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Au(III) π-Allyl Complexes: Synthesis, Structure, Reactivity, and Catalytic Applications

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Dedicated to Mats Tilset

π-Allyl complexes of transition metals are key species in organometallic chemistry and homogeneous catalysis. Palladium(II) π-allyl complexes in particular, have gained a lot of attention, but their isoelectronic gold(III) counterparts long remained elusive. However, this situation changed during the last few years. This concept article describes the preparative routes, characterization, structure and reactivity of such species, together with their catalytic applications. The influence of the ancillary ligand at gold, either (P,C)/(N,C)-cyclometalated or (P,N)-hemilabile, is analysed in detail. The Au(III) and Pd(II) π-allyl complexes are also compared to highlight the similarities and differences.

1. Introduction

Despite the spectacular progress achieved over the past ten years concerning Au(III) complexes featuring carbon-based π-ligands (alkenes, alkynes, arenes),[1–3] Au(III) π-allyl complexes remained elusive until very recently.[4] This is all the more surprising that the related Pd(II) π-allyl complexes are key species in organometallic chemistry, both in terms of bonding/coordination and reactivity/catalytic applications (cf. the Tsuji-Trost reaction).[5–7]

It is only a few years ago that the first Au(III) π-allyl complexes could be isolated. They were reported simultaneously by our group and Tilset's group, using (P,C) and (N,C)-cyclometalated ligands, respectively.[8,9] From there on, the chemistry of Au(III) π-allyl complexes was explored systematically and thoroughly,[10–12] ranging from fundamental aspects such as their synthesis, characterization and geometric/electronic structure, to their reactivity towards nucleophiles, and finally their catalytic applications (Figure 1). These studies are summarized and analyzed herein, with special emphasis on the role and impact of the ancillary ligand at gold. Particular attention is given to the specific features of the Au(III) π-allyl complexes when compared to their Pd(II) counterparts.

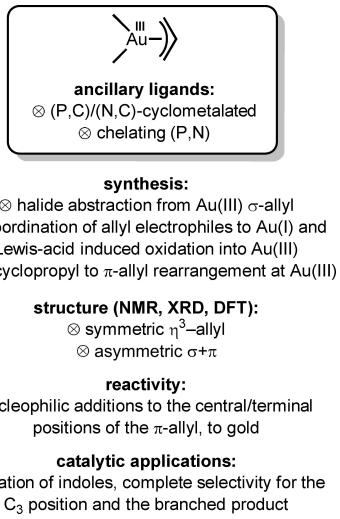

Figure 1. Au(III) π-allyl complexes: from their preparation and characterization, to their reactivity and catalytic application.

2. Preparation of Au(III) π-Allyl Complexes

In 2020, we reported the preparation of (P,C)-cyclometalated Au(III) π-allyl complexes **3** by halide abstraction from their respective Au(III) σ-allyl complexes **2** thereby allowing for the η^3 coordination of the allyl moiety (Scheme 1a).[8] The (P,C) Au(III) σ-allyl complexes were conveniently prepared by reaction of (P,C)AuI_2 complexes **1** with the appropriate allyl Grignard reagent (Scheme 1a). Both the parent Au(III) π-allyl complex (**3**, R′ = H) and the closely related methallyl complex (**3**, R′ = Me) were prepared. Simultaneously, Tilset and co-workers prepared

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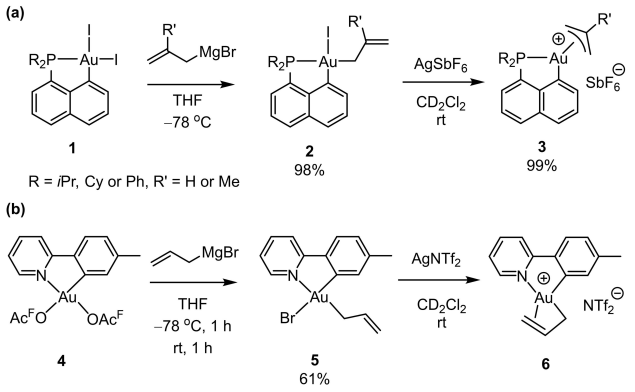


Scheme 1. Preparation of Au(III) π-allyl complexes **3** and **6** ($OAc^F = OCOCF_3$) upon halide abstraction from σ-allyl complexes **2** and **5**. The yields given for complex **2** and **3** are for R = *i*Pr and R' = H. No yield reported for **6** as it starts to decompose at the same time as it forms.

the (N,C)-cyclometalated Au(III) π-allyl complex **6** by a closely related method (Scheme 1b).[9] Reaction of $(N,C)Au(OAc^F)_2$ ($OAc^F = OCOCF_3$) **4** with allyl magnesium bromide followed by halide abstraction of **5** with $AgNTf_2$ and concomitant η^3 coordination of the π-allyl moiety led to the formation of complex **6**. Although prepared similarly, Au(III) π-allyl complexes **3** and **6** showed a striking difference in terms of stability. Whereas complexes **3** are stable at room temperature for weeks, complex **6** rapidly decomposes at room temperature. The bonding of the allyl moiety in complexes **3** and **6** turned out to be quite different, and we have chosen to draw the complexes in their most representative form (symmetric η^3-allyl *versus* asymmetric σ + π-coordination, as discussed below).

