



HAL
open science

Gold(III) π -Allyl Complexes

Jessica Rodriguez, György Szalóki, E. Daiann Sosa Carrizo, Nathalie Saffon-Merceron, Karinne Miqueu, Didier Bourissou

► **To cite this version:**

Jessica Rodriguez, György Szalóki, E. Daiann Sosa Carrizo, Nathalie Saffon-Merceron, Karinne Miqueu, et al. Gold(III) π -Allyl Complexes. *Angewandte Chemie International Edition*, 2020, 59 (1511), 10.1002/anie.201912314 . hal-02398796

HAL Id: hal-02398796

<https://hal.science/hal-02398796>

Submitted on 11 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Gold(III) π -Allyl Complexes

Jessica Rodriguez,^[a] György Szalóki,^[a] E. Daiann Sosa Carrizo,^[b] Nathalie Saffon-Merceron,^[c] Karinne Miqueu,^[b] Didier Bourissou*^[a]

[a] Laboratoire Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier/CNRS UMR 5069, 118 Route de Narbonne, 31062 Toulouse Cedex 09 (France). E-mail: dbouriss@chimie.ups-tlse.fr

[b] Institut de Chimie de Toulouse (FR 2599), 118 Route de Narbonne, 31062 Toulouse Cedex 09, France.

[c] CNRS/UNIV PAU & PAYS ADOUR, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, (IPREM UMR 5254), Hélioparc, 2 Avenue du Président Angot, 64053 Pau Cedex 09 (France)

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]

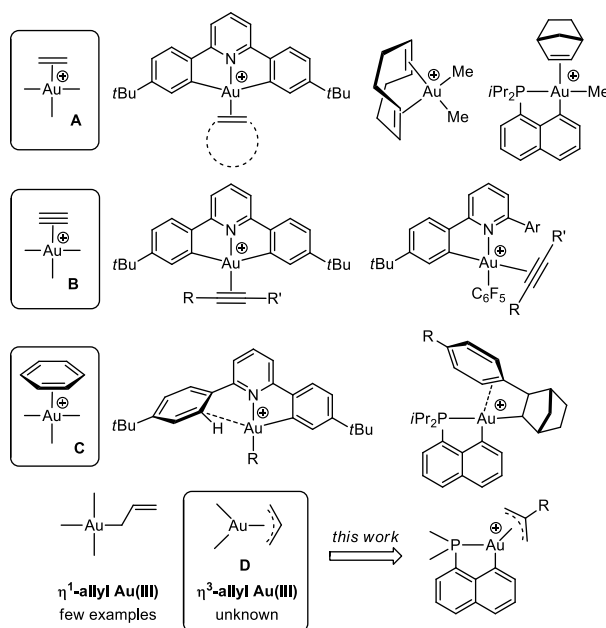


Figure 1. Known gold(III) π -complexes **A-C** with alkenes, alkynes and arenes, and targeted gold(III) π -allyl complexes **D**.

We have shown in previous studies that (P,C) cyclometallated gold(III) complexes are readily accessible by chelation-assisted oxidative addition of *per*-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]

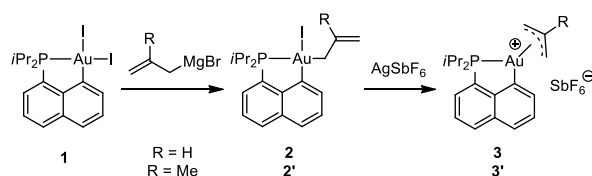
In this work, we envisioned to prepare and study gold(III) π -allyl complexes taking advantage of the stability imparted by the (P,C) chelate. As disclosed hereafter, thermally and air-stable species were readily obtained and fully characterized. Their η^3 -structure was thoroughly analysed by experimental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

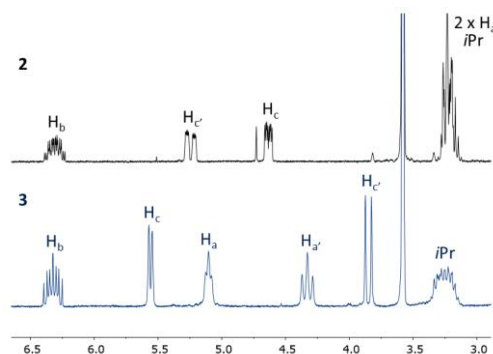
Complex **2** was then reacted with AgSbF₆ to abstract the iodine ligand and release a coordination site at gold for the double bond of the allyl group. According to ^{31}P NMR spectroscopy, this lead instantaneously to a single new species. After removal of the silver salts upon filtration over Celite, 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).



