



HAL
open science

Synthesis, structure and reactivity of an NHC silyl gold(I) complex

Maximilian Joost, Nathalie Saffon-Merceron, Abderrahmane Amgoune, Didier Bourissou

► **To cite this version:**

Maximilian Joost, Nathalie Saffon-Merceron, Abderrahmane Amgoune, Didier Bourissou. Synthesis, structure and reactivity of an NHC silyl gold(I) complex. *Organometallics*, 2019, 38 (19), pp.3494-3497. 10.1021/acs.organomet.9b00574 . hal-02398795

HAL Id: hal-02398795

<https://hal.science/hal-02398795>

Submitted on 8 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.

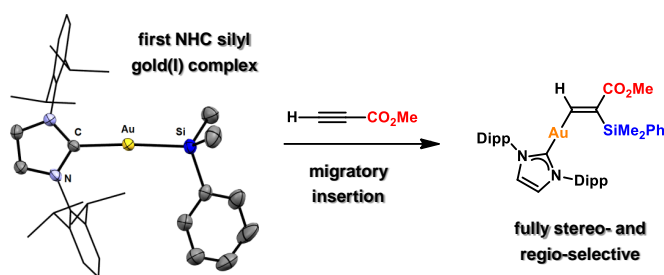
Synthesis, structure and reactivity of an NHC silyl gold(I) complex

Maximilian Joost,[†] Nathalie Saffon-Merceron,[‡] Abderrahmane Amgoune[†] and Didier Bourissou^{*,†}

[†]CNRS, Université Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA, UMR 5069), 118 Route de Narbonne, 31062 Toulouse Cedex 09, France. E-mail: dbouriss@chimie.ups-tlse.fr Web: <http://lhfa.cnrs.fr/index.php/equipes/lbpb>

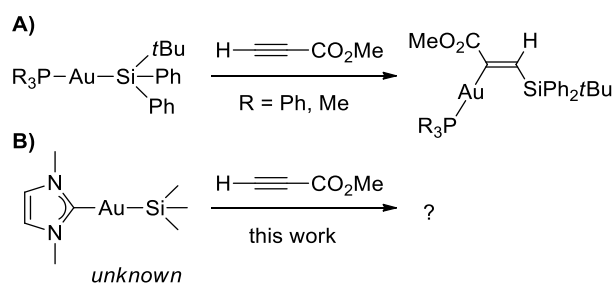
[‡]Institut de Chimie de Toulouse (FR 2599), 118 route de Narbonne, 31062 Toulouse Cedex 9, France

ABSTRACT: The first example of a silyl gold(I) complex stabilized by an *N*-heterocyclic carbene (NHC) was synthesised and fully characterized, including crystallographically. The *syn* insertion of methyl propiolate into the Au–Si bond leading to a vinyl gold complex is reported. As substantiated by X-ray diffraction analysis, the reaction proceeds with opposite regioselectivity compared to that observed previously with phosphine silyl gold(I) complexes.



During the last 15 years, homogeneous gold catalysis has evolved rapidly and now occupies a prominent position in organic chemistry.^{1–6} The activity of gold catalysts is based largely on the π -acidic property of cationic gold complexes, allowing for the activation of CC multiple bonds towards nucleophilic attack.⁷ While this activation mode is nowadays well understood and broadly used, other reaction patterns commonly encountered in transition metal catalysis, e.g. oxidative addition, reductive elimination or migratory insertion, are much less explored.

In the context of an ongoing research program in our group devoted to the investigation of unusual elementary steps at gold,⁸ we reported in 2013 reactions of phosphine silyl gold(I) complexes with alkynes and allenes. This work provided unambiguous evidence for *syn* insertion reactions at gold (Scheme 1A),^{9,10} a process in sharp contrast with the outer-sphere *anti* addition pathway usually encountered in gold catalysis.^{11,12} A comprehensive mechanistic study revealed that a 2-step coordination-insertion mechanism is operating.¹⁰ Migratory insertion of alkenes into Au(III)–C bonds were then authenticated.^{13–17}

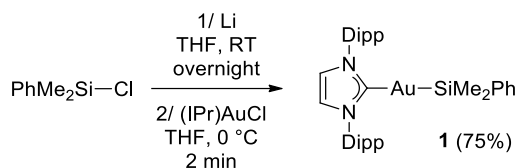


Scheme 1. Reaction of methyl propiolate with phosphine versus NHC silyl gold(I) complexes.