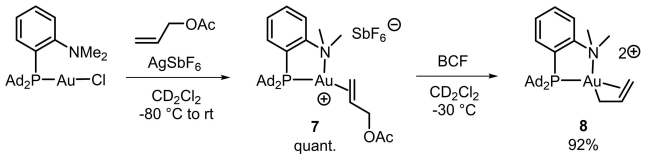
With the first two cyclometalated Au(III) π-allyl complexes being prepared *via* a redox neutral halide abstraction from the σ-allyl precursors, the question arose if they could be formed *via* oxidation from Au(I) to Au(III) as is often the case for their isoelectronic Pd(II) π-allyl analogues. In other words, can Au(III) π-allyl complexes be prepared from allyl electrophiles and Au(I), akin to the Pd(0)/Pd(II) elementary step in the Tsuji-Trost reaction?

While Au(I) is infamous for its reluctance to undergo oxidative addition, recent efforts have shown that carefully selecting the ligand allows for the oxidative addition to proceed.[13] In particular, the hemilabile (P,N) type ligand Me-Dalphos has been demonstrated to be very efficient in triggering Au(I)/Au(III) oxidation.[14] Due to the sterically demanding adamantyl substituents on the phosphorus atom, the nitrogen lone pair points towards the Au center, resulting in a lowering of the barrier for oxidative addition.[13c] With this in mind, allyl acetate was reacted with the *in situ* formed $(P,N)Au(I)^+$ (Scheme 2).[11] Unlike its Pd(0) analogues, the Au(I) to Au(III) oxidation did not proceed spontaneously and instead, the Au(I) π-alkene complex **7** was formed quantitatively. Despite the enhanced π-backdonating ability of gold induced by bending, the $(P,N)Au^+$ fragment was reluctant to undergo oxidation.

David Vesseur obtained his bachelor degree in 2018 at the University of Amsterdam (UVA) and Vrije Universiteit Amsterdam (VU), he then continued his studies at the UVA to obtain his master degree in 2020, during this he spend one year in the research group of Dr. Bas de Bruin developing new ways to access Co(III) carbene radicals. In 2020, he started his PhD under the supervision of Dr. Didier Bourissou at the Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA). His research focuses on ligand-enabled Au(I)/Au(III) oxidation and the stabilization of coinage metal carbenes.

Marte Sofie Martinsen Holmsen obtained her master degree in 2013 from the University of Oslo, Norway, where she worked with N-heterocyclic carbene complexes under the supervision of Professor Mats Tilset. She then pursued her PhD in the same group working with fundamental studies on cyclometalated Au(III) complexes. In 2020, she moved to Toulouse, France, where she did a postdoc with Dr. Didier Bourissou at the Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA). In 2021 she was awarded a FRINATEK mobility grant from the Reseach Council of Norway for a two years postdoctoral stay in the group of Dr. Didier Bourissou and thereafter a year in the group of Professor Mats Tilset.

Didier Bourissou obtained his PhD from Toulouse University. He then spent one year as research associate at the Ecole Polytechnique. Appointed as a Chargé de Recherche CNRS in 1998, he was promoted Directeur de Recherche in 2006. From 2006 to 2018, he has been Associate Professor at the Ecole Polytechnique. He has been Director of the Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA) from 2011 to 2020. He was awarded the Bronze (2005) and Silver (2016) Medals of the CNRS, the Clavel Lespiau Distinction (2006) and Del Duca Grant (2020) from the French Academy of Sciences, the Acros (2009) and Organic Division (2018) Awards from the French Chemical Society in recognition of his work. His research interests concern new bonding situations and reactivity patterns arising from the main group elements, the transition metals and their interplay. He has pioneered ambiphilic ligands in the mid 2000's and developed the concept of σ-acceptor ligands. Part of his research deals with non-innocent pincer complexes and in biodegradable polymers (ring-opening polymerization, organic and dual catalysis, drug delivery systems). He is also very much interested in the organometallic chemistry and catalytic applications of the coinage metals, in particular gold. He has been awarded an ERC Advanced grant in 2023 to explore Gold-Redox chemistry.



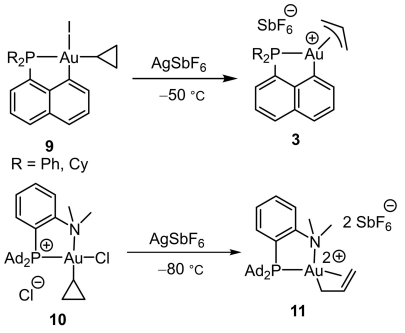
Scheme 2. Formation of the Au(I) π-alkene complex **7** and subsequent Lewis acid-assisted oxidation to give the Au(III) π-allyl complex **8**. SbF_6^- and AcO–BCF^- counter-anions for **8**.

However, addition of the strong Lewis acid tris(pentafluorophenyl)borane (BCF) resulted instantaneously in abstraction of the acetate. The ensuing Au(III) π-allyl complex **8** is stable up to −30 °C and was fully characterized using multinuclear NMR.

