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Substituent Effects and the Mechanism of Gold to Alkene Benzylidene Transfer Employing a Gold Sulfonium Benzylide Complex

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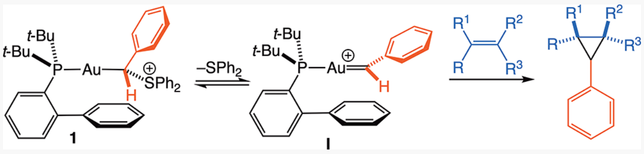

ABSTRACT: Aliphatic and aromatic alkenes react rapidly and efficiently with the gold sulfonium benzylide complex $[(\mathbf{P})\text{AuCHPh}(\text{SPh}_2)]^+\{\text{B}[3,5\text{-CF}_3\text{C}_6\text{H}_3]_4\}^-$ [**P** = P (*t*-Bu)$_2$*o*-biphenyl; **1**] at room temperature via the cationic two-coordinate gold benzylidene complex $[(\mathbf{P})\text{AuCHPh}]^+$ (**I**) to form phenycyclopropanes. The reactivity of *p*-substituted vinyl arenes toward **I** decreased with the decreasing electron donor ability of the vinyl arene ($\rho = -1.49 \pm 0.15$), and the reactivity of aliphatic alkenes toward **I** depended strongly on the number of alkyl groups attached to the more substituted alkene terminus. Benzylidene transfer to *cis*- and *trans*-*β*-methylstyrene occurred with complete retention of the alkene configuration. Benzylidene transfer to vinyl arenes led to predominant formation of *cis*-cyclopropanes (dr = 4.1: 1 to 13.9:1), whereas benzylidene transfer to aliphatic alkenes was generally less selective (dr = 1.3:1 to 5.1:1). All our experimental observations were consistent with a concerted, asynchronous, electrophilic benzylidene transfer mechanism. The diastereoselectivity of benzylidene transfer was interpreted in the framework of a transition state model involving a near *anti*-periplanar arrangement of the carbene Au═C and alkene C═C bonds.

■ INTRODUCTION

Cationic gold carbene complexes have been invoked as intermediates in numerous gold(I)-catalyzed transformations involving a diverse array of carbene precursors including diazo compounds, cyclopropenes, enynes, propargyl acetates, cycloheptatrienes, and simple alkynes in combination with a nucleophilic oxidant.[1,2] One of the most common pathways for the consumption of these gold carbene intermediates under catalytic conditions is via gold to alkene carbene transfer (cyclopropanation).[2] Despite prevalence of gold to alkene carbene transfer, our understanding of the mechanisms of these processes remains somewhat limited and is derived primarily from indirect experimental observations such as the product ratios, relative rates, and stereoselectivity[2] of catalytic reactions and from computational studies,[2−12] although no unified mechanism has emerged. Rather, these computational studies provide support for (1) concerted and stepwise pathways, (2) front-side or back-side displacement of the $(\text{L})\text{Au}^+$ fragment, and (3) a perpendicular, gauche, or *anti*-periplanar arrangement of the Au═C carbene bond and the alkene C═C bond in the transition state for carbene transfer. The preferred reaction pathway is presumably determined by the steric and electronic properties of the $(\text{L})\text{Au}^+$ fragment and the alkene.[2−12]

Motivated in part by the desire to gain insight into the mechanisms of gold to alkene carbene transfer, there has been considerable effort directed toward the synthesis of reactive, well-defined gold carbene complexes.[1] From these efforts, a small handful of weakly stabilized gold carbene complexes that undergo gold to alkene carbene transfer have been identified (Figure 1).[12−14] Unfortunately, these complexes have proven to be largely intractable for more detailed investigations of the mechanisms of gold to alkene carbene transfer owing to their extreme reactivity, thermal instability, and generation from strong Lewis acids.[12−14] As an alternative to these gold carbene complexes, we have recently demonstrated benzylidene transfer from the isolable gold sulfonium benzylide complex $[(\mathbf{P})\text{AuCHPh}(\text{SPh}_2)]^+\{\text{B}[3,5\text{-CF}_3\text{C}_6\text{H}_3]_4\}^-$ [**P** = P(*t*-Bu)$_2$*o*-biphenyl; **1**] to both aromatic and aliphatic alkenes within minutes at room temperature in solution without Lewis acid

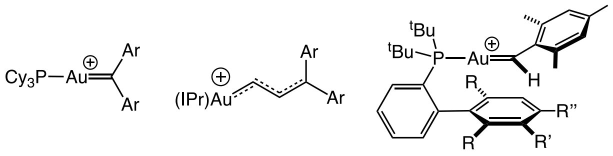

Figure 1. Well-defined gold carbene complexes that undergo carbene transfer to alkenes [Ar = 4-$\text{C}_6\text{H}_4\text{OMe}$; IPr = 1,3-bis(2,6-bis(diisopropylphenyl))imidazol-2-ylidene].

