

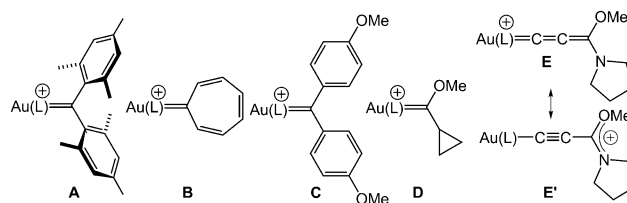
# Synthesis and Characterization of a Gold Vinylidene Complex Lacking $\pi$ -Conjugated Heteroatoms\*\*

Robert J. Harris and Ross A. Widenhoefer\*

**Abstract:** Hydride abstraction from the gold (disilyl)ethynyl complex  $[(P)Au\{\eta^1-C\equiv CSi(Me)_2CH_2CH_2Si(Me)_2H\}]$  ( $P = P(tBu)_2o$ -biphenyl) with triphenylcarbenium tetrakis(pentafluorophenyl)borate at  $-20^\circ C$  formed the cationic gold  $(\beta,\beta$ -disilyl)vinylidene complex  $[(P)Au=C=CSi(Me)_2CH_2CH_2Si(Me)_2]^+ B(C_6F_5)_4^-$  with  $\geq 90\%$  selectivity.  $^{29}Si$  NMR analysis of this complex pointed to delocalization of positive charge onto both the  $\beta$ -silyl groups and the  $(P)Au$  fragment. The C1 and C2 carbon atoms of the vinylidene complex underwent facile interconversion ( $\Delta G^\ddagger = 9.7$  kcal mol $^{-1}$ ), presumably via the gold  $\pi$ -disilacyclohexyne intermediate  $[(P)Au\{\eta^2-C\equiv CSi(Me)_2CH_2CH_2Si(Me)_2\}]^+ B(C_6F_5)_4^-$ .

Cationic gold carbene complexes are widely invoked as intermediates in a range of gold-catalyzed transformations including enyne<sup>[1]</sup> and propargyl carboxylate cycloaddition,<sup>[2]</sup> alkyne oxidation,<sup>[3]</sup> and alkene cyclopropanation.<sup>[4,5]</sup> Although the intermediacy of gold carbenes in these transformations is generally accepted, there remains considerable debate regarding the electronic structure of the Au–C bond,<sup>[6–9]</sup> due in large part to the dearth of suitable model complexes for structural and/or spectroscopic interrogation. It is therefore significant that within the past year well-defined gold carbene complexes that 1) lack  $\pi$ -conjugated heteroatoms (**A**, **B**),<sup>[7,10]</sup> 2) display alkylidene transfer behavior (**C**),<sup>[8]</sup> or 3) contain a cyclopropyl group at C1 (**D**)<sup>[9]</sup> have been reported (Scheme 1), which provide new insight into the electronic structure and behavior of gold carbene complexes.<sup>[11,12]</sup>

Gold vinylidene complexes of the form  $[(L)Au=C=CR_2]^+$  constitute a particularly intriguing class of gold carbene complexes that have attracted considerable recent interest. These species have been invoked as intermediates in a number of transformations,<sup>[13]</sup> most notably the gold-catalyzed polycyclization of *o*-dialkynyl arenes.<sup>[14]</sup> Although the existence of gold vinylidene complexes is supported by both indirect experimental evidence and computation,<sup>[14]</sup> direct experimental evidence for these complexes is absent.<sup>[15]</sup> The only relevant model complexes are the Fischer-type gold allenylidene complexes **E** ( $L = IPr$  or  $PCy_3$ ;  $IPr = 1,3$ -bis(2,6-diisopropylphenyl)imidazol-2-ylidene,

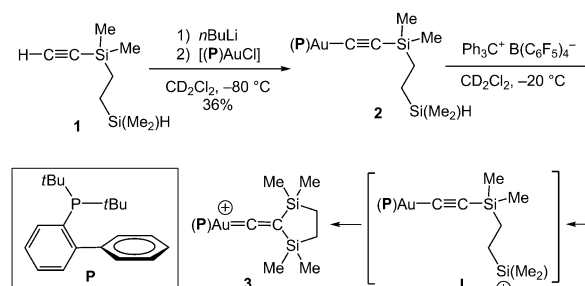


**Scheme 1.** Recent examples of gold carbenoid complexes ( $L = N$ -heterocyclic carbene or tertiary phosphine).<sup>[5–9]</sup>

Cy = cyclohexyl), which are significantly biased toward the oxonium/iminium contributor **E'** owing to the presence of two  $\pi$ -conjugated heteroatoms (Scheme 1).<sup>[16]</sup> Herein we report the synthesis and characterization of a cationic gold vinylidene complex that lacks  $\pi$ -conjugated heteroatoms.

