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Direct Observation of Aryl Gold(I) Carbenes that Undergo Cyclopropanation, C–H Insertion, and Dimerization Reactions

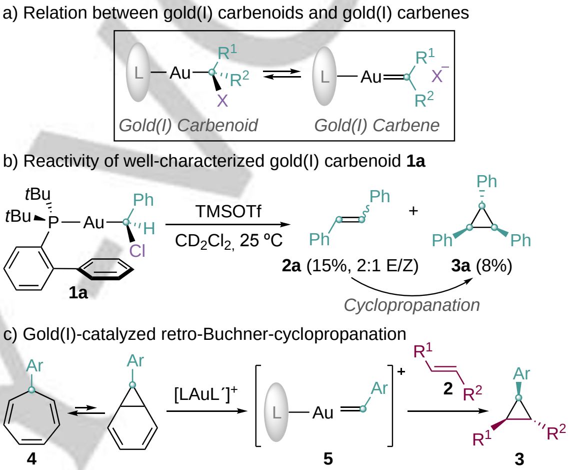
Cristina García-Morales,[a,b] Xiao-Li Pei,[a] Juan M. Sarria Toro,[a] and Antonio M. Echavarren[a,b]*

Dedication ((optional))

Abstract: *Mesityl gold(I) carbenes lacking heteroatom stabilization or shielding ancillary ligands have been generated and spectroscopically characterized from chloro(mesityl)methylgold(I) carbenoids bearing JohnPhos-type ligands by chloride abstraction with $GaCl_3$. The aryl carbenes react with PPh_3 and alkenes to give stable phosphonium ylides and cyclopropanes, respectively. Oxidation with pyridine N-oxide and intermolecular C–H insertion to cyclohexane have also been observed. In the absence of nucleophiles, a bimolecular reaction, similar to that observed for other metal carbenes, leads to a symmetrical alkene.*

Gold(I) carbenes have attracted great interest from the outset of the homogeneous gold catalysis era[1] and have been the center of debate regarding their structures and, in particular, the degree of stabilization provided by the π-backdonation from gold(I) to carbon.[2,3] Indeed, recent studies on well-characterized gold(I) carbene complexes have shown that these species can be considered from metal-stabilized carbocations to metal carbenes depending on the nature of the ancillary donating ligand(s) on gold(I).[3,4,5,6,7] However, these stabilized complexes require the presence of heteroatoms[4] or highly conjugated systems[5] at the carbene moiety and shielding ancillary ligands[6] or bidentate phosphines[7] at the metal center and, with very few exceptions,[8] do not display the reactivity proposed for the intermediate species involved in catalysis.

Metal carbenoids are species in which the metal is bound to a sp^3 carbon bearing a good leaving group that can generate a metal carbene upon ionization (Scheme 1a).[3a, 9] Based on this relationship, we have recently developed a method for the preparation of chloromethylgold(I) carbenoids that after chloride abstraction display typical reactivity of gold(I) carbenes in solution.[10] During the course of our investigation, preliminary results suggested that [JohnPhosAuCHPhCl] (**1a**), after chloride abstraction, generates stilbene (**2a**), which undergoes cyclopropanation by an undetected phenyl gold(I) carbene intermediate (Scheme 1b).[10] The observed cyclopropanation closely resembles the reactivity displayed by aryl gold(I) carbenes **5** generated by gold(I)-catalyzed retro-Buchner reaction of cycloheptatrienes **4** (Scheme 1c).[11] Although these arylidene complexes (**5**) have never been observed in solution, such species have been detected in the gas phase.[12,13]

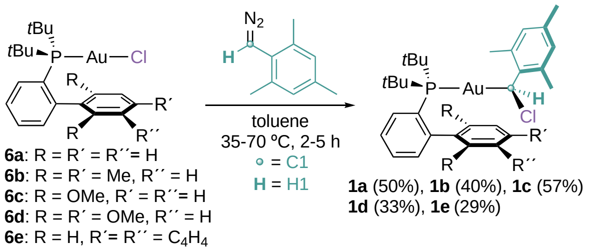

a) Relation between gold(I) carbenoids and gold(I) carbenes

b) Reactivity of well-characterized gold(I) carbenoid **1a**

c) Gold(I)-catalyzed retro-Buchner-cyclopropanation

Scheme 1. General concepts and reactivity of [JohnPhosAuCHPhCl] (**1a**) carbenoid.