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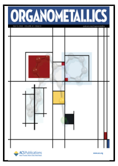

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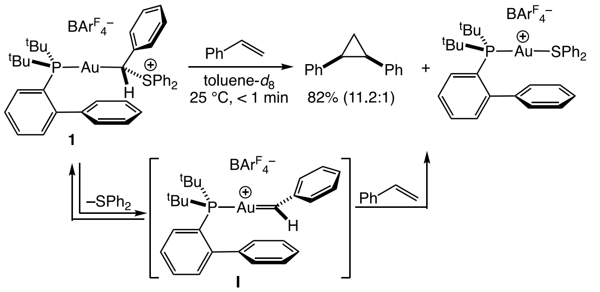
activation (Scheme 1).[15−19] Importantly, kinetic analysis of benzylidene transfer to styrene established a mechanism initiated by reversible sulfide dissociation from **1** to form the cationic, two-coordinate gold benzylidene complex **I** followed by irreversible benzylidene transfer to styrene (Scheme 1).[15]

Scheme 1. Gold to Alkene Benzylidene Transfer Employing the Gold Sulfonium Benzylide Complex 1



The facile generation of the gold benzylidene complex **I** from the thermally stable precursor **1** and subsequent benzylidene transfer to alkenes offer an opportunity to investigate the mechanisms of gold to alkene benzylidene transfer in solution while avoiding the complications associated with free carbene complexes. Gold to alkene benzylidene transfer is likewise not easily studied under catalytic conditions. For example, Echavarren et al. have demonstrated gold-catalyzed benzylidene transfer to alkenes employing 7-arylcycloheptatriene derivatives[20−22] or phenyldiazomethane[23] as carbene precursors. However, the temperatures required in the former transformation led to concomitant cis/trans isomerization of the resulting 1,2-diarylcyclopropanes, while the latter transformation was restricted to *p*-methoxystyrene as a carbene acceptor.[20−23] Herein, we report the effect of alkene substitution on the relative reactivity and diastereoselectivity of benzylidene transfer from **I** employing the gold sulfonium benzylide complex **1**. These efforts provide new insight into the mechanism and transition state geometry of gold to alkene carbene transfer.

■ RESULTS

Gold(I) to Alkene Benzylidene Transfer. To evaluate the effect of alkene substitution on the relative reactivity and diastereoselectivity of benzylidene transfer from **I**, the gold sulfonium benzylide complex **1** was treated with an excess (≥10 equiv each) of a mixture of two different alkenes in toluene at 25 °C for 3 h, and the reaction mixture was analyzed by GC. Product yields were determined in separate experiments via the reaction of **1** with a slight excess (~3 equiv) of a single alkene in either toluene or toluene-d_8 containing an internal standard followed by ^{1}H NMR or GC analysis of the crude reaction mixture. The major and minor diastereomers of the phenylcyclopropanes formed via benzylidene transfer from **I** were assigned unambiguously via ^{1}H NMR analysis and by comparison to the ^{1}H NMR spectra and GC traces of authentic samples of phenylcyclopropanes.

An initial set of experiments evaluated the effect of the electron donor ability of the alkene on the relative reactivity and diastereoselectivity of benzylidene transfer from **I** to the *para*-substituted vinyl arenes $H_2C{=}CH_2(4\text{-}C_6H_4R)$ (R = OMe, Me, H, Cl, and CN). The reactivity of the vinyl arenes toward **I** decreased by a factor of ~27 as the electron donor ability of the vinyl arene decreased from R = OMe to R = CN. A plot of $\log(k_X/k_H)$ versus the Hammett σ parameter was linear with a reaction constant of $\rho = -1.49 \pm 0.15$ (Figure 2, $R^2 = 0.97$), whereas a plot of $\log(k_X/k_H)$ versus the Hammett σ^+ parameter gave slightly poorer correlation ($R^2 = 0.94$). Benzylidene transfer to these *p*-substituted vinyl arenes formed predominantly the *cis*-cyclopropane with diastereomeric ratios ranging from 4.1:1 to 13.9:1. There was no obvious correlation between the diastereoselectivity of benzylidene transfer and the electron donor ability of the alkene. Although the diastereomeric ratio increased from 5.1:1 to 13.9:1 as the electron donor ability of the vinyl arene decreased from R = OMe to R = Cl (Table 1, entries 1−4), benzylidene transfer to the most electron-deficient vinyl arene (R = CN) formed a 4.1:1 mixture of *cis-*/*trans*-cyclopropanes (Table 1, entry 5). Periodic monitoring of reaction mixtures revealed no change in the diastereomeric ratio, arguing strongly against isomerization under reaction conditions.

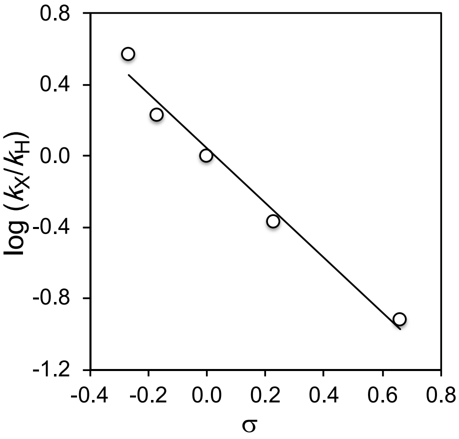
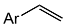
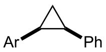
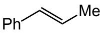
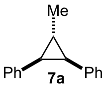
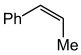
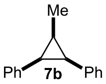
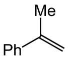
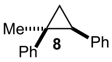
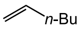
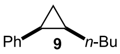
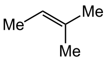
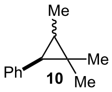
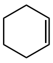
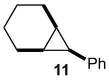
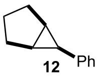
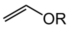
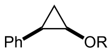
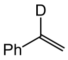
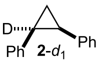
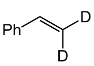
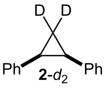


Figure 2. Plot of $\log(k_X/k_H)$ versus the Hammett σ parameter for benzylidene transfer from **1** to *p*-substituted vinyl arenes in toluene at 25 °C.

