Ag(NHC^H)_2]^{3-} anions (Fig. 11b) [34].

3. Applications in catalysis

One of the most important applications of chiral imidazolium-based carboxylate compounds and their corresponding chiral NHC-carboxylate ligands is their use in asymmetric catalysis [25]. In this sense, we have investigated the Kabachnik–Fields synthesis of chiral α-aminophosphonates using Zn and Ag complexes as catalysts with (*S,S*)–HL^R and (*S*)-HL^R ligands, but unfortunately no significant enantio-selectivity was observed [27,28]. On the contrary, interesting results were found in the Mo-catalyzed asymmetric oxidation of prochiral sulfides using aqueous hydrogen peroxide as oxidant and the presence of an imidazolium-based dicarboxylic compound, (*S,S*)-HL^R or (*R,R*)-HL^R, as the chiral inductor. Under mild conditions, chiral alkyl aryl sulfoxides with high yields and moderate enantioselectivities were obtained [30,31]. The catalyst was generated *in-situ* by reacting aqueous [Mo(O)(O_2)_2(H_2O)_n] with HL^R in the presence of [PPh_4]Br. The asymmetry is undoubtedly generated by the HL^R compound, as evidenced by the fact that the reaction performed with (*R,R*)-HL^{iPr} gave an enantiomeric excess comparable to that of its (*S,S*)–enantiomer, but with an opposed sense of the sulfoxide chirality. According to spectroscopic data and DFT calculations, the catalytic species was identified as the binuclear oxi-dodiperoxidomolybdenum(VI) complex [PPh_4]{[Mo(O)(O_2)_2(H_2O)]_2(μ-L^R)}, in which the bridging L^R ligand coordinates molybdenum in κ^1-*O* mode (Fig. 12). The origin of enantioselectivity was also theoretically investigated [31]. The optimized structures {[Mo(O)(O_2)_2(H_2O)]_2(μ-L^R)}⁻ show hydrogen bonds between the O—H from the water ligand and the noncoordinated oxygen atom of the carboxylate group of (L^R)⁻. Furthermore, for R = ^iPr, ^iBu, ^sBu and ^tBu, there is a subtler interaction between one C—H bond of the alkyl group and one oxygen atom of one of the peroxido ligands (nonclassical C—H⋯O hydrogen bond).

Na_3[Ag(NHC^H)_2]

Na_3[Ag{(*S,S*)-NHC^R}_2] (R = Me, ^iPr)

Na_3[Ag{(*R,R*)-NHC^R}_2] (R = Me, ^iPr, ^iBu, ^sBu)
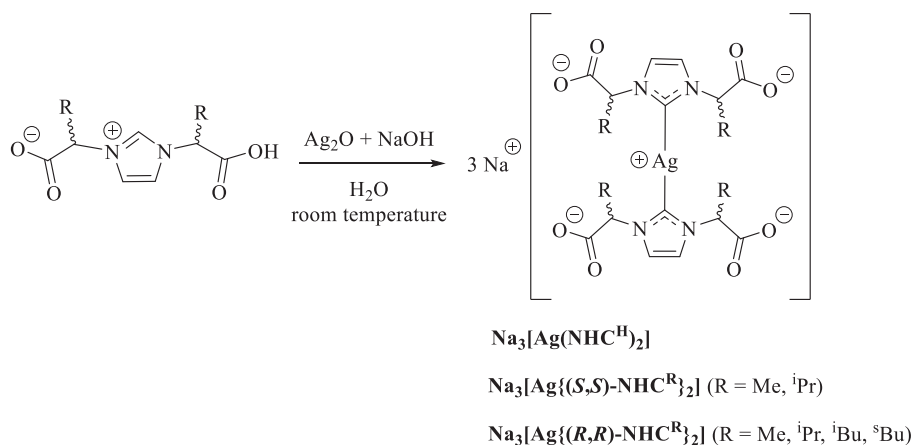
Scheme 8. Synthesis of NHC-dicarboxylate silver complexes Na_3[Ag(NHC^R)_2].

