

Axially Chiral Allenyl Gold Complexes

Alice Johnson, Antonio Laguna, and M. Concepción Gimeno*

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain

S Supporting Information

ABSTRACT: Unprecedented allenyl gold complexes have been achieved starting from triphenylpropargylphosphonium bromide. Two different coordination modes of the allene isomer of triphenylphosphoniumpropargylide to gold have been found depending on the gold oxidation state. Bromo-, pentafluorophenyl-, and triphenylphosphine-gold(I) allenyl complexes were prepared in which the α carbon coordinates to the gold(I) center. A chiral pentafluorophenyl-gold(III) allenyl complex with the gold atoms coordinated to the γ carbon was also prepared. All the complexes have been structurally characterized by X-ray diffraction showing the characteristic distances for a C=C=C unit.

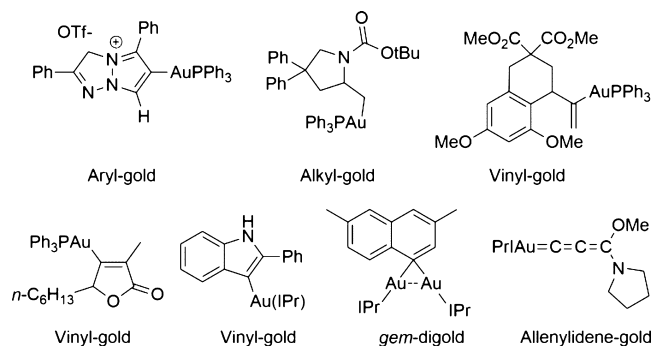


Figure 1. Some Au–C species isolated in gold-catalyzed reactions. IPr = 1,3-Bis(diisopropylphenyl)imidazole-2-ylidene.

Homogeneous gold catalysis is a powerful tool to promote a broad range of organic transformations for the formation of C–C and C–X bonds.¹ Gold catalysts are excellent soft π -acids capable of activating carbon–carbon multiple bonds toward intra- or internucleophilic attack. In gold-catalyzed transformations numerous organogold intermediates have been proposed to support the reaction mechanisms and consequently there is a need to understand the role of each metal–carbon coordination step. Therefore, great interest has arisen in the formation, stability, and reactivity of organo-gold complexes.² Several types of gold–carbon bonds are known within organometallic gold chemistry. Gold(I) and gold(III) alkyl/aryl or alkynyl complexes are well-known.³ Gold alkene/alkyne complexes are known for gold(I),⁴ with interesting examples obtained recently upon insertion of alkynes into Au–F,⁵ Au–H,⁶ or Au–Si⁷ bonds, and the first alkene species for gold(III) have been synthesized by insertion of allenes into the Au(III)–H bond.⁸ However, these organogold intermediates in gold-catalyzed reactions have only been very recently isolated⁹ and include gold-aryl,¹⁰ gold-alkyl,¹¹ gold(I)-vinyl,¹² gem-diaurated gold(I) species,^{12b,13} carbenoid gold(I) derivatives,¹⁴ and gold(I) and gold(III) allenylidenes (Figure 1).¹⁵ In these latter, a classical discussion of the Au=C bond, from carbocation vs carbene to carbocation vs allenylidene, is commented upon.^{14,15a,c}

Although much of the work in gold catalysis has focused on alkyne functionalization, allenes have been proven as very versatile substrates for gold-catalyzed transformations.¹⁶ The gold catalyst can coordinate to either of the allenic double bonds, and the regioselectivity of the subsequent nucleophilic attack depends on the structure of the substrate.^{16c}

Four different *endo*- or *exo*-cyclization compounds can be obtained, depending upon whether the nucleophilic attack takes place at the terminal or the central carbon atom. For this reason it

is extremely challenging to obtain the allene intermediate. Until recently very little information on the coordination of gold(I) to allenes was available and none on the coordination of gold(III) to allenes. Malacria et al. reported computational studies of the interaction of (*R*)-1,3-dimethyl allene in the presence of AuX₃ or Au⁺ showing that η^2 complexes involving one of the two orthogonal C=C bonds are the most stable form (Figure 2).¹⁷