cis- and *trans-β*-Methylstyrene were nominally less reactive than styrene toward **I**, and both formed exclusively (≥20:1) the methyldiphenylcyclopropane diastereomer possessing a cis arrangement of phenyl groups with retention of the original alkene configuration (Table 1, entries 6 and 7). In comparison, *α*-methylstyrene was slightly more reactive than styrene toward **I** but was less diastereoselective (dr = 2.7:1; Table 1, entry 8). 1-Hexene was ~190 times less reactive toward **I** than styrene and was also less diastereoselective (dr = 2.7:1; Table 1, entry 9). However, the reactivity of aliphatic alkenes toward benzylidene transfer depended strongly on the number of alkyl groups attached to the more substituted alkene terminus. For example, 2-methyl-2-butene was ~210 times more reactive toward **I** than 1-hexene, whereas cyclopentene and cyclohexene were only ~2 times more reactive than 1-hexene (Table 1, entries 9−12). The diastereoselectivity of benzylidene transfer to these aliphatic alkenes ranged from 1.3:1 for 2-methyl-2-butene and cyclopentene to 5.1:1 for cyclohexene (Table 1, entries 10−12). Ethyl and *n*-butyl vinyl ethers were 1.4−1.9 times more reactive toward **I** than styrene and formed alkoxy phenylcyclopropanes with modest (~2:1) diastereoselectivity (Table 1, entries 13 and 14).

To probe the extent of C−C bond formation to the more and less substituted alkene carbon atoms in the transition state

Table 1. Relative Reactivities of Alkenes and Diastereoselectivities of the Reaction of the Gold Carbenoid Sulfonium Benzylide Complex 1 (6.1 mM) with Alkenes in Toluene or Toluene-d_8 at 25 °C for 3 h[a]

entry	alkene	cyclopropane[b]	rel reactivity	dr	yield (%)[c]
					
1	Ar = Ph	2	1.00 ± 0.01	11.21 ± 0.01	82[d]
2	Ar = 4-C_6H_4OMe	3	3.29 ± 0.03	5.11 ± 0.09	87[d]
3	Ar = 4-C_6H_4Me	4	1.48 ± 0.03	6.69 ± 0.01	67
4	Ar = 4-C_6H_4Cl	5	0.37 ± 0.06	13.92 ± 0.07	69
5	Ar = 4-C_6H_4CN	6	0.116 ± 0.004	4.10 ± 0.01	62
6		 7a	0.77 ± 0.03	≥20	74
7		 7b	0.75 ± 0.01	≥20	84
8		 8	1.11 ± 0.04	2.7 ± 0.1	88
9		 9	$5.3 \pm 0.2 \times 10^{-3}$	2.71 ± 0.02	76[d]
10		 10	1.12 ± 0.04	1.30 ± 0.02	82
11		 11	$1.07 \pm 0.04 \times 10^{-2}$	5.09 ± 0.04	79[d]
12		 12	$1.5 \pm 0.1 \times 10^{-2}$	1.32 ± 0.03	71
					
13	R = Et	13	1.9 ± 0.1	2.10 ± 0.01	83
14	R = *n*-Bu	14	1.41 ± 0.05	1.81 ± 0.02	76
15		 2-d_1	0.98 ± 0.02	10.63 ± 0.01	—
16		 2-d_2	0.96 ± 0.03	9.81 ± 0.01	—

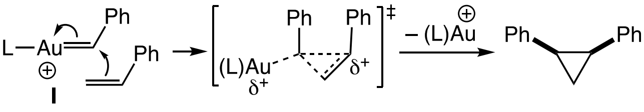
[a] See the Experimental Section for details. [b] Major diastereomer depicted if known. [c] Yield determined by GC analysis unless noted otherwise. [d] Yield taken from ref 15.

for benzylidene transfer from **I**, we determined the secondary kinetic isotope effects (KIEs) resulting from deuteration of the Cα or Cβ position of styrene (Table 1, entries 15 and 16). To this end, benzylidene transfer to α-deuteriostyrene occurred with a deuterium KIE of k_H/k_D = 1.02 ± 0.02, whereas benzylidene transfer to β,β-deuteriostyrene occurred with a deuterium KIE of k_H/k_D = 1.04 ± 0.03 (Table 1, entries 15 and 16.)

■ DISCUSSION

Aliphatic and aromatic alkenes and vinyl ethers react with the gold sulfonium benzylide complex **1** at 25 °C via the cationic gold benzylidene complex **I** generated via sulfide dissociation from **1** to form phenylcyclopropanes with modest to high cis selectivity.[15] All of our observations made in the context of the present study are consistent with a concerted, asynchronous mechanism for benzylidene transfer from **I** initiated by nucleophilic attack of the alkene on the electrophilic carbene carbon atom with more advanced C−C bond formation to the less substituted alkene carbon atom (or the β-carbon atom of a vinyl arene) and with concomitant positive polarization of the second alkene carbon atom (Scheme 2). Electrophilic cleavage of the (**P**)Au^+ fragment via the interaction of the Au−C bond with the nascent positively polarized alkene carbon atom then releases the cyclopropane.

Scheme 2. Proposed Mechanism for Benzylidene Transfer from I to Styrene

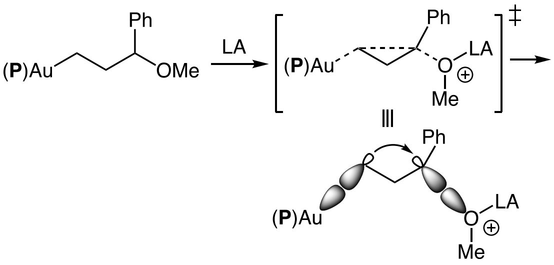


The negative reaction constant of $\rho = -1.49 \pm 0.15$ determined for benzylidene transfer to *p*-substituted vinyl arenes confirmed the electrophilic nature of the gold benzylidene complex **I** and established the accumulation of positive charge on the more substituted alkene carbon atom in the transition state for benzylidene transfer to these vinyl arenes. Further supporting this contention, electron-neutral and electron-rich vinyl arenes, alkyl vinyl ethers, and 2-methyl-2-butene were considerably more reactive with respect to benzylidene transfer than 1-hexene. Conversely, available evidence argues against the accumulation of positive charge on both alkene carbon atoms. For example, both *cis*- and *trans*-β-methylstyrene were less reactive toward **I** than styrene (Table 1, entries 6 and 7), and similarly, the reactivity of cyclopentene and cyclohexene toward **I** was comparable to that of 1-hexene but much less than that of 2-methyl-2-butene (Table 1, entries 11 and 12).

