EDGE ARTICLE

Ionization of gold (γ-methoxy)vinyl complexes generates reactive gold vinyl carbene complexes†

Nana Kim and Ross A. Widenhoefer ID *

Cationic gold vinyl carbene/allylic cation complexes of the form (*E*)-[(L)AuC(H)C(H)CAr$_2$]$^+$ OTf$^-$ {L = IPr, Ar = Ph [(*E*)-**5a**], L = IPr, Ar = 4-C$_6$H$_4$OMe [(*E*)-**5b**], L = P(*t*-Bu)$_2$*o*-biphenyl, Ar = 4-C$_6$H$_4$OMe [(*E*)-**5c**]} were generated in solution *via* Lewis acid-mediated ionization of the corresponding gold (γ-methoxy)vinyl complexes (*E*)-(L)AuC(H)C(H)C(OMe)Ar$_2$ at or below −95 °C. Complexes (*E*)-**5b** and (*E*)-**5c** were fully characterized in solution employing multinuclear NMR spectroscopy, which established the predominant contribution of the aurated allylic cation resonance structure and the significant distribution of positive charge into the γ-anisyl rings. Complex (*E*)-**5b** reacted rapidly at −95 °C with neutral two-electron, hydride, and oxygen atom donors exclusively at the C1 position of the vinyl carbene moiety and with *p*-methoxystyrene to form the corresponding vinylcyclopropane. In the absence of nucleophile (*E*)-**5a** decomposed predominantly *via* intermolecular carbene dimerization whereas formation of 1-aryl-5-methoxy indene upon ionization of (*Z*)-(IPr)AuC(H)C(H)C(OMe)(4-C$_6$H$_4$OMe)$_2$ [(*Z*)-**6b**] implicated an intramolecular Friedel–Crafts or electrocyclic Nazarov pathway for the decomposition of the unobserved vinyl carbene complex (*Z*)-[(IPr)AuC(H)C(H)C(4-C$_6$H$_4$OMe)$_2$]$^+$ OTf$^-$ [(*Z*)-**5b**].

Introduction

Cationic gold carbene complexes have been invoked as intermediates in a diverse range of gold(I)-catalyzed transformations[1–3] and, for this reason, considerable effort has been directed toward understanding the structure and reactivity of these complexes.[4] A particularly important subset of the reactive gold carbene complexes is the gold vinyl carbene/allylic cation complexes, with the potential for both the delocalization of positive charge on the Au, C1, and/or C3 atoms and diverse reaction pathways (Fig. 1). Cationic gold vinyl carbene

complexes have been invoked as intermediates in range of gold-catalyzed transformations employing cyclopropenes,[5–8] propargyl carboxylates,[9,10] propargyl ethers,[11] enynes,[12] ene-allenes,[13] vinyl diazo compounds,[14] and norcaradienes as vinyl carbene precursors.[15]

Notwithstanding the insight provided through the computational analysis of Toste and Goddard,[16] information regarding the structure and reactivity of cationic gold vinyl carbene complexes is scarce, owing in large part to the absence of suitable model complexes for interrogation.[4] Only three cationic gold vinyl carbene/allylic cation complexes (**1–3**) have been characterized, each of which contains either a C1 or multiple C3 oxygen atoms (Fig. 2).[17,18] As such, neither the electronic structure nor reactivity of complexes **1–3** is likely to mimic that of the reactive vinyl carbenes generated under gold(I) catalysis.[1–3,5–15] Indeed, well defined, two-coordinate gold carbene complexes that display reactivity analogous to their catalytic counterparts, gold to alkene carbene transfer in
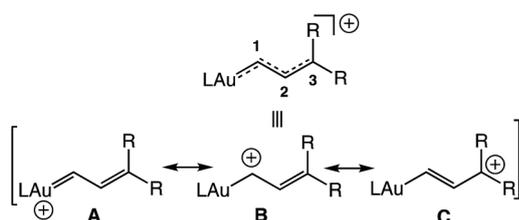

Fig. 1 Potential resonance contributors and composite representation of an unstabilized gold vinyl carbene/allylic cation complex.

