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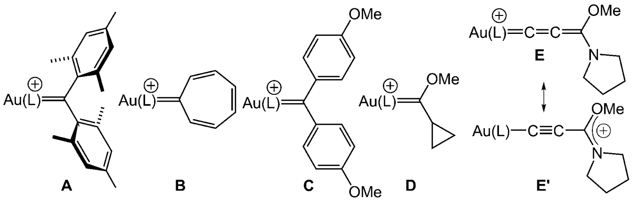
Synthesis and Characterization of a Gold Vinylidene Complex Lacking π-Conjugated Heteroatoms[**]

*Robert J. Harris and Ross A. Widenhoefer**

***Abstract:** Hydride abstraction from the gold (disilyl)ethylacetylide complex $[(\mathbf{P})Au\{\eta^1\text{-}C{\equiv}CSi(Me)_2CH_2CH_2SiMe_2H\}]$ ($\mathbf{P} = P(tBu)_2o$-biphenyl) with triphenylcarbenium tetrakis(pentafluorophenyl)borate at −20°C formed the cationic gold (β,β-disilyl)vinylidene complex $[(\mathbf{P})Au{=}C{=}CSi(Me)_2CH_2CH_2Si(Me)_2]^+B(C_6F_5)_4^-$ with ≥ 90% selectivity. ^{29}Si NMR analysis of this complex pointed to delocalization of positive charge onto both the β-silyl groups and the (**P**)Au fragment. The C1 and C2 carbon atoms of the vinylidene complex underwent facile interconversion ($\Delta G^{\neq} = 9.7$ kcal mol^{-1}), presumably via the gold π-disilacyclohexyne intermediate $[(\mathbf{P})Au\{\eta^2\text{-}C{\equiv}CSi(Me)_2CH_2CH_2Si(Me)_2\}]^+B(C_6F_5)_4^-$.*

Cationic gold carbene complexes are widely invoked as intermediates in a range of gold-catalyzed transformations including enyne[1] and propargyl carboxylate cycloaddition,[2] alkyne oxidation,[3] and alkene cyclopropanation.[4,5] 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,[6–9] 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 π-conjugated heteroatoms (**A**, **B**),[7,10] 2) display alkylidene transfer behavior (**C**),[8] or 3) contain a cyclopropyl group at C1 (**D**)[9] have been reported (Scheme 1), which provide new insight into the electronic structure and behavior of gold carbene complexes.[11,12]

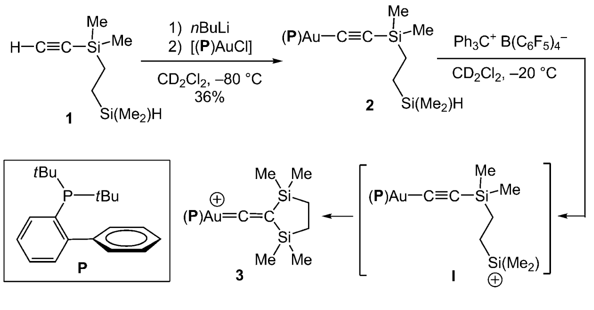
Gold vinylidene complexes of the form $[(L)Au{=}C{=}CR_2]^+$ constitute a particularly intriguing class of gold carbene complexes that have attracted considerable recent interest. These species have been invoked as intermediates in a number of transformations,[13] most notably the gold-catalyzed polycyclization of *o*-dialkynyl arenes.[14] Although the existence of gold vinylidene complexes is supported by both indirect experimental evidence and computation,[14] direct experimental evidence for these complexes is absent.[15] 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, Cy = cyclohexyl), which are significantly biased toward the oxonium/iminium contributor **E′** owing to the presence of two π-conjugated heteroatoms (Scheme 1).[16] Herein we report the synthesis and characterization of a cationic gold vinylidene complex that lacks π-conjugated heteroatoms.



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

Toward the generation of a cationic gold vinylidene complex lacking π-conjugated heteroatoms, we targeted gold (β,β-disilyl)vinylidene complexes generated by addition of a pendant silylium ion to the C≡C bond of a gold acetylide complex. This approach was inspired by studies from the research groups of Lambert,[17] Siehl,[18,19] and Müller,[19–23] who have both documented and exploited the stabilization of alkyl and vinyl carbenium ions by β-SiC hyperconjugation.[24] To this end, treatment of disilylethylacetylene **1** with *n*BuLi followed by auration of the resulting lithium acetylide with [(**P**)AuCl] (**P** = P(*t*Bu)$_2$*o*-biphenyl) led to isolation of the gold (disilylethyl)acetylide complex $[(\mathbf{P})Au\{\eta^1\text{-}C{\equiv}CSi(Me)_2\text{-}CH_2CH_2SiMe_2H\}]$ (**2**) in 36% yield (Scheme 2). Treatment of **2** with triphenylcarbenium tetrakis(pentafluorophenyl)borate in CD_2Cl_2 at −20°C for 10 min led to hydride abstraction and cyclization, presumably via the transient silylium ion species **I**, to form the (β,β-disilyl)vinylidene complex **3** with ≥ 90% selectivity, as determined by ^{31}P NMR analysis.[25]

Although **3** was stable in solution for short periods (≤ 5 min) at room temperature, concentration or attempted precipitation at −20°C led to rapid decomposition, and **3** was therefore characterized in solution by spectroscopy. The low-temperature (−80°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 (β,β-disilyl)vinylidene complex **3**.