Despite the positive polarization of the alkene in the transition state for benzylidene transfer from **I**, our experimental observations strongly support an asynchronous concerted mechanism in preference to a stepwise pathway involving a free carbenium ion. Key evidence in support of this contention includes (1) the modest reaction constant ($\rho = -1.49 \pm 0.15$) and superior fit of the rate data for benzylidene transfer to *p*-substituted vinyl arenes to the Hammett σ parameter as compared to the Hammett σ^+ parameter,[24] (2) the comparable reactivity of vinyl ethers and styrene toward **I**, and (3) the complete retention of the alkene configuration for benzylidene transfer to *cis*- and *trans*-β-methylstyrene.[25] The negligible secondary deuterium KIEs resulting from deuteration of either the styrene Cα (k_H/k_D = 1.02 ± 0.2) or Cβ (k_H/k_D = 1.04 ± 0.3) position point to an early transition state, consistent with the modest reaction constant for benzylidene transfer to *p*-substituted vinyl arenes.[26,27] For example, the cyclopropanation of styrene-d_8 with ethyldiazoacetate catalyzed by an iron porphyrin complex occurred with an inverse deuterium KIE of k_H/k_D = 0.87 ± 0.07, which was interpreted as resulting from $sp^2 \rightarrow sp^3$ rehybridization in the transition state for carbene transfer.[26]

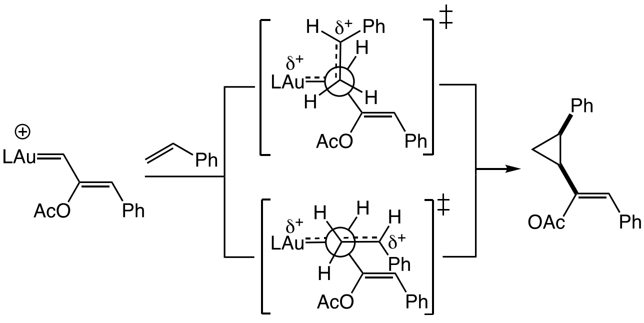
Transition State Geometry. A number of transition state geometries have been proposed and supported by computation for gold to alkene carbene transfer ranging from a perpendicular to an *anti*-periplanar arrangement of the Au═C and C═C bonds.[2−12] Relevant to this discussion of the transition state geometry for gold to alkene carbene transfer, we have recently reported the formation of cyclopropanes via ionization of (γ-methoxy)alkyl gold(I) complexes.[28] Isotopic labeling and related stereochemical experiments established the inversion of the configuration at the carbon atoms α and γ to gold, consistent with a W-shaped transition state involving electrophilic attack of the nascent electrophilic γ-carbon atom on the back lobe of the carbon−gold σ bond (Scheme 3), as has similarly been established for cyclopropanation of γ-functionalized alkyl iron complexes.[29−31] In a similar manner, the mechanism for gold to alkene benzylidene transfer from **I** depicted in Scheme 2 also involves electrophilic cleavage of the Au−C bond via the interaction with the nascent electrophilic γ-carbon atom to gold. For this reason, we posit that electrophilic displacement of (**P**)Au^+ in the transition state for gold to alkene benzylidene transfer from **I** also occurs via back-side displacement of the (**P**)Au^+ fragment via electrophilic attack of the γ-carbon atom on the back lobe of the Au−C bond.

Scheme 3. Lewis Acid-Mediated Cyclopropanation of a (γ-Methoxy)alkyl Gold(I) Complex through a W-Shaped Transition State



One of the first proposals regarding transition state geometry for gold to alkene carbene transfer was forwarded by Toste et al. in 2005 to rationalize the predominant formation of *cis*-cyclopropane in the gold-catalyzed cyclopropanation of styrene with propargylic acetates. This transition state model invoked a near perpendicular arrangement of the alkene C═C bond and the Au═C bond of the presumed gold vinylidene intermediate (Scheme 4).[32,33] The observed diastereoselectivity was presumed to result from unfavorable steric interactions between the alkene phenyl substituent and the gold-bound phosphine ligand in the transition state leading to the *trans*-cyclopropane that were absent in the transition state leading to the *cis*-cyclopropane. Although a perpendicular arrangement of the Au═C and C═C bonds would similarly account for the predominant formation of *cis*-1,2-diphenylcyclopropane via benzylidene transfer from **I** to styrene, the perpendicular arrangement of the alkene C═C bond and the carbene Au═C bond appears incompatible with the requirement for back-side displacement of the (**P**)Au^+ fragment through a concerted carbene transfer process.

