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Theoretical Study on the Ring-Opening Reactions of Cyclopropenes Mediated by a Au^{I} Complex

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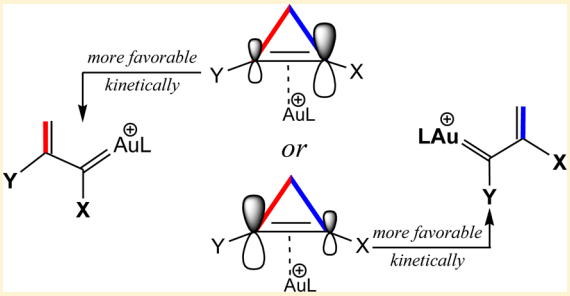
Supporting Information

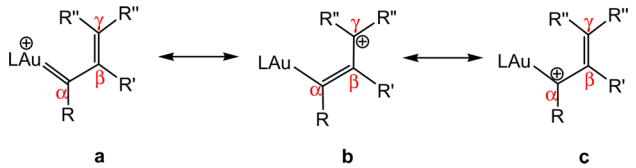
ABSTRACT: DFT calculations have been carried out in order to rationalize and predict the ring-opening regioselectivity of substituted cyclopropenes in the presence of gold(I) catalysts. It has been shown that the regioselectivity of these ring-opening processes is driven by the relative π-donor ability of the substituents on the cyclopropene double bond (C1 and C2). A stronger π-donor substituent at C2 favors Au(I)-induced polarization of the double bond toward C1, resulting in preferential breaking of the C1−C3 bond. An excellent correlation between $\Delta E^{\ddagger}$ and the difference in the C1−C2 p(π) orbital population was observed for a broad range of substituents, providing a useful predictive model for gold-induced cyclopropene ring-opening. Furthermore, it was found that the stability of the resulting gold-stabilized allyl-cation intermediates do not follow the same trend as the ring-opening reaction energies. Generally, the more facile ring-opening process led to the less thermodynamically stable intermediate, which lacked stabilization of the carbocation by a π-donor in the α-position.



INTRODUCTION

Cyclopropenes have been widely used as substrates for a broad range of transition-metal-catalyzed reactions;[1] however, their reactivity with gold catalysts has only been investigated since 2008.[2] Cyclopropenes have proven to be excellent substrates for homogeneous gold complexes and one of their most typical modes of reactivity involves rapid ring-opening reactions to provide an organogold intermediate. This intermediate can be considered as a hybrid between a gold carbenoid **a** and gold-stabilized allyl cations **b** and **c** (Scheme 1). The ring-opened organogold intermediates can undergo cationic reactivity associated with **b** (or **c**), such as nucleophilic addition with alcohols,[3] thiols,[4] amines, and aromatic systems.[5] Alternatively, carbenoid-type reactivity associated with **a** is observed in reactions such as cyclopropanation.[3a,6]

Scheme 1



We recently reported a facile gold-catalyzed rearrangement of cyclopropenylmethyl acetates to (*Z*)-acetoxydienes, which proceeded via a C2−C3 ring-opening process to give organogold intermediate **2** (Figure 1).[7] This intermediate then underwent nucleophilic attack by the pendant acetate, thereby displaying cationic reactivity. Cossy and Meyer demonstrated that related cyclopropenes **4** without a C1 substituent underwent an alternative ring-opening via the C1−C3 bond to give organogold intermediate **5**. Interestingly, this intermediate displayed carbenoid-type reactivity by undergoing cyclopropanation with the pendant allyl group.[6] This substituent-dependent switch in ring-opening regioselectivity prompted us to initiate a theoretical investigation into the directing effect of the cyclopropene C1 and C2 substituents. Given the range of reactivity associated with organogold intermediates such as **2** and **5**, guiding principles regarding the effect of cyclopropene substituents on the regiochemistry of gold-catalyzed ring-opening would represent an important toolkit of information for the synthetic community. Herein, we show that the kinetics of the gold-catalyzed ring-opening process is governed by the relative π-donor ability of the substituents on the cyclopropene double bond and that

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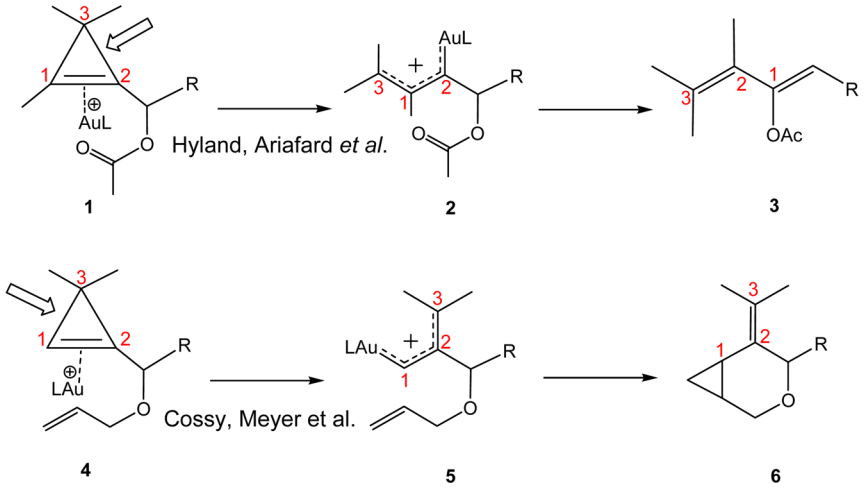