As a further extension of this work, we have now investigated analogous silyl gold(I) featuring *N*-heterocyclic carbenes (NHCs) instead of phosphines (Scheme 1B). NHCs play a major role in gold catalysis¹⁸ and have been shown to stabilize a large set of reactive gold(I) compounds, including species not accessible with other ancillary ligands. Most noteworthy are the gold(I) fluoride and hydride complexes reported by Nolan, Sadighi and Toste.^{19–23} Unlike silyl copper(I) complexes which are well known and commonly involved in catalytic transformations,^{24–26} analogous silyl gold(I) species remain scarce. NHC boryl gold(I) complexes have been reported^{27,28} but to the best of our knowledge, NHC silyl gold(I) complexes are hitherto unknown. Here we report the synthesis and characterization of such a compound, namely [(IPr)Au(SiMe₂Ph)] (**1**) (IPr = 1,3-bis(2,6-diisopropyl)phenyl-imidazol-2-ylidene). It is shown to react with methyl propiolate via *syn* insertion of the alkyne and opposite regioselectivity compared to that observed with phosphine silyl gold(I) complexes.

In analogy to the synthesis of phosphine silyl gold(I) complexes,^{9,10} we envisioned to prepare an NHC silyl gold(I) complex *via* salt metathesis between an NHC gold(I) chloride precursor and a lithiosilane. The commercially available complex [(IPr)AuCl] (IPr = 1,3-bis(2,6-diisopropyl)phenylimidazol-2-ylidene) was chosen as precursor. Phosphine silyl(I) gold complexes require important steric protection at silicon to be isolated, typically SiPh₃, Si(*t*Bu)Ph₂ or Si(SiMe₃)₃.^{9,10,29,30} We surmised that the strong σ -donor character and high steric demand of IPr might enable the synthesis of an NHC silyl gold(I) complex featuring relatively small substituents at silicon. Starting from chlorodimethylphenylsilane and lithium metal, the corresponding lithiosilane was prepared and *in situ* reacted with [(IPr)AuCl] (Scheme 2). The ensuing complex **1** was thereby

obtained as a white solid in 75% isolated yield. It was characterized by multi-nuclear NMR spectroscopy and high-resolution mass spectrometry (HRMS).



Scheme 2. Synthesis of complex **1**. Dipp = (2,6-diisopropyl)phenyl.

The following data are diagnostic for a silyl gold complex. The ^{29}Si NMR spectrum of **1** exhibits a singlet resonance at $\delta = 12.9$ ppm, in the same range that those previously reported for phosphine silyl gold(I) complexes.^{9,10} In the ^{13}C NMR spectrum, a singlet resonance at $\delta = 217.4$ ppm is observed for the carbene carbon, significantly shifted downfield compared to that of [(IPr)AuCl] ($\delta = 175.1$ ppm).³¹ The downfield shift of the carbene signal results from the strong *trans* influence of the silyl group³² and is comparable to that reported by Sadighi for the hydride complex [(IPr)AuH] ($\delta = 204.9$ ppm).²³

The molecular structure of **1** was further analysed by X-Ray diffraction (Figure 1). Accordingly, complex **1** was found to adopt a discrete monomeric structure in the solid state, without Au...Au intermolecular interaction (the shortest Au...Au distance exceeds 8 Å). The gold atom is two-coordinate and quasi-linearly bonded to the NHC and silyl ligands (CAuSi 171.6(1)°). The bond distances associated with both ligands give further indications with regard to the *trans* influence of the silyl group. The Au–C bond is elongated in complex **1** compared to [(IPr)AuCl] (from 1.942(3) Å to 2.091(4) Å), even more than in the hydride complex [(IPr)AuH] (2.045(3) Å).²³ The Au–Si bond of **1** (2.344(1) Å) is similar to those reported for phosphine silyl gold(I) complexes (2.354(4) Å to 2.3629(16) Å).^{9,10,29,30,33} The gold atom is strongly shielded by the flanking bulky Dipp groups of the NHC, likely imparting kinetic stabilization to the complex.