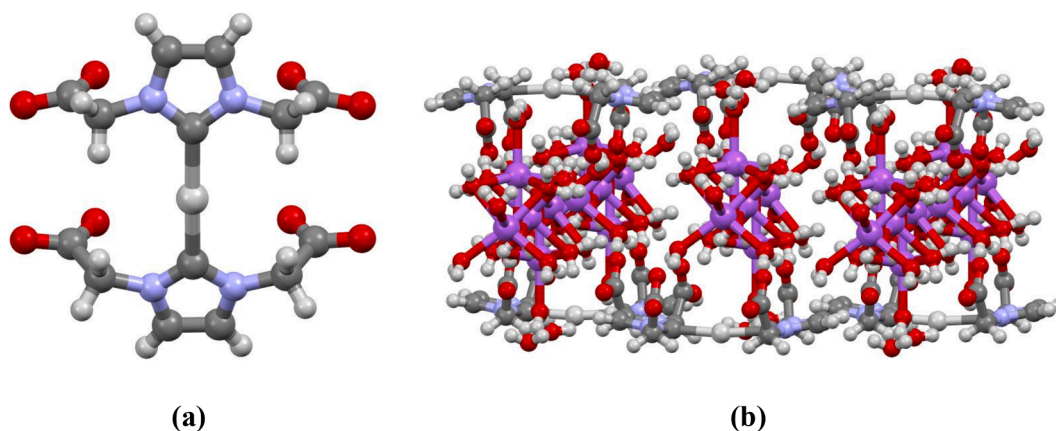**Fig. 11.** Structure of the complex $Na_3[Ag(NHC^H)_2]$: (a) anionic part; (b) crystal packing. Colour codes as in Figs. 1 and 7.
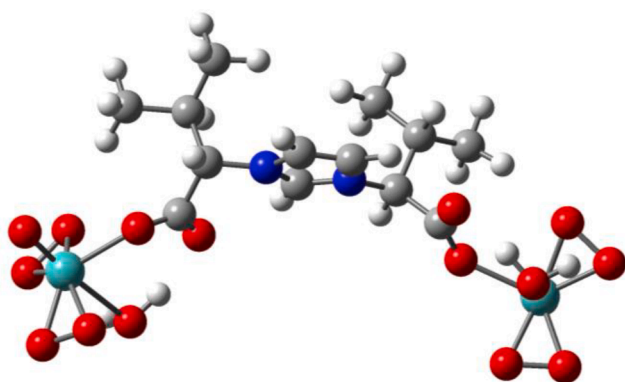

Fig. 12. Optimized structure of the species $\{[Mo(O)(O_2)_2(H_2O)]_2[\mu\text{-}(S,S)\text{-}L^{iPr}]\}^-$.

Interestingly, these compounds are those in which an asymmetric process is observed, while for compounds without this C—H···O interaction, low or null activity was found. We demonstrated that the step that governs the enantioselectivity was the oxido-transfer to the sulfide [50]. In fact, the transition states of the oxido-transfer to the substrate PhMeS of two complexes $[Mo(O)(O_2)_2(H_2O)(\kappa^1\text{-}O\text{-}L^R)]^-$ (R = H and $L^R = (S,S)$–L^{iPr}) were located. For R = H, which obviously gave racemic sulfoxide, the calculated $\Delta\Delta G^{\neq}$ is essentially 0 kcal•mol^{-1}, meanwhile for the chiral species the formation of (R)-sulfoxide is favored with a $\Delta\Delta G^{\neq}$ of *ca.* 2 kcal•mol^{-1} [31].

4. Biological applications: Antimicrobial and antitumoral

The emerging problem of antimicrobial resistance to common antibiotics led to active research to look for new biocide agents that exhibits low toxicity to humans. In recent decades, silver complexes, which contain imidazole-based [51] or NHC ligands [52], have been used as antimicrobial agents in various medical applications. In this field, our contribution was the investigation of antimicrobial activity versus Gram-negative bacteria *E. coli* and *P. aeruginosa* of carboxylate complexes $\{Ag[(S,S)\text{-}L^R]\}_n$, $\{Ag[(R,R)\text{-}L^R]\}_n$ [32] and of NHC complexes $\{Ag[(S)\text{-}NHC^{Mes,R}]\}_n$, $\{Ag[(R)\text{-}NHC^{Mes,Me}]\}_n$ [33], which were evaluated by MIC and MBC measurements (minimal inhibitory concentration and minimal bactericidal concentration, respectively). In both cases, several MIC and MBC values are lower than that of silver cation of AgNO$_3$, as reference, confirming that the activity is not only due to silver, but a combined effect between the silver cation and the corresponding ligand, whose precursor HL^R did not show biocidal activity.

Concerning carboxylate-silver compounds, the complex $\{Ag[(S,S)\text{-}L^{Me}]\}_n$ is the most effective antimicrobial agent for *E. coli*, while for *P. aeruginosa* both $\{Ag[(S,S)\text{-}L^{Me}]\}_n$ and $\{Ag[(R,R)\text{-}L^{iPr}]\}_n$ show the best antimicrobial properties. Interestingly, from the observed MIC and MBC values, the complexes $\{Ag[(R,R)\text{-}L^R]\}_n$ (R = Me, ^{i}Pr) showed slightly better antimicrobial properties than those of their enantiomeric derivatives $\{Ag[(S,S)\text{-}L^R]\}_n$. This fact reveals an unusual chirality–antimicrobial relationship, which could most likely be related to the mechanism of action of these compounds. The eutomers for both bacteria are complexes $\{Ag[(R,R)\text{-}L^R]\}_n$ (R = Me, ^{i}Pr), which were prepared with precursor ligands obtained from the non-proteinogenic amino acid. In particular, $\{Ag[(R,R)\text{-}L^{Me}]\}_n$ had a wider applicability as an antimicrobial agent and its behavior was confirmed by the effect on biofilm formation [32]. Of all carboxylate-silver compounds, [Ag(L^H)]$_n$ and $\{Ag[(R,R)\text{-}L^{Me}]\}_n$ had interesting properties to be considered as effective antimicrobial agents and possible alternatives to classical drugs.

