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Gold(III) π -Allyl Complexes

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Abstract: Gold(III) π -complexes have been authenticated recently with alkenes, alkynes and arenes. The key importance of Pd(II) π -allyl complexes in organometallic chemistry (Tsuji-Trost reaction) prompted us to explore gold(III) π -allyl complexes, which have remained so far elusive species. The (P,C)Au(III)(allyl) and (methallyl) complexes **3** and **3'** were readily prepared and isolated as thermally and air-stable solids. Spectroscopic and crystallographic analyses combined with detailed DFT calculations support tight quasi-symmetric η^3 -coordination of the allyl moiety. The π -allyl gold(III) complexes are activated towards nucleophilic additions, as substantiated with β -diketo enolates.

The last decade has witnessed spectacular progress in gold(III) chemistry. The variety of well-defined gold(III) complexes has been significantly expanded.^[1] Their unique luminescence and biological properties open exciting perspectives in material science and medicine.^[2,3] Applications in catalysis are also developing rapidly,^[4] including towards asymmetric transformations.^[5] In addition, numerous studies have been performed to improve our basic knowledge of gold(III) complexes from both structure and reactivity viewpoints.^[6] Most noticeable in this respect are the π -complexes resulting from side-on coordination of unsaturated hydrocarbons to gold(III) (Figure 1).^[7,8] The field was pioneered by Bochmann and Tilset in 2013 who independently reported the first π -alkene gold(III) complexes **A**.^[9] It was not until 2017 that gold(III) complexes featuring π -coordinated alkynes and arenes **B**^[10] and **C**^[11] were unambiguously authenticated. It is worth noting that gold(III) π -complexes are relevant to important reactivity paths: outer-sphere nucleophilic addition / migratory insertion for alkenes and alkynes, and C–H activation (auration) for arenes.

One missing class of gold(III) π -complexes in this picture are the π -allyl complexes, which are key species in organometallic chemistry, in particular within the frame of the Pd-catalyzed Tsuji-Trost reaction.^[12] Indeed, very little is known so far about gold(III) π -allyl complexes **D**. A few σ -allyl species have been described,^[13,14] while, to the best of our knowledge, precedents for side-on coordination of an allyl moiety to gold(III) are limited to $[(\pi\text{-allyl})\text{AuMe}_2]$. The latter complex was not directly observed, but based on mass spectrometry studies in the gas phase, it was proposed to form upon reaction of dimethyl aurate (AuMe_2)⁻ with allyl iodide and its η^3 -structure was inferred computationally.^[15]

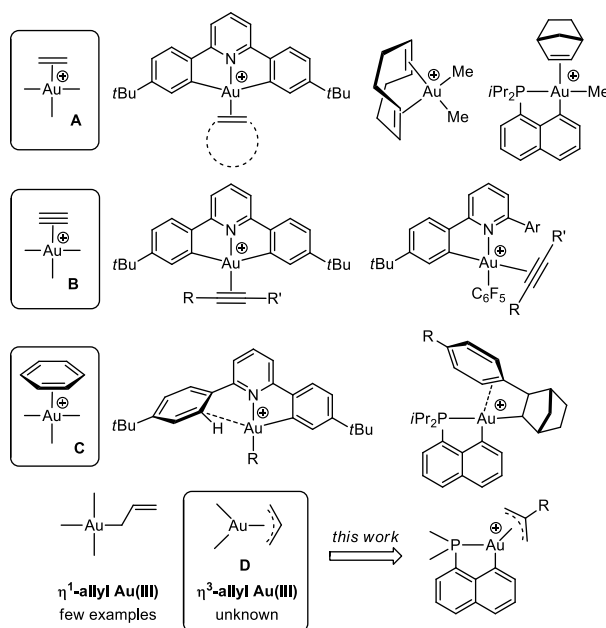


Figure 1. Known gold(III) π -complexes **A-C** with alkenes, alkynes and arenes, and targeted gold(III) π -allyl complexes **D**.

