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

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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_6H_4OMe [(E)-5b], L = $P(t-Bu)_2o$ -biphenyl, Ar = 4- C_6H_4OMe [(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 aurred 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_6H_4OMe)₂ [(Z)-6b] implicated an intramolecular Friedel–Crafts or electrocyclic Nazarov pathway for the decomposition of the unobserved vinyl carbene complex (Z)- $[(IPr)AuC(H)C(H)C(4-C_6H_4OMe)_2]^+ OTf^-$ [(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

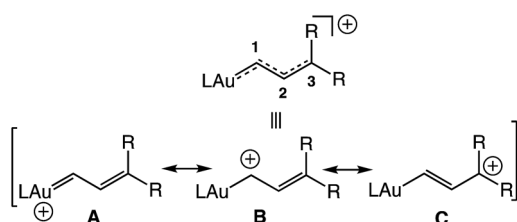


Fig. 1 Potential resonance contributors and composite representation of an unstabilized gold vinyl carbene/allylic cation complex.

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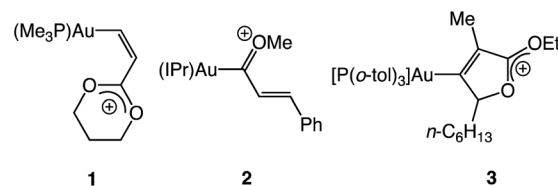


Fig. 2 Gold vinyl carbene/allylic cation complexes possessing π -conjugated oxygen atoms, depicted in the form of the predominant oxonium resonance contributor.

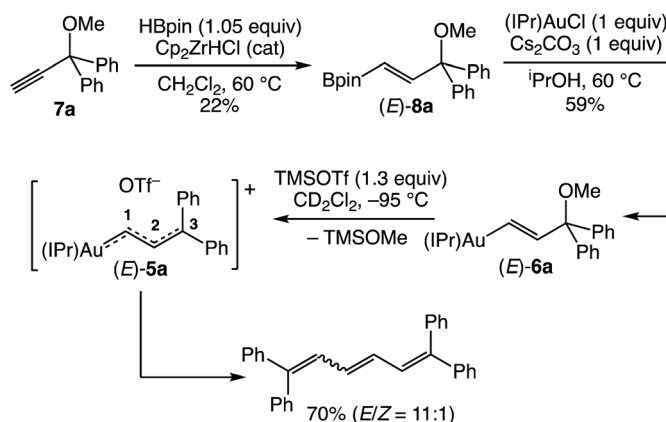


particular, are exceedingly rare.^{19,20} Although weakly-stabilized vinyl carbene complexes are known for a range of transition metals,²¹ the properties of cationic gold(I), including high d-electron count, electronegativity²² and poor $d \rightarrow \pi$ back bonding,⁴ likely render the electronic 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 auroated 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)CPh₂]⁺ OTf⁻ [(*E*)-**5a**] for initial investigation (Scheme 2). The requisite gold (γ,γ -diphenyl)vinyl complex (*E*)-(IPr)AuC(H)=C(H)C(OMe)Ph₂ [(*E*)-**6a**] was synthesized in two steps from propargylic ether **7a** *via* zirconium-catalyzed hydroboration²⁷ followed by transmetalation of the resulting boronic ester (*E*)-**8a** with (IPr)AuCl (Scheme 2).²⁸ Treatment of (*E*)-**6a** with trimethylsilyl trifluoromethanesulfonate (TMSOTf) in CD₂Cl₂ at -95°C led to immediate (<1 min) formation of a bright orange/red solution that became colorless over the course of ~ 10 s. ¹H NMR analysis of the resulting solution at -95°C revealed formation of trimethylsilyl methyl ether (TMSOMe) in $92 \pm 5\%$ yield, which established that efficient ionization of (*E*)-**6a** had occurred, but no resonances were observed that could be