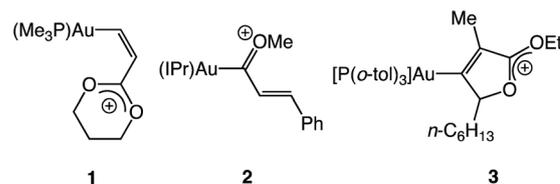*French Family Science Center, Duke University, Durham, North Carolina, USA. E-mail: rwidenho@chem.duke.edu*

Fig. 2 Gold vinyl carbene/allylic cation complexes possessing π-conjugated oxygen atoms, depicted in the form of the predominant oxonium resonance contributor.

particular, are exceedingly rare.[19,20] Although weakly-stabilized vinyl carbene complexes are known for a range of transition metals,[21] the properties of cationic gold(I), including high d-electron count, electronegativity[22] and poor d → π back bonding,[4] likely render the electronic structure and reactivity of cationic gold vinyl carbene complexes distinct from these related complexes.

We have recently reported the synthesis of the cationic, two coordinate gold(I) diphenylallenylidene complex **4** and related complexes, generated via the Lewis acid-mediated ionization of the corresponding gold (γ-methoxy)acetylide complexes (Scheme 1),[23,24] and which represent rare examples of cationic gold carbene complexes lacking π-conjugated heteroatoms.[25,26] The efficiency and facility of the γ-ionization process suggested that a similar approach might provide access to particularly reactive gold vinyl carbene/allylic cation complexes. Indeed, here we report that ionization of gold (γ-methoxy-γ,γ-diaryl) vinyl complexes generates cationic, two-coordinate gold vinyl carbene complexes that react rapidly at −95 °C with a range of nucleophiles, including alkenes, and that decompose in the absence of nucleophile via inter- or intramolecular pathways. The spectroscopy of these complexes points to strong contribution of the aurated allylic cation resonance form and stabilization by the γ-aryl groups.

Results and discussion

Guided by our investigation of cationic gold allenylidene complexes,[23] we targeted the gold γ,γ-(diphenyl)vinylcarbene/ allylic cation complex (E)-[(IPr)AuC(H)C(H)CPh$_2$]$^+$ OTf$^-$ [(E)-**5a**] for initial investigation (Scheme 2). The requisite gold (γ,γ-diphenyl)vinyl complex (E)-(IPr)AuC(H)=C(H)C(OMe)Ph$_2$ [(E)-**6a**] was synthesized in two steps from propargylic ether **7a** via zirconium-catalyzed hydroboration[27] followed by trans-metallation of the resulting boronic ester (E)-**8a** with (IPr)AuCl (Scheme 2).[28] Treatment of (E)-**6a** with trimethylsilyl trifluoromethanesulfonate (TMSOTf) in CD$_2$Cl$_2$ at −95 °C led to immediate (<1 min) formation of a bright orange/red solution that became colorless over the course of ~10 s. ^{1}H NMR analysis of the resulting solution at −95 °C revealed formation of trimethylsilyl methyl ether (TMSOMe) in 92 ± 5% yield, which established that efficient ionization of (E)-**6a** had occurred, but no resonances were observed that could be
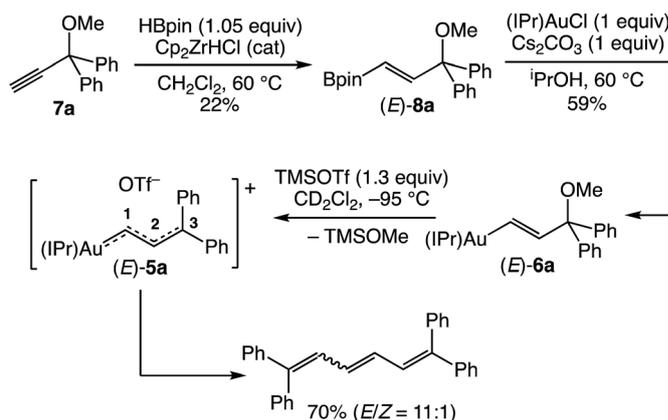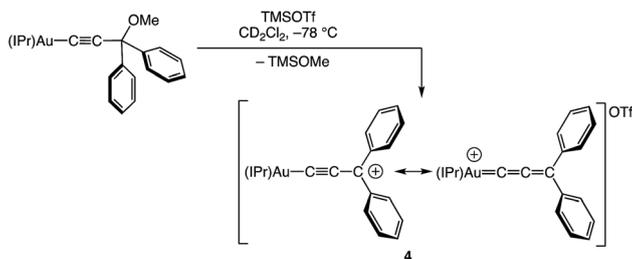

Scheme 2 Synthesis and thermal decomposition of gold vinyl carbene/allylic cation complex (E)-**5a**.