Gold has been shown to display rich reactivity in combination with strained carbocycles,[15] and recently the ring-opening of alkylidene cyclopropanes by Au(III) was reported.[16] Therefore we wondered if Au(III) π-allyl complexes could be formed *via* a redox neutral rearrangement from their isomeric σ-cyclopropyl, driven by the release of strain energy.[12]

To test this synthetic approach, the (P,C)-cyclometalated Au(III) σ-cyclopropyl complex **9** and the (P,N)-chelated Au(III) σ-cyclopropyl complex **10** were prepared (Scheme 3). For the rearrangement to proceed, a coordination site had to be liberated, which could be done by halide abstraction with $AgSbF_6$. In both cases, the reaction led cleanly to the ring-opened product. However, the temperature at which the rearrangement occurred depended strongly on the ligand used. For the (P,C)-cyclometalated Au(III) σ-cyclopropyl **9**, the rearrangement occurred already at −50 °C. Whereas the chelated biscationic (P,N)-chelated Au(III) σ-cyclopropyl complex **10** undergoes rearrangement already at −80 °C and is complete when −60 °C is reached. Changing the phenyl substituents on **9** to the more electron-donating cyclohexyl did not noticeably change the temperature at which the ring-opening proceeded.

The ring-opening process was investigated in-depth using DFT calculations. The free energy profile for the σ-cyclopropyl to π-allyl rearrangement for complex **9-Ph** is given in Figure 2. The lowest barriers were found for the ring-opening where the distal σ(CC) bond was cleaved. For the (P,C) Au(III) σ-cyclopropyl complex, a barrier of 19.8 kcal/mol was found while for the



Scheme 3. Formation of Au(III) π-allyl complexes **3** and **11** from their corresponding Au(III) σ-cyclopropyl complexes **9** and **10** by halide abstraction.

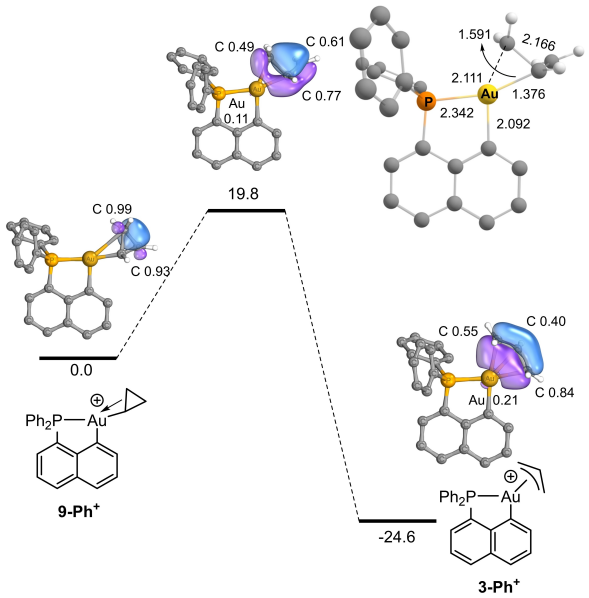


Figure 2. Computed energy profile for the ring-opening of the (P,C) Au(III) σ-cyclopropyl complex **9-Ph** to give the corresponding π-allyl complex **3-Ph**. ΔG values in kcal/mol, main distances in Å. Profile computed in the gas phase at the B3PW91/SDD + f(Au), 6–31G** (other atoms) level of theory and main IBOs accounting for the ring-opening of the distal σ(CC) bond along the reaction path (numbers relate to the fraction of electrons of the doubly occupied orbital assigned to each atom).

(P,N) Au(III) σ-cyclopropyl complex, a lower activation barrier of 15.7 kcal/mol was found matching the experimental trend. Several other mechanistic pathways were considered, *e.g.* β-H elimination and insertion of Au into the σ(CC) bond, but these were found to not be energetically competitive.

A deeper look into the ring-opening process showed that the rotation of the two CH_2 moieties along the Intrinsic Reaction Coordinate (IRC) proceeds *via* a disrotatory ring-opening process. For analysis of the electron flow associated with the rearrangement, the intrinsic bond orbitals (IBO) were inspected. Here, the most noteworthy observation was the progressive conversion of the distal σ(CC) bond into a 3-center π-orbital (Figure 2), in line with an electrocyclic ring-opening.

Upon halide abstraction from σ-cyclopropyl complexes **9** and **10**, a cationic coordinatively unsaturated Au(III) intermediate is formed. This type of complexes can engage in weak interactions such as agostic interactions with surrounding ligands or substrates.[17] In the case of the σ-cyclopropyl complexes, it can be envisioned that the σ(CC) bond engages in a donor-acceptor interaction with the gold center resulting in an agostic interaction. While C–H agostic interactions have been described before with gold, this is not the case for C–C agostic interactions.[17a] Cyclopropyl has high ring strain resulting in bent *banana* bonds that are more prone to agostic interactions.[18] Natural Bond Orbital (NBO) analysis on the cationic 3-coordinate (P,C) Au(III) σ-cyclopropyl complex **9-Ph**$^+$ showed donor-acceptor interactions with weak donations from the proximal and distal σ(CC) bonds to Au (2.9 and 4.6 kcal/mol, respectively). For the dicationic (P,N) Au(III) σ-cyclopropyl complex, similar agostic interactions were found, with donor-

acceptor interactions of 6.9 kcal/mol between the proximal σ(CC) bond and gold, and 6.4 kcal/mol between the distal σ(CC) bond and gold.