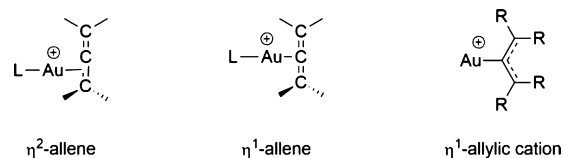


Figure 2. Gold(I) allene complexes.

Gold(I)- π -allene species have been reported by Widenhoefer et al., confirming that the η^2 -allene form with coordination of the cationic gold fragment to the less substituted C=C bond of the allene was the most stable. A few η^2 -allene complexes bearing N-heterocyclic or phosphine ligands have also been prepared.¹⁸ The η^1 -allylic form represented in Figure 2 has been isolated with a tetraaminoallene gold complex.¹⁹ No σ -coordination of gold(I) to the outer carbon atoms of the allene has been reported, and no gold(III)-allene derivative is known to date. σ -Metal allenyls are almost unknown, and these interesting species are either generated *in situ* in the reaction medium or proposed as key intermediates of more complex process.²⁰ Among the scarce σ -metal allenyls described are those reported by Auman et al. by addition of a tertiary phosphine²¹ or more recently of a N-

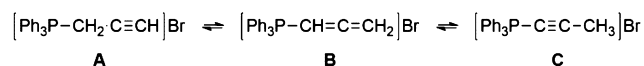
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heterocyclic carbene to an alkynyl Fischer carbene.²² The lack of gold allenyl derivatives encouraged us to search for new precursors able to produce σ species and with the aim of achieving substitution at both the outer allenic carbon atoms. This would lead to the synthesis of appealing chiral allenyl gold complexes. Taking this into account, we envisaged that use of a stable source of allene compounds, triphenylpropargylphosphonium bromide, could be a suitable method to achieve our goal.

Triphenylpropargylphosphonium bromide is a phosphonium salt of a stabilized ylide. The alkynyl group provides the stability by facilitating the delocalization of electron density. This compound is unusual in that it has three isomers (Scheme 1)

Scheme 1. Isomers of Triphenylpropargylphosphonium Bromide



and will readily isomerize into the allene form, **B**, in various nonpolar solvents. It is also possible to obtain an isomer with the triple bond in the α,β position by simply refluxing in polar solvent for several hours.²³

Triphenylpropargylphosphonium bromide has great potential for the formation of coordination complexes due to having various coordination sites and isomeric forms (Figure 3). There

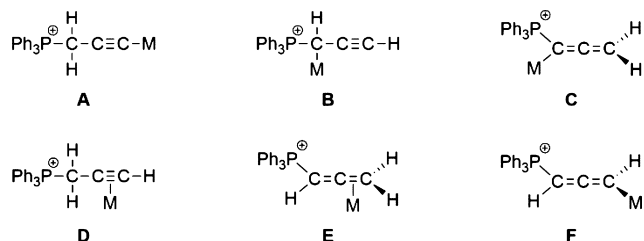


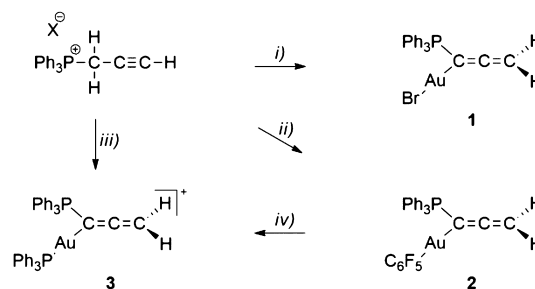
Figure 3. Coordination possibilities of triphenylpropargylphosphonium bromide.