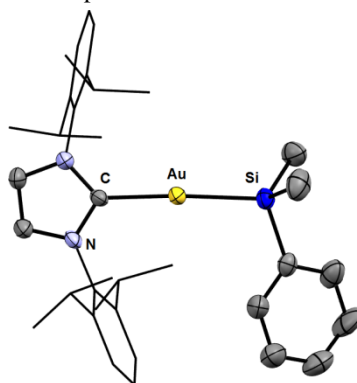
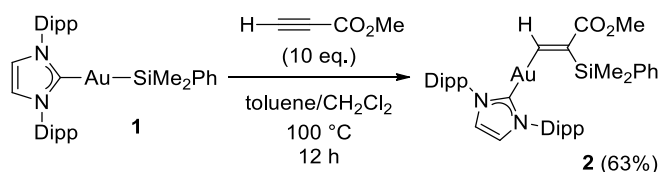


Figure 1. Molecular structure of complex **1** determined by single crystal X-ray diffraction. Hydrogen atoms and solvent molecule are omitted and Dipp groups are simplified for clarity. Selected bond lengths [Å] and angles [°]: C–Au 2.091(4), Au–Si 2.344(1), CAuSi 171.6(1).

Subsequently, the reactivity of the NHC silyl gold(I) complex **1** towards methyl propiolate was investigated (Scheme 3). The reaction was performed in a toluene/dichloromethane (1:1) solution with an excess of alkyne (10 equiv.). The mixture was heated to 100 °C in a sealed vessel and monitored by ^{29}Si NMR spectroscopy. Accordingly, complex **1** was found to be slowly consumed to give a new compound **2** associated with a singlet ^{29}Si NMR resonance at $\delta = -13.6$ ppm. This chemical shift is in the typical range of (vinyl)dimethylphenylsilyl groups.^{34,35} Complete conversion was achieved after 12 hours of heating. Simple work-up afforded complex **2** as a white crystalline solid in 63% isolated yield. It was characterized by NMR spectroscopy, HRMS and X-ray crystallography.



Scheme 3. Reaction of complex **1** with methyl propiolate.

HRMS confirmed the formation of a 1:1 adduct between complex **1** and methyl propiolate. A peculiar feature in the ^1H NMR spectrum of **2** is the singlet resonance at $\delta = 9.20$ ppm for the vinylic proton. Indeed, lower chemical shifts, in the 8.0–8.5 ppm range, were observed for the analogous products deriving from phosphine silyl gold(I) complexes.^{9,10} The associated ^{13}C NMR signal is also much more deshielded for the NHC complex **2** ($\delta = 171.5$ ppm) than for the related phosphine compounds ($\delta = 140$ – 145 ppm).^{9,10} It is noteworthy that the carbene signal is shifted downfield by about 20 ppm upon reaction with methyl propiolate (from $\delta = 217.4$ ppm for **1**, to $\delta = 196.7$ ppm for **2**), in line with the presence of a group with weaker *trans* influence at gold.

To confirm the connectivity of complex **2** and assess its regio- and stereochemistry, an X-ray diffraction analysis was performed. The obtained molecular structure of **2** is shown in Figure 2.