Toward the generation of a cationic gold vinylidene complex lacking  $\pi$ -conjugated heteroatoms, we targeted gold  $(\beta,\beta$ -disilyl)vinylidene complexes generated by addition of a pendant silylium ion to the  $C\equiv C$  bond of a gold acetylide complex. This approach was inspired by studies from the research groups of Lambert,<sup>[17]</sup> Siehl,<sup>[18,19]</sup> and Müller,<sup>[19–23]</sup> who have both documented and exploited the stabilization of alkyl and vinyl carbenium ions by  $\beta$ -SiC hyperconjugation.<sup>[24]</sup> To this end, treatment of disilylethynylacetylene **1** with *n*BuLi followed by auration of the resulting lithium acetylide with  $[(P)AuCl]$  ( $P = P(tBu)_2o$ -biphenyl) led to isolation of the gold (disilylethynyl)acetylide complex  $[(P)Au\{\eta^1-C\equiv CSi(Me)_2CH_2CH_2Si(Me)_2H\}]$  (**2**) in 36% yield (Scheme 2). Treatment of **2** with triphenylcarbenium tetrakis(pentafluorophenyl)borate in  $CD_2Cl_2$  at  $-20^\circ C$  for 10 min led to hydride abstraction and cyclization, presumably via the transient silylium ion species **I**, to form the  $(\beta,\beta$ -disilyl)vinylidene complex **3** with  $\geq 90\%$  selectivity, as determined by  $^{31}P$  NMR analysis.<sup>[25]</sup>

Although **3** was stable in solution for short periods ( $\leq 5$  min) at room temperature, concentration or attempted precipitation at  $-20^\circ C$  led to rapid decomposition, and **3** was therefore characterized in solution by spectroscopy. The low-temperature ( $-80^\circ C$ )  $^{31}P$  and  $^{29}Si$  NMR spectra of **3** displayed single resonances at  $\delta = 58.3$  and  $\delta = 33.5$ , respectively, and

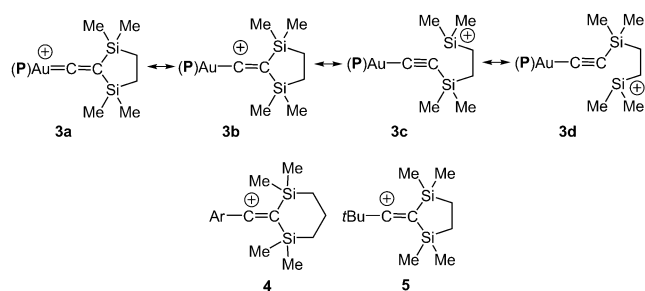


**Scheme 2.** Synthesis of gold  $(\beta,\beta$ -disilyl)vinylidene complex **3**.

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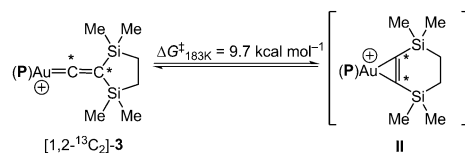
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201501474>.