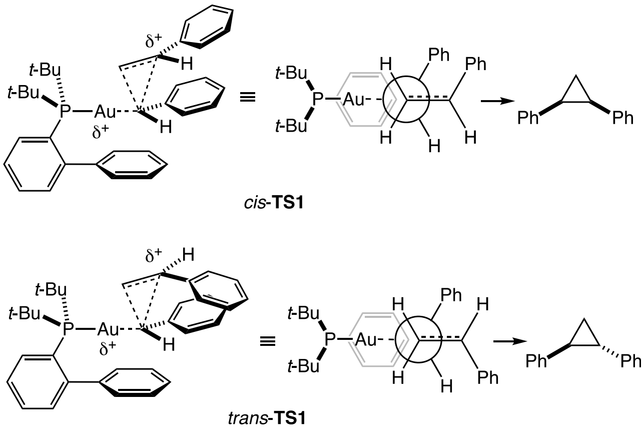
Scheme 4. Renditions of the Transition State Geometries for Vinylidene Transfer from (L)Au (L = PMe_3) to Styrene Proposed by Toste et al. (Top Pathway) and Derived Computationally by Soriano and Marco-Contelles (Bottom Pathway)



In contrast to the Toste model, computational modeling of the transition state for gold to styrene vinylidene transfer by Soriano and Marco-Contelles supported a near *anti*-periplanar arrangement of the carbene Au═C bond and the styrene C═C bond via a concerted yet highly asynchronous mechanism (Scheme 4).[10] In contrast to the Toste proposal, this transition state geometry is in accord with the requirement for back-side, electrophilic displacement of the (L)Au^+ fragment. Interestingly, preferential formation of the *cis*-cyclopropane was attributed to the presence of stabilizing $\pi-\pi$ stacking interactions in the transition state leading to the *cis*-cyclopropane that are absent in the transition state leading to the *trans*-cyclopropane (Scheme 4). Computational modeling of the transition state for vinylidene transfer from gold to 1-methylcyclopentene also predicted a nearly *anti*-periplanar arrangement of the carbene Au═C bond and the alkene C═C bond with a slight (1.8:1) preference for formation of the *cis*-cyclopropane.[10]

Echavarren et al. subsequently reported the computational analysis of the transition state for gold to alkene vinylidene transfer in the context of the gold-catalyzed cyclopropanation of alkenes with 7-vinyl 1,3,5-cycloheptatrienes (retro-Buchner).[9] This analysis both corroborated Soriano and Marco-Contelles' transition state model and provided insight into the influence of the P(t-Bu)$_2$$o$-biphenyl supporting ligand on the transition state geometry.[9] In particular, Echavarren et al.'s calculations supported a concerted, asynchronous mechanism with a near *anti*-periplanar arrangement of the carbene Au═C bond and the styrene C═C bond, through which stabilizing $\pi-\pi$ stacking and dispersion interactions are responsible for the preferential formation of *cis*-cyclopropanes. In this model, the vinylidene ligand adopts an orientation parallel to the protruding phenyl ring of the P(t-Bu)$_2$$o$-biphenyl (**P**) ligand, and the alkene approaches the carbene Au═C bond on the face opposite the blocking phenyl group.

The transition state model for benzylidene transfer from **I** to styrene depicted in Figure 3 is inspired by the models



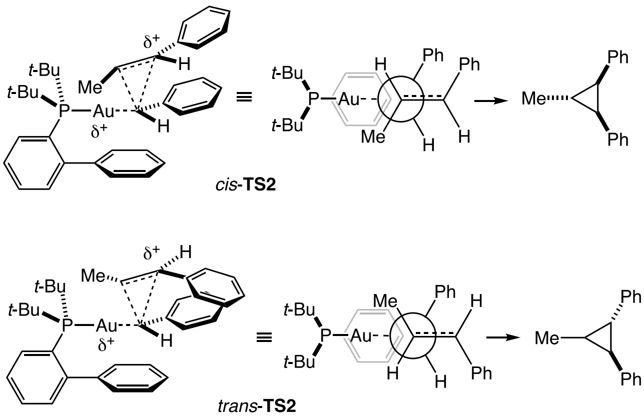
cis-**TS1**

trans-**TS1**

Figure 3. Proposed transition state geometries *cis*-**TS1** (favored) and *trans*-**TS1** (disfavored) for benzylidene transfer from **I** to styrene leading to *cis*- and *trans*-1,2-diphenylcyclopropane, respectively.

proposed by Soriano and Marco-Contelles and Echavarren et al. and accounts for most of our experimental observations regarding the effects of alkene substitution on the relative reactivity and diastereoselectivity of gold to alkene benzylidene transfer from **I** and also satisfies the condition of back-side displacement of the (**P**)Au$^+$ fragment. Salient features of the proposed transition state model include (i) the near *anti*-periplanar arrangement of the carbene Au═C bond and the alkene C═C bonds, (ii) the approximately parallel arrangement of the benzylidene phenyl group and the protruding phenyl ring of the *o*-biphenyl phosphine ligand, and (iii) attack of the alkene on the open face of the benzylidene ligand (Figure 3). The transition state leading to the *cis*-cyclopropane (*cis*-**TS1**) is presumably stabilized by $\pi-\pi$ interactions that are absent in the transition state leading to the *trans*-cyclopropane (*trans*-**TS1**). The experimentally determined 11.2:1 cis/trans ratio for benzylidene transfer from **I** to styrene at 25 °C corresponds to $\Delta\Delta G^{\ddagger}$ = 1.43 kcal/mol for *cis*-**TS1** relative to *trans*-**TS1** (Figure 3).