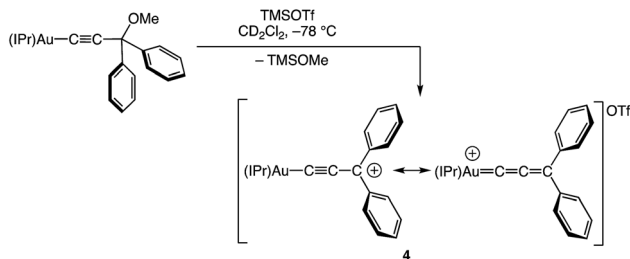
Scheme 2 Synthesis and thermal decomposition of gold vinyl carbene/allylic cation complex (*E*)-**5a**.

attributed to (*E*)-**5a**. Rather ¹H NMR analysis revealed formation of a $\sim 11:1$ 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 CDFCl₂/CD₂Cl₂ and analysed immediately by ¹H 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

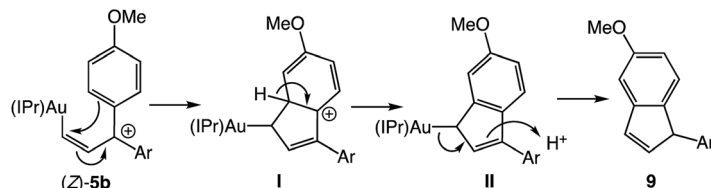
	(<i>E</i>)- 5a ^a	(<i>E</i>)- 5b ^b	(<i>E</i>)- 5c ^c
δ H1	10.83	9.51	8.89
δ H2	8.18	7.71	7.83
δ C1	—	243.7	252.3
δ C2	—	146.9	148.2
δ C3	—	185.7	185.6
$J_{\text{H1,H2}}$	17.5	17.8	17.4
$J_{\text{C1,C2}}$	—	48	—
$J_{\text{C2,C3}}$	—	48	—

^a -110°C in CDFCl₂/CD₂Cl₂. ^b -95°C in CD₂Cl₂. ^c -90°C in CD₂Cl₂.



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



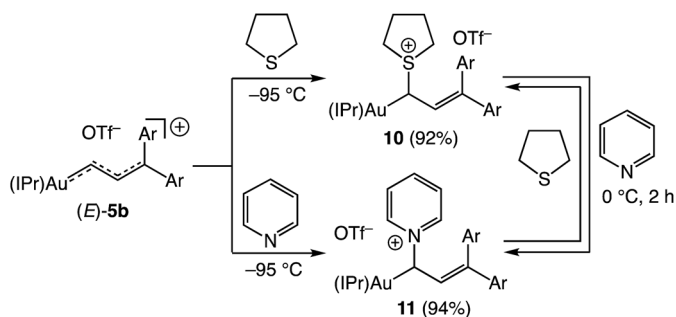


Scheme 5 Proposed mechanism of the conversion of (Z)-5b to 9.

end, the gold vinyl complex (Z)-6b was synthesized in two steps from propargyl ether 7b via rhodium-catalyzed, anti-selective hydroboration³⁴ followed by transmetalation of boronic ester (Z)-8b (Scheme 4).

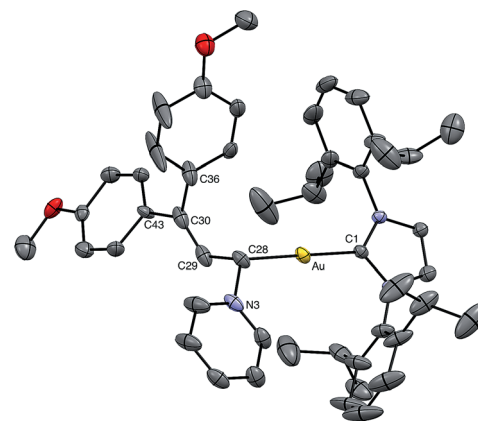
Ionization of (Z)-6b with TMSOTf at $-95\text{ }^{\circ}\text{C}$ formed a pale orange solution that displayed no resonances in the ^1H NMR spectrum that could be attributed to vinyl carbene complex (Z)-5b.[§] Rather, warming this solution above $-50\text{ }^{\circ}\text{C}$ led to formation of the 1-aryl-5-methoxy indene 9 in 58% yield (^1H NMR; Scheme 4). Because 1-aryl indenenes are less stable than are the isomeric 3-aryl indenenes,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-1*H*-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 ($\Delta G^{\ddagger} \approx 16\text{ kcal mol}^{-1}$).

