

Dinuclear Gold(I) Complexes Bearing N,N'-Allyl-Bridged Bisimidazolylidene Ligands

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Abstract: A novel N,N'-allyl-bridged bisimidazolium salt and a novel dinuclear Ag(I) and a Au(I) NHC complex are reported. Both metallacyclic complexes have a twisted structural shape due to the rigid allylic system and form two different isomers relating to the position of the double bonds. The allyl-group shows photoisomerisation, but no reactivity towards bases for the additional coordination of Pd(II).

Gold(I) N-heterocyclic carbene (NHC) complexes are increasingly attractive in various research fields including catalysis, medicinal chemistry or photochemistry.^[1] NHC moieties emerged as highly versatile class of ligands with tunable electronic, steric, hydro- and lipophilic properties, which allows the access to very stable late transition metal complexes.^[2] Multidentate carbene ligands (e.g. bisimidazol-2-ylidenes) in particular form very stable dinuclear Au(I) complexes in a metallacyclic fashion.^[3] This class of complexes displays important characteristics such as luminescence properties (aurophilic interactions) or high stability under physiological conditions.^[4] In the case of bisimidazol-2-ylidenes, the modification of the bridging unit is a promising strategy for inserting functional groups.^[5] Recently, different dinuclear Au(I)-complexes bearing bridge-functionalised bisimidazol-2-ylidene moieties (hydroxy and carboxyl groups) have been described.^[6] The functionalisation of the methylene bridge enhances water solubility and leads to isomerisation of the

corresponding Au(I) complexes (syn/anti arrangement of the methylene bridge). The complex with mesityl N-substituents exhibits moderate cytotoxicity towards human cancer cell lines.^[7]

NHC moieties (strong donors) combined with alkenyl/allylic groups (hemilabile ligands) give interesting late transition metal complexes (e.g. palladium) with relevant catalytic and anti-bacterial properties.^[8] Additionally, the presence of an olefin functionality in dinuclear Au(I) complexes exhibit photochromic properties showing a wavelength-depending [2 + 2]-photocycloaddition.^[9] Furthermore, olefin-based ligand moieties undergo a reversible photo-isomerisation from E- to Z-configuration.^[10] Based on these considerations, the synthesis and characterisation of a novel allyl-bridged bisimidazolium salt and the corresponding Ag(I) and Au(I) complexes are presented in this work. Aiming to prepare novel hetero-metallic Au(I)-Pd(II) complexes, the reactivity of the allyl bridge under basic conditions is investigated. Furthermore, photo irradiation experiments were conducted to demonstrate the reactivity of the allyl-bridge towards photocycloaddition or -isomerisation.

The N,N'-allyl-bridged bisimidazolium salt (*E*)-L1-X₂ (X=Br or PF₆) was prepared after heating a reaction mixture of 1-mesitylimidazole and 2,3-dibromo-propanol as described in the literature (Scheme 1).^[5-6] The initially desired asymmetrically bridge-functionalised L2-X₂ was not obtained due to elimination reactions occurring at high temperature (110 °C) leading to the unsaturated allyl-bridge (C3). Therefore, two different literature-known elimination pathways can be ruled out, both taking place after the first nucleophilic substitution of a bromide of the bridging agent. The first pathway can involve a Wagner-Meerwein rearrangement with elimination of water.^[11] On the contrary, in the second route, the other bromide is first eliminated (HBr) and the hydroxyl group is finally substituted by the nucleophilic imidazole.^[12] It has been recently reported that functional groups located in the proximity of imidazolium/imidazolylidene systems are susceptible to elimination

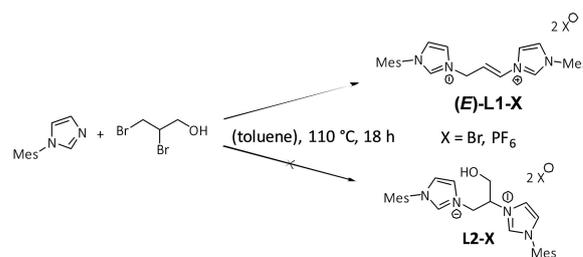
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Scheme 1. Synthesis of (*E*)-L1-X₂. Mes = mesityl or 2,4,6-trimethylphenyl. L2-X₂ represents the initially desired product.

