Vinylimidazole coordination modes to Pt and Au metal centers†

Sirpa Jääskeläinen, Igor O. Koshevoy, Sari Suvanto, Tiina Ryhänen and Pipsa Hirva

The coordination modes of 1-vinylimidazole to platinum and gold were studied. Complexes [PtCl₂(Hvinylimidazole)]H₂O (1), [Au(vinylimidazole)₂][AuBr₂]⁻ (2), [Hvinylimidazole][AuCl₄]⁻ (3), and [Hvinylimidazole][AuBr₄]⁻ (4) were prepared and structurally characterized. Compound 1 is the first structurally characterized transition metal complex containing a protonated vinylimidazole, which is coordinated through the vinyl group in the side-on position. In compound 2, the neutral ligands coordinate through the imidazole nitrogens to the reduced gold(1) center and the charge balancing counter anion [Au(II)Br₂]⁻ has a short Au–Au contact with the cationic part. In 3 and 4, the acidic reaction conditions lead to the protonation of the imidazole nitrogen and an ion pair with tetrahalogenide gold(III) is obtained. The tendency to different crystallized products is attributed to the combination of the metal and the halogen properties with the reaction conditions. Computational chemistry was used to explain the preference of the vinyl coordination type, as well as in the interpretation of the spectroscopic details and the nature of the intra- and intermolecular interactions present in the solid state.

Introduction

1-Vinylimidazole or N-vinylimidazole is a two nitrogen containing, five-membered, aromatic compound with the vinyl group at one of the nitrogen atoms. Imidazoles, in general, are important in biomolecules, pharmaceutical applications and in industrial utilization as corrosion inhibitors. Vinylimidazole is particularly known for its homo and co-polymers. The monomer is easily polymerized through the vinyl group by exploiting UV-irradiation, heat or activator agents. Furthermore, vinylimidazole monomers can be quaternized to ionic liquids and polymerized through the side chains. The active imidazolone nitrogens in these polyionic hydrogels effectively bind metal atoms. Due to the mechanical stability, strength and recoverability of the materials, diverse applications in polymer anchored metal catalysts, drug delivery, and water purification are produced.

In the context of transition metal complexes, the most probable coordination sites in 1-vinylimidazole are the imidazole nitrogen and the vinyl group. The substituent at the heteroatom blocks up the possibility for tautomerism typical of the original imidazole. The non-coordinated nitrogen atom is slightly basic and protonation of this site is possible. The high tendency to coordination to metal centers and formation of molecular complexes, as in the case of polymeric structures, is a source of diverse applications such as pharmacologically active species.

A survey of the CCDC database and literature reveals that exclusively nitrogen bound ligands are present in transition metal vinyl imidazole complexes. A quite large selection of complexes for lighter transition metals is published. However, going towards the heavier metals, the number of synthesized and characterized complexes is reduced. In group ten in the periodic table, Ni has several vinylimidazole derivatives, while only the octahedral [PdCl₂(vinylimidazole)₄]Cl₂ is crystallographically characterized for platinum.

Among the coinage metals, copper has several derivatives of this ligand. The most common coordination type is octahedral, but also tetrahedral complexes are known. Typically, these have two or four vinylimidazole ligands. The catena compounds, where Cu centers with 1-vinylimidazole ligands and ReCl₆-units are connected through chloro bridges, have shown magnetic properties. Surprisingly, no compounds of Ag or Au have been reported. In group twelve, Zn and Cd form MOF complexes with auxiliary linking ligands, and the vinylimidazoles coordinate monodentately.
Ruthenium has a unique cluster derivative [HRu₃(CO)₁₀(vinylimidazole)], where the deprotonated ligand acts as a bidentate bridging C₅N-ligand. The imidazole carbon between the nitrogen atoms is utilized in coordination, but the vinyl group remains intact.⁶²

A similar type of ligand, 4-vinylpyridine typically coordinates through the nitrogen atom, as in the complexes of Cu,⁴³ Pt,⁴⁴,⁴⁵ Os,⁵⁰,⁵³–⁵⁷ Co,⁵⁸,⁵⁹ Rh,⁶⁰ Ir,⁶¹ Pd,⁶² Pt,⁶³,⁶⁴ and Au.⁶⁵,⁶⁶ 2-vinylpyridine can form five-membered cyclometalated complexes with the high versatility of applications in the fields of biological, catalytic and luminescence properties.⁶⁴

In this work we concentrated on the reactions of vinylimidazole with late transition metals, Pt and Au, to clarify the relative reactivity of the imidazole group or the vinyl group towards the metal ions. The experimental crystal structures of the products were analyzed via X-ray diffraction, NMR, IR and Raman spectroscopy, and computational DFT methods.