We have shown in previous studies that (P,C) cyclometallated gold(III) complexes are readily accessible by chelation-assisted oxidative addition of *perr*-halogeno naphthylphosphines^[16] and enable to access new gold(III) species, including π and σ complexes.^[11a,17] The (P,C) cyclometallated gold(III) complexes also possess rich reactivity^[18] and display high catalytic activity in the hydroarylation of alkynes.^[4e]

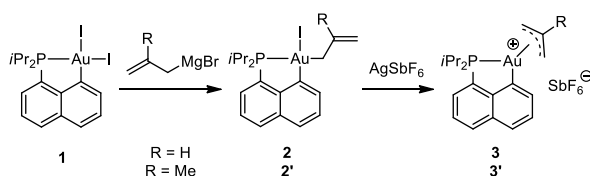
In this work, we envisioned to prepare and study gold(III) π -allyl complexes taking advantage of the stability imparted by the (P,C) chelate. As disclosed hereafter, thermally and air-stable species were readily obtained and fully characterized. Their η^3 -structure was thoroughly analysed by experimental and theoretical means, and some reactivity studies have been performed.

Complex **2** was prepared by Mg to Au transmetalation (Scheme 1).^[19] Addition of a stoichiometric amount of allylmagnesium bromide to the (P,C) cyclometallated gold(III) precursor **1** rapidly and cleanly afforded **2** which was isolated as a stable yellowish solid in 98% yield. The structure of **2** was deduced from high-resolution mass spectrometry (HRMS) and multinuclear NMR spectroscopy. η^1 coordination of the allyl is apparent from the ^1H and ^{13}C NMR signals of the Au-CH₂ group (δ ^1H 3.2 ppm and δ ^{13}C 48.2 ppm) and from the vinylic signals observed for the pendant CH=CH₂ moiety. The NMR pattern of the allyl group in **2** is very similar to those met in the few known Au(III) species.^[13] Complex **2** is obtained as a single stereoisomer, with the allyl chain in *trans* position to phosphorus. This is apparent from the large J_{PC} coupling constant (98.9 Hz) of the Au-CH₂ group and consistent with the electronic dissymmetry of the (P,C) ligand.^[11a,17,18]

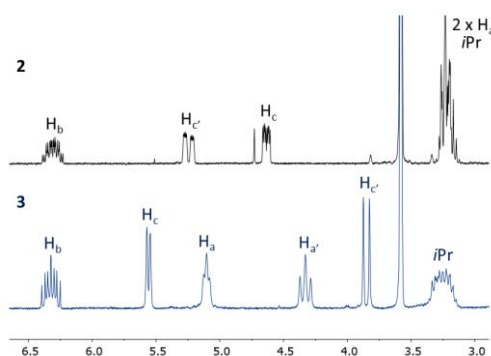
Complex **2** was then reacted with AgSbF₆ to abstract the iodine ligand and release a coordination site at gold for the double bond of the allyl group. According to ^{31}P NMR spectroscopy, this lead instantaneously to a single new species. After removal of the silver salts upon filtration over Celite, complex **3** was isolated in quantitative yield as a white stable powder (no sign of decomposition detected after 6 weeks upon storage under air). Complex **3** was characterized by HRMS, elemental analysis and multinuclear NMR spectroscopy. The ^{31}P NMR signal appears at δ 88.1 ppm, deshielded by 17 ppm compared to that of **2**. Most significant is the deshielding and splitting of the Au-CH₂ signal (from a unique signal in ^1H NMR at δ ~ 3.2 ppm for **2** to two distinct signals at δ 4.33 and 5.11 ppm for **3**) and the equalization of the ^{13}C chemical shifts of the two CH₂ groups (from δ 48.2/110.2 ppm for **2**, to δ 83.3/76.3 ppm for **3**). The J_{PC} coupling constant of the CH₂ group *trans* to phosphorus significantly decreases (from 98.9 to 31.8 Hz). All these data are diagnostic of an η^3 -allyl type structure (see Figure 2).