Figure 1. Examples showing the effect of substituents at C1 and C2 on the gold catalyzed ring-opening regioselectivity of cyclopropenes.

thermodynamic stability of the resulting organogold intermediates is a function of the π-basicity of the α-substituent.

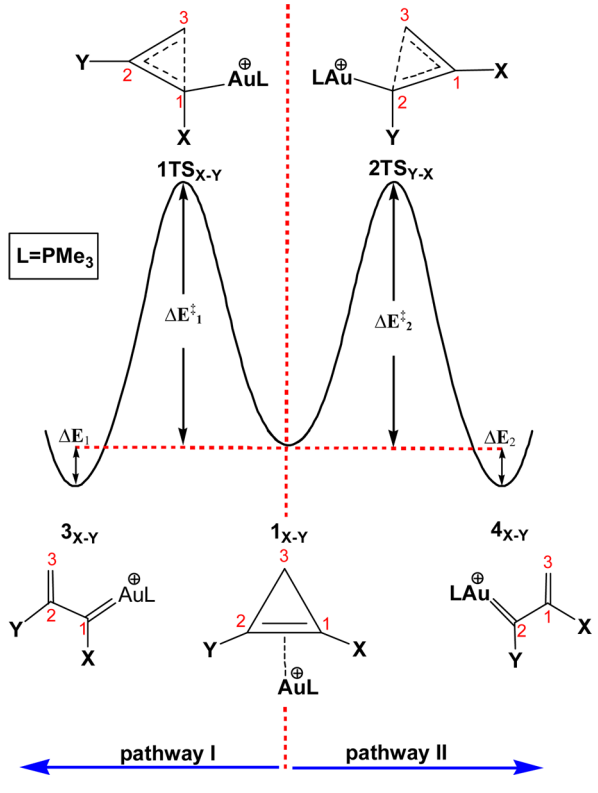
COMPUTATIONAL DETAILS

Gaussian 09[8] was used to fully optimize all the structures reported in this paper at the B3LYP level of density functional theory (DFT).[9] The effective-core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ)[10] was chosen to describe Au. The 6-31G(d) basis set was used for other atoms.[11] A polarization function of ξ_f = 1.050 was also added to Au.[12] This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory as those for the structural optimization. Transition states were located using the Berny algorithm. Intrinsic reaction coordinate (IRC)[13] calculations were used to confirm the connectivity between transition structures and minima. To further refine the energies obtained from the B3LYP/BS1 calculations, we carried out single-point energy calculations for all of the structures with a larger basis set (BS2) in dichloromethane using the CPCM solvation model[14] at the B3LYP level. BS2 utilizes the quadruple-ζ valence def2-QZVP[15] basis set on Au and the 6-311+G(2d,p) basis set on other atoms. We have used the electronic energies obtained from the B3LYP/BS2//B3LYP/BS1 calculations in dichloromethane throughout the paper unless otherwise stated. The atomic orbital populations were calculated on the basis of natural bond orbital (NBO) analyses.[16]

RESULTS AND DISCUSSION

Kinetic Preference. To study the gold-catalyzed regioselectivity of cyclopropene ring-opening using DFT calculations, a range of unsymmetrical 1,2-disubstituted cyclopropenes were identified as representative substrates. We performed our calculations by using L = PMe_3 as the coordinated ligand to Au(I) for all the species involved in the ring-opening reaction. Various X and Y substituents for $\mathbf{1}_{X-Y}$ (Scheme 2) are considered, where X = H, Me, Ph and Y = H, Me, CH_2OH, $SiMe_3$, PH_2, OH, F, Cl, CN, Ph, p-$C_6H_4NO_2$. As depicted in Scheme 1, starting from $\mathbf{1}_{X-Y}$, two different pathways are conceivable for ring-opening (pathways **I** and **II**). In pathway **I**, the cleavage of the C1−C3 bond occurs through transition structure $\mathbf{1TS}_{X-Y}$ and leads to the formation of $\mathbf{3}_{X-Y}$. In comparison, in pathway **II**, the C2−C3 bond is cleaved and $\mathbf{4}_{X-Y}$ is formed by passing transition structure $\mathbf{2TS}_{X-Y}$. We have represented $\mathbf{3}_{X-Y}$ and $\mathbf{4}_{X-Y}$ as the gold carbenoid, but it is known that these intermediates display both cationic and carbene-type reactivity depending upon exact nature of L and other substituents.[2g]