attributed to (E)-**5a**. Rather ^{1}H NMR analysis revealed formation of a ~11 : 1 mixture of (E)- and (Z)-1,1,6,6-tetraphenylhexa-1,3,5-triene in 70% combined yield, presumably generated via homocoupling of the vinyl carbene groups of (E)-**5a** (Scheme 2).[20,29] In an effort to directly observe vinyl carbene (E)-**5a**, a solution of (E)-**6a** was treated with TMSOTf at −110 °C in CDFCl$_2$/CD$_2$Cl$_2$ and analysed immediately by ^{1}H NMR spectroscopy. The resulting spectrum was broadened and largely uninterpretable, but displayed a pair of mutually-coupled doublets at δ 10.83 and 8.18 (J = 17.5 Hz), assigned to the C1 and C2 vinylic protons, respectively, of (E)-**5a** (Table 1).

Table 1 Selected NMR data for gold vinyl carbene complexes (E)-**5**. δ Values reported in ppm; J values reported in Hz

	(E)-**5a**^{a}	(E)-**5b**^{b}	(E)-**5c**^{c}
δH1	10.83	9.51	8.89
δH2	8.18	7.71	7.83
δC1	—	243.7	252.3
δC2	—	146.9	148.2
δC3	—	185.7	185.6
J$_{H1,H2}$	17.5	17.8	17.4
J$_{C1,C2}$	—	48	—
J$_{C2,C3}$	—	48	—

^{a} −110 °C in CDFCl$_2$/CD$_2$Cl$_2$. ^{b} −95 °C in CD$_2$Cl$_2$. ^{c} −90 °C in CD$_2$Cl$_2$.

Scheme 1 Synthesis of gold allenylidene complex **4** [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene].

In an effort to enhance the stability of the gold vinyl carbene/allylic cation complex to allow more rigorous spectroscopic interrogation and reactivity analysis, we turned our attention to the gold γ,γ-bis(anisyl)vinyl carbene/allylic cation complex (E)-[(IPr)AuC(H)C(H)C(4-C$_6$H$_4$OMe)$_2$]$^+$ OTf$^-$ [(E)-**5b**]. To this end, ionization of gold vinyl complex (E)-**6b** in CD$_2$Cl$_2$ at −95 °C led to immediate (<1 min) formation of the bright red-orange solution of (E)-**5b** in 96 ± 5% yield (^{1}H NMR), which persisted indefinitely at this temperature (Scheme 3). In a similar manner, ionization of the phosphine-supported gold vinyl complex (E)-**6c** at −95 °C led to formation of (E)-**5c** in 95% yield (^{1}H NMR; Scheme 3), which darkened noticeably over the course of several hours at −95 °C.

Complexes (E)-**5b** and (E)-**5c** were fully characterized by NMR spectroscopy at or below −85 °C (Table 1). For example, the ^{13}C NMR spectrum of (E)-**5b** displayed downfield resonances at δ 243.7, 146.9, and 185.7 assigned to the C1, C2, and C3 carbon atoms, respectively, of the vinyl carbene/allylic cation moiety. These resonances as well as $^1J_{C1,C2}$ and $^1J_{C2,C3}$ were unambiguously assigned *via* ^{13}C NMR analysis of the corresponding ^{13}C-labelled isotopomer (E)-[(IPr)Au^{13}C(H)^{13}C(H)C(4-C$_6$H$_4$OMe)$_2$]$^+$ OTf$^-$ [(E)-**5b**-^{13}C$_2$]. The ^{13}C NMR spectrum of (E)-**5b** also displayed a pair of downfield resonances at δ 168.3 and 167.6 assigned to the chemically inequivalent methoxy-bound aromatic carbon atoms. These resonances were shifted significantly downfield relative to those of neutral (E)-**6b** (δ 140), which points to the significant delocalization of positive charge onto the γ-anisyl rings of (E)-**5b**.[30]

The ^{1}H NMR spectrum of (E)-**5b** at −95 °C displayed two mutually-coupled doublets at δ 9.51 and 7.71 (J = 17.8 Hz)

Scheme 3 Syntheses of gold vinyl carbene/allylic cation complexes (E)-**5b** and (E)-**5c**.

Fig. 3 Fluxional behaviour of (E)-**5b**.

