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PAPER

Computational studies on the mechanism of the gold(i)-catalysed rearrangement of cyclopropenes†

Maximillian S. Hadfield, L. Jonas L. Häller, Ai-Lan Lee,* Stuart A. Macgregor,* James A. T. O'Neill and Ashley M. Watson

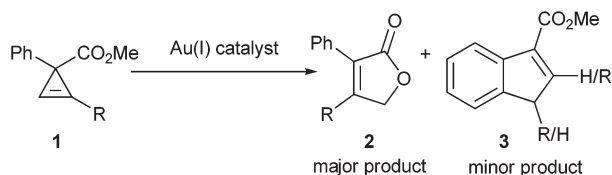
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Density functional theory calculations have been employed to investigate the mechanism of gold(i)-catalysed rearrangements of cyclopropenes. Product formation is controlled by the initial ring-opening step which results in the formation of a gold-stabilised carbocation/gold carbene intermediate. With 3-phenylcyclopropene-3-methylcarboxylate, the preferred intermediate allows cyclisation *via* nucleophilic attack of the carbonyl group and hence butenolide formation. Further calculations on simple model systems show that substituent effects can be rationalised by the charge distribution in the ring-opening transition state and, in particular, a loss of negative charge at what becomes the β -position of the intermediate. With 1-C₃H₃R cyclopropenes (R = Me, vinyl, Ph), ring-opening therefore places the substituent at the β -position.

Introduction

Interest in organic transformations catalysed by cationic gold(i) complexes has undergone a dramatic increase in recent years.¹ The majority of homogenous gold-catalysed reactions draw on the superb Lewis acidity of gold(i) for activation of carbon π -systems such as alkynes and allenes.^{1d} One of the research efforts within our group is exploring the diverse chemistry of gold-catalysed reactions with *cyclopropenes*.^{2,3} In addition to developing novel intermolecular reactions, we have also presented results regarding the *intramolecular* rearrangements⁴⁻⁶ of cyclopropenes, *e.g.* **1** to give butenolides **2** and indenes **3** (Scheme 1).^{3a}

Scheme 1 Gold(i)-catalysed rearrangement of **1**.

School of Engineering and Physical Sciences, Chemistry – William H. Perkin Building, Heriot-Watt University, Edinburgh EH14 4AS, UK. E-mail: A.Lee@hw.ac.uk, S.A.Macgregor@hw.ac.uk; Tel: +44(0)131-4518030/+44(0) 131 451 8031

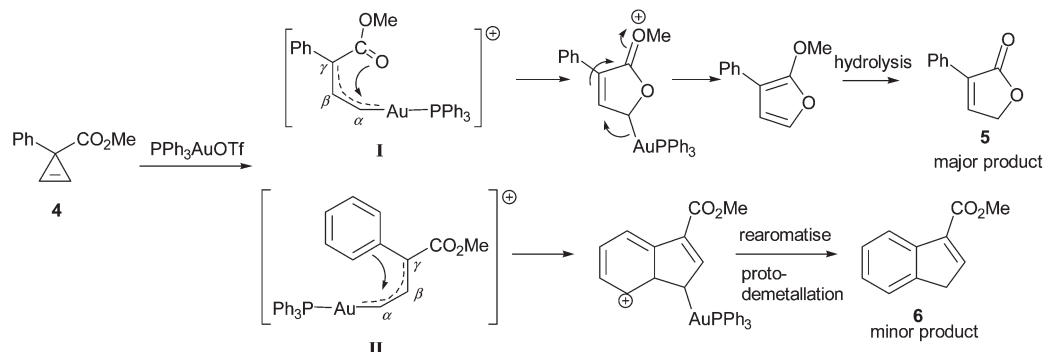
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Table 1 The effect of substituents

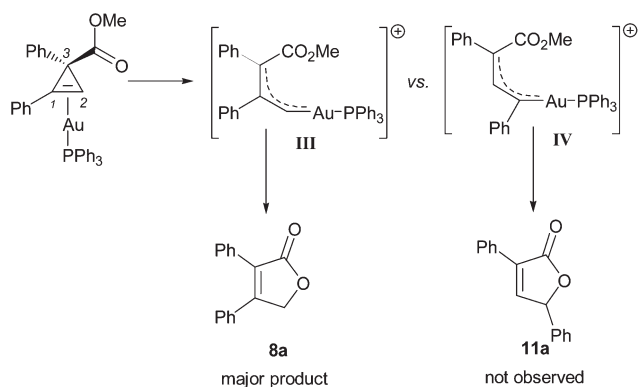
Entry	R	Yield 5/8	Yield 6/9 + 10^a	Ratio 9 : 10^b
1 ^c	H	52%	20%	—
2	Ph	53%	18%	1 : 1
3	<i>p</i> -OMeC ₆ H ₄	50%	20%	2.6 : 1
4	<i>p</i> -FC ₆ H ₄	50%	18%	1 : 3

^a Isolated yields. ^b Determined by ¹H-NMR analysis. ^c Toluene, 80 °C, 18 h.