Scheme 2



The activation energies for the ring-opening pathways **I** and **II** are represented by $\Delta E^{\ddagger}_1$ and $\Delta E^{\ddagger}_2$, respectively. The calculated $\Delta E^{\ddagger}_1$ and $\Delta E^{\ddagger}_2$ values for all substrates are listed in Table 1. The energy difference between $\Delta E^{\ddagger}_1$ and $\Delta E^{\ddagger}_2$ is represented by $\Delta E^{\ddagger}$ ($\Delta E^{\ddagger} = \Delta E^{\ddagger}_1 - \Delta E^{\ddagger}_2$) (Table 1). The $\Delta E^{\ddagger}$ values determine the kinetic preference for the ring-opening; positive values indicate that the cleavage of C2−C3 bond is preferred and negative values indicate that the cleavage of C1−C3 bond is favored.

It is interesting to note that, for X = H, the ring-opening, in most cases, occurs through pathway **I** (except for Y = $SiMe_3$), while for X = Ph, the ring-opening preferentially proceeds through pathway **II** (except for Y = OH). For X = Me, the regioselectivity of the ring-opening is dictated by the identity of the Y-substituents; pathway **I** is favored for Y = OH, Ph, F, and

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Table 1. Calculated Activation Energies (kcal/mol) for the Ring-Opening of All the Cyclopropenes Studied and the p_π Orbital Populations at C1 and C2 of $\mathbf{1}_{x\text{-}y}$ (See Scheme 2)

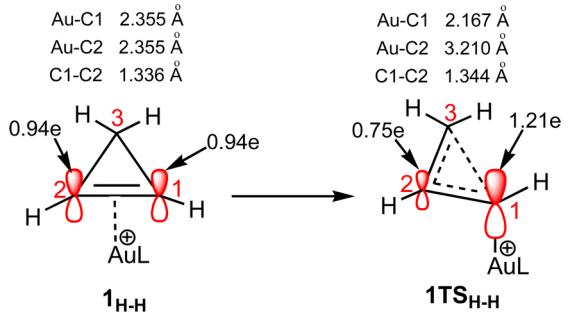
entry	X	Y	$\Delta E^{\ddagger}_1$	$\Delta E^{\ddagger}_2$	$\Delta E^{\ddagger} = \Delta E^{\ddagger}_1 - \Delta E^{\ddagger}_2$	p_π(C1)	p_π(C2)	$\Delta n = p_\pi(C1) - p_\pi(C2)$
1	H	OH	2.9	22.7	−19.8	1.31	0.68	0.63
2	H	Ph	4.8	18.1	−13.3	1.26	0.70	0.56
3	H	F	1.4	13.1	−11.7	1.22	0.72	0.50
4	H	*p*-$C_6H_4NO_2$	4.3	14.9	−10.6	1.23	0.71	0.52
5	H	Me	6.4	16.9	−10.5	1.08	0.78	0.40
6	H	Cl	3.8	12.7	−8.9	1.15	0.83	0.32
7	H	CH_2OH	6.7	13.3	−6.6	1.00	0.87	0.13
8	H	PH_2	8.5	13.3	−4.8	1.13	0.85	0.28
9	H	CN	11.4	11.7	−0.3	0.95	0.96	−0.01
10	H	$SiMe_3$	12.3	11.6	0.7	0.96	0.90	0.06
11	Me	OH	2.9	14.2	−11.3	1.21	0.75	0.46
12	Me	Ph	8.9	13.2	−4.3	1.10	0.84	0.26
13	Me	F	6.4	7.9	−1.5	1.06	0.87	0.19
14	Me	*p*-$C_6H_4NO_2$	12.0	12.3	−0.3	1.00	0.93	0.07
15	Me	Cl	9.6	8.3	1.3	0.96	1.02	−0.06
16	Me	CH_2OH	12.7	10.3	2.4	0.88	1.01	−0.13
17	Me	PH_2	14.5	9.7	4.8	0.90	1.07	−0.17
18	Me	$SiMe_3$	19.6	11.2	8.4	0.80	1.09	−0.29
19	Me	CN	18.4	7.9	10.4	0.82	1.10	−0.28
20	Ph	OH	4.6	9.7	−5.1	1.19	0.80	0.39
21	Ph	F	5.9	*a*		0.78	0.99	−0.21
22	Ph	Cl	10.5	3.5	7.0	0.76	1.17	−0.40
23	Ph	PH_2	16.7	7.6	9.0	0.78	1.23	−0.45
24	Ph	$SiMe_3$	22.0	12.1	9.9	0.72	1.27	−0.55
25	Ph	CN	21.4	7.3	14.1	0.70	1.26	−0.56

[a]The ring opening was calculated to occur without any barrier.

p-$C_6H_4NO_2$ substituents while pathway **II** is preferred for Y = Cl, CH_2OH, PH_2, $SiMe_3$, CN, and H substituents.