Herein, we report the generation and spectroscopic characterization of mesityl gold(I) carbenes from stable carbenoids **1a**-**e** bearing JohnPhos-type ligands. These gold(I) carbenes display the same reactivity towards alkenes as the intermediates of the retro-Buchner reaction and many other gold(I)-catalyzed transformations.[11] Importantly, the gold(I) carbenes undergo bimolecular homocoupling to form the corresponding symmetrical alkene, by a process reminiscent to that shown by electrophilic and nucleophilic metal carbenes.



Scheme 2. Synthesis of chloro(mesityl)methylgold(I) carbenoids **1a**-**e**.

Gold(I) carbenoids **1a**-**e** were obtained by reaction of complexes **6a-e** with mesityl diazomethane, and their structures were confirmed by X-ray diffraction (Scheme 2).[14]. Remarkably, upon addition of $GaCl_3$ to carbenoid **1a** in CD_2Cl_2 at -90 ºC, the solution turned deep red suggesting the formation of mesityl gold(I) carbene **5a**, which could be characterized by NMR techniques (Table 1). Although gold(I) carbenoids bearing JohnPhos and different substitution patterns in the aryl group were tested under the same conditions, the generation of gold(I) carbenes could not

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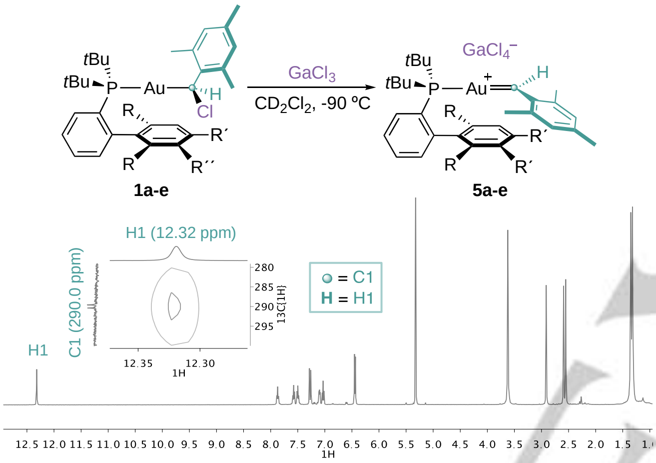
be detected by NMR in those cases.[15] Although **5a** partially decomposed at -90 ºC, mesityl gold(I) carbenes **5b-e** were stable until -70 ºC. These are the first monosubstituted gold(I) carbenes that have been characterized spectroscopically. Complexes **5a-e** present a characteristic signal in ^{1}H NMR at δ 11.74-12.67 ppm corresponding to H1 (Scheme 3, Table 1). The carbenic carbons (C1) resonate at δ 284.6-290.0 ppm as a doublet (^2J (^{13}C-^{31}P) = 96.8 – 99.8 Hz), within the range of previously characterized gold(I) carbenes (225-321 ppm).[4,5,6,7] In addition, clear correlations between the carbenic carbon (C1) and proton (H1) were observed in the ^{1}H-^{13}C HSQC spectra.[16] DFT calculations for **1b´-c´** and **5b´-c´** complexes at the B3LYP-D3/6-31G(d,p) + SDD(Au) level of theory led to computed ^{1}H NMR, ^{13}C NMR chemical shifts for H1, C1 and ^1J(^{1}H1-^{13}C1) constants consistent with the experimental results (Table 1). Furthermore, mesityl gold(I) carbenes **5a-e** were detected in gas phase by ESI-MS from carbenoid complexes **1a-e**.



Scheme 3. Generation of mesityl gold(I) carbenes **5a**-**e**. ^{1}H NMR and selected region of ^{1}H-^{13}C HSQC spectra of gold(I) carbene **5c** in CD$_2$Cl$_2$ at -90 ºC.