**Scheme 3.** Resonance contributors to gold vinylidene complex **3** along with vinyl cations **4** and **5**.

the  $^1\text{H}$  NMR spectrum of **3** at  $-80^\circ\text{C}$  displayed a 9:2:6 ratio of resonances at  $\delta = 1.31$  (d,  $J_{\text{PH}} = 15.5$  Hz), 1.14 (s), and 0.47 (s) corresponding to the *tert*-butyl, Si-CH<sub>2</sub>, and Si-CH<sub>3</sub> protons, respectively. Together, these spectroscopic features established both the cyclization of **2** and the high symmetry (static or time-averaged) of gold vinylidene complex **3**. The significant downfield shift of the  $^{29}\text{Si}$  NMR resonance of **3** relative to the C(sp)-Si resonance of neutral acetylide precursor **2** ( $\delta = -20.6$ ;  $\Delta\delta = +54$ ) points to accumulation of positive charge on the  $\beta$ -silicon atoms of **3**, as represented by resonance structures **3c** and **3d** (Scheme 3). A number of studies have shown that  $\beta$ -SiC hyperconjugation in  $\beta$ -silyl-substituted carbenium ions increases with the increasing electron demand of the electron-deficient carbon atom.<sup>[26]</sup> Müller et al. extended and quantified this relationship by establishing a correlation between the downfield shift of the  $^{29}\text{Si}$  NMR chemical shift ( $\Delta\delta$ ) of the  $\alpha$ -aryl- $\beta$ , $\beta$ -disilylvinyl cations **4** relative to their neutral arylacetylene precursors versus the Hammett  $\sigma^+$  parameter.<sup>[22]</sup> It is therefore worth noting that the  $\Delta\delta$  value for **3** is significantly less than that of the analogous  $\alpha$ -*tert*-butyl- $\beta$ , $\beta$ -disilylvinyl cation **5** ( $\Delta\delta = 86$ ),<sup>[23,27]</sup> which suggests that the electron-donor ability of the (P)Au fragment in **3** significantly exceeds that of a *tert*-butyl group, in accord with our previous analysis of Au $\rightarrow$ C electron donation in the cyclopropyl carbene complex **D**.<sup>[9]</sup> The IR spectrum of **3** displayed an absorbance at  $1955\text{ cm}^{-1}$  assigned to the vinylidene C=C stretch, which is similar to those observed for cations **4**.<sup>[21]</sup>

Although the  $^{13}\text{C}$  NMR spectrum of **3** at  $-90^\circ\text{C}$  was likewise consistent with a highly symmetric structure, the key C1 and C2 vinylidene resonances could not be detected, even upon extended acquisition. However,  $^{13}\text{C}$  NMR analysis of the doubly labeled isotopomer  $[1,2-^{13}\text{C}_2]\text{-3}$  at  $-90^\circ\text{C}$  displayed broad multiplets at  $\delta = 206$  (dd,  $J_{\text{CP}} = 110$  Hz,  $J_{\text{CC}} = 60$  Hz) and  $\delta = 112$  (d,  $J_{\text{CC}} = 60$  Hz) corresponding to the vinylidene C1 and C2 atoms, respectively (Scheme 4). As the temperature was raised, these resonances broadened further and disappeared into the baseline between  $-70$  and  $-50^\circ\text{C}$ . Although these resonances did not coalesce at  $25^\circ\text{C}$ , they reappeared unchanged when the solution was again cooled to  $-90^\circ\text{C}$ .  $^{13}\text{C}$ -Spin saturation transfer analysis of  $[1,2-^{13}\text{C}_2]\text{-3}$  at  $-90^\circ\text{C}$  confirmed interconversion of the C1 and C2 vinylidene carbon atoms and established an energy barrier of  $\Delta G^\ddagger_{183\text{K}} = 9.7\text{ kcal mol}^{-1}$  for this process. The simplest mechanism that accounts for interconversion of the C1 and C2



**Scheme 4.** Fluxional behavior of gold vinylidene isotopomer  $[1,2-^{13}\text{C}_2]\text{-3}$ .

vinylidene carbon atoms of **3** involves 1,2-silyl migration to generate the unobserved gold  $\eta^2$ -disilacyclohexyne intermediate  $[(\text{P})\text{Au}\{\eta^2\text{-C}\equiv\text{CSi}(\text{Me})_2\text{CH}_2\text{CH}_2\text{Si}(\text{Me})_2\}]^+ \text{B}(\text{C}_6\text{F}_5)_4^-$  (**II**; Scheme 4).<sup>[28]</sup> Similar fluxional behavior has been documented for  $\beta$ , $\beta$ -disilylvinyl cations possessing an  $\alpha$ -SiR<sub>3</sub> or  $\alpha$ -GeR<sub>3</sub> group.<sup>[23]</sup>

In summary, we have synthesized the gold ( $\beta$ , $\beta$ -disilyl)vinylidene complex **3** by hydride abstraction/cyclization of neutral gold acetylide complex **2**. Complex **3** represents the first example of a gold vinylidene complex and a rare example of a gold carbene complex that lacks  $\pi$ -conjugated heteroatoms.<sup>[7,10]</sup> The C1 and C2 vinylidene atoms of **3** undergo facile interconversion ( $\Delta G^\ddagger_{183\text{K}} = 9.7\text{ kcal mol}^{-1}$ ), presumably via the gold  $\pi$ -disilacyclohexyne intermediate **II**.  $^{29}\text{Si}$  NMR analysis of **3** points to delocalization of positive charge onto both the  $\beta$ -silyl groups and the (P)Au fragment. Ongoing efforts are directed toward further quantifying the extent of Au $\rightarrow$ C electron donation in these complexes.

**Keywords:** bonding modes · carbene ligands · carbenoids · gold · vinylidenes

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