Scheme 4 Generation and decomposition of gold vinyl carbene/allylic cation complex (Z)-**5b**.

assigned to the C1 and C2 protons, respectively, and a pair of singlets at δ 3.89 and 3.96 assigned to the chemically inequivalent aryl methoxy protons. As the temperature was raised, the methoxy resonances broadened and coalesced at −42 °C, albeit with significant decomposition, which provided an energy barrier of $\Delta G^{\ddagger}_{231K} = 10.5$ kcal mol^{-1} for interconversion of the anisyl groups of (E)-**5b** (Fig. 3). Both the facile rotation about the C2–C3 bond of (E)-**5b** and the significant delocalization of positive charge onto the γ-anisyl rings of (E)-**5b** point to the predominant contribution resonance structures **D** to the electronic structure of (E)-**5b** (Fig. 4), which is likewise consistent with the significantly greater thermal stability of (E)-**5b** relative to (E)-**5a**.

Warming a solution of (E)-**5b** at −40 °C ($t_{1/2}$ = 35 min) or (E)-**5c** at −60 °C ($t_{1/2} \approx$ 10 min) led to decomposition to form unidentified mixtures of products that included neither the products of intramolecular Friedel–Crafts alkylation nor carbene dimerization as determined by GCMS and LCMS analysis. We were somewhat surprised by the absence of Friedel–Crafts/Nazarov reactivity for complexes (E)-**5**, which is well documented for 1-aryl allylic cations[31,32] and which is directly implicated in the gold(I)-catalyzed ring-opening of aryl cyclopropenes.[5,6] We reasoned that the less stable gold Z-vinyl carbene complexes, which are generated as the kinetic products of cyclopropene ring opening,[33] might be more susceptible toward intramolecular cyclization processes than are the E-vinyl carbene complexes. To evaluate this hypothesis, we sought the independent synthesis of vinyl carbene complex (Z)-**5b**.‡ To this

Fig. 4 Resonance structures **D** representing delocalization of positive charge onto the γ-anisyl rings of (E)-**5b**.
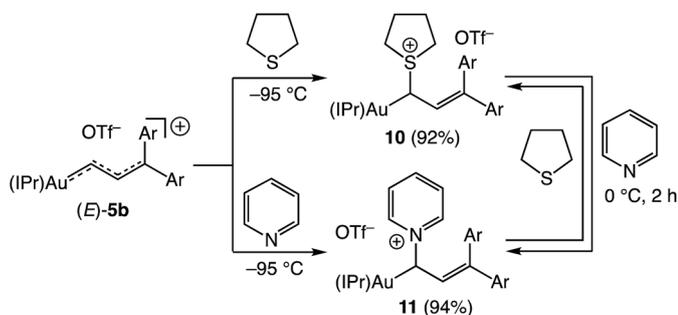
Scheme 5 Proposed mechanism of the conversion of (Z)-**5b** to **9**.

end, the gold vinyl complex (Z)-**6b** was synthesized in two steps from propargyl ether **7b** *via* rhodium-catalyzed, anti-selective hydroboration[34] followed by transmetallation of boronic ester (Z)-**8b** (Scheme 4).

Ionization of (Z)-**6b** with TMSOTf at −95 °C formed a pale orange solution that displayed no resonances in the ^{1}H NMR spectrum that could be attributed to vinyl carbene complex (Z)-**5b**.§ Rather, warming this solution above −50 °C led to formation of the 1-aryl-5-methoxy indene **9** in 58% yield (^{1}H NMR; Scheme 4). Because 1-aryl indenes are less stable than are the isomeric 3-aryl indenes,[35] **9** must be formed kinetically, which points to a mechanism for the conversion of (Z)-**5b** to **9** involving intramolecular Friedel–Crafts alkylation or electrocyclic Nazarov-type cyclization followed by selective protonation of the γ-position of gold allyl intermediate **II** through an S_E' pathway (Scheme 5). Interestingly, (3-phenyl-1H-inden-1-yl) gold(I) complexes very similar to intermediate **II** have been recently isolated *via* thermal rearrangement of neutral (3,3-diphenylcycloprop-1-en-1-yl)gold(I)complexes and were shown to undergo protodeauration with HCl predominantly through an S_E' pathway.[36,37] The facility of the intramolecular Friedel–Crafts/Nazarov reaction of (Z)-**5b** and the failure to form **9** in the decomposition of (E)-**5b** therefore suggests that the energy barrier for E/Z isomerization of (E)-**5b** exceeds that of the lowest energy decomposition pathway available to (E)-**5b** ($\Delta G^{\ddagger} \approx$ 16 kcal mol^{-1}).