reactions.^[6c] The respective ¹H-NMR spectrum confirms the formation of (E)-L1-Br₂ and both chemical shifts of the olefinic protons of the allyl-bridge shows coupling constants (14.2 Hz) in the range for E-configuration.^[12] Adequate single crystals for X-ray diffraction analysis were obtained for (E)-L1-Br₂ by slow diffusion of diethyl ether into a saturated solution of (E)-L1-Br₂ in acetonitrile, which crystallised in the monoclinic space group P 2₁/n. An ORTEP-style view of the molecular structure of (E)-L1-Br₂, together with selected bond lengths and angles are given in Figure 1. The crystal structure demonstrates unambiguously the formation of the allyl-bridge.

A summary of the crystal data, structure solution and refinement parameters are given in the supporting information (SI, Table 1). The shorter bond length of C13–C14 (1.310(4) Å) localizes the double bond in the structure when compared to saturated C14–C15 bond (1.454(4) Å). In addition, the angles around the C13–C14 bond as well as the dihedral angle N1–C13–C14–C15 (–178.5(3)°) are also typical for olefins and the bridge shows E-configuration confirming the results of NMR spectroscopy. Apart from that, no significant differences in bond lengths and angles were observed when compared to the bisimidazolium salt with saturated C3-bridge described in the literature.^[13] Aiming to increase the solubility of (E)-L1-Br₂ in organic solvents, a salt metathesis to (PF₆)[–] was conducted in water, yielding (E)-L1-(PF₆)₂ (89%) in high purity. The resulting compound has been structurally characterised by NMR spectroscopy, electrospray ionisation-mass spectrometry (ESI-MS) and elemental analysis.

Treatment of (E)-L1-(PF₆)₂ with Ag₂O in acetonitrile following a literature procedure gave the respective Ag(I) complex ^A(EE)-Ag₂(L1)₂ (Scheme 2).^[6a,b]

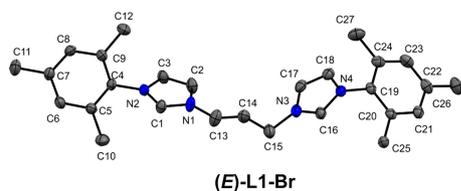
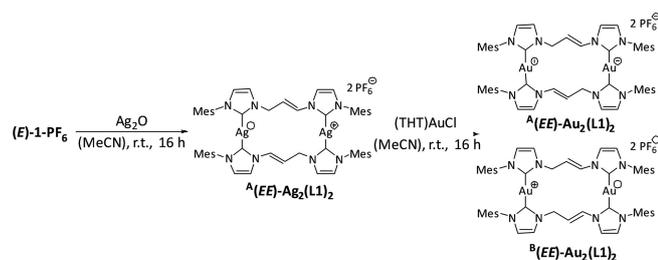


Figure 1. ORTEP-style view of the cationic fragment of ligand precursor (E)-L1-Br₂. All atoms are shown using ellipsoids at a probability level of 50%. Hydrogen atoms and counter-anions are omitted for clarity. Relevant bond lengths [Å] and angles [°]: C13–C14 1.310(4), C14–C15 1.454(4), N1–C1–N2 108.1(3), N3–C16–N4 109.0(3), N1–C13–C14 122.7(3), C13–C14–C15 122.7(3), C14–C15–N3 111.8(3).