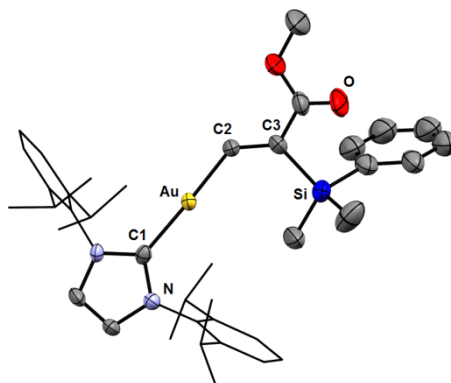


Figure 2. Molecular structure of complex **2** determined by single crystal X-ray diffraction. Hydrogen atoms and solvent molecule are omitted and Dipp groups are simplified for clarity. Selected bond lengths [Å] and angles [°]: C1–Au 2.033(3), Au–C2 2.023(4), C2–C3 1.342(5), C1AuC2 174.3(1), AuC2C3 132.4(3), C2C3Si 126.5(3), AuC2C3Si 4.4(6).

Accordingly, the gold complex **2** was found to adopt a two-coordinate linear structure without Au⋯Au intermolecular interaction. Despite significant steric crowding, the C=C double bond only slightly deviates from trigonal planar geometry (6° torsion). Most noticeable is the *cis* arrangement of the Au and Si atoms, meaning that the alkyne inserted in a *syn* fashion into the Au–Si bond of **1**, as in the case of phosphine silyl gold(I) complexes.^{9,10} However, the regioselectivity is opposite to that observed with phosphines as ancillary ligands. The vinylic proton sits in the position α to gold, meaning that the silyl and carboxyethyl groups are in *gem* positions to each other. A reasonable explanation for this regioselectivity may be the steric bulk of the Dipp groups of the carbene. The formed regioisomer is indeed the one minimizing steric repulsion, the carboxyethyl group being located in *trans* position to the NHC ligand.

In summary, the first example of a silyl gold(I) complex stabilized by an *N*-heterocyclic carbene was synthesized and fully characterized, including by single-crystal X-ray diffraction. In contrast with analogous phosphine complexes, the presence of sterically hindered substituents at silicon is not necessary to impart stability and enable isolation of the complex. The NHC silyl gold(I) complex slowly reacts with methyl propiolate *via* migratory insertion into the Au–Si bond. The transformation is fully stereo- and regio-selective. The gold and silicon atoms add in a *cis* fashion (in line with a concerted inner-sphere process). The ester group positions in *trans* position to the NHC ligand, minimizing steric repulsion. These results illustrate the generality of the insertion of alkynes into Au–Si bonds. It is interesting to note that changing the ancillary substituent at gold, from a phosphine to an NHC, reverses the regioselectivity of the migratory insertion.

The silyl and vinyl gold complexes **1** and **2** stand as well-defined molecular versions of key reactive species proposed by Stratakis to account for the silylation of alkynes catalyzed by supported gold nanoparticles.^{36,37}

Future work from our group will aim to extend further the variety of NHC gold complexes and generalize the migratory insertion process to other Au–element bonds.