Results and discussion
Reactions and structural studies

The reaction of 1-vinylimidazole with K₂PtCl₄ in water solution led to the formation of a white product, which by spectroscopic measurements and elemental analysis was interpreted as the square planar [PtCl₂(vinylimidazole)₂] with nitrogen coordinated ligands. This is in good agreement with the earlier reported catalytic and luminescence properties.⁶⁴

On the other hand, the reaction of 1-vinylimidazole with K₂PtCl₄ in acidic medium generated a novel vinylimidazole derivative type [PtCl₃(vinylimidazole)]H₂O (1), where the partially protonated ligand is bound to metal through the vinyl group in side-on geometry (Fig. 1a). The Pt(s) center has further three chloro ligands in the perpendicular plane against the C=C bond of 1.395(2) Å. The Pt–C(6) bond is 2.135(2) Å and Pt–C(7) is slightly shorter 2.109(2) Å, showing a strong side-on coordination type of the vinyl group. The sum of the van der Waals radii of Pt and C is 3.45 Å. The Pt–Cl bonds are 2.2972(5) and 2.2922(5) Å in the cis-position and 2.3056(5) Å in the trans-position to the vinylimidazole.

Reaction of vinylimidazole with AuBr₃ in organic aprotic THF solvent led to the formation of an ion pair [Au(vinylimidazole)₂][AuBr₂]⁻ (2) (Fig. 2). In the cation, two neutral ligands are attached to the Au(i) center via imidazole nitrogens, the vinyl groups remaining unreacted. Anionic [Au(i)Br₂]⁻ acts as the counter ion. Therefore, reduction of the metal with partial oxidation of the bromines has taken place during coordination.

The coordination at both gold atoms is almost ideal T-shape with Au–Au–N bond angles of 90.8(2)° and 91.0(2)°. The Au–N distances are 2.018(5) and 2.017(5) Å. The C=C bond lengths in vinyl groups are considerably shorter, 1.306(10) and 1.300(10) Å, than in 1. The Au–Au distance is 3.1200(5) Å, which is slightly shorter than the sum of the van der Waals radii of two gold atoms (3.32 Å). The cationic part is planar and the Br–Au–Br moiety lies perpendicular to this plane.

The ion pairs form a chain structure in the solid state via hydrogen bonds (Fig. 3). The bromine forms an intramolecular hydrogen bond of 3.0687(8) Å to H(2). The bromine atoms have also several short contacts of 2.8839(7)–3.0437(8) Å to hydrogens of neighboring ion pairs.

The nature of the hydrogen bonding network was further studied computationally by analyzing the charge density of an extended model by Quantum Theory of Atoms in Molecules (QTAIM). The model with four adjacent ion pairs was cut directly from the experimental crystal structure (see Fig. S1 in the ESI†) and analyzed using the DFT wavefunction. The results for the properties of the electron density are shown in Table 1.

The [Au(vinylimidazole)₂][AuBr₂]⁻ ion pairs show a large number of relatively weak intermolecular hydrogen bonds to the adjacent ion pairs, explaining the packing of the ions into rows. The properties of the electron density, such as small ρ, the ratio between potential energy density and kinetic energy density |V|/G < 1, and interaction energy EINT < 10 kJ mol⁻¹, all point out to typical noncovalent intermolecular hydrogen bonds. In addition, the aurophilic Au(1)···Au(2) interactions at BCP 3 exhibit slightly larger strength with EINT of ~26 kJ mol⁻¹. Notably, the aurophilic interactions to the neighboring cations.
have comparable strength ($E_{\text{INT}} = -13 \text{ kJ mol}^{-1}$ at BCP 6),
enhancing the self-assembly of the ion pairs. Furthermore, $\pi-\pi$
interactions form between vinyl groups and the imidazole rings
of the adjacent ion pairs, explaining the torsional behavior of
the N-ligands as they stack together.