Nucleophilic trapping of a cationic gold vinyl carbene complex represents one of the most common terminating steps of catalytic transformations involving these intermediates.[5,7,8] In a similar manner, treatment of (E)-**5b** with either tetrahydrothiophene (THT) or pyridine at −95 °C in CD$_2$Cl$_2$ led to immediate (<1 min) disappearance of the distinctive red color to form pale yellow solutions of the gold allyl carbenoid

complexes **10** and **11**, respectively, in >90% yield (^{1}H NMR; Scheme 6). These complexes were characterized in solution, and in the case of **11**, by X-ray crystallography (Fig. 5). For example, selective attack of THT at the C1 vinyl carbene carbon atom of (E)-**5b** was established by a pair of mutually-coupled doublets at δ 3.22 and 5.60 (J = 11.5 Hz) assigned to the aliphatic C1 and vinylic C2 protons, respectively of **10**. In the solid state, **11** adopts a slightly distorted linear conformation (C1–Au–C28 = 177°) with the C1 allylic carbon atom adopting a distorted sp^3 geometry with a larger Au–C28–C29 angle (115°) and smaller Au–C28–N3 and N3–C28–C29 angles (108°) (Fig. 5). Treatment of **10** (15 mM) with pyridine (1 equiv.) at 0 °C for 2 h led to formation of an equilibrium 1.25 : 1 mixture of **11** : **10** (K_{eq} = 1.8 ± 0.1; Scheme 6). Kinetic analysis of the conversion of **10** to **11** established first-order approach to equilibrium through 2.5 half-lives with forward and reverse rate constants k_f = 4.1 ± 0.9 × 10^{-4} s^{-1} and k_r = 2.3 ± 0.5 × 10^{-4} s^{-1}. The first-order kinetic behaviour points to a dissociative mechanism for the interconversion of **10** and **11** involving free (E)-**5b**.

Oxygen atom transfer to the C1 position of a gold vinyl carbene intermediate has been invoked in the gold-catalyzed reactions of cyclopropenes with diphenylsulfoxide.[7,38,39] In a similar manner, treatment of (E)-**5b** with 4-picoline N-oxide (4-
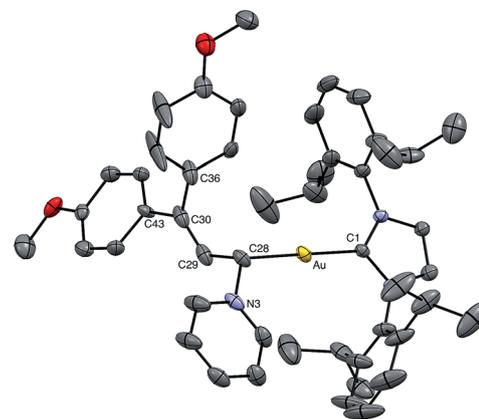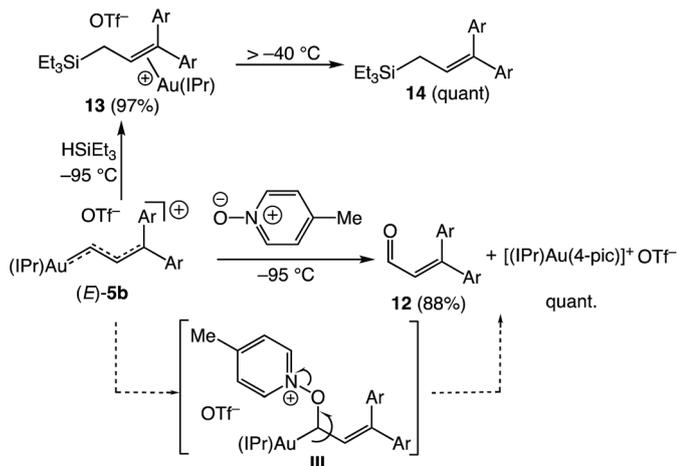

Fig. 5 ORTEP diagram of **11**. One of two crystallographically independent molecules is depicted with ellipsoids shown at the 50% probability level with counterion and hydrogen atoms omitted for clarity. Selected bond distances (Å) and bond angles (deg) for **11**: Au–C1 = 2.005(4), Au–C28 = 2.067(5), C28–C29 = 1.495(5), C29–C30 = 1.343(7), C28–N3 = 1.515(6), C30–C36 = 1.501(8), C30–C43 = 1.55(1), C1–Au–C28 = 177.4(2), Au–C28–C29 = 115.6(3), Au–C28–N3 = 107.8(3), N3–C28–C29 = 108.3(4), C28–C29–C30 = 125.5(5), C29–C30–C43 = 126.1(9), C29–C30–C36 = 121.6(5), C36–C30–C43 = 112.0(9).