To demonstrate the versatility of the σ-cyclopropyl to π-allyl rearrangement, (N,C) cyclometalated complexes **12** were included in the study (Scheme 4). Like complexes **9** and **10**, they undergo ring-opening upon liberation of a coordination site at gold. However, the rearrangement does not start before room temperature is reached, at which point the π-allyl complex decomposes, preventing a clean transformation. The rigidity of the backbone of the ancillary ligand (tolyl-pyridine *versus* benzoquinoline) did not influence the ring-opening to any significant degree, this observation was in good agreement with the calculated barriers for the ring-opening (27.1 and 26.4 kcal/mol for tolyl-pyridine and benzoquinoline, respectively).

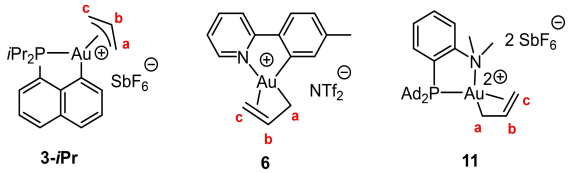
3. Characterization and Structure of Au(III) π-Allyl Complexes

Complexes **3**, **6** and **11** were unambiguously authenticated by multinuclear NMR spectroscopy.[8,9,11] Complexes **3** and **6** were also characterized by single crystal X-ray diffraction analysis. In the case of **6**, connectivity was established, but twinning and disorder in the crystals led to poor data quality, thus the optimized structure for complex **6** will be used herein when comparing with the other π-allyl complexes.

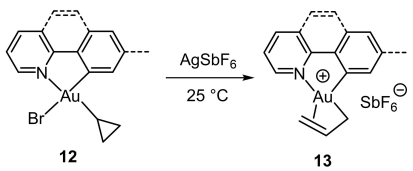
The ancillary ligands employed in complexes **3, 6** and **11** have major differences in their electronic properties with the (P,C) ligand being close to electronically symmetric, whereas the (N,C) and (P,N) ligands are highly asymmetric due to P and C being significantly more donating than N. This difference is reflected in the bonding of the π-allyl moiety and thus the stability of the ensuing complexes (Table 1). Complex **3-*i*Pr** is stable at room temperature, whereas complexes **6** and **11** rapidly decompose at this temperature.

With the naphthyl-based (P,C) ligand employed in complexes **3**, bench stable complexes were obtained featuring a quasi-symmetric η^3 coordination of the allyl moiety.[8] The symmetric coordination of the allyl in complex **3-*i*Pr** is illustrated by the equalization of the ^{13}C NMR chemical shifts of the two terminal carbons C^a and C^c of the π-allyl moiety (δ 83/76 *versus* δ 48/110 in the corresponding σ-allyl complex **2-*i*Pr**) together with the similar bond lengths found for C^a–C^b and C^b–C^c and the small variation found in the distance between Au and the three carbon atoms of the π-allyl moiety. In complexes **6** and **11**, the picture is very different.[9,11,12] Here, the terminal carbons C^a and C^c are found at significantly different ^{13}C NMR chemical shifts (δ 50/106 for **6** and δ 67/115 for **11**) indicating σ + π coordination of the allyl moiety where C^a remains bonded in a σ-fashion, similarly to the σ-allyl precursors, and the double bond of the allyl moiety is π-coordinated to gold.[19] This is in line with the larger difference in *trans* influence (C > P ≫ N) of the two ends of the chelating ligand in complexes **6** and **11** compared to **3-*i*Pr** and the following thermodynamic preference of having the higher *trans* influence σ-end of the allyl moiety *trans* to the lower *trans* influence end of the ancillary ligand (aryl-*N* and $ArMe_2N$ in complexes **6** and **11**, respectively). The asymmetric coordination of the allyl ligand was also observed in the optimized structures of complexes **6** and **11**. In both cases C^a is bound significantly tighter to gold compared to C^b and C^c, indicating significant σ-character of the Au–C^a bond. Moreover, the bonding situation in complexes **3-*i*Pr**, **6** and **11** was analyzed by the atoms-in-molecules (AIM) approach showing noticeable differences between the different complexes (Table 2). For complex **3-*i*Pr**, bond critical points (BCP) are found between both the terminal carbons of the allyl ligand and gold, whereas for complexes **6** and **11**, BCP is *only* found between gold and the terminal carbon of the allyl moiety *trans* to N (C^a). Furthermore, in complex **3-*i*Pr**, the associated electron densities (ϱ) and the Bader's delocalization indexes (δ) are very similar, indicating a highly delocalized allyl moiety. In contrast, in complexes **6** and **11**, very different values are obtained when comparing C^a–C^b and C^b–C^c, showing a significant double bond character for the latter bond.