In the reaction of the ligand with either NaAuCl$_4$ or HAuCl$_4$
in water solution containing HCl, protonation of the ligand
took place giving compound $[\text{Hvinylimidazole}]^+\text{[AuCl}_4^-$(3)
(Fig. 4) with a disordered structure. Thus, the protonated ligand
does not coordinate to the metal like in the case of platinum.
This type of ion pair was earlier known for instance for
apyridine.$^{68}$ In the solid state, a network supported by hydrogen
bonds H(3)–Cl(1) of 2.4256(5) Å and H(7B)–Cl(4) of 2.9059(5)
and 2.9139(5) Å was obtained (Fig. 4).

The synthesis of $[\text{Hvinylimidazole}]^+\text{[AuBr}_4^-$(4)
from AuBr$_3$
in acidic HBr solution proceeded analogously to that of 3. The
crystal structure and spectroscopic data showed a similar
structure type to 3, but in this case with no disorder.

**IR and FT-Raman spectroscopy**

The appearance of the $\nu$(N–H) vibration at 3281, 3254 and
3256 cm$^{-1}$ supports the protonation of the imidazole nitrogen
in compounds 1, 3 and 4. The interpretation of the spectra was
verified via computational simulation at the DFT level of theory
on optimized molecular models. The experimental and simu-
lated spectra are shown in Fig. S6–S8 (ESI†).

### Table 1

Properties of the electron density in the selected BCPs for an
extended model $\{[\text{Au(vinylimidazole)}_2]^+\text{[AuBr}_2^-\}$ of compound 2. For
the numbering scheme of the BCPs, see Fig. S1.

| BCP# | Type | $\rho$ (e Å$^{-3}$) | $|V|$ G | $E_{\text{INT}}$ (kJ mol$^{-1}$) |
|------|------|-------------------|--------|-----------------|
| 1    | Au(1)–N(3) | 0.898             | 1.37   | -278            |
| 1'   | Au(1)–N(3A) | 0.899             | 1.38   | -275            |
| 2    | C(6)–C(7)  | 2.398             | 3.73   | -777            |
| 2'   | C(6A)–C(7A) | 2.408             | 3.73   | -784            |
| 3    | Au(1)–Au(2) | 0.175             | 1.12   | -26             |
| 4    | Au(2)–H(4)  | 0.048             | 0.80   | -5              |
| 4'   | Au(2)–H(2)  | 0.057             | 0.82   | -6              |
| 5    | Br(1)–H(4)  | 0.044             | 0.74   | -4              |
| 5'   | Br(1)–H(2)  | 0.054             | 0.73   | -5              |
| 6    | Au(1)–Au(1') | 0.105             | 1.03   | -13             |
| 7    | Au(1)–Br(1') | 0.073             | 0.89   | -7              |
| 8    | Br(2)–H(5)  | 0.040             | 0.75   | -3              |
| 9    | Br(2)–H(7)  | 0.042             | 0.76   | -4              |
| 10   | ($\pi-\pi$)vinyl | 0.023             | 0.82   | -2              |
| 11   | ($\pi-\pi$)imidazole | 0.042             | 0.80   | -4              |
Table 2. Selected calculated Raman signals for 1 and 2, and the free 1-vinylimidazole (L) and [vinylimidazole]⁺ (HL). Experimental values are given in parentheses were resolved.

| Vibration | 1   | 2   | L      | HL     |
|-----------|-----|-----|--------|--------|
| ν(N–H)    | 3468 (3281) | —   | —      | 3431   |
| ν(C–H)L   | 3141 (3152) | 3111 (3113) | 3106 (3108) | 3102   |
| ν(C–H)    | 3009 (3026) | 2968 [n.r.] | 3014 (3044) | 3040   |
| ν(C–H)    | 2967 (2951) | 2994 [n.r.] | 2993 (2999) | 2997   |
| ν(C–C)    | 1441 (1408) | 1632 (1645) | 1625 (1653) | 1627   |
| ν(C–C)    | 1315 (1322) | 1370 (n.r.) | 1375 (1367) | 1331   |
| ω(M–C)    | 544 (503)   | —    | —      | —      |
| ω(M–C)    | 476 (456)   | —    | —      | —      |
| ω(M–N)    | —            | 239 (n.r.) | —      | —      |

n.r. = not resolved.