The electron distribution analysis during the reaction can help us to understand the origin of the regioselectivity of the ring-opening. Our calculations for the cyclopropene with X = Y = H show that in order for the C1−C3 bond to be broken, the C1−C2 π-bond should be polarized toward the C1 atom. The NBO analysis shows that in transition structure $\mathbf{1TS_{H-H}}$, due to this polarization, the population of C1 p(π) orbital increases by 0.27e while that of C2 p(π) decreases by 0.19e (Scheme 3).

Scheme 3



$\mathbf{1_{H-H}}$ $\mathbf{1TS_{H-H}}$

This indicates that the essential requirement for the ring-opening is the polarization of C1−C2 π-bond mediated by the Au catalyst. The result of this π-bond polarization is the shortening of the Au−C1 distance and the lengthening of the Au−C2 and C1−C2 distances (Scheme 3). This might viewed as a nucleophilic attack of the cyclopropene double bond onto AuL^+, which then results in concomitant C1−C3 bond breaking.

As depicted in Table 1, the regioselectivity of the ring-opening is controlled by the identity of the X and Y substituents. If the π-donor ability of Y is stronger than X, the C1−C2 π-bond is polarized toward the C1 atom and, as a result, the electron distribution of the π-bond in $\mathbf{1_{X-Y}}$ becomes more similar to $\mathbf{1TS_{X-Y}}$. In such a case, the transition structure $\mathbf{1TS_{X-Y}}$ is reached more easily than $\mathbf{2TS_{X-Y}}$ because a smaller change in the electron distribution of the π-bond is required. For example, the electron distribution of the π-bond in $\mathbf{1_{H-OH}}$ (entry 1) resembles that in $\mathbf{1TS_{H-OH}}$ due to the strong π-donor character of OH (Scheme 4). This effect causes $\mathbf{1TS_{H-OH}}$ to lie only 2.9 kcal/mol above $\mathbf{1_{H-OH}}$. In contrast, to reach the transition structure $\mathbf{2TS_{H-OH}}$, a large change in electron distribution of the π-bond is required (Scheme 4), leading to a high activation energy for ring-opening ($\Delta E^{\ddagger}_2$ = 22.7 kcal/mol). As such, C1−C3 bond breaking is favored for Y = OH.

Our calculations show that the energy difference between the transition structures $\mathbf{1TS_{X-Y}}$ and $\mathbf{2TS_{X-Y}}$ hinges on the population difference between the C1p(π) and C2p(π) orbitals of $\mathbf{1_{X-Y}}$. If the p(π) orbital population of C1 is larger than that of C2, $\mathbf{1TS_{X-Y}}$ is more stable than $\mathbf{2TS_{X-Y}}$ ($\Delta E^{\ddagger} < 0$) and if the p(π) orbital population of C1 is smaller than that of C2, $\mathbf{1TS_{X-Y}}$ is less stable than $\mathbf{2TS_{X-Y}}$ ($\Delta E^{\ddagger} > 0$). The absolute amount of the $\Delta E^{\ddagger}$ value (Table 1) depends on how strong the π-donor ability of Y relative to X is. The stronger the π-donor ability of Y relative to X, the more negative the $\Delta E^{\ddagger}$ value and the weaker the π-donor ability of Y relative to X, the more positive the ΔE value. For example, in the case of $\mathbf{1_{H-OH}}$ (entry 1), where OH is a strong π-donor group and H has no π effect, the population of C1 p(π) orbital is about 0.63e greater than that of C2 p(π) orbital. This large difference in the population of the p(π) orbitals leads to a large negative value for $\Delta E^{\ddagger}$

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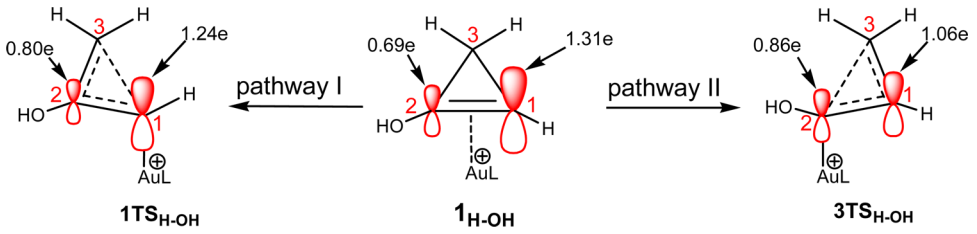
Scheme 4