Scheme 2. Synthesis of ^A(EE)-Ag₂(L1)₂ and of the isomer-mixture ^{A/B}(EE)-Au₂(L1)₂. THT=Tetrahydrothiophene. Isomer ratio A/B: 46/54

The complex ^A(EE)-Ag₂(L1)₂ was characterised by NMR spectroscopy, ESI-MS and elemental analysis. The ¹H-NMR spectrum shows the coupling constants of the olefinic bridge-protons to be 14.2 Hz, confirming that the E-configuration is maintained. Single crystals of ^A(EE)-Ag₂(L1)₂, suitable for X-ray diffraction analysis, were obtained by slow diffusion of diethyl ether into a solution of the respective complex in acetonitrile. The complex crystallises in the orthorhombic space group P b c n. The single crystal structure of ^A(EE)-Ag₂(L1)₂ presents a dinuclear complex bearing two N,N'-allyl-bridged bisimidazolylidene ligands. The respective ORTEP-style view of the molecular structure together with selected bond lengths and angles are presented in Figure 2. A summary of the crystal data, structure solution and refinement parameters are given in the SI (Table 1).

The bond lengths of both olefins C4–C5/C32–C33 are again shorter (~1.32 Å) than C5–C6/C31–C32 (~1.49 Å). The complex shows a twisted shape with angles of 57.33° (Ag1) and 52.76° (Ag2) between the mean planes of the NHCs bound to the same Ag atom. This might be caused by the rigid olefin-bridge with E-configuration. This conformation is different from the one adopted by the dinuclear complexes bearing bisimidazolylidene ligands with saturated C3-bridges, which show a parallel structural motif. The Ag–C bond lengths as well as the C–Ag–C bond angles show no significant differences to other published dinuclear Ag(I) complexes.^[3] The silver nuclei have a distance of 5.3 Å and are not in the range for argentophilic interactions.^[14]

Transmetalation of ^A(EE)-Ag₂(L1)₂ with Au(THT)Cl (THT = tetrahydrothiophene) yields the respective gold(I) complexes ^{A/B}(EE)-Au₂(L1)₂ (A/B, Scheme 2). ¹H-NMR analysis shows the presence of two different resonance patterns indicating the formation of different isomers. The olefinic chemical shifts of the allyl bridges of both isomers show again typical coupling constants for E-configuration. In the case of the second isomer ^B(EE)-Au₂(L1)₂, only one signal is observed for both allylic CH₂ groups showing the formation of the C₂-symmetric isomer B. In addition, elemental analysis and ESI-MS are in accordance with the theoretical values of the gold complex. Suitable crystals for SC-XRD were obtained by slow diffusion of diethyl ether into a saturated solution of ^{A/B}(EE)-Au₂(L1)₂ in acetonitrile. The single crystal structure of ^A(EE)-Au₂(L1)₂ shows the same structure

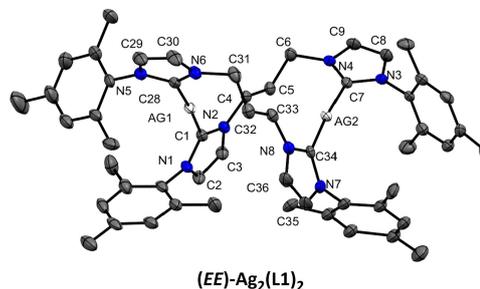


Figure 2. ORTEP-style view of the cationic fragment of complex ^A(EE)-Ag₂(L1)₂. All atoms are shown using ellipsoids at a probability level of 50%. Hydrogen atoms and counter-anion are omitted for clarity. Relevant bond lengths [Å] and angles [°]: Ag–C1/C7/C28/C34 2.067(5)–2.076(5), C5/C31–C6/C32 1.495(6)–1.496(7), C4/C32–C5/C33 1.323(7)–1.326(7), C7/C28–Ag–C34/C1 175.0(2)–176.0(2).

when compared to ${}^A(EE)\text{-Ag}_2(\text{L1})_2$. A summary of the crystal data, structure solution and refinement parameters are given in the SI (Table 1). The ORTEP-style view of the molecular structure of ${}^A(EE)\text{-Au}_2(\text{L1})_2$, together with selected bond lengths and angles are given in Figure 3.