REFERENCES

- (1) Hashmi, A.S.K.; Hutchings, G.J. Gold Catalysis. *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936.
- (2) Hashmi, A.S.K. Gold-Catalyzed Organic Reactions. *Chem. Rev.* **2007**, *107*, 3180–3211.
- (3) Li, Z.; Brouwer C.; He, C. Gold-Catalyzed Organic Transformations. *Chem. Rev.* **2008**, *108*, 3239–3265.
- (4) Corma, A.; Leyva-Pérez, A.; Sabater, M.J. Gold-Catalyzed Carbon–Heteroatom Bond-Forming Reactions. *Chem. Rev.* **2011**, *111*, 1657–1712.
- (5) Boorman, T.C.; Larrosa, I. Gold-mediated C–H bond functionalisation. *Chem. Soc. Rev.* **2011**, *40*, 1910–1925.
- (6) Hashmi, A.S.K.; Toste, D.F. *Modern Gold Catalyzed Synthesis*, Wiley-VCH, Weinheim, 2012.
- (7) Fürstner, A.; Davies, P.W. Catalytic Carbophilic Activation: Catalysis by Platinum and Gold π Acids. *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449.
- (8) Joost, M.; Amgoune, A.; Bourissou, D. Reactivity of Gold Complexes towards Elementary Organometallic Reactions. *Angew. Chem. Int. Ed.* **2015**, *54*, 15022–15045.
- (9) Joost, M.; Gualco, P.; Mallet-Ladeira, S.; Amgoune, A.; Bourissou, D. Direct *syn* Insertion of Alkynes and Allenes into Au–Si bonds. *Angew. Chem. Int. Ed.* **2013**, *52*, 7160–7163.
- (10) Joost, M.; Estévez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. Mechanisms of *syn*-Insertion of Alkynes and Allenes into Gold-Silicon Bonds: a Comprehensive Experimental / Theoretical Study. *J. Am. Chem. Soc.* **2014**, *136*, 10373–10382.
- (11) Hashmi, A.S.K. Homogeneous Gold Catalysis Beyond Assumptions and Proposals—Characterized Intermediates. *Angew. Chem. Int. Ed.* **2010**, *49*, 5232–5241.
- (12) Echavarren, A.M.; Obradors, C. Intriguing mechanistic labyrinths in gold(I) catalysis. *Chem. Commun.* **2014**, *50*, 16–28.
- (13) Rekhroukh, F.; Brousses, R.; Amgoune, A.; Bourissou, D. Cationic Gold(III) Alkyl Complexes: Generation, Trapping and Insertion of Norbornene. *Angew. Chem. Int. Ed.* **2015**, *54*, 1266–1269.