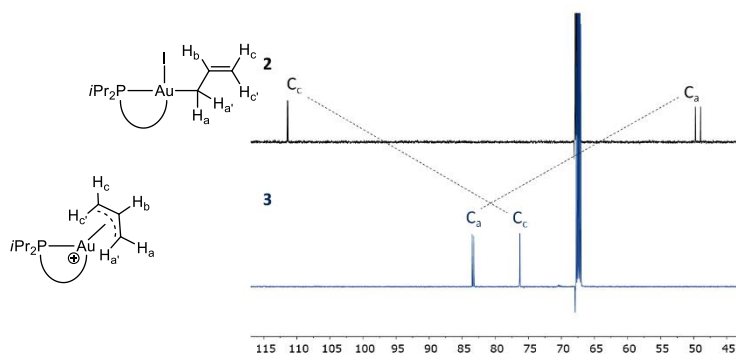


Figure 2. NMR spectra (selected zones) of the neutral σ -allyl and cationic π -allyl gold(III) complexes **2** and **3** in d_8 -THF. Top: Allylic zone of the ^1H NMR spectra. Bottom: ^{13}C NMR spectra, C_a/C_c signals.

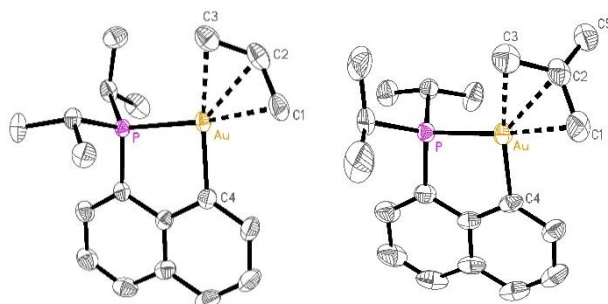


Figure 3. Molecular structures of the π -allyl gold(III) complexes **3** (left) and **3'** (right). Thermal ellipsoids drawn at 50% probability, hydrogen atoms, counter anion and disordered atoms are omitted. Selected bond lengths (\AA): (**3**) Au-C1 2.195(12), Au-C2 2.226(8), Au-C3 2.275(9), C1-C2 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 - 57.2° 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'**.

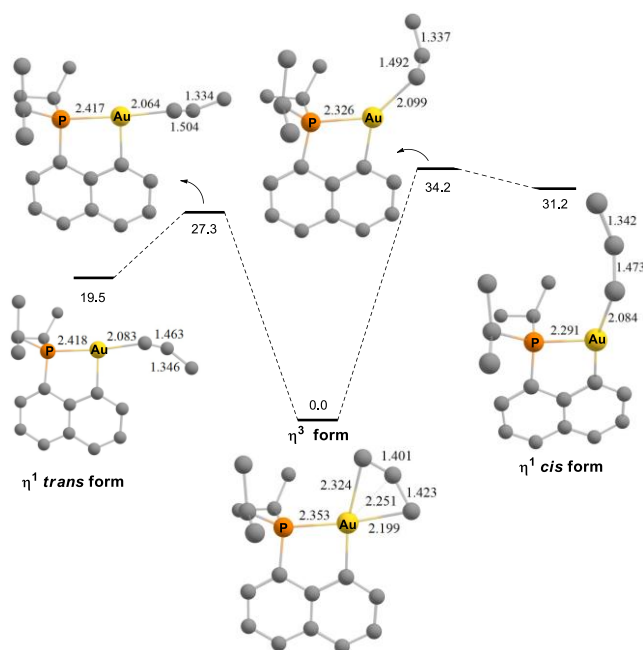


Figure 4. Potential energy surface computed for the cationic allyl gold(III) complex **3** showing the η^3 and η^1 forms (ΔG in kcal/mol).

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]

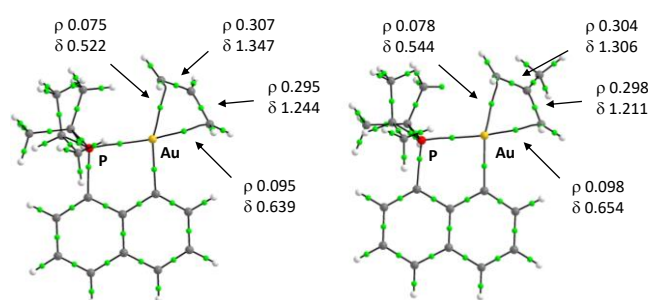
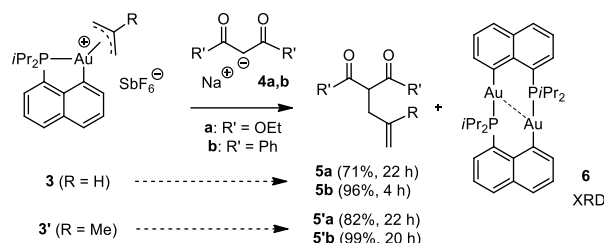


Figure 5. Atoms-in-molecules (AIM) molecular graph calculated for the π -allyl gold(III) complexes **3** and **3'** with relevant bond paths, bond critical points (BCP, green circles), electron densities (ρ in e/bohr³) and delocalization indices (δ).