Table 1. Selected measured and calculated NMR data.[a]

Complex	Method	H1 (ppm)	C1 (ppm)	^1J (^{1}H1-^{13}C1) (Hz)
5a	Exp[b]	12.35 (4.92)	290.0 (69.7)[d]	-
	DFT[c]	12.12 (4.22)	280.8 (72.2)	125.2 (144.2)
5b	Exp[b]	12.67 (4.28)	287.9 (71.8)	129.8 (143.9)
	DFT[c]	12.17 (4.24)	280.2 (71.2)	124.4 (143.4)
5c	Exp[b]	12.32 (4.17)	290.0 (73.7)	127.8 (144.3)
	DFT[c]	12.09 (4.30	278.9 (75.4)	126.1 (144.6)
5d	Exp[b]	12.57 (4.24)	289.0 (71.4)[d]	-
	DFT[c]	12.03 (4.69)	274.6 (74.0)	125.6 (144.4)
5e	Exp[b]	11.74 (3.26)	284.6 (70.7)[d]	-
	DFT[c]	11.06 (-)	272.4 (-)	125.4 (144.4)

[a] Data for the corresponding carbenoid precursor in parenthesis. [b] -90 ºC in CD$_2$Cl$_2$. [c]Computed at 25 ºC in CH$_2$Cl$_2$. [d] 25 ºC in toluene-*d*$_8$.

The calculated structure **5c'** shows the mesitylidene fragment parallel to the lower ring of the biaryl ligand plane (Figure 1, top).[17] The computed Au-C1 (2.026 Å) and C1-C2 (1.401 Å) bond distances for **5c'** are slightly shorter than those for carbenoid precursor **1c**, Au-C1 (X-ray: 2.085 Å, computed: 2.095 Å) and C1-C2 (X-ray: 1.498 Å, computed: 1.502 Å). The reactivity of electrophilic gold(I) carbenes is dominated by the LUMO orbital, which in the case of **5c´** is located over the occupied d$_{xz}$(Au) orbital at gold and the 2p$^\pi$-system of the carbene ligand (Figure 1, bottom left). A NBO analysis for **5c´** revealed two main electronic contributions involved in the π-orbital stabilization of C1. First, a small π-backdonation with d$_{xz}$(Au) to 2p$^\pi$(C1) donor-acceptor interaction (24.4 Kcal/mol) and 3.7% contribution of 2p$^\pi$(C1) in the corresponding NLMO (Figure 1, bottom right), along with a lone pair at C2 (2p$^\pi$(C2)) highly polarized towards C1 (23.5% on 2p$^\pi$(C1)).18 The calculated energy barrier to Au-C1 ($\Delta G^‡$ = 1.3 kcal/mol) and C1-C2 ($\Delta G^‡$ = 18.6 kcal/mol) bond rotation supported the low Au-C1 bond π-character and a significant C1-C2 π-bond. Although for these species the benzyl carbocation structure predominates, back-donation from gold is expected to be higher for other alkyl-substituted gold(I)-carbenes generated under catalytic conditions.

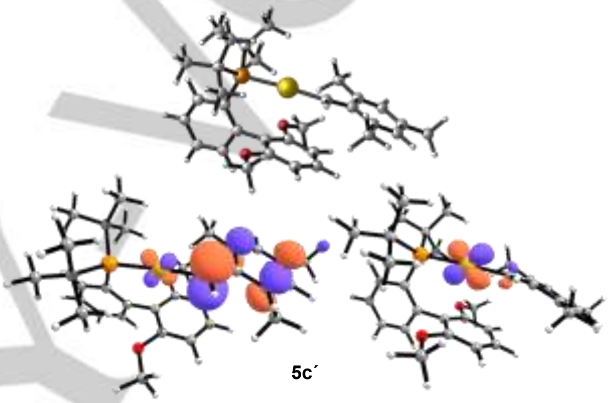
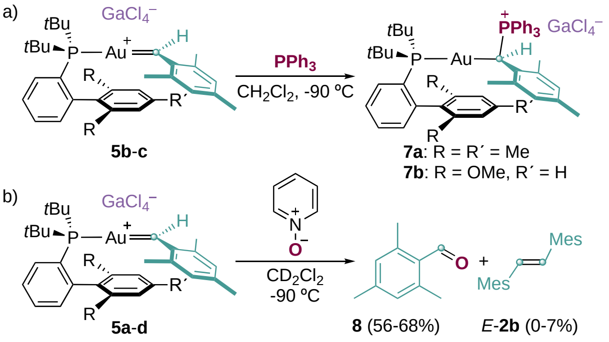


Figure 1. Top: Optimized geometry for carbene **5c´**. Bottom left: plot for the LUMO orbital for complex **5c´**. Bottom right: plot for the NLMO associated to Au-to-C1 π-backdonation for complex **5c´.** Cutoff: 0.05.