Table 1. Selected NMR, XRD and DFT data for complexes **3-*i*Pr**, **6** and **11** illustrating their striking differences in bonding.[8,9,11,12]

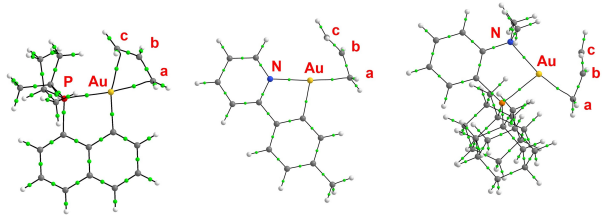


Stable at RT *Quasi-symmetric* *Non-fluxional*	*Unstable at RT* *Asymmetric (σ+π)* *Fluxional*	*Unstable at RT* *Asymmetric (σ+π)* *Non-fluxional*
NMR data		
	δ C^a, C^c	
δ 83, 76	δ 50, 106	δ 67,115
	δ H^a, $H^{a'}$	
δ 5.1, 4.3	δ 3.8 (2H)	δ 5.5, 4.5
Bond lengths [Å] (XRD or *DFT*)		
	C^a–C^b, C^b–C^c	
1.422 (14), 1.386(12)	*1.438, 1.382*	*1.437, 1.385*
	Au–C^a, Au–C^b, Au–C^c	
2.195(12), 2.226(8), 2.275(9)	*2.090, 2.224, 2.329*	*2.134, 2.269, 2.405*



Scheme 4. Formation of the (N,C) Au(III) π-allyl complexes **13** from their corresponding Au(III) σ-cyclopropyl complexes **12** by halide abstraction.

Table 2. Atoms-in-molecules (AIM) molecular graphs for complexes **3-*i*Pr**, **6** and **11** with relevant bond paths, bond critical points (BCP, green circles), electron densities (ϱ in e bohr^{-3}) and delocalization indexes (δ).



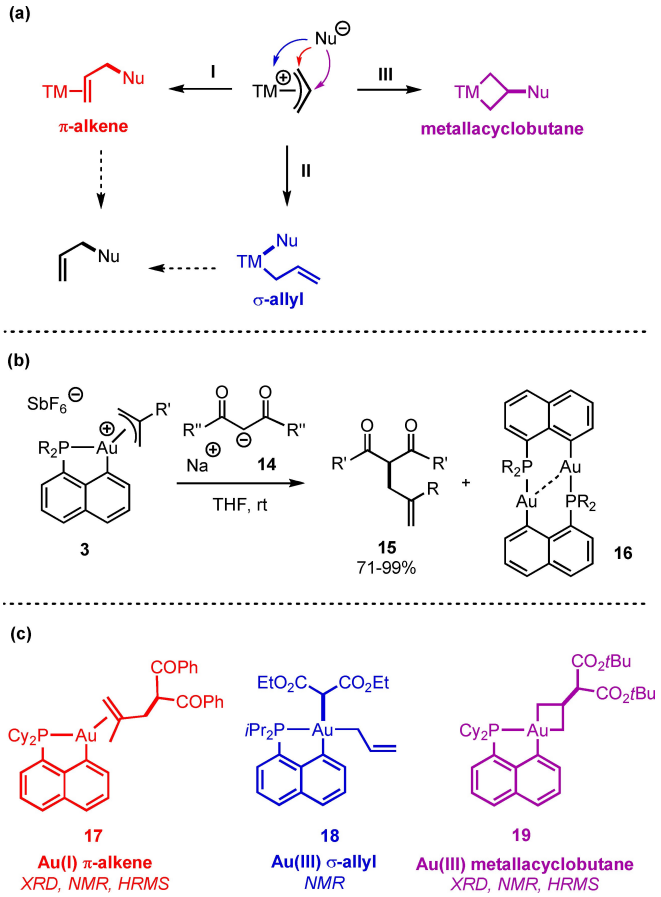
3-*i*Pr	6	11
	Au-C^a	
ρ 0.095, δ 0.639	ρ 0.121, δ 0.791	ρ 0.109, δ 0.729
	Au-C^c	
ρ 0.075, δ 0.522	–	–
	C^a-C^b	
ρ 0.295, δ 1.244	ρ 0.282, δ 1.144	ρ 0.290, δ 1.173
	C^b-C^c	
ρ 0.307, δ 1.347	ρ 0.318, δ 1.454	ρ 0.318, δ 1.415

The dynamic properties of π-allyl complexes play an important role when they are employed in catalysis.[7] The large electronic dissymmetry provided by the ancillary ligand and the following σ+π coordination of the allyl moiety observed in complexes **6** and **11** may point towards a higher fluxionality in these complexes, but this was only observed experimentally for complex **6**.[9,11,12] DFT calculations showed that for complex **6**, the η^1 forms are *ca* 12 kcal mol^{-1} higher in energy than the η^3 form, and the free energy barriers for the involved coordination, rotation and re-coordination processes are not too high (< 18 kcal/mol). The dynamic behavior of complex **6** was evident from its ^{1}H NMR spectrum. The two protons H^a are found as one resonance in contrast to what is normally observed in π-allyl complexes (including that of **3** and **11**, see Table 1). This phenomenon indicates that double bond decoordination followed by rotation around the AuCH$_2$-CHCH$_2$ and re-coordination occurs relatively fast at the NMR timescale leading to the coalescence of the two H^a resonances. The same phenomenon was not observed for the two H^c, indicating that the η^3-η^1-η^3 interconversion only occurs *trans* to Aryl-*C* in line with the asymmetric σ+π bonding of the allyl moiety with the thermodynamic preference of having the σ-character *trans* to Aryl-*N*. Lowering the temperature to *ca* −80 °C, and thereby slowing down the η^3-η^1-η^3 interconversion process, led to the observation of the coexisting η^3 (with the resonances of the two H^a now decoalesced) and η^1 forms of complex **6**. In contrast, for complex **11**, the difference in free energy between the η^3 and η^1 forms ($\triangle$G = 36.5 kcal mol^{-1}) is three times as large as that of **6**, explaining why no fluxionality was observed for complex **11**.