The related methallyl complexes **2'** and **3'** were prepared similarly using 2-methylallyl magnesium chloride (Scheme 1).^[19] The NMR features of **3'** very much resemble those of **3**. In particular, η^3 -coordination of the methallyl group to gold is apparent from the ^{13}C NMR signals of the two terminal CH₂ units, that both resonate as doublets at δ ~ 80 ppm (δ 83.24 ppm, $J_{\text{PC}} = 34.2$ Hz and δ 74.90 ppm, $J_{\text{PC}} = 2.9$ Hz).

The dynamics of π -allyl complexes has attracted much attention and plays a key role in their reactivity (especially when regioselectivity and stereoselectivity come into play).^[12] The possibility of the π -allyl moiety bonded to Au(III) in complex **3** to rotate and/or shift from η^3 to η^1 coordination was investigated by variable temperature NMR spectroscopy. No significant change was detected in the temperature range -70 to +110°C, indicating rigid coordination and the absence of fluxional behaviour (Figure S13).^[19]



Scheme 1. Synthesis of the neutral σ -allyl and cationic π -allyl gold(III) complexes **2**^(a) and **3**^(a).



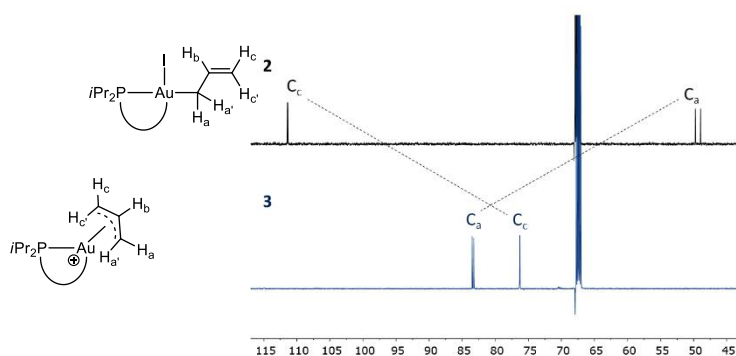


Figure 2. NMR spectra (selected zones) of the neutral σ -allyl and cationic π -allyl gold(III) complexes **2** and **3** in d_6 -THF. Top: Allylic zone of the ^1H NMR spectra. Bottom: ^{13}C NMR spectra, C_a/C_c signals.

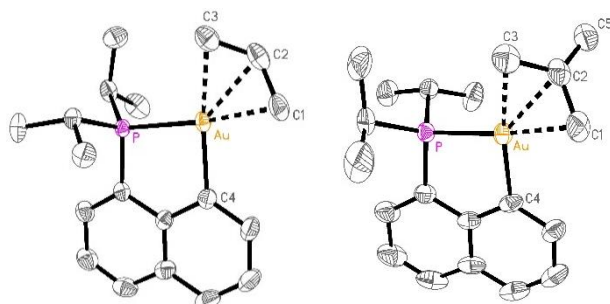


Figure 3. Molecular structures of the π -allyl gold(III) complexes **3** (left) and **3'** (right). Thermal ellipsoids drawn at 50% probability, hydrogen atoms, counter anion and disordered atoms are omitted. Selected bond lengths (\AA): (**3**) Au-C1 2.195(12), Au-C2 2.226(8), Au-C3 2.275(9), C1-C2 1.422(14), C2-C3 1.386(12), (**3'**) Au-C1 2.169(5), Au-C2 2.238(5), Au-C3 2.240(5), C1-C2 1.406(8), C2-C3 1.400(8), C2-C5 1.512(8).

Crystals of **3** and **3'** suitable for X-ray diffraction analysis were grown from dichloromethane solutions (Figure 3).^[19,20] Complexes **3** and **3'** adopt separate ion-pair structures with no significant intermolecular Au...Au contacts (shortest distance $> 7 \text{ \AA}$). The gold center is in square-planar environment. The allyl fragment is coordinated facially and makes an angle of $56.7\text{--}57.2^\circ$ with the (P,C)Au coordination plane. The metrics for the Au-CH₂/Au-CH(Me) (2.169-2.275 \AA) and H₂C-CH(Me) bonds (1.386-1.422 \AA) are very comparable to those reported for Pd and Pt π -(meth)allyl complexes.^[21] Of note, the Au-C1 / Au-C3 distances differ by only 0.08 \AA and the C1-C2 / C2-C3 bond lengths differ by only 0.04 \AA , indicating quasi-symmetric coordination of the π -allyl moiety to Au in both complexes **3** and **3'**.