Vinyllic ν(C–C) in the free ligand lies at 1630 cm⁻¹ (computational value at 1626 cm⁻¹). In 1 it is clearly shifted to a lower frequency of 1437 cm⁻¹ (simulated 1441 cm⁻¹), which is attributed to π-bonded C–C ligands like ethylene and related ligands.⁶⁹ In a σ-bonded ligand, the shift is typically to higher frequencies. In 2, 3 and 4, ν(C–C) appears at 1640 cm⁻¹ (sim. 1632), so the shift is not remarkable.

The Raman spectra were measured for complexes 1 and 2 in the solid state and for vinylimidazole in the liquid form, and also simulated at the DFT level of theory using single molecular models to facilitate interpretation. The computational values are given in Table 2, and an example of the interpretation of the most important signals for compound 1 is given in Fig. S4 and S5 (ESI†).

The full interpretation of the solid state Raman spectra was possible only for the platinum complex 1, which yielded the best quality experimental spectrum. Fig. S4 and S5 (ESI†) compare the experimental and simulated signals, which were further interpreted by animation of the vibrations. Even though the wavenumbers do not exactly match because all signals in the simulation do not scale similarly, the general appearance of the spectra is similar enough to allow interpretation (Table 2).

The coordination mode of 1 and 2 can most easily be seen in the stretching vibration of the C–C double bond of the vinyl group, which is strongly shifted to smaller wavenumbers in the platinum complex 1, but shows a similar value to that in the free vinylimidazoles for the gold complex 2. The same, but less clear trend is seen in the ν(C–H) values of the CH₂ protons of the vinyl group, as well as in the scissor vibration of the CH₂ protons. Furthermore, clear Pt–C(vinyl) signals could be obtained in the spectrum of 1, verifying the side-on coordination of the metal.

The poor quality of the experimental Raman spectrum of compound 2, resulting from the degradation of the crystals during the measurement, did not allow all the signals to be resolved, most importantly the Au–N stretching frequency. However, indirect evidence on the coordination mode could be obtained by the absence of interaction with the vinyl group, since ν(C–C) and ν(C–H) were not shifted compared to the free 1-vinylimidazole. Additionally, there was no N–H stretching signal, which verified the coordination of the ligand in the non-protonated form.

It has been observed in the previous computational Raman studies of platinum complexes that the effect of temperature and isosteres of chlorine complicate the situation and some contradiction among the assignments exists.⁷⁰,⁷¹

NMR spectroscopy

The ¹H NMR spectra of all compounds were measured in d₆-DMSO solvent and interpreted by comparison with the spectrum of the free ligand. The spectra are presented in Fig. S2 (ESI†).

Compound 1 shows two sets of sharp peaks with a very similar pattern to the free ligand shifted to slightly larger chemical shifts. One possibility to the two sets of signals is the existence of another isomer with a non-protonated and possibly N-coordinated ligand. This suggestion is supported by the observation that the imidazole protons (2, 4, and 5) in isomer b show the same chemical shifts as in the spectrum of 2, while the peaks of the crystallized product appear at the same location as in 3. The protonation of the vinylimidazole ligand was computationally found to charge the charge distribution especially in the aromatic ring of the free ligand, which could explain the difference in the chemical shift values.

The spectrum of 2, as in the case of 1, has also a pattern of two signal sets shifted toward higher chemical shifts. In this case, the small difference in chemical shifts suggests quite similar structures for the isomers, indicating the presence of two compounds in solution, probably due to the rotation around the Au(1)–Au(2), Au(1)–N(3/3A), and N(1/1A)–C(6/6A) bonds. The major compound has reasonably sharp signals. However, the minor compound shows broad signals, which can be assumed to arise from hydrogen bonding of the protons to the near-by quadrupole bromines. Since the rotation in solution can be rather free around single bonds, in the minor isomer the protons can have short contact with bromines. The elemental analysis indicates the presence of one pure product. The NMR spectra of 3 and 4 are similar with one set of peaks describing one pure product without the possibility of fluxionality.

Overall, the most notable shift of the signals is observed at the imidazolic H(2) proton signal in those structures, where protonation of the ligand has taken place. This shift can be interpreted to have originated from the protonation of the imidazole nitrogen N3, which was found to modify considerably the calculated charge distribution of the whole imidazole ring and especially the charge of C(2) and H(2).