is the possibility for linear coordination of metal atoms at the alkynyl group, **A**, coordination at the α -carbon to give both the ylide-alkynyl isomer, **B**, and the allenyl isomer, **C**. Side-on π -type coordination is also possible with the triple bond in the alkyne isomer, **D**, to the double bond of the allene isomer, **E**. Finally coordination at the γ -carbon gives the chiral allenyl species **F**. The only previous uses of triphenylpropargylphosphonium bromide as a ligand are in ruthenium complexes, form **C**,^{24a} and recently platinum complexes in which coordination type **D** is observed.^{24b}

The dependence of the isomeric form of solution state triphenylpropargylphosphonium bromide on solvent polarity was studied by NMR spectroscopy, showing that only in the very polar DMSO is the alkyne form **A** maintained. The shift of the CH proton at 3.46 ppm is characteristic of a shielded proton next to a $\text{C}\equiv\text{C}$ triple bond. The CH proton will be deshielded as a result of being next to a $\text{C}=\text{C}$ double bond and in close proximity to the positively charged phosphorus atom of the triphenylphosphine, resulting in a higher chemical shift (see Supporting Information (SI)). Interestingly, the reaction of the phosphonium bromide with $[\text{AuX}(\text{tht})]$ ($\text{X} = \text{Cl}, \text{C}_6\text{F}_5$; tht = tetrahydrothiophene), in the presence of cesium carbonate, in which there is first deprotonation at the α -carbon and subsequent

displacement by the ylide of the labile tht in the gold complexes, gives the unprecedented allenyl gold species $[\text{AuX}(\text{Ph}_3\text{PC}=\text{C}=\text{H}_2)]$ ($\text{X} = \text{Br}$ (**1**), C_6F_5 (**2**)) (isomer **C**, Scheme 1).

Scheme 2. Synthesis of the Allenyl Gold(I) Derivatives^a



^a(i) $\text{X} = \text{Br}$, $[\text{AuCl}(\text{tht})]$, Cs_2CO_3 ; (ii) $\text{X} = \text{Br}$, $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$, Cs_2CO_3 ; (iii) $\text{X} = \text{OTf}$, $[\text{Au}(\text{acac})(\text{PPh}_3)]$; (iv) $[\text{Au}(\text{PPh}_3)_2]\text{OTf}$.

Complexes **1** and **2** were obtained with good yields, 63% and 85%, respectively, and have been characterized by IR and NMR spectroscopy (see SI). The absorption for the allene $\text{C}=\text{C}=\text{C}$ fragment appears in the IR at around 1906 cm^{-1} . In the ^1H NMR spectra, the $=\text{CH}_2$ protons appear as a doublet around 4 ppm, as a consequence of the coupling with the phosphorus atom. In the ^{13}C APT spectrum of **1**, the allenic carbons $\text{C}=\text{C}=\text{CH}_2$ appear at 83.8, 216.5, and 65.6 ppm, respectively. For complexes **2** and **3** not all of the allenic carbons can be observed, with resonances at 215.9 and 64.0 ppm for **2** and at 66.5 ppm for **3**.

The molecular structures of **1** and **2** were determined by X-ray diffraction methods (see Figure 4). The expected linear

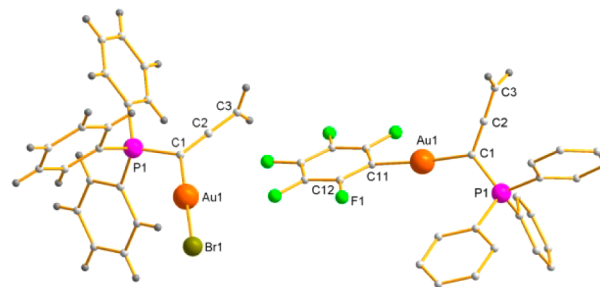


Figure 4. Structures of complexes **1** and **2**.