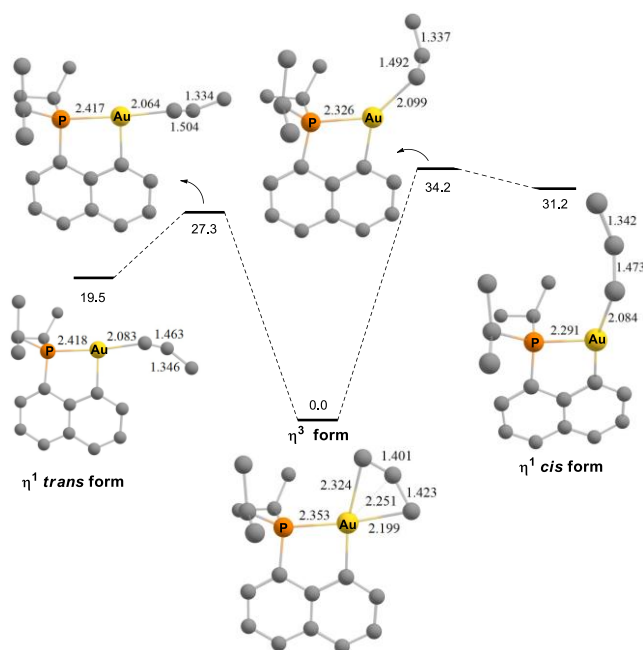


Figure 4. Potential energy surface computed for the cationic allyl gold(III) complex **3** showing the η^3 and η^1 forms (ΔG in kcal/mol).

The structure of the π -allyl gold(III) complexes **3** and **3'** was analysed computationally. DFT calculations were performed on the actual complexes at the B3PW91/SDD+f(Au),6-31G** (other atoms) level of theory. The optimized geometries reproduce closely those determined crystallographically (Figure S25).^[19] The computed NMR data (^1H , ^{13}C chemical shifts, J_{PC} coupling constants) are also in very good agreement with those observed experimentally (Table S2).^[19] The potential energy surface of **3** was scrutinized and two local energy minima were located with the allyl group η^1 -coordinated to gold in *trans* or *cis* to phosphorus (and a pending $\text{CH}=\text{CH}_2$ moiety) (Figure 4). They are much less stable than the ground-state η^3 structure (by 19.5 and 31.2 kcal/mol, respectively). In line with the non-fluxional behaviour noted upon variable-temperature NMR, the activation barriers computed for η^3 to η^1 interconversion exceed 27 kcal/mol.^[22]

The bonding situation of the gold(III) complexes **3** and **3'** in their π -allyl ground-states was then analysed using the Atoms-in-Molecules (AIM) approach (Figure 5). Bond critical points (BCP) are found between Au and the terminal carbon atoms. The associated electron densities ρ (0.075 / 0.078 and 0.095 / 0.098 e/bohr³) and delocalization indexes δ (0.522 / 0.544 and 0.639 / 0.654) are similar. This is indicative of quasi-symmetry η^3 coordination of the allyl group to gold. Consistently, the allyl moiety is highly delocalized, as apparent from the Bader bond indexes for the two CHCH_2 moieties (1.244 / 1.211 and 1.347 / 1.306).^[23]