Gold(I) carbenes **5b-c** were trapped by PPh$_3$ at -90 ºC affording phosphonium ylide complexes **7a-b**, whose structures were confirmed by X-ray diffraction (Scheme 4a). Complexes **7a-b** resemble the phosphonium ylide gold adducts previously used to detect aryl gold(I) carbenes in gas phase.[12a-c,f,13] In our reactivity studies, small amounts of 2,4,6-trimethylbenzaldehyde (**8**) were detected corresponding to the oxidation of gold(I) carbenes with oxygen.[19] Indeed, we observed instantaneous formation of aldehyde **8** as the only organic product when oxygen was bubbled through solutions of gold(I) carbenes **5a-d** at -90 ºC.[20] Clean oxygen atom transfer also took place by treatment of **5a-d** with pyridine *N*-oxide at -90 ºC (Scheme 4b). Similar reactivity has been observed for other gold(I) carbenes.[5]



Scheme 4. a) Synthesis of phosphonium ylide complexes **7a-b**. b) Oxygen transfer from pyrine *N*-oxide. Yields determined by ^{1}H NMR using Ph$_2$CH$_2$ as internal standard. Mes = 2,4,6-trimethylphenyl.

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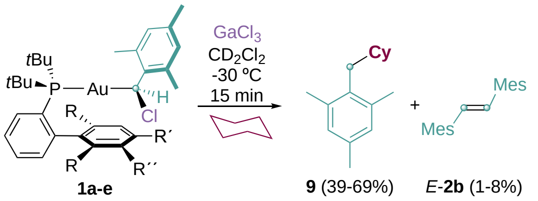
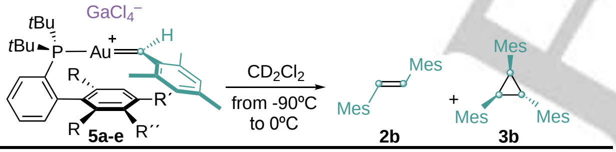
To date, none of the isolated gold(I) carbenes have been shown to undergo C–H insertion into alkanes. In contrast, gold(I) carbenes **5a**-**e**, generated at -30 ºC from **1a**-**e** in the presence of cyclohexane, undergo clean C–H insertion to give **9** in 39-69% yield (Scheme 5).



Scheme 5. Gold(I)-promoted C–H insertion. Yields determined by ^{1}H NMR using Ph$_2$CH$_2$ as internal standard. Mes = 2,4,6-trimethylphenyl.

In the reactions of **5a**-**d** with pyridine *N*-oxide and cyclohexane, traces of *E*-1,2-dimesitylethene (*E*-**2b**) were also detected (Schemes 4b and 5). Alkene *E*-**2b** was cleanly formed, together with the corresponding chloride-bridged digold(I) complexes (**10a**-**e**),[21] when solutions of **5a-e** in CD$_2$Cl$_2$ were warmed up from -90 ºC to -30 or 0 ºC (Table 2). Significant amounts of cyclopropane **3b** were also obtained in some cases (Table 1, entries 1,3, and 5). Analysis of the reactivity of gold(I) carbene **5c**[22a] shows that *E*-**2b** was initially formed between -70 and -40 ºC. Then, around -40 ºC, cyclopropane **3b** and small amounts of *Z*-**2b** were also detected. The formation of *E*-**2b** follows a second order dependence on the concentration of complex **5b**.[22b] Related bimolecular couplings to form symmetrical alkenes have been observed as common decomposition pathways for rhenium methylidenes,[23,24] ruthenium carbenes[25,26] as well as typical Fischer[27] and Schrock carbenes.[28]

Table 2. Alkene and cyclopropane formation.[a]