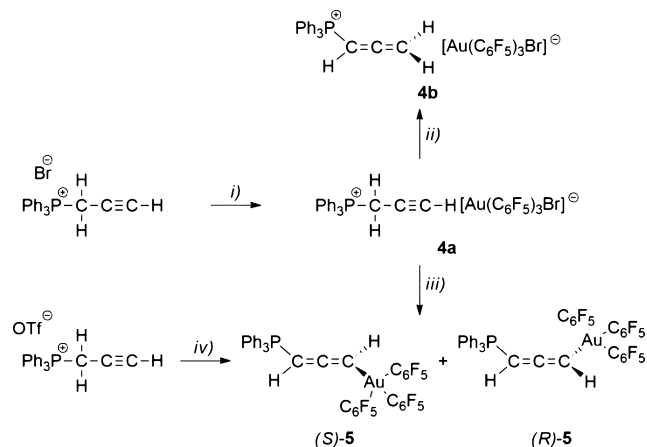
coordination around the gold(I) centers can clearly be seen in the molecular structure of **1** or **2** with angles of $179.66(10)^\circ$ and $175.24(9)^\circ$, respectively. The $\text{Au}-\text{C}$ distances are within the values found for σ $\text{Au}-\text{C}$ bonds. The similarity of the bond lengths $\text{C}(1)-\text{C}(2)$ and $\text{C}(2)-\text{C}(3)$, 1.296(5) and 1.304(5) Å for **1** and 1.304(4) and 1.300(4) Å for **2**, highlights the presence of the allenyl isomer. These are also comparable to the carbon-carbon bond length in ethene, 1.34 Å.

Reaction of triphenylpropargylphosphonium triflate with $[\text{Au}(\text{acac})(\text{PPh}_3)]$ did successfully produce complex **3**; however, the yield was low, 50%, and the ^{31}P NMR spectrum showed the product was impure. A more effective synthetic route to **3** was the reaction of **2** with $[\text{Au}(\text{PPh}_3)_2]\text{OTf}$, which produced complex **3** cleanly and in a higher yield (60%). The driving force of the process is the formation of the stable $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)]$, which can be easily separated due to its high solubility in organic solvents.

The molecular structure of **3** was determined by X-ray diffraction methods (see SI). Linear coordination about the gold(I) center in **3** is observed with a slight distortion which results from the bulky triphenylphosphine groups. The carbon–carbon bond lengths in the allenyl, 1.293(16) and 1.290(19) Å, are typical of those for a carbon–carbon double bond. The Au–C bond distance is 2.063(11) Å, which is similar to those found for complexes **1** and **2**.

With the aim of obtaining gold(III) derivatives with allenes which are unknown in the literature, we carried out the reaction of triphenylpropargylphosphonium bromide with the gold(III) derivative [Au(C₆F₅)₃(tht)] in dichloromethane resulting in the formation of the phosphonium salt **4a**, in which the alkyne triple bond is maintained (Scheme 3). Attempts to coordinate the

Scheme 3. Synthesis of the Allenyl Gold(III) Derivatives^a



^a(i) [Au(C₆F₅)₃(tht)]; (ii) Cs₂CO₃; (iii) NaH; (iv) [Au(C₆F₅)₃(tht)], Cs₂CO₃.