4. Reactivity and Catalytic Applications of Au(III) π-Allyl Complexes

Nucleophilic addition to π-allyl complexes is a key elementary step in transition metal catalysis, most notably in the well-known Pd-catalysed Tsuji-Trost reaction.[7] Most common is the outer-sphere nucleophilic addition to one of the terminal positions of the π-allyl (Scheme 5a, path I) leading to π-alkene complexes and ultimately the allylation products. The nucleophilic addition can also occur at the metal itself leading to σ-allyl complexes which can then undergo reductive elimination to release the allylation product (Scheme 5a, path II). Less common, but present in the literature, is the nucleophilic addition to the central position of the π-allyl leading to the formation of a metallacyclobutane (Scheme 5a, path III).[20,21]

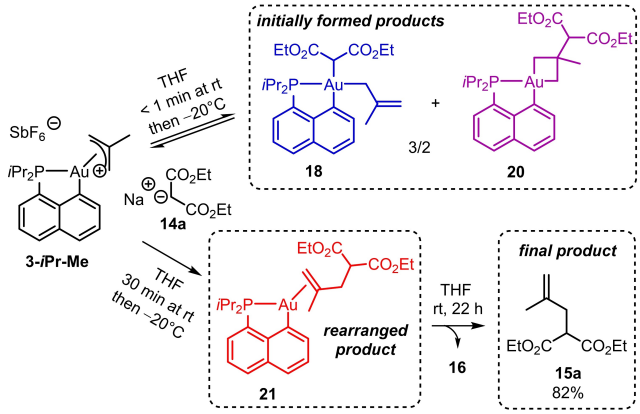
The reactivity of Au(III) π-allyl complexes **3** towards β-diketo enolates **14** was thoroughly investigated.[8,10] In all cases studied, the desired allylation products **15** originating from nucleophilic addition to the terminal position of the π-allyl were ultimately obtained in good yields (71–99%) together with the Au(I) dimer **16** (Scheme 5b). However, after close inspection of these



Scheme 5. (a) Possible reactive sites for the nucleophilic addition to transition metal π-allyl complexes. (b) Reactivity of complexes **3** (R = *i*Pr or Cy, R′ = H or Me) towards β-diketo enolates **14** (R″ = OEt, O*t*Bu or Ph). (c) Examples of characterized complexes (**17**–**19**) showing nucleophilic addition to the central and terminal position of the π-allyl, as well as to gold.

reactions both experimentally and computationally, they turned out to be much more complex than first anticipated. Nucleophilic addition to all sites (paths I, II and III) turned out to be possible and competitive. Four combinations of Au(III) π-allyl complexes **3** and nucleophiles **14** were studied in detail by multinuclear low temperature NMR spectroscopy and DFT calculations. It was found that, depending on the combination of Au(III) π-allyl complex and nucleophile, additions to all the different positions were indeed possible and complexes **17**–**19** could all be authenticated in solution by NMR spectroscopy. Complexes **17** and **19** were also isolated and characterized crystallographically and by high resolution mass spectrometry (HRMS). NMR spectroscopy together with DFT calculations showed that the nucleophilic additions to the central position of the π-allyl and to gold itself were reversible, explaining why ultimately, the coupling products **15** originating from the nucleophilic addition to the terminal position is observed in all cases studied.

The reaction of the Au(III) π-allyl complex **3-*i*Pr-Me** with the β-diketo enolate **14a** was the most complex, but also the most fascinating. In this case, nucleophilic addition to all possible sites could be authenticated within the same reaction



Scheme 6. Reaction of the π-allyl Au(III) complex **3-*i*Pr-Me** with the β-diketo enolate **14a**.

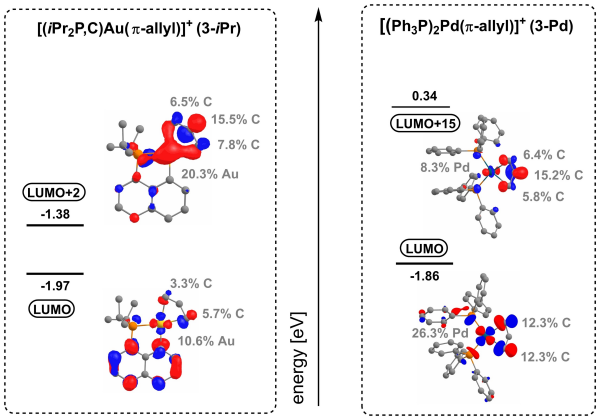


Figure 3. Key Molecular Orbitals (MO) computed for complexes **3-iPr** and **3-Pd**. Energy of the MOs in eV, cutoff: 0.05. Contribution of the main atoms in each MO in %.