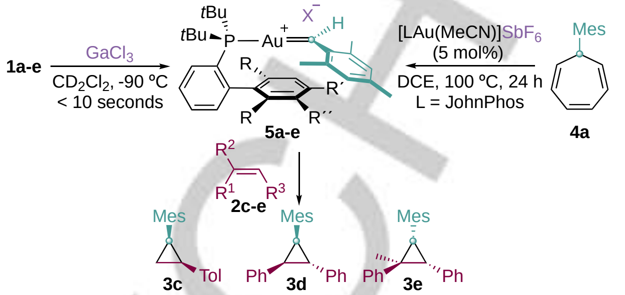


Entry	Complex	T [ºC]	**2b** [%]	*E*/*Z* ratio	**3b** [%]
1	**5a**	-10	25	12:1	36
2	**5b**	-20	68	> 60:1	< 1
3	**5c**	-10	27	9:1	39
4	**5d**	-30	62	> 60:1	< 1
5	**5e**	0	7	> 60:1	83

[a] ^{1}H NMR yields using 1,3,5-tris(trifluoromethyl)benzene as internal standard. Mes = 2,4,6-trimethylphenyl.

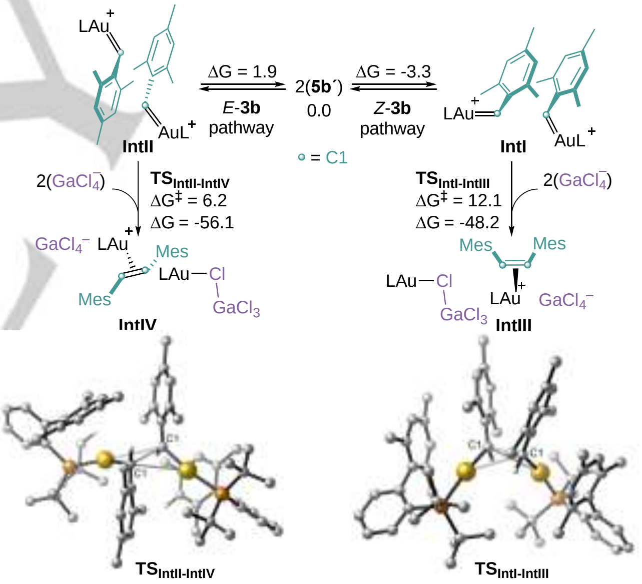
As suggested by the competitive cyclopropanation observed in the formal dimerization of the carbene fragments leading to **2b** (Table 2), substituted alkenes **2c**-**e** readily react at -90 ºC with gold(I) carbenes **5a-e** to form the corresponding cyclopropanes **3c**-**e** (Table 3, entries 1-5).[29] Importantly, the gold(I)-catalyzed retro-Buchner reaction[11,30] of aryl cycloheptatriene **4a** in the presence of alkenes **2c**-**d** also leads to cyclopropanes **3c**-**e** (Table 3, entry 6), which strongly suggests that mesityl gold(I) carbene **5a** is also generated under catalytic conditions. The lower yields of **3c**-**e** obtained under catalytic conditions can be explained by the steric hindrance introduced by the mesityl group in the rate-determining cleavage of the cyclopropane bond of the norcaradiene in tautomeric equilibrium with the cycloheptatriene.

Table 3. Cyclopropanation by carbenes **5a-e** from carbenoids **1a**-**e** (left) or through decarbenation of **4a** (right).[a]



Entry	Precursor	**3c** [%][b]	**3d**	**3e**[b]
1	**1a**	99	80	99 (2.3:1)
2	**1b**	87	90	99 (3:1)
3	**1c**	99	99	99 (1:1.2)
4	**1d**	99 (1:1.5)[31]	99	72 (1:2.1)
5	**1e**	99	90	99 (3.5:1)
6	**4a**	32	38	17 (1:7.5)

[a] ^{1}H NMR yields using Ph$_2$CH$_2$ as internal standard. [b] Diastereomeric ratio in parenthesis. DCE = 1,2-dichloroethane, Mes = 2,4,6-trimethylphenyl.



Scheme 6. Calculated reaction profile for the bimolecular coupling of gold(I) carbene **5b´**. L = MeJohnPhos. DFT calculations were carried out at the B3LYP-D3/6-31G(d,p) + SDD on Au and Ga. CH$_2$Cl$_2$ was represented with the PCM. Free energies in Kcal/mol.