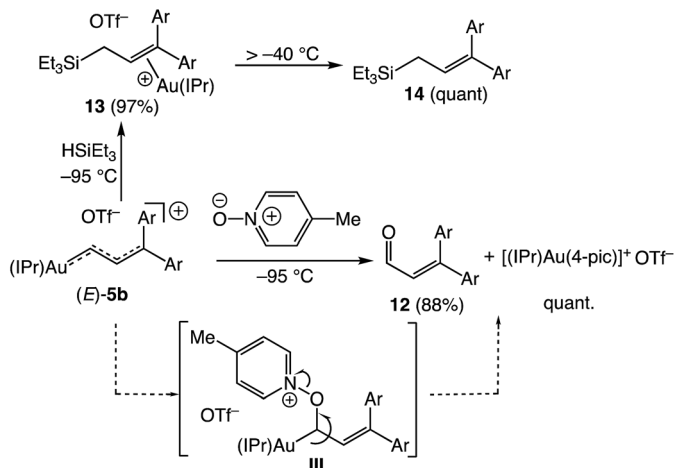
Nucleophilic trapping of a cationic gold vinyl carbene complex represents one of the most common terminating steps of catalytic transformations involving these intermediates.^{5,7,8} In a similar manner, treatment of (E)-5b with either tetrahydrothiophene (THT) or pyridine at $-95\text{ }^{\circ}\text{C}$ in CD_2Cl_2 led to immediate (<1 min) disappearance of the distinctive red color to form pale yellow solutions of the gold allyl carbenoid

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

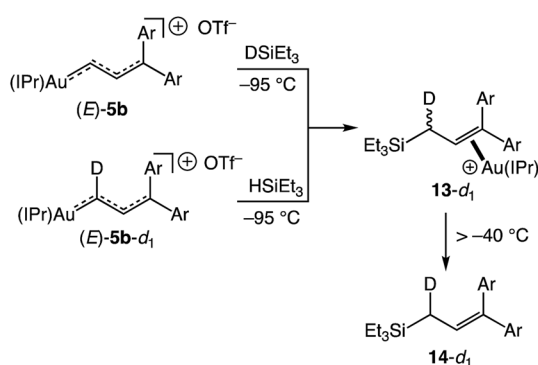
complexes 10 and 11, respectively, in >90% yield (^1H NMR; Scheme 6). These complexes were characterized in solution, and in the case of 11, by X-ray crystallography (Fig. 5). For example, selective attack of THT at the C1 vinyl carbene carbon atom of (E)-5b was established by a pair of mutually-coupled doublets at δ 3.22 and 5.60 ($J = 11.5\text{ Hz}$) assigned to the aliphatic C1 and vinylic C2 protons, respectively of 10. In the solid state, 11 adopts a slightly distorted linear conformation ($\text{C1-Au-C28} = 177^{\circ}$) 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 $0\text{ }^{\circ}\text{C}$ for 2 h led to formation of an equilibrium 1.25 : 1 mixture of 11 : 10 ($K_{\text{eq}} = 1.8 \pm 0.1$; 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 $k_{\text{f}} = 4.1 \pm 0.9 \times 10^{-4}\text{ s}^{-1}$ and $k_{\text{r}} = 2.3 \pm 0.5 \times 10^{-4}\text{ s}^{-1}$. 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 diphenylsulfide.^{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 (\AA) and bond angles (deg) for 11: $\text{Au-C1} = 2.005(4)$, $\text{Au-C28} = 2.067(5)$, $\text{C28-C29} = 1.495(5)$, $\text{C29-C30} = 1.343(7)$, $\text{C28-N3} = 1.515(6)$, $\text{C30-C36} = 1.501(8)$, $\text{C30-C43} = 1.55(1)$, $\text{C1-Au-C28} = 177.4(2)$, $\text{Au-C28-C29} = 115.6(3)$, $\text{Au-C28-N3} = 107.8(3)$, $\text{N3-C28-C29} = 108.3(4)$, $\text{C28-C29-C30} = 125.5(5)$, $\text{C29-C30-C43} = 126.1(9)$, $\text{C29-C30-C36} = 121.6(5)$, $\text{C36-C30-C43} = 112.0(9)$.