In addition to providing a rationale for the preferential formation of *cis*-cyclopropanes via benzylidene transfer to monosubstituted vinyl arenes, the transition state model depicted in Figure 3 accounts for the nominal stereochemical influence of the substituent on the alkene carbon atom proximal to gold, such as the C3 methyl substituent of 2-methyl-2-butene (Table 1, entry 10) or the methyl group of *cis*- and *trans*-*β*-methylstyrene (Table 1, entries 6 and 7). In these cases, the methyl substituent on the alkene carbon atom proximal to gold will experience a similar steric interaction with the phosphorus-bound *tert*-butyl groups in the transition state regardless of which alkene *π*-face attacks the carbene carbon atom (Figure 4). The transition state model depicted in Figure 3 also accounts for the nominal stereoselectivity observed for benzylidene transfer to monosubstituted aliphatic alkenes and enol ethers, owing to the absence of stabilizing $\pi-\pi$ stacking interactions (Table 1, entries 9, 13, and 14). Conversely, some aspects of stereocontrol for benzylidene transfer from **I** to alkenes are less obviously explained by the transition state model depicted in Figures 3 and 4. These observations include the low stereoselectivity for benzylidene transfer to *α*-methylstyrene and the good diastereoselectivity for benzylidene transfer to cyclohexene (Table 1, entries 8 and 11).



cis-**TS2**

trans-**TS2**

Figure 4. Proposed transition state geometries *cis*-**TS2** (favored) and *trans*-**TS2** (disfavored) for benzylidene transfer from **I** to *trans*-*β*-methylstyrene.

Comparisons to Other Carbene Transfer Processes. As noted above, the negative reaction constant of $\rho = -1.49 \pm 0.15$ determined for benzylidene transfer from **I** to *p*-substituted vinyl arenes confirmed the electrophilic nature of the gold benzylidene complex **I** and allows for meaningful comparisons to be made to a number of transition metal-mediated or catalyzed carbene transfer processes for which Hammett analyses have been performed. For example, the reaction constant determined for benzylidene transfer from **I** is more negative than those observed for alkene cyclopropanation with ethyl diazoacetate catalyzed by iron(II) ($\rho = -0.68 \pm 0.07$)[26] or rhodium(I) porphyrin complexes ($\rho \approx 0$),[27] or copper(I) pyrazolyl borate complexes (ρ = −0.85 to −1.2),[34,35] or for alkene cyclopropanation with the dichlorocarbene generated from phenyl(bromodichloromethyl)mercury ($\rho = -0.62 \pm 0.05$).[36] Conversely, the reaction constant determined for benzylidene transfer from **I** is similar to the value for alkene cyclopropanation with CH_2I_2 mediated by diethylzinc ($\rho = -1.61 \pm 0.05$)[37] and is less negative than that for alkene cyclopropanation with *gem*-dihalides mediated by copper ($\rho = -2.4 \pm 0.3$)[38] or for ethylidene transfer from the cationic iron ethylidene complex $Cp(CO)_2FeCHCH_3^+$ ($\rho^+ = -2.66$).[39] Worth noting is the slight attenuation of the reaction constant for benzylidene transfer from **I** relative to the value reported by Echavarren et al. for the tandem cycloisomerization/cyclopropanation of 1,6-enynes catalyzed by $[(\mathbf{P})Au(NCMe)]^+$ ($\rho = -1.9 \pm 0.3$).[4] This slight discrepancy may be attributed to the greater electronic stabilization provided by the phenyl group of **I** relative to the cyclopropyl group in the enyne cycloisomerization/cyclopropanation process.

Comparison to Benzylidene Transfer from $(CO)_5$WCHPh. In addition to benzylidene transfer from **I**, efficient benzylidene transfer to alkenes has been realized under mild conditions from well-defined tungsten,[40−44] iron,[45−47] chromium,[43,44] and ruthenium[45] benzylidene complexes. Most notably, Casey et al. and subsequently Doyle et al. investigated the effect of alkene substitution on the relative reactivity and diastereoselectivity of tungsten to alkene benzylidene transfer employing the pentacarbonyl tungsten benzylidene complex $(CO)_5$WCHPh (Table 2).[40−42] Similar to benzylidene transfer from **I**, available evidence for benzylidene transfer from $(CO)_5$WCHPh points to a concerted, asynchronous, electrophilic carbene transfer process with the accumulation of positive charge on the more substituted alkene carbon atom and with back-side electro-

Table 2. Relative Reactivities and Diastereoselectivities for Alkene Cyclopropanation with I at 25 °C and with $(CO)_5$WCHPh at −78 °C

	1		$(CO)_5$WCHPh	
alkene	rel reactivity[a]	dr	rel reactivity[a,b]	dr[b]
styrene	1.0	11	1.0	9.7
ethyl vinyl ether	1.9	2.1	41	7.6
n-butyl vinyl ether	1.4	1.8	54	5.8
cyclopentene	0.015	1.3	0.015	2.6
1-hexene	0.0053	2.7	0.011	0.84
2-methyl-2-butene	1.1	1.3	2.0	94

[a] Relative reactivities are not normalized between systems. [b] Data taken from refs 40−42.

philic displacement of the $(CO)_5W$ fragment.[40−42] As such, the data collected by Casey et al. and Doyle et al. on the one hand, and the data reported herein on the other, allow for the comparison between benzylidene transfer from early and late transition metal benzylidene complexes (Table 2).

Employing log/log plots, Doyle et al. established correlations between the alkene-dependent diastereoselectivity and reactivity of stoichiometric alkene cyclopropanation employing $(CO)_5WCHPh$ with the alkene-dependent diastereoselectivity and reactivity of rhodium-catalyzed alkene cyclopropanation employing phenyldiazomethane and $Rh_2(OAc)_4$ across the same series of alkenes.[42] These correlations suggested that the factors that control the reactivity and diastereoselectivity of alkenes toward benzylidene transfer were similar in both systems.[42] Conversely, analysis of similar log/log plots comparing the alkene-dependent reactivities and diastereoselectivities of benzylidene transfer from **I** to the alkene-dependent reactivities and diastereoselectivities of benzylidene transfer from $(CO)_5WCHPh$ revealed no obvious correlation in either case (Figures S1 and S2). The lack of correlation suggests, perhaps not unsurprisingly, that the factors that control the reactivity and diastereoselectivity of benzylidene transfer from **I** differ markedly from those that control the reactivity and diastereoselectivity of benzylidene transfer from $(CO)_5WCHPh$.