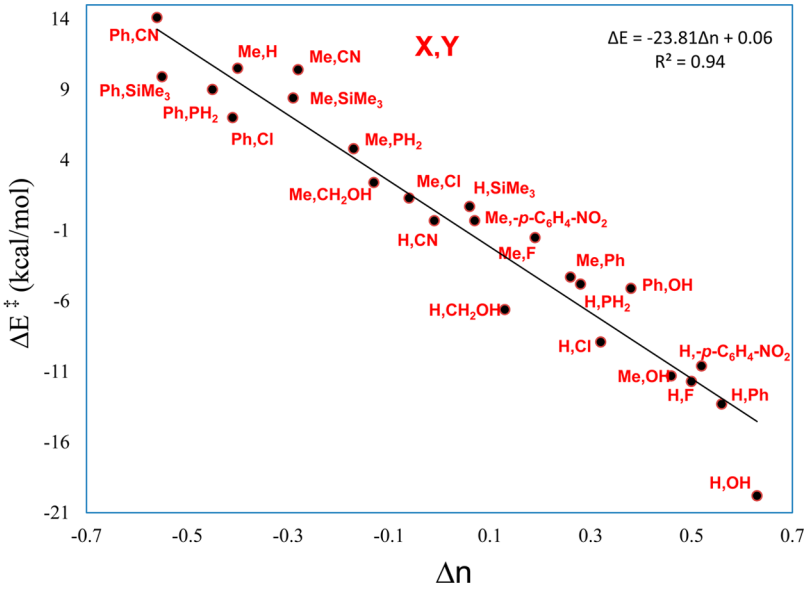


Figure 2. Plot of the values of $\Delta E^{\ddagger}$ against Δn (see Table 1) for all cases studied.

Table 2. Calculated Reaction Energies (kcal/mol) for the Ring-Opening of All the Cyclopropenes Studied and the LUMO Energies (eV) for Intermediates 3_{X-Y} (E_{LUMO1}) and 4_{X-Y} (E_{LUMO2}) (See Scheme 2)

entry	X	Y	ΔE_1	ΔE_2	$\Delta E = \Delta E_1 - \Delta E_2$	E_{LUMO1}	E_{LUMO2}	$\Delta E_{LUMO} = E_{LUMO1} - E_{LUMO2}$
1	H	OH	−1.8	−25.0	23.2	−4.76	−3.76	−1.01
2	H	Ph	0.3	−13.1	13.4	−4.65	−4.33	−0.32
3	H	F	−14.5	−27.4	12.9	−5.03	−4.44	−0.60
4	H	*p*-$NO_2C_6H_4$	−2.7	−11.7	9.0	−4.82	−4.84	0.03
5	H	Me	−3.0	−9.7	6.7	−4.63	−4.33	−0.30
6	H	Cl	−8.6	−20.8	12.2	−5.01	−4.63	−0.38
7	H	CH_2OH	−6.0	−13.2	7.2	−4.63	−4.33	−0.30
8	H	PH_2	0.6	−14.9	15.5	−4.73	−4.25	−0.49
9	H	CN	−5.6	−11.6	6.0	−5.20	−5.50	0.30
10	H	$SiMe_3$	2.6	0.5	2.1	−4.54	−4.57	0.03
11	Me	OH	−8.6	−28.0	19.4	−4.30	−3.62	−0.68
12	Me	Ph	−1.3	−4.8	3.5	−4.25	−4.22	−0.03
13	Me	F	−16.4	−23.3	6.9	−4.54	−4.30	−0.24
14	Me	*p*-$NO_2C_6H_4$	−1.2	−1.1	−0.1	−4.38	−4.71	0.33
15	Me	Cl	−9.6	−14.9	5.3	−4.57	−4.52	−0.05
16	Me	CH_2OH	−5.7	−3.1	−2.6	−4.19	−4.11	−0.08
17	Me	PH_2	0.3	−8.5	8.8	−4.30	−4.14	−0.16
18	Me	$SiMe_3$	3.3	8.0	−4.7	−4.00	−4.25	0.24
19	Me	CN	−6.3	−5.5	−0.8	−4.73	−5.17	0.44
20	Ph	OH	−10.1	−23.0	12.9	−4.30	−3.65	−0.65
21	Ph	F	−20.6	−19.9	−0.7	−4.52	−4.38	−0.14
22	Ph	Cl	−10.9	−10.9	0.0	−4.49	−4.54	0.05
23	Ph	PH_2	−1.9	−5.6	3.7	−4.27	−4.16	−0.11
24	Ph	$SiMe_3$	−2.1	10.9	−13.0	−4.00	−4.19	0.19
25	Ph	CN	−5.6	1.3	−6.9	−4.63	−5.44	0.82