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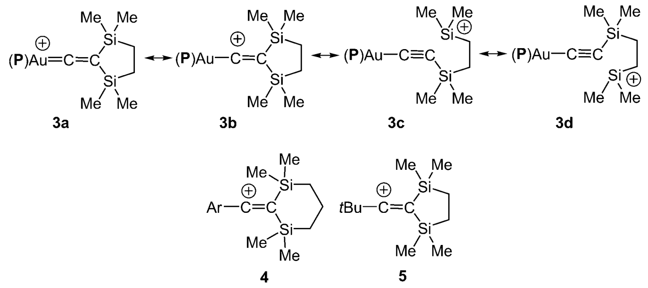
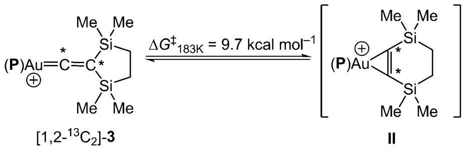


Scheme 3. Resonance contributors to gold vinylidene complex **3** along with vinyl cations **4** and **5**.

the ^{1}H NMR spectrum of **3** at −80 °C displayed a 9:2:6 ratio of resonances at $\delta = 1.31$ (d, $J_{PH} = 15.5$ Hz), 1.14 (s), and 0.47 (s) corresponding to the *tert*-butyl, Si-CH$_2$, and Si-CH$_3$ 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}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 β-silicon atoms of **3**, as represented by resonance structures **3c** and **3d** (Scheme 3). A number of studies have shown that β-SiC hyperconjugation in β-silyl-substituted carbenium ions increases with the increasing electron demand of the electron-deficient carbon atom.[26] Müller et al. extended and quantified this relationship by establishing a correlation between the downfield shift of the ^{29}Si NMR chemical shift (Δδ) of the α-aryl-β,β-disilylvinyl cations **4** relative to their neutral arylacetylene precursors versus the Hammett σ^+ parameter.[22] It is therefore worth noting that the $\Delta\delta$ value for **3** is significantly less than that of the analogous α-*tert*-butyl-β,β-disilylvinyl cation **5** ($\Delta\delta = 86$),[23,27] 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→C electron donation in the cyclopropyl carbene complex **D**.[9] The IR spectrum of **3** displayed an absorbance at 1955 cm^{-1} assigned to the vinylidene C=C stretch, which is similar to those observed for cations **4**.[21]

Although the ^{13}C NMR spectrum of **3** at −90 °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}C NMR analysis of the doubly labeled isotopomer [1,2-^{13}C$_2$]-**3** at −90 °C displayed broad multiplets at $\delta = 206$ (dd, $J_{CP} = 110$ Hz, $J_{CC} = 60$ Hz) and $\delta = 112$ (d, $J_{CC} = 60$ 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 °C. Although these resonances did not coalesce at 25 °C, they reappeared unchanged when the solution was again cooled to −90 °C. ^{13}C-Spin saturation transfer analysis of [1,2-^{13}C$_2$]-**3** at −90 °C confirmed interconversion of the C1 and C2 vinylidene carbon atoms and established an energy barrier of $\Delta G^{\ddagger}_{183\text{K}} = 9.7$ kcal mol^{-1} for this process. The simplest mechanism that accounts for interconversion of the C1 and C2 vinylidene carbon atoms of **3** involves 1,2-silyl migration to generate the unobserved gold η^2-disilacyclohexyne intermediate $[(\mathbf{P})\text{Au}\{\eta^2\text{-}\overline{\text{C}{\equiv}\text{CSi(Me)}_2\text{CH}_2\text{CH}_2\text{Si}}\text{(Me)}_2\}]^+\ \text{B(C}_6\text{F}_5)_4^-$ (II; Scheme 4).[28] Similar fluxional behavior has been documented for β,β-disilylvinyl cations possessing an α-SiR$_3$ or α-GeR$_3$ group.[23]



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

In summary, we have synthesized the gold (β,β-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 π-conjugated heteroatoms.[7,10] The C1 and C2 vinylidene atoms of **3** undergo facile interconversion ($\Delta G^{\ddagger}_{183\text{K}} = 9.7$ kcal mol^{-1}), presumably via the gold π-disilacyclohexyne intermediate **II**. ^{29}Si NMR analysis of **3** points to delocalization of positive charge onto both the β-silyl groups and the (**P**)Au fragment. Ongoing efforts are directed toward further quantifying the extent of Au→C electron donation in these complexes.

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

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[27] Unfortunately, no correlation between the $\Delta\delta$ and σ^+ values has been established for α-aryl-β,β-disilylvinyl cations in which the β-silicon atoms are part of a five-membered ring, such as in **3** and **5**. As such, no definitive assignment of the electron-donor ability of the (**P**)Au fragment of **3** can be determined from these data.

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