${}^A(EE)\text{-Au}_2(\text{L1})_2$ crystallises in the orthorhombic space group $Pbcn$ and all Au–C bond lengths as well as C–Au–C bond angles are in the range of dinuclear Au(I) complexes showing no notable differences. The twisted shape of the complex features angles of 55.58° (Au1) and 50.58° (Au2) between the mean planes of the NHCs bound to the same Au atom and arranges the gold(I) nuclei with a distance of 5.4 \AA to each other, which is closer than in the dinuclear complex with a saturated C3-bridge.^[15] Nevertheless, this distance is still not in the range for aurophilic interactions.^[14]

The photochemical behavior of the N,N'-allyl bridge as well as the reactivity in presence of bases were investigated for ${}^A/B(EE)\text{-Au}_2(\text{L1})_2$ and $(E)\text{-L1-(PF}_6)_2$, (Scheme 3).

Firstly, irradiation experiments of the isomer-mixture ${}^A/B(EE)\text{-Au}_2(\text{L1})_2$ at 366 nm were conducted to analyse a possible [2 + 2]-photocycloaddition between both allyl-bridges similarly to a comparable reported dinuclear complex.^[9] In the case of ${}^A/B(EE)\text{-Au}_2(\text{L1})_2$, a purple precipitate (most likely gold nanoparticles) was observed after irradiation for 16 h and the full ${}^1\text{H-NMR}$ spectrum shows traces of imidazolium protons in the range of 9–10 ppm. Nevertheless, this complex seems to be sufficiently

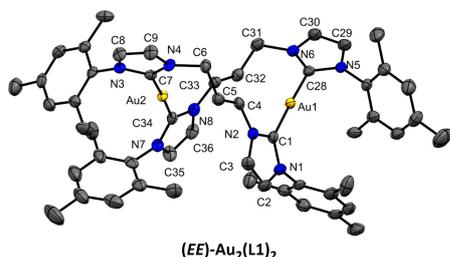
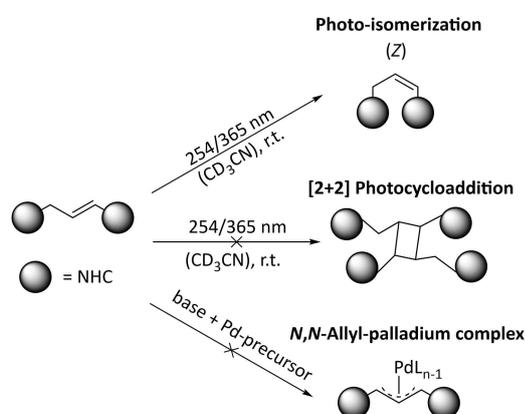


Figure 3. ORTEP-style view of the cationic fragment of complex ${}^A(EE)\text{-Au}_2(\text{L1})_2$. All atoms are shown using ellipsoids at a probability level of 50%. Hydrogen atoms and counter-anion are omitted for clarity. Relevant bond lengths [\AA] and angles [$^\circ$]: Au–C1/C7/C28/C34 2.019(5)–2.026(5), C5/C31–C6/C32 1.500(7)–1.501(7), C4/C33–C5/C32 1.315(7)–1.320(7), N–C4/C33 1.413(6)–1.423(6), C7/C28–Au–C34/C1 177.1(2).



Scheme 3. Reactivity studies of the N,N'-allyl-bridge.

UV-light stable. In addition to the formation of traces of the imidazolium-type decomposition product, at least two new major species have been observed, which show the same resonance pattern when compared to the starting gold complexes (Figure 4). The coupling constants of the new olefinic protons in the range of 6.0–6.5 ppm change from ${}^3J \approx 14 \text{ Hz}$ to ${}^3J \approx 8\text{--}9 \text{ Hz}$, indicating a photo-isomerisation switching from *E*- to *Z*-conformation. No [2 + 2]-photocycloaddition was observed as no cyclobutene-related chemical shifts (expected as product of the photocycloaddition) were found in the full spectrum (SI-Figure 10).