Au(C₆F₅)₃ unit to the ylide by subsequent reaction with excess cesium carbonate were unsuccessful, resulting in a prototropic isomerization giving the allene isomer, **4b**. Reaction of **4a** with the stronger base, sodium hydride, resulted in deprotonation, isomerization to the allene isomer, and coordination of Au(C₆F₅)₃ to the γ -carbon atom to give both enantiomers of **5** as a racemic mixture and in a yield of 65% (isomer F in Figure 3). This result is remarkable, as there is a regioselectivity of the gold(III) compared to the gold(I) species and an axially chiral derivative is produced. Complex (\pm)-**5** was also prepared by the more synthetically simple route in which triphenylpropargylphosphonium triflate is reacted stoichiometrically with [Au(C₆F₅)₃(tht)] in the presence of excess cesium carbonate. In this case a phosphonium salt analogous to **4b** is not produced, since the triflate anion is too weakly coordinating to bind to the gold center. The ¹H NMR spectrum of complex (\pm)-**5** confirms the coordination of the gold(III) center to the γ -carbon atom, as the protons of the outer allenic carbons each appear as a doublet of doublets by coupling themselves and also coupling with the phosphorus atom. In the ¹³C APT spectrum of (\pm)-**5**, the allenic carbons C=C=CH₂ appear at 86.4, 205.6, and 65.6, respectively, downshielded compared with those of the gold(I) species.

The formation of complex (\pm)-**5** by deprotonation at the γ -carbon atom is unusual, as the hydrogen atom at the α -carbon of the ylide would be more acidic since a negative charge here would be stabilized by the positively charged phosphorus of the triphenylphosphine group. It is likely that the triphenylphosphine

and the tris(pentafluorophenyl) gold(III) groups are too sterically bulky to be in close proximity resulting in regioselectivity in the coordination to the γ -carbon.

The molecular structure of **5** was unambiguously determined by X-ray diffraction methods, and the molecular structure diagram is shown in Figure 5. Complex (\pm)-**5** is a chiral allenyl

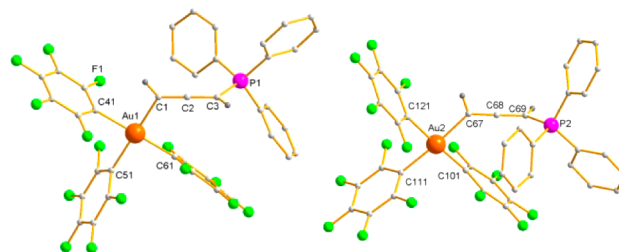


Figure 5. Structures of both enantiomers of complex (\pm)-**5**.

derivative which crystallizes in the space group *P*2₁/*c* with both the (*S*) and (*R*) enantiomers in the asymmetric unit. The bond lengths C(1)–C(2) of 1.276(7) Å and C(2)–C(3) of 1.322(9) Å for the (*S*) enantiomer and C(67)–C(68) of 1.276(9) and C(68)–C(69) of 1.322(9) Å for the (*R*) enantiomer are typical of those for carbon–carbon double bonds. The Au–C bond distances are very similar to the carbon atoms of the allene. A square planar coordination is observed about the gold(III) centers.

Several experiments have been carried out in order to determine the stability and reactivity of these derivatives (see SI). The complexes are thermally stable, and no dynamic NMR effects have been observed at low/high temperature. A protodesaturation experiment was carried out with complex **3**, using stoichiometric amounts of a solution of HCl in diethyl ether at room temperature, showing formation of [AuCl(PPh₃)] and the phosphonium salt in a few hours. This protodesaturation process may be relevant in a catalytic cycle as the key step before the release of a possible catalyst.²⁵ The stability of these allenyl species probably arises as a result of the presence of an electron-withdrawing phosphonium group. In summary, here we have synthesized unprecedented allenyl gold(I) derivatives, with the gold center coordinated to the most substituted α carbon atom and with the typical Au–C distances for a σ bond (isomer C). The use of a bulky gold(III) derivative changes the regioselectivity and an axially chiral gold(III) compound is produced, with coordination of the gold(III) center to the less substituted γ carbon (isomer F). Our work represents some unprecedented examples in the field of gold allene derivatives, and these interesting species open the possibility for preparation of a wide range of outstanding organogold derivatives, some of which could be crucial as possible intermediates in gold catalyzed reactions.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedure, NMR and X-ray diffraction data. CCDC-996108 (1), -996109 (2), -996110 (3), and -996111 ((\pm)-**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

gimeno@unizar.es

Notes

The authors declare no competing financial interest.

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