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($\Delta E^{\ddagger}$ = −19.8 kcal/mol). In comparison, in the case of $\mathbf{1}_{\mathbf{Me-OH}}$ (entry 11), where Me is a π-donor group but the π-donor ability of Me is weaker than OH, $\Delta E^{\ddagger}$ is calculated to be only −11.3 kcal/mol. The less negative value of $\Delta E^{\ddagger}$ in this case is related to the smaller difference in population of the p(π) orbitals (Δn = 0.46e). In the case where X = Me and Y = Ph (entry 12), $\Delta E^{\ddagger}$ is found to be negative (−4.3 kcal/mol), supporting the fact that Ph is a stronger π-donor than Me. Translating this back to the experimental results in Figure 1, the breaking of the C2−C3 bond in our acetoxy-diene forming reaction can be rationalized by the stronger π-donor ability of the Me group compared to the CH(R)OAc group. Conversely, the $CH(R)OCH_2CH{=}CH_2$ group in Cossy and Meyer's system is a stronger π-donor than H, resulting in C1−C3 ring-opening.

Interestingly, we found an excellent correlation between the $\Delta E^{\ddagger}$ and Δn values (R^2 = 0.94) (Figure 2).[17] This surprising result suggests that, regardless of the nature of X and Y, the regioselectivity of the ring-opening is heavily dictated by the p(π) orbital populations of C1 and C2 in the adduct complex $\mathbf{1}_{\mathbf{X-Y}}$. In other words, the energy difference between the transition structures $\mathbf{1TS}_{\mathbf{X-Y}}$ and $\mathbf{2TS}_{\mathbf{X-Y}}$ is reliant on how large the C1 p(π) orbital is populated as compared to the C2 p(π) orbital in $\mathbf{1}_{\mathbf{X-Y}}$.

Thermodynamic Preference. Another interesting result that needs further attention is the thermodynamic preference for $\mathbf{3}_{\mathbf{X-Y}}$ against $\mathbf{4}_{\mathbf{X-Y}}$ (Scheme 2). The relative energy for intermediates $\mathbf{3}_{\mathbf{X-Y}}$ and $\mathbf{4}_{\mathbf{X-Y}}$ are represented by ΔE_1 and ΔE_2, respectively. The calculated ΔE_1 and ΔE_2 values for all products are listed in Table 2. The energy difference between ΔE_1 and ΔE_2 is represented by ΔE ($\Delta E = \Delta E_1 - \Delta E_2$) (Table 2). The positive ΔE values indicate that the formation of $\mathbf{4}_{\mathbf{X-Y}}$ is thermodynamically preferred, while the negative values indicate that the formation of $\mathbf{3}_{\mathbf{X-Y}}$ is thermodynamically favored.

We found that the activation barriers do not follow the same trend as in the ring-opening reaction energies; i.e., a more stable transition state does not lead to a more stable product (Tables 1 and 2). For instance, the transition structure $\mathbf{1TS}_{\mathbf{H-OH}}$ is by 19.8 kcal mol^{-1} more stable than $\mathbf{2TS}_{\mathbf{H-OH}}$, while the intermediate obtained from $\mathbf{1TS}_{\mathbf{H-OH}}$ ($\mathbf{3}_{\mathbf{H-OH}}$) is by 23.2 kcal mol^{-1} less stable than the intermediate obtained from $\mathbf{2TS}_{\mathbf{H-OH}}$ ($\mathbf{4}_{\mathbf{H-OH}}$) (Figure 3). A similar result for the gold(I)-catalyzed rearrangement of 3-phenylcyclopropene-3-methylcarboxylate to butenolide and indene was also obtained in a previous study by Hadfield et al.[18]

As depicted in Scheme 1, the product of the ring-opening can be considered as a hybrid between a gold carbenoid **a** and gold-stabilized allyl cations **b** and **c**. We believe that contributor **c** is the most suitable representation in our system because Au(I) is a weak π-donor center and in **c** the positive charge is completely localized on the α-carbon atom, which allows stabilization if the R substituent is a π-base group. In such a case, the relative stability of $\mathbf{3}_{\mathbf{X-Y}}$ and $\mathbf{4}_{\mathbf{X-Y}}$ mainly depends on how strong the π-basicity of X is compared to Y; if X is a stronger π-base than Y, $\mathbf{3}_{\mathbf{X-Y}}$ is more stable than $\mathbf{4}_{\mathbf{X-Y}}$; otherwise, it is less stable. The strength of π-basicity of the X and Y substituents is reflected in the LUMO energy of the intermediates $\mathbf{3}_{\mathbf{X-Y}}$ and $\mathbf{4}_{\mathbf{X-Y}}$. Because the LUMO of the intermediate is mainly made of the p_π orbitals of α- and γ-carbon atoms, a π-base substituent on the α-carbon atom is capable of destabilizing the LUMO, as shown in Scheme 5; the stronger the π-basicity of substituent at α-position, the more destabilized the LUMO. A larger destabilization of the LUMO leads to a greater stabilization of its bonding orbital, thereby giving a more stable intermediate.