Both proton coupled and proton decoupled ¹³C NMR spectra of the vinylimidazole ligand in the basic form as well as HCl treated vinylimidazole to simulate the protonation were measured (Fig. S3, ESI†), but only the proton decoupled spectra of the products (1–4) were obtained. Comparison of the experimental and the calculated⁷²–⁷⁴ spectra is given in Table S1 (ESI†). The spectra show the remaining vinylimidazole assembly in all cases. In complexes 1, 3 and 4, containing the protonated ligands, the signal of C(6) is slightly shifted to lower values as in the case of the protonated free ligand. Otherwise, the structure of the spectrum remains practically unchanged. The presence of different types of metals and paramagnetic species as well as the
solvent effect has earlier shown to cause peculiarities in the spectrum appearance of 1-vinylimidazole and even the relative positions of the signals can change.\textsuperscript{75,76}

**Stability of the coordination modes**

In order to find explanation for the preferred coordination mode in the Pt or Au vinylimidazoles, we performed computational optimization for models mimicking both N-coordination (A) of the deprotonated ligand and the side-on coordination (B) to the vinyl group of the protonated ligand. Since the HOMO–LUMO energy gap can give information on the relative stability of the models, the highest occupied and the lowest unoccupied orbitals along with the corresponding energies of the small molecular models are presented in Fig. 5.

There is a clear difference in the frontier molecular orbitals of the N-coordinated cations. With platinum, the strong involvement of the metal d orbitals in both the HOMO and LUMO stabilizes their energy, leading to a small energy gap. In contrast, the LUMO of the gold cation is expanded over the two ligands without contribution from the metal center, which destabilizes strongly the LUMO energy and leads to a large energy gap and hence to very stable coordination. The opposite is true in the C–C coordination mode B, where the LUMO of the Au complex concentrates over the MX orbitals, again stabilizing LUMO energy, whereas in the Pt complex the LUMO is expanded mostly on the ligand π orbitals. According to the frontier orbital energies, platinum would prefer coordination to the vinyl group and gold would prefer N-coordination of the 1-vinylimidazole, provided that the Au(III) center is reduced to Au(I). It should be noted that we also tested the side-on coordination with Au(i), and even though the stability of the product, $\Delta \varepsilon = 4.58$ eV, was slightly larger than for Au(III), the preferred coordination mode would still be A. Experimentally, we tested also the reaction HAuCl\textsubscript{4} + vinylimidazole in THF solution. The crystals formed showed again the structure of 3. The $^1$H NMR spectrum of the reaction mixture verified this, but two minor products were present, thus other coordination modes are possible for gold.

**Experimental**

**Materials and methods**

Commercially available reagents AuBr\textsubscript{3} (99%, Alfa Aesar), HAuCl\textsubscript{4} \textsubscript{3}H\textsubscript{2}O (Au 49.5%, Alfa Aesar), NaAuCl\textsubscript{4} \textsubscript{2}H\textsubscript{2}O (99%, Sigma Aldrich), K\textsubscript{2}PtCl\textsubscript{4} (99.9% Alfa Aesar) and 1-vinylimidazole (99%, Alfa Aesar) were used without purification. The organic solvents were dried using molecular sieves. Infrared spectra were measured from KBr pellets using a Shimadzu IRAffinity-1 Fourier transform infrared spectrophotometer in the range of 4000–400 cm\textsuperscript{-1}. The elemental analysis was performed on a varioMICRO V1.7. The $^1$H NMR spectra were recorded on a Bruker Avance 400 MHz or Bruker AMX 400 MHz spectrometer. Raman spectra were recorded on a Renishaw inVia Raman Microscope with 514 nm excitation laser wavelength. Raman shifts ranging from 3200–100 cm\textsuperscript{-1} were collected.

**Crystal structure determination**

The crystals of 1–4 were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 150 K. The X-ray

![Fig. 5](image-url)  
**Fig. 5** The appearance of the HOMO and LUMO in the N-coordinated cationic models [1A]\textsuperscript{2+} (Pt) and [2A]\textsuperscript{+} (Au), and the C,C-coordinated model [1B] (Pt) and [2B]\textsuperscript{+} (Au).
### Table 3: Crystal data and structure refinement for 1–4