Scheme 6 Reactions of (E)-**5b** with THT and pyridine and interconversion of **10** and **11**. Yields determined by ^{1}H NMR spectroscopy *versus* internal standard.

Scheme 7 Reactions of (E)-**5b** with 4-picoline-N-oxide and HSiEt₃. Yields determined by ^{1}H NMR spectroscopy *versus* internal standard.
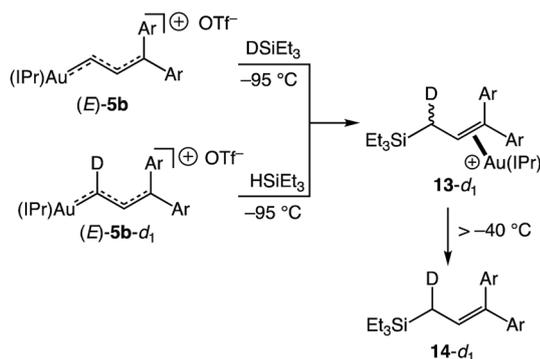
Scheme 8 Reaction of (E)-**5b** with DSiEt₃ and reaction (E)-**5b**-d_1 with HSiEt₃.

PNO) (1.9 equiv.) in CD_2Cl_2 at −95 °C for ~1 min led to formation of 3-arylcinnamaldehyde **12** in 88% yield and the 4-picoline gold complex [(IPr)Au(4-pic)]$^+$ OTf$^-$ in quantitative yield (Scheme 7). This outcome is consistent with selective oxygen atom transfer to the C1 carbon atom of the vinyl carbene moiety of (E)-**5b** followed by elimination from the unobserved α-oxopyridinium intermediate **III**. Related to this, treatment of
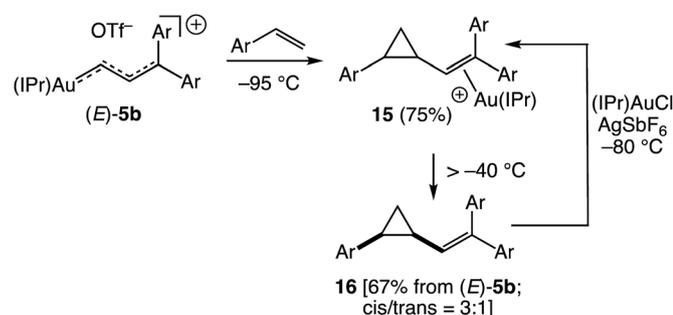
Scheme 9 Reaction of (E)-**5b** with p-methoxystyrene and independent synthesis of π-(vinyl cyclopropane) complex **15**.

(E)-**5b** with triethylsilane at −95 °C led to immediate (<1 min) and selective formation of the cationic gold π-allyl silane complex **13**, presumably *via* hydride addition to the C1 position of (E)-**5b** followed by silyldeauration of the resulting gold allyl intermediate through an S_E pathway.[40] Warming this solution above −40 °C led to decomplexation and formation of allylic silane **14** in quantitative yield. Both the reaction of (E)-**5b** with DSiEt₃ and the reaction of the deuterated isotopomer (E)-**5b**-d_1 with HSiEt₃ at −95 °C led selective incorporation of deuterium into the allylic position to form **13**-d_1 as a ~1 : 1 mixture of diastereomeric isotopomers, pointing to a stepwise deauration/complexation process (Scheme 8).