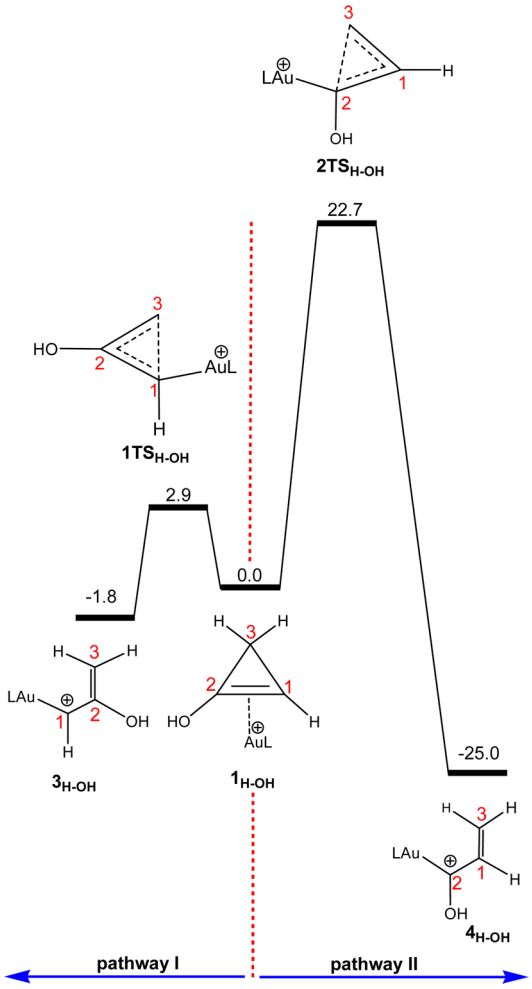
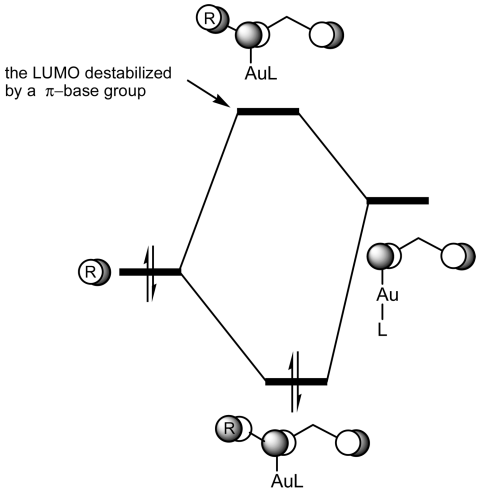


Figure 3. Computed energy profile for the ring-opening of a cyclopropene with X = H and Y = OH by PMe_3Au^+ through the pathways **I** and **II**. The relative potential energies are given in kcal/mol.

Scheme 5



These results suggest that the higher stability of $\mathbf{4}_{\mathbf{H-OH}}$ compared to $\mathbf{3}_{\mathbf{H-OH}}$ is due to the presence of the strong π-base OH substituent at the α-position. Our calculations show that

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the LUMO of $\mathbf{4}_{\mathbf{H-OH}}$ lies 1.0 eV higher than that that of $\mathbf{3}_{\mathbf{H-OH}}$ (Figure 4). The strong antibonding interaction between the α-carbon and the OH substituent in the LUMO of $\mathbf{4}_{\mathbf{H-OH}}$ is indicative of the fact that the OH is a powerful π-base.

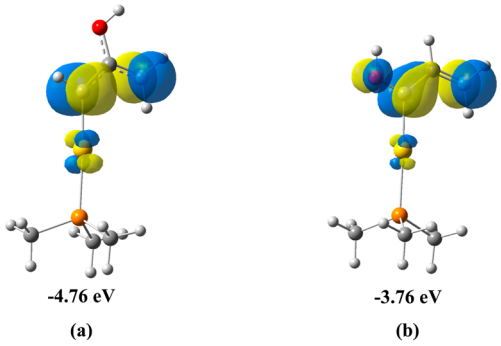

Figure 4. Spatial plot of the lowest unoccupied molecular orbital (LUMO) along with its energy for (a) $\mathbf{3}_{\mathbf{H-OH}}$ and (b) $\mathbf{4}_{\mathbf{H-OH}}$.