Regarding the NHC complexes $\{Ag[(S)\text{-}NHC^{Mes,R}]\}_n$ and $\{Ag[(R)\text{-}NHC^{Mes,Me}]\}_n$, the latter complex showed the best antimicrobial properties, from the observed MIC and MBC values, which were significantly better than those of its enantiomeric derivative $\{Ag[(S)\text{-}NHC^{Mes,Me}]\}_n$. Again, this result revealed a chirality–antimicrobial relationship, closely related to that previously described above. Comparison of MIC and MBC values of the complexes $\{Ag[(S)\text{-}NHC^{Mes,R}]\}_n$ (R = Me, ^{i}Pr and ^{i}Bu) showed that the steric nature of the R alkyl group in the NHC ligand clearly affected antimicrobial activity. Silver complexes with the less biocidal activity are that with the bulkier R alkyl group. These facts reveal a clear structure–antimicrobial effect relationship, which is surely related to its mechanism of action [33].

The *in vitro* antitumoral activity of complexes $Na_3[Ag(NHC^R)_2]$ was evaluated by determining half inhibitory concentrations (IC$_{50}$) against four human tumor cell lines and one human non-cancerous HaCaT cells. These complexes showed cytotoxic activity against all cancer cell lines. In general, their activities are slightly lower, or in some cases comparable, to related complexes, but all of them are less active than cisplatin [34]. The IC$_{50}$ values clearly reveal two structure–anticancer effect relationships. First, antitumoral activity decreases when the steric properties of the R alkyl group are increased in $Na_3[Ag(NHC^R)_2]$ complexes, as we similarly observed in the antimicrobial activity of the complexes $\{Ag[NHC^{Mes,R}]\}_n$ [33]. Second, the different anticancer behavior of enantiomerically related complexes, where, for example, the activity of $Na_3[Ag\{(S,S)\text{-}NHC^{iPr}\}_2]$ is clearly better than that of $Na_3[Ag\{(R,R)\text{-}NHC^{iPr}\}_2]$, for all cancer cell lines tested [34]. This chirality-anticancer correlation is related to the analogous chirality-antimicrobial relationship that we observed in the study of silver complexes, previously discussed [33], although in this case the complex containing the NHC ligand obtained from the natural amino acid displays major antitumoral activity.

5. Conclusions and future perspectives

The use of the Debus–Radziszewski reaction (Scheme 1) is a fruitful synthetic route that allows the incorporation of enantiopure amino acids (natural or non-proteinogenic) into several chiral ligand precursors, such as imidazole-carboxylate, imidazolium-carboxylate and imidazolium-dicarboxylate (Scheme 2). From these compounds, NHC-carboxylate and NHC-dicarboxylate ligands can also be prepared (Scheme 2). These ligands stabilize transition metal centers, usually by chelation or as bridging units, and are well suited for the construction of interesting 3D architectures at the solid state. Furthermore, for those prepared from amino acids, their chirality at the ligand is quite appropriate for their use in enantioselective transition-metal catalysis. In the last decade, our research group has become interested in this family of compounds and their uses as transition-metal ligands in the area of coordination polymers and asymmetric catalysis, as well as their possible applications as antimicrobial and antitumoral agents. In this contribution, we have summarized our recent results and here we highlight some of the most important findings. From a structural point of view, we have evidenced new coordination modes for chiral imidazole-carboxylate and imidazolium-dicarboxylate ligands in coordination polymers of sodium and silver metals and we have reported the first structural characterization of these coordination polymers with ligands derived from non-proteinogenic amino acids. From a theoretical point of view, we rationalized the bonding capabilities of these ligands through the analysis of their frontier MOs. In the area of catalysis, a combined experimental and theoretical study of the asymmetric oxidation of prochiral sulfides has demonstrated the subtle behavior of imidazolium-dicarboxylate as a chiral inductor in such a process through a non-classical hydrogen bond between one C—H bond of the alkyl R group and one oxygen atom of one of the peroxido ligands. In terms of biological and medical applications, we have found several interesting relationships between the antimicrobial and antitumoral activity and the specific chirality of the silver complexes and between this activity and the nature of the R group of the amino acid precursor. Currently, further studies are in progress in the area of coordination polymers with the aim of controlling the growth of the coordination polymer through the design of the imidazolium-dicarboxylate ligand. In the area of bioinorganic applications, further research is in progress to evaluate the biological activities of chemically related silver complexes as therapeutic agents and to analyze the action mechanism of these complexes.

CRediT authorship contribution statement

Carlos J. Carrasco: Investigation, Data curation, Validation. **Francisco Montilla:** Investigation, Data curation, Conceptualization, Validation. **Eleuterio Álvarez:** Investigation, Data curation, Conceptualization, Validation. **María del Mar Conejo:** Investigation, Data curation, Conceptualization, Validation. **Antonio Pastor:** Investigation, Data curation, Conceptualization, Validation. **Agustín Galindo:** Supervision, Validation, Data curation, Writing – original draft, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

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