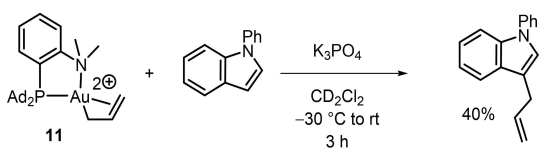
(Scheme 6). Initially, the formation of σ-allyl complex **18** and auracyclobutane **20** (in a 3/2 ratio) was observed. Warming the reaction mixture to 25 °C for *ca.* 30 min before cooling back to −20 °C led to the quantitative formation of Au(I) π-alkene complex **21**. Finally, the C-allylated product **15a** was released from the Au(I) π-alkene complex **21** at room temperature with concomitant formation of Au(I) dimer **16**.

As mentioned previously, nucleophilic addition to the terminal position of Pd(II) π-allyl complexes usually dominates, and nucleophilic addition to the central position remains a curiosity.[20,21] To rationalize the different reactivity of Pd(II) and Au(III) π-allyl complexes, the Molecular Orbitals relevant for the nucleophilic additions to $[(P,C)Au(\pi\text{-allyl})]^+$ **3-*i*Pr** and the related $[(Ph_3P)_2Pd(II)(\pi\text{-allyl})]^+$ complex **3-Pd** were computed (see Figure 3 for selected data).[10] Significant differences between the Au(III) and Pd(II) π-allyl complexes were discovered. While in both cases, the LUMO has large contributions on the terminal carbons (C_{term}) and the metal itself, only in **3-*i*Pr** vacant orbitals with significant contributions of the central carbon (C_{cent}, 15.5 %) can be found at accessible energies (LUMO + 2, only 0.6 eV above the LUMO). In contrast, for complex **3-Pd**, it is not before LUMO + 15, lying 2.2 eV above the LUMO, where a significant participation of C_{cent} is found. This explains why nucleophilic attack to the central position of the π-allyl and formation of auracyclobutanes is so much more favourable than palladacyclobutanes.

The limited stability of (N,C) Au(III) π-allyl complex **6** prevented its reactivity towards nucleophiles to be studied in detail. However, attempts at obtaining single crystals of a *gem*-dimethylallyl complex led to the authentication of a water adduct which may result from nucleophilic addition to the central position of the π-allyl followed by protodeauration.[22]

The stoichiometric reaction of (P,C) Au(III) π-allyl complexes **3** with carbon based nucleophiles demonstrated the feasibility of C–C bond formation *via* nucleophilic attack to Au(III) π-allyls. While being fundamentally interesting, it was not a synthetically relevant method for C–C bond formation due to the use of stoichiometric amounts of gold. In order to achieve catalytic allylation *via* Au(III) π-allyl intermediates, a Au(I)/Au(III) redox cycle was envisioned similar to Ir, Ru and Pd catalysts. Here, (P,N) Au(III) π-allyl complexes were considered as good candidates as the (P,N) ligand enable to cycle between Au(I)/Au(III) as has been shown to great success in catalytic C–C, C–N and C–S coupling reactions.[14]

To demonstrate the feasibility of C–C coupling, the (P,N) Au(III) π-allyl complex **11** was reacted with one equivalent of *N*-phenyl indole as a synthetically relevant nucleophile (Scheme 7).[11] The C3 allylated product was obtained as the

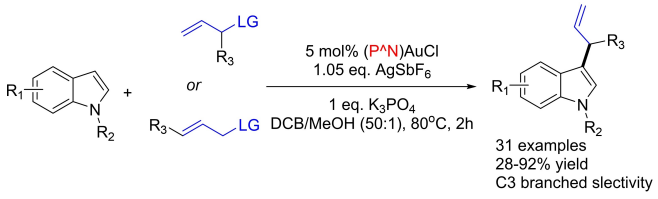


Scheme 7. Stoichiometric reactivity of the (P,N) Au π-allyl complex **11** with indole as the nucleophile.

only product, as expected with the more nucleophilic nature of the C3 position of indoles. The ability of the Me-Dalphos ligated Au complex to cycle through Au(I)/Au(III) catalytic cycles combined with the formation of a single product in the stoichiometric reaction made it a good candidate for catalytic allylation.

After optimization of the reaction conditions, it was found that the allylation could proceed with catalytic amounts of (P,N)AuCl (Scheme 8). For the catalytic transformation, $AgSbF_6$ was used to carry out the functions of both halide abstraction from the initial (P,N)AuCl and to replace BCF as a Lewis acid to promote the oxidation of the π-alkene complex. While the transformation worked well with a variety of allyl substrates (alcohols, acetates, carbonates, phosphates and halides), the investigation of the scope was achieved on allyl acetates and alcohols which are the most valuable synthetically. Control experiments showed that it was indeed the gold catalyst that promoted the reaction and only traces of the allylation product were observed without it.