The LUMO energies for intermediates $\mathbf{3}_{\mathbf{X-Y}}$ (E_{LUMO1}) and $\mathbf{4}_{\mathbf{X-Y}}$ (E_{LUMO2}) are given in Table 2. Our calculations show that a larger difference between the LUMO energies of $\mathbf{3}_{\mathbf{X-Y}}$ and $\mathbf{4}_{\mathbf{X-Y}}$ (ΔE_{LUMO}) gives rise to a stronger thermodynamic preference for one of the intermediates. We found a relatively good correlation between the ΔE_{LUMO} and ΔE values (R^2 = 0.83) (Figure 5).[19,20] This result confirms that the π-basicity of substituent at α-position plays a significant role in determining the stability of intermediate $\mathbf{3}_{\mathbf{X-Y}}$ compared to $\mathbf{4}_{\mathbf{X-Y}}$.

CONCLUSION

We have shown by DFT calculations that the regioselectivity of cyclopropene ring-opening by Au(I)-catalysts can be predicted on the basis of relative π-donor ability of the C1 and C2 substituents; these results are consistent with our previous experimental results[7] and those of Cossy and Meyer.[6] It is possible to conclude that cyclopropenylcarbinol derivatives, which are readily synthesized, can lead to very selective ring-opening processes by choice of the group at C1. For example, when C2 is CH_2OH almost complete selectivity for pathway **II** can be expected if C1 is a methyl group and selective pathway **I** ring-opening will be observed if C1 is hydrogen. It is also clear that cyclopropenes with a C1 phenyl group, which are readily prepared by cyclopropenation of phenylacetylene derivatives, represent a class of cyclopropenes amenable to highly selective gold-catalyzed ring-opening processes. It is interesting to note that for trimethylsilyl-substituted cyclopropenes, the β-silicon effect is not a strong director of ring-opening regiochemistry. Even in the case of X = H and Y = $SiMe_3$ there is only a slight preference for pathway **II**, suggesting that the silicon group may not a good choice of group to direct cyclopropene ring-opening with gold-catalysts. It has also been demonstrated that the thermodynamic stability of the ring-opened product is controlled by the π-basicity of the α-substituent. Further work is ongoing in our laboratories to experimentally investigate the substituent-dependent reactivity of the organo-gold intermediates.

ASSOCIATED CONTENT

Supporting Information

Complete ref 8 and tables giving Cartesian coordinates of all optimized structures along with electronic and Gibbs free energies as well as the activation and reaction energies calculated using B3LYP/BS2//B3LYP//BS1 in the gas phase (kcal/mol) for the ring-opening of all the cyclopropenes. Figures showing the plot of the values of $\Delta E^{\ddagger}$ in the gas phase against Δn for all the cases studied and the plot of the values of ΔE in the gas phase against ΔE_{LUMO} for a number of the studied cyclopropenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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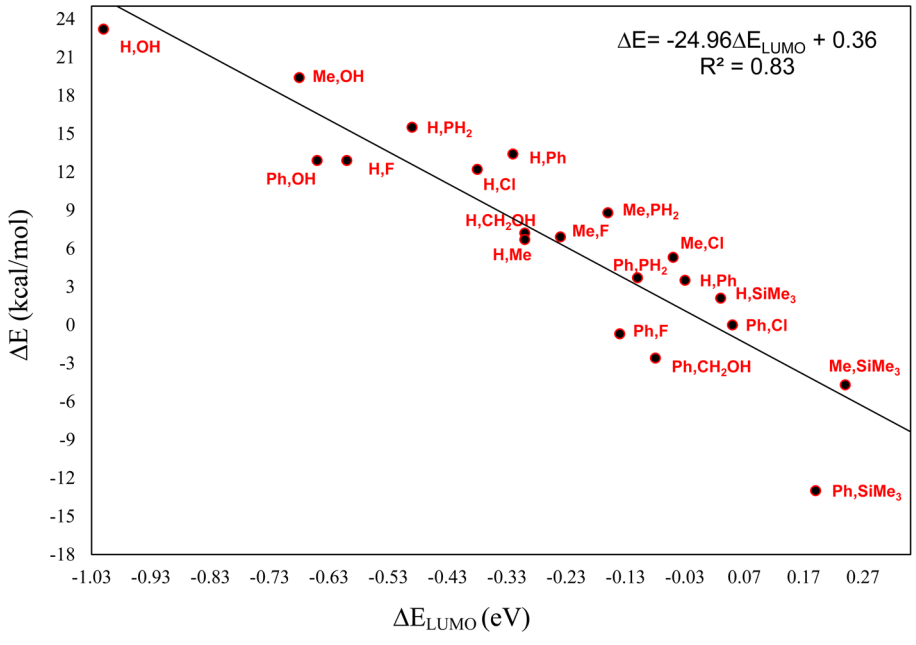

Figure 5. Plot of the values of ΔE against ΔE_{LUMO} (see Table 2) for a number of the studied cyclopropenes.

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Notes

The authors declare no competing financial interest.

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(20) A correlation with R^2 = 0.77 was found when the gas phase electronic energies for ΔE are plotted against ΔE_{LUMO} (Figure S2, Supporting Information).