Analysis of the data collected in Table 2 points to some similarities and some key differences in the behavior of **I** and $(CO)_5WCHPh$ toward alkenes. For example, the relative reactivities of styrene, 1-hexene, cyclopentene, and 2-methyl-2-butene are similar in both systems (Table 2). Conversely, vinyl ethers were >40 times more reactive than styrene toward $(CO)_5WCHPh$, whereas vinyl ethers were less than twice as reactive as styrene toward **I** (Table 2), perhaps pointing to greater carbenium ion character in the transition state for benzylidene transfer from $(CO)_5WCHPh$ as compared to **I**. With respect to the effect of alkene substitution on the diastereoselectivity of benzylidene transfer, the most conspicuous difference between benzylidene transfer from $(CO)_5WCHPh$ and **I** is the strong stereochemical influence of the substituent on the less substituted alkene carbon atom in the former case and the general absence of such an influence in the latter case. This difference is exemplified by 2-methyl-2-butene, which undergoes benzylidene transfer from $(CO)_5WCHPh$ with 94:1 diastereoselectivity as compared to 1.3:1 diastereoselectivity in the case of benzylidene transfer from **I** (Table 2).[46,48] This difference points to the very different steric profiles of the $(CO)_5W$ fragment in the octahedral $(CO)_5WCHPh$ as compared to the $(\mathbf{P})Au^+$ fragment in the linear, two-coordinate gold complex.

■ CONCLUSIONS

We have analyzed the effects of alkene substitution on the relative reactivity and diastereoselectivity of gold to alkene benzylidene transfer from the two-coordinate gold benzylidene complex **I** employing the isolable gold sulfonium benzylide complex **1** as a convenient carbene precursor. The results of these studies were consistent with a concerted, asynchronous mechanism for benzylidene transfer from **I** initiated by nucleophilic attack of the alkene on the electrophilic carbene carbon atom with more advanced C−C bond formation to the less substituted alkene carbon atom of an aliphatic alkene or *β*-carbon atom of a vinyl arene and with concomitant positive polarization of the second alkene carbon atom. Electrophilic cleavage of the $(\mathbf{P})Au^+$ fragment via the interaction of the Au−C bond with the nascent positively polarized alkene carbon atom releases the cyclopropane.

Guided by computational modeling of the transition states for gold to alkene vinylidene transfer,[9,10] the diastereoselectivity of benzylidene transfer from **I** was interpreted in the framework of a transition state involving a near *anti*-periplanar arrangement of the Au═C carbene bond and the C═C alkene bond with alkene attack on the benzylidene *π*-face opposite the protruding phenyl group of the *o*-biphenylphosphine supporting ligand. According to this model, preferential formation of *cis*-cyclopropanes via benzylidene transfer from **I** to vinyl arenes can be attributed to stabilizing *π*−*π* interactions in the transition state leading to the *cis*-cyclopropane that are absent in the transition state leading to the *trans*-cyclopropane. This model also predicts that alkyl substitution at either alkene carbon atom will impart a minimal stereochemical influence on benzylidene transfer, in accord with experimental observations. The apparent lack of steric control of the diastereoselectivity of gold to alkene benzylidene transfer is presumably due to the linear, two-coordinate geometry of the gold benzylidene complex and the symmetric arrangement of the two phosphorus-bound *tert*-butyl groups. The absence of steric control of benzylidene transfer from **I** points to an inherent limitation to stereocontrol in gold to alkene carbene transfer processes involving aliphatic alkenes.

■ EXPERIMENTAL SECTION

General Methods. Reactions were performed under a nitrogen atmosphere employing standard Schlenk and glovebox techniques unless specified otherwise. NMR spectra were obtained on a Varian spectrometer operating at 400 MHz unless noted otherwise. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 30 m × 320 *μ*m polydimethylsiloxane capillary column and a flame ionization detector. An oven temperature gradient of 50−300 °C with a ramp rate of 20 °C/min was employed. Toluene-d_8 was dried over Na/benzophenone, distilled, and stored over 3 Å molecular sieves in a glovebox prior to use. Toluene was purified by passage through columns of activated alumina under nitrogen. All alkenes including deuterated styrenes (Sigma Aldrich) and all other reagents were obtained through major chemical suppliers and used as received. Complex **1** was synthesized employing a published procedure.[15] A cis/trans mixture of **2** was obtained from Alfa Aesar. Authentic samples of phenylcyclopropanes **3**,[50,51] **4**,[51,52] and **5**[51,52] were isolated as mixtures of cis/trans diastereomers via the reaction of the appropriate *α*,*β*-unsaturated ketone with hydrazine and NaOH (Kishner reaction) employing the procedure reported by Casey et al.[41] Cyclopropane **6** was synthesized as a cis/trans mixture via copper-mediated cyanation of **5** employing the procedure reported by Hixson and Garrett.[49,51] Cyclopropanes **7a**,[50] **7b**,[53] **8**,[54] **9**,[41,55] **10**,[41] **11**,[56] **12**,[41] **13**,[41] and **14**[41] were isolated from the stoichiometric reaction of **1** with the corresponding alkene employing a published procedure.[15] Reported errors correspond to the standard deviation of triplicate GC measurements applying standard methods for propagation of error (see the Supporting Information).