|   | 1          | 2          | 3          | 4          |
|---|------------|------------|------------|------------|
| **Empirical formula** | C₆H₆Cl₄N₄O Pt | C₁₀H₁₂Br₂Au₂N₄ | C₃H₈Au₂N₂ | C₈H₇Br₄AuN₂ |
| fₒ (g mol⁻¹) | 414.58 | 741.99 | 433.89 | 611.73 |
| **Space group** | P2₁/n | P2₁/n | P2₁/n | P2₁/n |
| a (Å) | 6.6036(13) | 7.3655(13) | 10.5561(2) | 7.9563(3) |
| b (Å) | 12.158(2) | 9.5071(16) | 8.2051(5) | 8.7084(3) |
| c (Å) | 12.513(2) | 14.007(2) | 12.2809(5) | 9.5630(3) |
| α (°) | 90 | 71.099(3) | 90 | 110.7660(10) |
| β (°) | 95.214(4) | 84.673(4) | 93.8790(10) | 92.5480(10) |
| γ (°) | 90 | 68.279(4) | 90 | 102.5670(10) |
| Z | 4 | 2 | 4 | 2 |
| ρcalcd (Mg m⁻³) | 2.752 | 2.860 | 2.716 | 3.433 |
| ρ(obsd) (Mg m⁻³) | 2.600 | 2.163 | 2.481 | 2.588 |
| θ range for data collection (°) | 3.351 to 20.555 | 3.269 to 28.998 | 2.463 to 29.994 | 2.742 to 32.203 |
| Refl. collected | 21 058 | 14 780 | 14 680 | 11 784 |
| Independent refl. | 6 022 | 4 535 | 3 902 | 2 408 |
| Final R indices | † | † | † | † |
| R || 0.0229 | 0.0348 | 0.0186 | 0.0205 |
| R || 0.0176, wR || 0.0372 | 0.0323, wR || 0.0757 | 0.00148, wR || 0.0341 | 0.0158, wR || 0.0354 | 0.0195, wR || 0.0365 | 0.0608 and −1.187 |

* † = Σ||Fₒ| − |F_c||/Σ|F_c|; wR₂ = (Σ[w(Fₒ² − F_c²)]²/Σ[w(Fₒ²)]²)¹/₂.

### Computational details

All calculations were performed by applying the Gaussian 09 software package. The optimized geometry and simulated infrared and Raman spectra of all the complexes were obtained by the B3LYP functional with the 6-311+G(d,p) basis set for non-metal atoms and the Def2-TZVPPD basis set for Pt and Au atoms.

To obtain the electronic properties of the solid state structure of 2, we performed topological charge density analysis with the QTAIM (Quantum Theory of Atoms in Molecules) method, which allowed us to access the nature of the bonding via calculating different properties of the electron density at the bond critical points (BCPs). The analysis was done with the AIMALL program using the wavefunction obtained from the single point DFT calculations of an extended model cut from the crystal structure.

### Synthesis of complexes 1–4

**[PtCl₆(Hvinylimidazole)]H₂O (1).** K₂PtCl₄ (51.7 mg, 0.125 mmol) was dissolved in 5 M HCl (2 ml) during 1 h stirring. Two drops (excess) of vinylimidazole was added. The yellow crystalline product was filtered and washed with water. Yield: 32.2 mg. Anal. calcd for PtCl₆N₂C₅H₉: C, 14.49; H, 2.19; N, 6.76. Found: C, 15.97; H, 2.10; N, 7.08%. Mp 205–207 °C (d). IR (KBr, cm⁻¹): ν(N–H) 3281, ν(C–C–C–C, vinyl) 1437 cm⁻¹. ¹H NMR (400 MHz, d₆-DMSO, 298 K, δ): 9.37 (H2, s), 8.19 (H5, s), 7.82 (H4, s), 7.69 (H6, m), 5.98 (H7, d) and 5.42 (H7, d) ppm. For isomer b: 8.63 (H2, s), 7.92 (H5, s), 7.33 (H4, s), 7.33 (H6, m), 5.97 (H7, d) and 5.16 (H7, d) ppm. For minor isomer: 8.65 (H2, br), 7.92 (H5, br), 7.41 (H4, s), 7.18 (H6, m), 5.73 (H7, d) and 5.16 (H7, d) ppm. For isomer c: 8.63 (H2, s), 7.92 (H5, s), 7.33 (H4, s), 7.69 (H6, m), 5.97 (H7, d) and 5.16 (H7, d) ppm. For minor isomer: 8.65 (H2, br), 7.92 (H5, br), 7.41 (H4, s), 7.18 (H6, m), 5.73 (H7, d) and 5.16 (H7, d) ppm.