To get a deeper insight into the mechanism of this rate-limiting bimolecular coupling, we performed DFT calculations with carbene **5b´** (Scheme 6). Our calculations suggest that association complex **IntI**, which is stabilized by face-to-face π-π interactions between the two mesitylidenes fragments and shows a relatively short C1-C1 distance (3.13 Å), is preferentially formed (ΔG = -3.3 kcal/mol) and can evolve through **TS$_{IntI-IntIII}$** (ΔG‡ = 12.1 kcal/mol) to form (η^2-*Z*-**5a**)gold(I) complex (**IntII**) in a highly exothermic process (ΔG = -48.2 kcal/mol). Alternatively, less stable association complex **IntII** (ΔG = 1.9 kcal/mol), with the optimal orientation of the mesitylidenes for *trans*-C1-C1 bond formation, can evolve *via* $\mathbf{TS}_{\mathbf{IntII-IV}}$ ($\Delta G^{\ddagger}$ = 6.2 kcal/mol) to form *E*-**2b**. At -35 ºC, the calculated *E*/*Z*-**2b** ratio ($\Delta\Delta G^{\ddagger}$= 0.6 kcal/mol, 3:1 *E*/*Z*) is in close agreement with the experimental results (2.4:1 *E*/*Z*). Related mechanisms have been proposed for the formation of alkenes from rhenium[23] and ruthenium[25] carbenes.

We also examined theoretically the reaction pathways for the cyclopropanation of *Z*-**2b** and *E*-**2b** by gold carbene **5b**´.[32] As we have found before for intermolecular cyclopropanations of intermediate gold(I) carbenes,[33] these reactions proceed by an asynchronous concerted mechanism with an activation barrier for *E*-**2b** ($\Delta G^{\ddagger}$ = 12.7 kcal/mol), 8.5 kcal/mol lower than that for *Z*-**2b** ($\Delta G^{\ddagger}$ = 21.2 kcal/mol).[32]

In summary, we have generated and characterized spectroscopically monosubstituted gold(I) carbenes for the first time in solution, which undergo representative transformations of intermediate gold(I) carbenes formed under catalytic conditions such as cyclopropanation, oxidation, and C−H insertion reactions. These aryl gold(I) carbenes correspond to the intermediates generated in the gold(I)-catalyzed decarbenation of cycloheptatrienes (retro-Buchner reaction). In the absence of other reagents, we observed dimerization to form preferentially the *E*-configured alkene by a process similar to that followed by other well-known metal carbenes, which places these highly electrophilic species among the metal carbene family, despite the weak back donation from gold(I) to the carbenic carbon.

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Keywords: carbenes • carbenoids • gold • cyclopropane • C−H insertion

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[14] CCDC 1887058 (**1a**), CCDC 1887068 (**1b**), CCDC 1887061 (**1c**), CCDC 1887064 (**1d**), CCDC 1887062 (**1e**), CCDC 1887059 (**7a**), CCDC 1887060 (**7b**), CCDC 1887067 (**10a**), CCDC 1887065 (**10c**), CCDC 1887063 (**S1**), CCDC 1887066 (**S2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] See Supporting Scheme S1 for alternative gold(I) carbenoids tested.

[16] See Supporting information for spectroscopy characterization for carbenes **5a**-**e**.

[17] Supporting information: Optimized structures and structural discussion on carbenes **5a**-**e** can be found in Figure S17 and Table S15.

[18] See Supporting information Figure S32: plot for the NLMO associated to lone pair at C2 ($2p^{\pi}$(C2)) for **5c**´.

[19] Oxidation of gold(I) carbenes under air: H. Zhan, L. Zhao, J. Liao, N. Li, Q. Chen, S. Qiu, H. Cao, *Adv. Synth. Catal.* **2015**, *357*, 46–50.

[20] Supporting information: See Scheme S1 for further information.

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[29] Cyclopropane **3b** undergoes partial cis to trans isomerization in the presence of $GaCl_3$, and therefore, the diastereoselectivity varies along the experiments.

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[31] The diastereomeric ratio can vary from along the experiment because small amounts of $GaCl_3$ can catalyze the isomerization of *cis*-**3c** to *trans*-**3c** (see supporting information Table S3).

[32] Supporting information: See Figures S31 and S33 for further DFT details.

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