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]

Acknowledgements

Financial support from the Centre National de la Recherche Scientifique and the Université de Toulouse is gratefully acknowledged. J. R. thanks the European Commission for a MCIF (Gold3Cat-799606). The "Direction du Numérique" of the Université de Pau et des Pays de l'Adour, MCIA (Mésocentre de Calcul Intensif Aquitain) and CINES under allocation A005080045 made by Grand Equipement National de Calcul Intensif (GENCI) are acknowledged for computational facilities. E. D. Sosa Carrizo thanks CDAPP for funding part of his post-doctoral contract.

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

- [1] R. Kumar, C. Nevado, *Angew. Chem.* 2017, 129, 2024–2046; *Angew. Chem. Int. Ed.* 2017, 56, 1994–2015.
- [2] a) V. W.-W. Yam, E. C.-C. Cheng, *Chem. Soc. Rev.* 2008, 37, 1806–1813; b) R. Visbal, M. C. Gimeno, *Chem. Soc. Rev.* 2014, 43, 3551–3574.
- [3] a) S. Medici, M. Peana, V. M. Nurchi, J. I. Lachowicz, G. Crisponi, M. A. Zoroddu, *Coord. Chem. Rev.* 2015, 284, 329–350; b) C. M. Che, R. W.-Y. Sun, *Chem. Commun.* 2011, 47, 9554–9560.
- [4] a) H. Schmidbaur, A. Schier, *Arab. J. Sci. Eng.* 2012, 37, 1187–1225; b) A. S. K. Hashmi, J. P. Weyrauch, M. Rudolph, E. Kurpejović, Hashmi *Angew. Chem.* 2004, 116, 6707–6709; *Angew. Chem. Int. Ed.* 2004, 43, 6545–6547; c) C.-Y. Wu, T. Horibe, C. B. Jacobsen, F. D. Toste, *Nature* 2015, 517, 449–454; d) W.-P. To, G. S.-M. Tong, W. Lu, C. Ma, J. Liu, A. L.-F. Chow, C.-M. Che, *Angew. Chem.* 2012, 124, 2708–2711; *Angew. Chem. Int. Ed.* 2012, 51, 2654–2657; e) C. Blons, S. Mallet-Ladeira, A. Amgoune, D. Bourissou, *Angew. Chem.* 2018, 130, 11906–11910; *Angew. Chem. Int. Ed.* 2018, 57, 11732–11736.
- [5] For asymmetric catalysis with well-defined gold(III) complexes, see: a) J.-F. Cui, H.-M. Ko, K.-P. Shing, J.-R. Deng, N. C.-H. Lai, M.-K. Wong, *Angew. Chem.* 2017, 129, 3120–3125; *Angew. Chem. Int. Ed.* 2017, 56, 3074–3079; b) P. T. Bohan, F. D. Toste, *J. Am. Chem. Soc.* 2017, 139, 11016–11019; c) J.