**[Au(vinylimidazole)]⁺[AuBr₄]⁻ (2).** The solution of vinylimidazole (51.0 mg, 0.542 mmol) in thf (1 ml) was added to the solution of AuBr₃ (66.1 mg, 0.151 mmol) in thf (2 ml). Clear crystals were obtained from the slow diffusion of diethyl ether to the reaction mixture at 4 °C in two weeks. Yield: 23.8 mg, 42%. Anal. calcd for Au₂Br₃C₅H₉Cl₂: C, 16.19; H, 1.63; N, 7.55. Found: C, 15.88; H, 1.72; N, 7.04%. IR (KBr, cm⁻¹): ν(C–C–C, vinyl) 1640 cm⁻¹. ¹H NMR (400 MHz, d₆-DMSO, 298 K, δ): 8.76 (H₂, s), 8.01 (H₅, s), 7.41 (H₄, s), 7.18 (H₆, m), 5.73 (H₇, d) and 5.16 (H₇, d) ppm. For minor isomer: 8.65 (H₂, br), 7.92 (H₅, br), 7.30 (H₄, br), 7.11 (H₆, m), 5.66 (H₇, br) and 5.09 (H₇, br) ppm. ¹C NMR (400 MHz, d₆-DMSO, 298 K, δ): 139.9 (C2), 138.0 (C4), 128.9 (C6), 120.8 (C6), 118.6 (C5), 108.5 (C7) ppm.

**[AuCl₄][Hvinylimidazole]⁺ (3).** From HAuCl₄, H₂AuCl₄·3H₂O (58.1 mg, 0.148 mmol) was dissolved in 5 M HCl (5 ml) and one
drop of vinylimidazole was added. After a few days the solid product was filtered and washed with water and dried. Yield: 36.0 mg, 56%.

From NaAuCl₄, NaAuCl₄·2H₂O (56.1 mg, 0.141 mmol) was dissolved in 5 M HCl (5 ml) and one drop of vinylimidazole was added. Yield: 34.5 mg, 56%. Anal. calc'd for AuCl₂N₂C₅H₇: C, 13.84; H, 1.63; N, 6.46. Found: C, 14.04; H, 1.60; N, 6.35%. Mp 158–159 °C. IR (KBr): ν(C=O) 1640 cm⁻¹. ¹H NMR (400 MHz, d₆-DMSO, 298 K, δ): 9.10 (H₂, s, 1H), 8.23 (H₅, s), 7.81 (H₄, s), 7.31 (H₆, m), 5.97 (H₇, d) and 5.41 (H₇, d) ppm. ¹³C NMR (400 MHz, d₆-DMSO, 298 K, δ): 150.4 (C₄), 125.9 (Cₙ), 114.8 (C₌), 115.7 (C₂), 110.7 (C₁), 108.9 (C₀). 

[ AuBr₄ ]⁻[Hvinylimidazole]⁺ (4). AuBr₄ (33.6 mg, 0.077 mmol) was dissolved in 5 M HBr (3 ml) and one drop of vinylimidazole was added. After a few days, the red solid was filtered, washed with water and dried. Yield: 35.8 mg, 76%. Anal. calc'd for AuBr₄N₂C₅H₇: C, 9.82; H, 1.15; N, 4.58. Found: C, 9.94; H, 1.23; N, 4.53%. Mp 158–159 °C. IR (KBr): ν(C=O) 1640 cm⁻¹. ¹H NMR (400 MHz, d₆-DMSO, 298 K, δ): 9.10 (H₂, s, 1H), 8.23 (H₅, s), 7.81 (H₄, s), 7.31 (H₆, m), 5.97 (H₇, d) and 5.41 (H₇, d) ppm. ¹³C NMR (400 MHz, d₆-DMSO, 298 K, δ): 150.4 (C₄), 125.9 (Cₙ), 114.8 (C₃), 115.7 (C₂), 110.7 (C₀).

**Conclusions**

1-Vinylimidazole has different coordination modes towards platinum and gold. Reaction conditions were found to have a major effect on the obtained crystalline products, which was attributed to the protonation/deprotonation of the 1-vinylimidazole free nitrogen in acidic/basic medium. Under the acidic conditions, the first protonation/deprotonation of the vinyl group is energetically more favorable than N-coordination, which explains the structure of complex 1. The stability of the molecular models was fully consistent with the experimentally obtained structures, which were verified via X-ray diffraction and IR, Raman, and NMR spectroscopy.

**Conflicts of interest**

There are no conflicts to declare.

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