- (14) Rekhroukh, F.; Estévez L.; Bijani, C.; Miqueu, K.; Amgoune, A.; Bourissou, D. Experimental and Theoretical Evidence for an Agostic Interaction in a Gold(III) Complex. *Angew. Chem. Int. Ed.* **2016**, *55*, 3414–3418.
- (15) Rekhroukh, F.; Estévez L.; Bijani, C.; Miqueu, K.; Amgoune, A.; Bourissou, D. Coordination-Insertion of Norbornene at Gold: a Mechanistic Study. *Organometallics* **2016**, *35*, 995–1001.
- (16) Rekhroukh, F.; Blons, C.; Estévez L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. Gold(III) arene complexes by insertion of olefins into Au(III)–aryl bonds. *Chem. Sci.* **2017**, *8*, 4539–4545.
- (17) Serra, J.; Font, P.; Sosa Carrizo, E. D.; Mallet-Ladeira, S.; Massou, S.; Parella, T.; Miqueu, K.; Amgoune, A.; Ribas, X.; Bourissou, D. Cyclometalated Gold(III) Complexes: Noticeable Differences between (N,C) and (P,C) Ligands in Migratory Insertion. *Chem. Sci.* **2018**, *9*, 3932–3940.
- (18) Marion, N.; Nolan, S.P. *N*-Heterocyclic carbenes in gold catalysis. *Chem. Soc. Rev.* **2008**, *37*, 1776–1782.
- (19) Collado, A.; Gómez-Suárez, A.; Oonishi, Y.; Slawin, A.M.Z.; Nolan, S.P. Synthesis, characterisation, and oxygen atom transfer reactions involving the first gold(I)-alkylperoxo complexes. *Chem. Commun.* **2013**, *49*, 10745–10747.
- (20) Egbert, J.D.; Slawin, A.M.Z.; Nolan, S.P. Synthesis of *N*-Heterocyclic Carbene Gold Complexes Using Solution-Phase and Solid-State Protocols. *Organometallics* **2013**, *32*, 2271–2274.
- (21) Laitar, D.S.; Müller, P.; Gray, T.G.; Sadighi, J.P. A Carbene-Stabilized Gold(I) Fluoride: Synthesis and Theory. *Organometallics* **2005**, *24*, 4503–4505.
- (22) Mankad, N. P.; Toste, F. D. C–C Coupling Reactivity of an Alkylgold(III) Fluoride Complex with Arylboronic Acids. *J. Am. Chem. Soc.* **2010**, *132*, 12859–12861.
- (23) Tsui, E.Y.; Müller, P.; Sadighi, J. P. Reactions of a Stable Monomeric Gold(I) Hydride Complex. *Angew. Chem. Int. Ed.* **2008**, *47*, 8937–8940.
- (24) Kleeberg, C.; Cheung, M. S.; Lin, Z.; Marder, T. B. Copper-Mediated Reduction of CO₂ with pinB–SiMe₂Ph via CO₂ Insertion into a Copper–Silicon Bond. *J. Am. Chem. Soc.* **2011**, *133*, 19060–19063.
- (25) Kleeberg, C.; Feldmann, E.; Hartmann, E.; Vyas, D. J.; Oestreich, M. Copper-Catalyzed 1,2-Addition of Nucleophilic Silicon to Aldehydes: Mechanistic Insight and Catalytic Systems. *Chem. Eur. J.* **2011**, *17*, 13538–13543.
- (26) Fujihara, T.; Tani, Y.; Semba, K.; Terao, J.; Tsuji, Y. Copper-Catalyzed Silacarboxylation of Internal Alkynes by Employing Carbon Dioxide and Silylboranes. *Angew. Chem. Int. Ed.* **2012**, *51*, 11487–11490.
- (27) Segawa, Y.; Yamashita, M.; Nozaki, K. Boryl Anion Attacks Transition-Metal Chlorides To Form Boryl Complexes: Syntheses, Spectroscopic, and Structural Studies on Group 11 Borylmetal Complexes. *Angew. Chem. Int. Ed.* **2007**, *46*, 6710–6713.
- (28) Zinser, C. M.; Nahra, F.; Falivene, L.; Brill, M.; Cordes, D. B.; Slawin, A.M.Z.; Cavallo, L.; Cazin, C.S.J.; Nolan, S.P. Synthesis and reactivity of [Au(NHC)(Bpin)] complexes. *Chem. Commun.* **2019**, *55*, 6799–6802.
- (29) Meyer, J.; Willnecker, J.; Schubert, U. Übergangsmetall-Silyl-Komplexe, 26. Gold(I)-Silyl-Komplexe *Chem. Ber.* **1989**, *122*, 223–230.
- (30) Oroz, M.M.; Schier, A.; Schmidbaur, H. (Trimethylphosphine)(triphenylsilyl)gold(I) and Related Compounds. *Z. Naturforsch. B* **1999**, *54*, 26–29.
- (31) de Frémont, P.; Scott, N.M.; Stevens, E.D.; Nolan, S.P. Synthesis and Structural Characterization of *N*-Heterocyclic Carbene Gold(I) Complexes. *Organometallics* **2005**, *24*, 2411–2418.
- (32) Zhu, J.; Lin, Z.; Marder, T.B. Trans Influence of Boryl Ligands and Comparison with C, Si, and Sn Ligands. *Inorg. Chem.* **2005**, *44*, 9384–9390.
- (33) Theil, M.; Jutzi, P.; Neumann, B.; Stammer, A.; Stammer, H.-G. Zur Insertion von Decamethylsilicocen in Nickel- und Gold-Chlor-Bindungen. *J. Organomet. Chem.* **2002**, *662*, 34–42.
- (34) Liepiņš, E.; Goldberg, Y.; Iovel, I.; Lukevics, E. ¹H, ¹³C and ²⁹Si NMR study of α - and β -silylstyrenes and their adducts with dichlorocarbene. *J. Organomet. Chem.* **1987**, *335*, 301–311.
- (35) Chen, H.-M.; Oliver, J.P. Silylcupration of acetylenes. *J. Organomet. Chem.* **1986**, *316*, 255–260.
- (36) Stratakis, M.; Garcia, H. Catalysis by Supported Gold Nanoparticles: Beyond Aerobic Oxidative Processes. *Chem. Rev.* **2012**, *112*, 4469–4506.
- (37) Lykakis, I.N.; Stratakis, M. Nanogold(0)-Catalyzed Addition of Heteroelement σ Linkages to Functional Groups. *Synthesis* **2019**, *51*, 2435–2454.