To provide further proof for the involvement of Au(III) π-allyl intermediates in the catalytic reaction, α and γ substituted allyl alcohols and acetates were investigated (Scheme 8). It was expected that the same ratio for linear and branched products is obtained if the reaction proceeds *via* π-allyl intermediates as is observed with Pd, Ir, Rh catalysts.[23] Subjecting the α and γ substituted allyls to the catalytic conditions indeed resulted in the formation of the same branched C3 allylated indoles independently of whether the α or γ position was substituted on the initial allyl. All tested substrates were completely selective for the branched isomer, with the exception of ethyl allyl acetate where a 95:5 ratio was obtained. To further probe the generality of the transformation, substituted α phenyl allyl acetates were tried with indoles containing different substitutions on the nitrogen and indole backbone. In all cases, complete selectivity for the C3 allylated branched product was observed with good to excellent yields (62–92%). Only when the C3 position of the indole was sterically hindered or the nucleophilicity lowered with electron withdrawing groups were lowered yields observed (35–56%). Good functional group compatibility was observed with the reaction tolerating C–F, C–Br and C–Si bonds. Notably when the C2 position of the indole was methylated, the allylated product was still obtained in high yields (76%) while for the previously reported arylation of indoles with the same (P,N)AuCl catalyst, no product was obtained.[14a]



Scheme 8. Ligand-enabled Au(I)/Au(III) catalytic allylation of indoles with allyl electrophiles.

The selectivity for the branched product could be elucidated when the Au(III) π-allyl intermediate was investigated computationally. The most stable optimized structure for the methyl substituted π-allyl was found with the Me group in the pseudoequatorial position, *trans* to the phosphorus (Figure 4). The LUMO showed a higher contribution to this carbon (20.7%) compared to the carbon *cis* to the phosphorus (13.9%). The higher contribution of the LUMO combined with the easier accessibility due to the less sterically demanding NMe_2 groups compared to the PAd_2 group offer an explanation to the observed selectivity for the branched product. When comparing these results with earlier reports on the allylation of indoles *via* transition metal π-allyls, the complementary nature of Au becomes clear. In the allylation of indoles with Pd catalysts, the linear product is obtained, while with Ir, usually branched products are observed. As for Ru catalysts, the selectivity is highly dependent on the ligand, with selectivities in favour of both the linear and branched product being reported as well as the formation of mixtures.[23]

5. Summary and Outlook

During the last three years, Au(III) π-allyl complexes have emerged as a very interesting and attractive class of compounds. The use of (P,C), (N,C) and (P,N) bidentate ligands was shown to impart enough stability to enable the characterization or even the isolation of such complexes. Various synthetic routes, with or without oxidation of gold, have been developed. Detailed analyses of their structure revealed either symmetric η^3 or asymmetric σ+π-coordination of the allyl moiety to gold, depending on the ancillary ligand. Rich reactivity towards nucleophiles was also substantiated, with possible additions to the terminal and central positions of the π-allyl, as well as to gold itself. The possibility to achieve catalytic transformation *via* Au(III) π-allyl complexes has also been demonstrated. Most noteworthy are the specific features of the Au(III) π-allyl complexes, compared to the isoelectronic Pd(II) species, making them valuable tools.

These first achievements are very exciting and for sure, much remains to be discovered and developed when it comes to Au(III) π-allyl complexes. The variety of ancillary ligands at Au(III) can certainly be further expanded, enabling

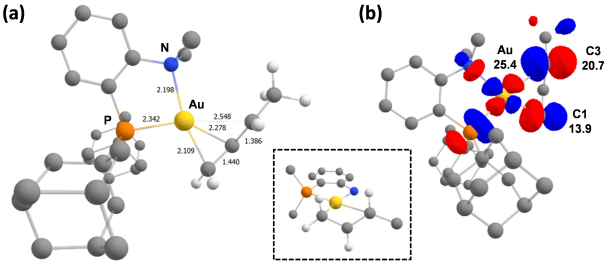


Figure 4. (a) Optimized geometry of the Au(III) π-allyl complex (P,N)Au[H_2CC-(H)CH(CH_3)]$^{2+}$ at the SDM(CH_2Cl_2)-B3PW91/SDD + f(Au),6-31G** (other atoms) level of theory (distances in Å). Simplified perspective view as inset chart. (b) Plot of the LUMO (cutoff: 0.05) with key atomic contributions in %.

to finely tune the structure and reactivity of the π-allyl moiety at Au(III).[13] Other catalytic transformations than the allylation of indoles are also most probably achievable *via* Au(III) π-allyl complexes. Selectivities complementary to the other transition metals may be encountered and transformations involving nucleophilic attack to the central position of the π-allyl may be developed. Recent pioneering contributions on enantioselective Au(I)/Au(III) catalysis also give credence to the possibility to achieve asymmetric gold-catalyzed allylation reactions.[24–26]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: π-allyl · cyclopropyl · gold · nucleophilic addition · palladium

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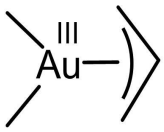
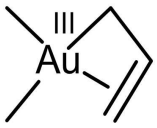
CONCEPT

Au(III) π-allyl complexes have recently been shown to be readily accessible and stable, as well as highly reactive towards nucleophiles, including in catalytic transformations. They display structural features and reactivity profiles that differ noticeably from the related Pd(II) π-allyl complexes, making them complementary and attractive for synthesis.





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