Relative Alkene Reactivity and Diastereoselectivity of Benzylidene Transfer. Toluene solutions of styrene (50 *μ*L, 1.22 M, 6.1 × 10^{-2} mmol) and *p*-methoxystyrene (50 *μ*L, 1.22 M, 6.1 × 10^{-2} mmol) were added simultaneously to a solution of **1** (10 mg, 6.1 × 10^{-3} mmol) in toluene (2 mL), and the resulting solution was stirred at 25 °C for 3 h. GC analysis of the resulting mixture revealed peaks corresponding to *cis*-**2** (6.923 min), *trans*-**2** (7.591 min), *cis*-**3** (8.491 min), and *trans*-**3** (9.156 min) in an 11.2:1.0:20.4:4.0 area ratio (Tables S1−S3). The reactivity of *p*-methoxystyrene ($R_{p\text{-methoxystyrene}}$) relative to styrene ($R_{\text{styrene}}$) was obtained by dividing the area of the GC peaks corresponding to **3** [$A_3 = cis\text{-}\mathbf{3} + trans\text{-}\mathbf{3}$] by the area of the GC peaks corresponding to **2** [$A_2 = cis\text{-}\mathbf{2} + trans\text{-}\mathbf{2}$] after correcting for the response factors for **2** (RF_2) and **3** (RF_3) relative to pentadecane (see below) according to the formula $(R_{p\text{-methoxystyrene}})/(R_{\text{styrene}}) = (A_3/RF_3)/(A_2/RF_2) = [(20.4 + 4.0)/(0.84)]/[(11.2 + 1.0)/(1.38)] = 3.29 \pm 0.03$ (Table 1, entry 2). The diastereoselectivities of benzylidene transfer to styrene and *p*-methoxystyrene (Table 1, entries 1 and 2) were determined from the area ratios $A_{cis\text{-}2}/A_{trans\text{-}2} = 11.21 \pm 0.01$ and $A_{cis\text{-}3}/A_{trans\text{-}3} = 5.11 \pm 0.09$, respectively.

The relative reactivities of *p*-methylstyrene, *p*-chlorostyrene, *p*-cyanostyrene, 2-methyl-2-butene, *cis*- and *trans*-*β*-methylstyrene, *α*-methylstyrene, and ethyl and *n*-butyl vinyl ethers toward benzylidene transfer were determined employing a procedure analogous to that used to determine the reactivity of *p*-methoxystyrene relative to styrene. The relative reactivities *α*-deuteriostyrene and *β*,*β*-dideuteriostyrene toward benzylidene transfer were determined relative to *p*-methylstyrene employing an analogous procedure. The relative reactivity of cyclopentene toward benzylidene transfer was determined from the reaction of cyclopentene (0.61 mmol), *p*-cyanostyrene (6.1×10^{-2} mmol, and **1** (6.1×10^{-3} mmol) in toluene at 25 °C for 3 h. The reactivity of cyclopentene ($R_{\text{cyclopentene}}$) relative to styrene (R_{styrene}) was determined according to the formula $(R_{\text{cyclopentene}})/(R_{\text{styrene}}) = [(A_{12}/RF_{12})/(A_6/RF_6)] \times ([p\text{-cyanostyrene}]/[\text{cyclopentene}]) \times [(A_6/RF_6)/(A_2/RF_2)] = 1.25 \times 0.10 \times 0.116 = 1.5 \pm 0.1 \times 10^{-2}$ (Table 1, entry 12). The relative reactivities of 1-hexene and cyclohexene were determined employing analogous procedures.

The diastereoselectivities of benzylidene transfer to all alkenes except *α*-methylstyrene were determined by GC analysis of the competition experiments described above. The diastereoselectivity of benzylidene transfer to *α*-methylstyrene was determined by ^{1}H NMR analysis of the crude reaction mixture generated from the reaction of **1** (10.0 mg, 6.11×10^{-3} mmol) with *α*-methylstyrene (2.17 mg, 1.83×10^{-2} mmol) in toluene-d_8 (1 mL) at 25 °C for 3 h. The diastereomeric ratio of **8** was determined by integrating the singlets at *δ* 1.91 and 1.16, corresponding to cyclopropyl methyl groups of *cis*-**8** and *trans*-**8**, respectively.

Yields of Gold to Alkene Benzylidene Transfer. A solution of **1** (10 mg, 6.1×10^{-3} mmol), *p*-methylstyrene (2.17 mg, 1.83×10^{-2} mmol), and pentadecane (1.30 mg, 6.1×10^{-3} mmol) in toluene (1 mL) was stirred at 25 °C for 3 h, and the solution was analyzed by GC. The yield of cyclopropane **4** was determined from the areas of the GC peaks corresponding to **4** ($A_4 = A_{cis\text{-}4} + A_{trans\text{-}4}$) and pentadecane ($A_{PD}$) at 6.569 min and from the response factor of **4** (RF_4) relative to pentadecane according to the formula yield of **4** (%) $= [(A_4/RF_4)/A_{PD}] \times 100$. All yields of gold to alkene benzylidene transfer that were not previously reported[15] were determined employing analogous procedures.

GC Response Factors for Phenylcyclopropanes. A solution of **2** (cis/trans = 1/1, 97.9 mg, 0.504 mmol) and pentadecane (98.8 mg, 0.465 mmol) in methylene chloride (30 mL) was analyzed by GC. The response factor of **2** (RF_2) relative to pentadecane was determined from the area of the peaks corresponding to **2** ($A_2 = A_{\mathbf{cis\text{-}2}} + A_{\mathbf{trans\text{-}2}}$) and pentadecane ($A_{PD}$) according to the formula $RF_2 = (A_2/[\mathbf{2}])/(A_{PD}/[\text{pentadecane}]) = 1.38 \pm 0.008$. Response factors for all remaining cyclopropanes were determined employing analogous procedures (Table S1). Isomeric phenylcyclopropanes were assumed to possess the same RF.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.2c00097.

Correlations plots, tables of data, and error analysis (PDF)

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Notes

The authors declare no competing financial interest.

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