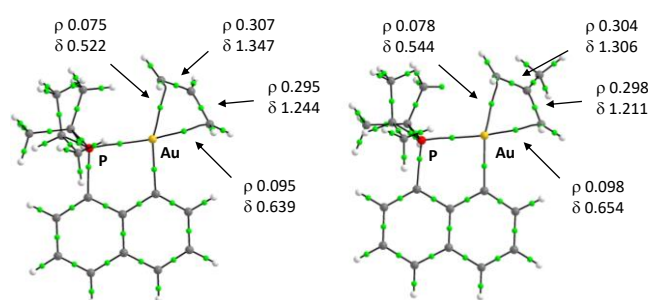
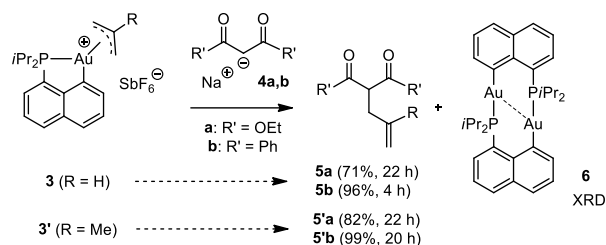


Figure 5. Atoms-in-molecules (AIM) molecular graph calculated for the π -allyl gold(III) complexes **3** and **3'** with relevant bond paths, bond critical points (BCP, green circles), electron densities (ρ in e/bohr³) and delocalization indices (δ).

Some reactivity studies were performed to assess the chemical behavior of the allyl gold(III) complexes and substantiate that π -coordination of the allyl moiety to gold mediates nucleophilic addition to it. Having in mind the Pd-mediated allylation of β -diketo derivatives (Tsuji-Trost reaction),^[12] we selected diethylmalonate **4a** as nucleophile (Scheme 2). A control experiment carried out with the neutral Au(III) η^1 -allyl complex **2** showed no sign of a reaction after several days at 20°C.^[19] In stark contrast, **4a** was found to react smoothly with the cationic η^3 -allyl Au(III) complex **3** under the same conditions. Within 22 hours, the expected coupling product **5a** was obtained in 71% yield (as deduced from comparison of NMR and GC-MS data with those of an authentic sample) along with the (P,C)-bridged dinuclear Au(I) complex **6** (as deduced from independent synthesis and X-ray crystallography).^[19] With the enolate of 1,3-

diphenylpropanedione **4b**, the reaction proceeds even faster and the coupling product **5b** is obtained in near quantitative yield within 4 hours. Similar nucleophilic addition reactions were observed with the methallyl complex **3'**. Of note, reaction of the dinuclear Au(I) complex **6** with allyl iodide^[24] was found to enable simple and efficient recycling of the (P,C) cyclometallated gold complex. Indeed, the neutral σ -allyl gold(III) complex **2** was thereby obtained in 92% yield within 3.5 hours at room temperature.



Scheme 2. Reactivity of cationic π -allyl gold(III) complexes **3** and **3'** with β -dicarbonyl carbanions.

In summary, π -allyl complexes of gold have been authenticated for the first time in the form of (P,C) cyclometallated thermally and air-stable gold(III) complexes. NMR spectroscopy, X-ray crystallography and DFT calculations substantiate tight quasi-symmetric η^3 -coordination of the allyl moiety. Reactions with β -diketo enolates show that side-on coordination to gold(III) activates the allyl moiety towards nucleophilic additions.

Further studies will aim to explore further the reactivity of π -allyl gold(III) complexes towards C- as well as heteroatom- and H-based nucleophiles, to study the reaction mechanism and to draw comparison with related Pd complexes. Better understanding of the structure and chemical behavior of π -allyl gold(III) complexes will certainly help in developing gold-catalyzed allylation reactions, which remain very rare so far.^[13b,25]

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Keywords: Allyl • π -Complexes • Gold • DFT • NMR • Nucleophilic Addition • XRD

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- [19] See Supporting Information for details.
- [20] Two orientations of the η^3 -allyl moiety co-exist in the solid state (up and down). For sake of clarity, only one is discussed.
- [21] The Cambridge Structural Database contains 1062 (respectively 149) hits for Pd (resp. Pt) η^3 -allyl complexes. The average value for the Pd–C (resp. Pt–C) bond length is 2.160 Å (resp. 2.250 Å) and the average value for the C–C bond length is 1.401 Å.
- [22] Upside/down flip of the allyl moiety by rotation around the CH₂–CH bond is associated with a rather large activation barrier as well (24.4 kcal/mol). Rotation of the η^3 -allyl around the Au–CH axis was also considered, but no relevant transition state could be located.[19]
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