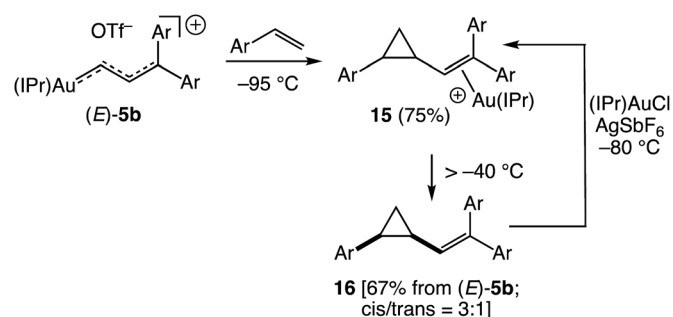


Scheme 7 Reactions of (*E*)-**5b** with 4-picoline-*N*-oxide and HSiEt_3 . Yields determined by ^1H NMR spectroscopy versus internal standard.



Scheme 8 Reaction of (*E*)-**5b** with DSiEt_3 and reaction (*E*)-**5b**- d_1 with HSiEt_3 .

PNO) (1.9 equiv.) in CD_2Cl_2 at $-95\text{ }^\circ\text{C}$ for ~ 1 min led to formation of 3-arylcinnamaldehyde **12** in 88% yield and the 4-picoline gold complex $[(\text{IPr})\text{Au}(4\text{-pic})]^+ \text{OTf}^-$ 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 $-95\text{ }^\circ\text{C}$ 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 $-40\text{ }^\circ\text{C}$ led to decomplexation and formation of allylic silane **14** in quantitative yield. Both the reaction of (*E*)-**5b** with DSiEt_3 and the reaction of the deuterated isotopomer (*E*)-**5b**- d_1 with HSiEt_3 at $-95\text{ }^\circ\text{C}$ led selective incorporation of deuterium into the allylic position to form **13**- d_1 as a $\sim 1 : 1$ 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 $-95\text{ }^\circ\text{C}$ led to immediate (< 3 min) consumption of (*E*)-**5b** to form the gold π -vinyl cyclopropane complex **15** (Scheme 9). Although ^1H NMR analysis of this solution at $-95\text{ }^\circ\text{C}$ 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 $-40\text{ }^\circ\text{C}$ led to decomplexation to form free vinyl cyclopropane **16** in 67% NMR yield from (*E*)-**5b** as a $\sim 3 : 1$ 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 $(\text{IPr})\text{AuCl}$ and AgSbF_6 in CD_2Cl_2 at $-80\text{ }^\circ\text{C}$. \blacktriangleleft

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 $-95\text{ }^\circ\text{C}$ 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

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Notes and references

‡ Fürstner has previously reported that attempted synthesis of the PCy₃-analogue of (*Z*)-**5a** via reaction of 1,1-diphenylcyclopropene with (PCy₃)PAuNTf₂ 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/AgSbF₆ produced a similar outcome.

§ Two discrete intermediates were detected by ¹H 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 AgSbF₆ in CD₂Cl₂ 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 ¹H 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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