Despite the dearth of examples of stoichiometric gold to alkene carbene transfer,[19,20] perhaps no process is more closely associated with the reactive gold carbene complexes, including vinyl carbene complexes, generated as catalytic intermediates.[1,2] It is therefore significant that vinyl carbene complex (E)-**5b** underwent facile gold to alkene carbene transfer with p-methoxystyrene. For example, treatment of (E)-**5b** with p-methoxystyrene (3 equiv.) at −95 °C led to immediate (<3 min) consumption of (E)-**5b** to form the gold π-vinyl cyclopropane complex **15** (Scheme 9). Although ^{1}H NMR analysis of this solution at −95 °C was complicated by the presence of free p-methoxystyrene and byproducts, a doublet was observed at δ 4.99 (J = 10.2 Hz), assigned to the vinyl proton of **15**, which corresponded to a 75% yield of **15** from (E)-**5b** (Scheme 9). Warming this solution of **15** above −40 °C led to decomplexation to form free vinyl cyclopropane **16** in 67% NMR yield from (E)-**5b** as a ~3 : 1 mixture of *cis/trans* isomers (Scheme 9). Assignment of the δ 4.99 resonance to the vinyl proton of **15** was confirmed by independent synthesis of **15** from reaction of **16** (*cis/trans* = 3 : 1) with a mixture of (IPr)AuCl and AgSbF₆ in CD_2Cl_2 at −80 °C.¶

Conclusions

We have generated highly reactive gold vinyl carbene/allylic cation complexes *via* low-temperature ionization of gold γ-methoxy-(γ,γ-diaryl)vinyl complexes. Spectroscopic analysis of vinyl carbene/allylic cation complex (E)-**5b** established the predominant contribution of the aurated allylic cation canonical form to the electronic structure of the vinyl carbene complex (C; Fig. 1) with significant delocalization of positive charge into the γ-anisyl groups. Indeed, the significantly greater stability of the γ,γ-bis(anisyl) vinyl carbene complex (E)-**5b** relative to the γ,γ-diphenyl vinyl carbene complex (E)-**5a** points to the importance of the p-methoxy groups in the stabilization of (E)-**5b**.[41] Complex (E)-**5b** reacted rapidly at −95 °C with neutral two-electron, hydride, and oxygen atom donors exclusively at the C1 position of the vinyl carbene/allylic cation moiety and with p-methoxystyrene to form vinyl cyclopropane. These transformations are close or direct analogues to processes attributed to gold vinyl carbene intermediates generated under catalytic conditions.[1–3,5–15] Two distinct pathways for decomposition of these gold vinyl carbene complexes in the absence of nucleophile were identified; complex (E)-**5a** decomposed predominantly *via* intermolecular carbene

homocoupling whereas formation of indene **9** upon ionization of (*Z*)-**6b** directly implicated an intramolecular Friedel–Crafts or electrocyclic Nazarov pathway for the decomposition of the unobserved vinyl carbene complex (*Z*)-**5b**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

‡ Fürstner has previously reported that attempted synthesis of the PCy$_3$-analog of (*Z*)-**5a** *via* reaction of 1,1-diphenylcyclopropene with (PCy$_3$)PAuNTf$_2$ led instead to rapid oligomerization of the cyclopropene.[19] In our hands, attempted synthesis of (*Z*)-**5b** *via* reaction of 1,1-(bisanisyl)cyclopropene with either (IPr)AuOTf or (IPr)AuCl/AgSbF$_6$ produced a similar outcome.

§ Two discrete intermediates were detected by ^{1}H NMR spectroscopy over the temperature range −95 to −30 °C. However, broadening, overlapping resonances, and the dearth of potentially diagnostic resonances precluded extraction of any meaningful information from these data.

¶ Reaction of **16** (*cis/trans* = 3 : 1, 1 equiv.) with a 1 : 1 mixture of (IPr)AuCl and AgSbF$_6$ in CD$_2$Cl$_2$ at −80 °C generated a single resonance [δ 4.99 (br d, J = 10.2 Hz)] that could be attributed to **15** and which constituted ~25% of the reaction mixture, the remainder being free **16**. This suggests that either (1) the vinylic ^{1}H resonances for the various diastereomers of **15** are coincidental or (2) only a single diastereomer of **15** is formed in detectable concentrations from this reaction. Therefore, the 75% yield determined for the conversion of (*E*)-**5b** to **15** (determined by integrating the δ 4.99 resonance relative to internal standard) represents a lower limit for the yield of **15** formed from (*E*)-**5b** and the 67% yield determined for **16** (determined by integrating the vinylic resonances of *cis*- and *trans*-**16** relative to internal standard after warming to room temperature and filtering through silica gel) points to decomposition of **16** under reaction conditions, which was confirmed experimentally. Treatment of (*E*)-**5b** with 1-(*p*-methoxyphenyl)-1,3-butadiene at −95 °C led to immediate consumption of (*E*)-**5b** but produced no products that could be attributed to either cyclopropanation or [4 + 3] cycloaddition.

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