Performing the same irradiation experiments for the bisimidazolium salt $(E)\text{-L1-(PF}_6)_2$ at 366 nm showed no change in configuration is observed. However, lowering the irradiation wavelength to 254 nm led to the formation of the *Z*-moiety with coupling constants ${}^3J \approx 9 \text{ Hz}$ (SI-Figures 11 & 12). This observation indicates that the presence of gold lowers the required energy for isomerisation. It might be reasonable that the purple gold nanoparticles formed “in traces” facilitate the photo-isomerisation, allowing a change of *E*-to *Z*-configuration at lower energies (366 nm). It is known from the literature that nanoparticles as photocatalysts^[16] or a third cation via metal-metal interaction^[17] can promote (photo)-isomerisation processes.

Besides the photochemical experiments, deprotonation of the N,N'-allyl-bridge of ${}^A/B(EE)\text{-Au}_2(\text{L1})_2$ was attempted in the presence of a palladium precursor and various bases aiming to synthesise a hetero-metallic system (reaction conditions are summarised in Table 2 in SI). Applying different bases in the presence of various palladium precursors did not result in the formation of a Pd-allyl complex. Aimed at understanding that behavior, the same reaction conditions were applied for the bisimidazolium salt $(E)\text{-L1-(PF}_6)_2$. Using a moderate base (K_2CO_3) led to the formation of N,N-allyl-palladium complex with the additional presence of the unconverted starting material, the Wanzlick-type dimer and its respective Pd-allyl complex (confirmed by 1D and 2D NMR and ESI MS, SI-Figures 13–20) Thus, the unsuccessful formation of a palladium-allyl complex in the case of ${}^A/B(EE)\text{-Au}_2(\text{L1})_2$ seems not to be a matter of base

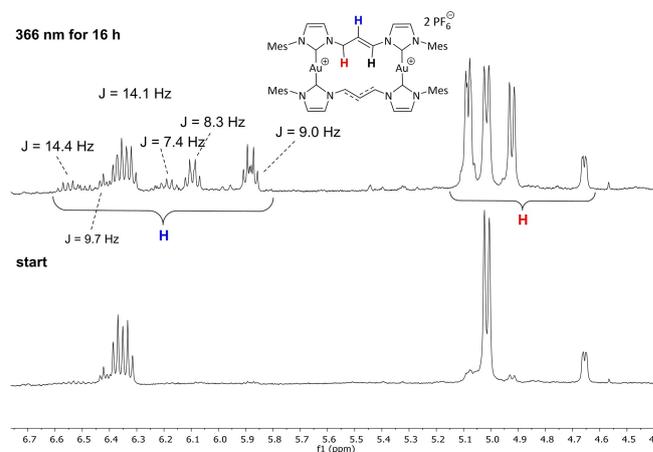


Figure 4. ${}^1\text{H NMR}$ spectra of ${}^A/B(EE)\text{-Au}_2(\text{L1})_2$ before irradiation (bottom) and after 16 h at 366 nm (top) in deuterated acetonitrile.

strength, but is rather caused through sterics or through the rigid twisted metallacycle. Applying smaller metals might circumvent these sterical problems, however synthesis of these metal complexes and their evaluation in this reaction are still ongoing.

Novel bisimidazolium bromide or $(PF_6)^-$ (*E*)-L1- X_2 salts are reported and further converted to the respective dinuclear complexes $^A(E)E-Ag_2(L1)_2$ and $^{A/B}(E)E-Au_2(L1)_2$. Elimination processes of the hydroxyl group occurring at higher temperatures yield *E*-configured allyl-bridges, as confirmed by evaluation of coupling constants in NMR spectra and by single crystal X-ray diffraction. Single crystal data of both complexes show a twisted shape approximating both nuclei. The gold complex isomerises, differing in the relative positioning of the double bonds. Irradiation of $^{A/B}(E)E-Au_2(L1)_2$ and of (*E*)-L1- $(PF_6)_2$ enables photo-isomerisation and conversion of *E* into *Z*-configuration. No hetero-metallic Au(I)-Pd(II) complex could be generated in the presence of bases and palladium precursors, which has been assigned to the high rigidity of $^{A/B}(E)E-Au_2(L1)_2$.

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Conflict of Interest

The authors declare no conflict of interest.

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