- Rodriguez, D. Bourissou, *Angew. Chem.* 2018, 130, 392–394; *Angew. Chem. Int. Ed.* 2018, 57, 386–388.
- [6] M. Joost, A. Amgoune, D. Bourissou, *Angew. Chem.* 2015, 127, 15234–15258; *Angew. Chem. Int. Ed.* 2015, 54, 15022–15045.
- [7] C. Blons, A. Amgoune, D. Bourissou, *Dalton Trans.* 2018, 47, 10388–10393.
- [8] For reviews on gold(I) π complexes, see: a) H. Schmidbaur, A. Schier, *Organometallics* 2010, 29, 2–23; b) R. E. M. Brooner, R. A. Widenhoefer, *Angew. Chem.* 2013, 125, 11930–11941; *Angew. Chem. Int. Ed.* 2013, 52, 11714–11724.
- [9] a) N. Savjani, D.-A. Roşca, M. Schormann, M. Bochmann, *Angew. Chem.* 2013, 125, 908–911; *Angew. Chem. Int. Ed.* 2013, 52, 874–877; b) E. Langseth, M. L. Scheuermann, D. Balcells, W. Kaminsky, K. I. Goldberg, O. Eisenstein, R. H. Heyn, M. Tilset, *Angew. Chem.* 2013, 125, 1704–1707; *Angew. Chem. Int. Ed.* 2013, 52, 1660–1663.
- [10] a) L. Rocchigiani, J. Fernandez-Cestau, G. Agonigi, I. Chambrier, P. H. M. Budzelaar, M. Bochmann, *Angew. Chem.* 2017, 129, 14049–14053; *Angew. Chem. Int. Ed.*, 2017, 56, 13861–13865; b) I. Chambrier, L. Rocchigiani, D. L. Hughes, P. M. H. Budzelaar, M. Bochmann, *Chem. Eur. J.* 2018, 24, 11467–11474.
- [11] a) F. Rekhroukh, C. Blons, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Chem. Sci.* 2017, 8, 4539–4545; b) L. Rocchigiani, J. Fernandez-Cestau, P. H. M. Budzelaar, M. Bochmann, *Chem. Commun.* 2017, 53, 4358–4361.
- [12] a) J. Hartwig in *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books, 1st ed., 2010; b) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* 1996, 96, 395–422; c) B. M. Trost, M. L. Crawley, *Chem. Rev.* 2003, 103, 2921–2943.
- [13] a) S. Komiyama, S. Ozaki, *Chem. Lett.* 1988, 17, 1431–1432; b) M. D. Levin, F. D. Toste, *Angew. Chem.* 2014, 126, 6325–6329; *Angew. Chem. Int. Ed.* 2014, 53, 6211–6215; c) M. D. Levin, T. Q. Chen, M. E. Neubig, C. M. Hong, C. A. Theulier, I. J. Kobylanskii, M. Janabi, J. P. O’Neil, F. D. Toste, *Science* 2017, 356, 1272–1276.
- [14] For π -allyl gold(I) complexes, see: a) A. S. K. Hashmi, A. M. Schuster, S. Litters, F. Rominger, M. Pernpointner, *Chem. Eur. J.* 2011, 17, 5661–5667; b) F. F. Mulks, P. W. Antoni, F. Rominger, A. S. K. Hashmi, *Adv. Synth. Catal.* 2018, 360, 1810–1821.
- [15] a) W. Nakanishi, M. Yamanaka, E. Nakamura, *J. Am. Chem. Soc.* 2005, 127, 1446–1453; b) N. J. Rijs, N. Yoshikai, E. Nakamura, R. A. J. O’Hair, *J. Am. Chem. Soc.* 2012, 134, 2569–2580.
- [16] J. Guenther, S. Mallet-Ladeira, L. Estevez, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* 2014, 136, 1778–1781.
- [17] a) F. Rekhroukh, L. Estévez, C. Bijani, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem.* 2016, 128, 3475–3479; *Angew. Chem. Int. Ed.* 2016, 55, 3414–3418; b) F. Rekhroukh, L. Estevez, C. Bijani, K. Miqueu, A. Amgoune, D. Bourissou, *Organometallics* 2016, 35, 995–1001; c) A. Pujol, M. Lafage, F. Rekhroukh, N. Saffon-Merceron, A. Amgoune, D. Bourissou, N. Nebra, M. Fustier-Boutignon, N. Mézailles, *Angew. Chem.* 2017, 129, 12432–12435; *Angew. Chem. Int. Ed.* 2017, 56, 12264–12267;

- [18] a) F. Rekhroukh, R. Brousses, A. Amgoune, D. Bourissou, *Angew. Chem.* 2015, 127, 1282–1285; *Angew. Chem. Int. Ed.* 2015, 54, 1266–1269; b) F. Rekhroukh, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* 2016, 138, 11920–11929.
- [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]
- [23] The related features for the η^3 cis form of complex 3 are Au–CH₂ (σ 0.127, σ AuC 0.853) and CH=CH₂ (σ 0.338, σ CC 1.712).[19]
- [24] For reviews on addition reactions to dinuclear gold(I) species, see: a) J. P. Fackler Jr, *Polyhedron* 1997, 16, 1–17; b) J. P. Fackler Jr, *Inorg. Chem.* 2002, 41, 6959–6972.
- [25] For rare examples of gold-catalyzed allylation and thio-allylation reactions, see: a) A. Quintavalla, M. Bandini, *ChemCatChem* 2016, 8, 1437–1453; b) M. O. Akram, P. S. Mali, N. T. Patil, *Org. Lett.* 2017, 19, 3075–3078; c) X. Ye, J. Wang, S. Ding, S. Hosseyni, L. Wojtas, N. G. Akhmedov, X. Shi, *Chem. Eur. J.* 2017, 23, 10506–10510; d) J. Wang, S. Zhang, C. Xu, L. Wojtas, N. G. Akhmedov, H. Chen, X. Shi, *Angew. Chem.* 2018, 130, 7031–7036; *Angew. Chem. Int. Ed.* 2018, 57, 6915–6920.