Some of our synthetic results are summarised in Table 1. In the presence of PPh₃AuCl and AgOTf (forming PPh₃AuOTf *in situ*) cyclopropene **4** rearranges to the butenolide **5** and indene **6** in 52% and 20% yield, respectively (toluene, 80 °C, 18 h, entry 1).⁸ We also found that Ph-substituted cyclopropene **7a** undergoes rearrangement under milder conditions, to furnish the butenolide **8a** in 53% yield (CH₂Cl₂, 20 °C, 2 h, entry 2).^{9,10} Butenolide formation occurs with high regioselectivity, whereas the indene by-products (18%) are formed in a 1 : 1 regioisomeric ratio of **9a** and **10a**. Changing the electronics on the aryl ring



Scheme 2 Proposed mechanism for the gold(I)-catalysed rearrangement of **4** to **5** and **6**.



Scheme 3 Intermediates leading to possible butenolide regioisomers **8a** and **11a**.

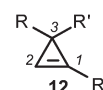
does not affect the preference for butenolide formation, nor its regioselectivity, although shifts in the balance between indenenes **9** and **10** are seen (entries 3 and 4).

Our proposed mechanism for the rearrangement of **4** to form **5** and **6** is shown in Scheme 2. Gold(I) induces ring-opening of the strained cyclopropene to form the gold-stabilised cationic/gold carbene stereoisomeric intermediates **I** and **II**.^{11,12} In **I** the ester moiety is *syn* to C^α and allows formation of butenolide **5** *via* intramolecular attack of the carbonyl oxygen onto C^α , followed by hydrolysis. Alternatively, in **II** the phenyl group is *syn* to the reactive centre and intramolecular attack of the phenyl substituent onto C^α could ultimately furnish the indene side-product **6**.

We postulated that the ratio of intermediates **I** and **II** determines the ratio of products **5** and **6**, and thus the ultimate selectivity of the reaction. Similarly, the two possible ring-opening reactions of **7a** (*via* cleavage of the C1–C3 or C2–C3 bonds) will give rise to intermediates **III** and **IV** (Scheme 3), precursors to butenolides **8a** and **11a**, respectively. The reasons for the selectivity for **8a** in this case are not clear. Steric arguments might suggest that Au(I) prefers to be delivered to the less hindered centre (C2 *vs.* C1) to give **III**. Alternatively, the ability of the Ph substituent to stabilise any build up of positive charge at C1 could also account for the preferential formation of **III** and thus **8a**.

In this paper we will assess these ideas by characterising the mechanism of these gold-catalysed rearrangements with density functional theory (DFT) calculations. Our study has three major

aims: (i) to account for the preferential formation of butenolides **2** over indenenes **3** in the reactions of cyclopropenes **1**; (ii) to explain the preferential formation of butenolide **8a** over its regioisomer **11a**; and (iii) to address, in a more general way, the impact of different substituents around the cyclopropene ring on the selectivity of these rearrangements. As the effect of substituents on the gold-catalysed ring-opening step is potentially relevant to all gold(I)-catalysed reactions with cyclopropenes,^{3,4,6} we shall initially focus on this last point by considering the ring-opening of simple cyclopropenes (**12**) at a simple model $\{Au(PH_3)\}^+$ fragment. Different substituents at the 3-position ($R = Me, Ph, CO_2Me$) or at the 1-position ($R'' = Me, vinyl$ and Ph) will be assessed. The mechanism of the intramolecular rearrangements of cyclopropenes **4** and **7a** at $\{Au(PPh_3)\}^+$ will then be addressed.



Results and discussion

(i) Ring-opening of *c*-C₃H₄ ($R = R' = R'' = H$ in **12**)

The results for the parent model system, $[Au(PH_3)(c-C_3H_4)]^+$, **13_{H/H}**, are shown in Fig. 1. Cyclopropene binds in a symmetrical fashion with Au–C1–C2 distances of 2.26 Å and a C1–C2 distance of 1.36 Å, the latter being 0.05 Å longer than in free cyclopropene. The ring-opening transition state, **TS(13-14)_{H/H}**, exhibits an elongated C1–C3 distance (1.62 Å) but the major motion is the slippage of Au towards C1 (Au–C1 = 2.13 Å, Au...C2 = 3.08 Å). The Au–C1 distance shortens further to 2.00 Å in the ring-opened intermediate **14_{H/H}** in which C1–C2 = 1.42 Å and C2–C3 = 1.38 Å.

The electronic structure of species such as **14_{H/H}** has been discussed in terms of a continuum of behaviour between the extremes of a gold-carbene and a gold-stabilised carbocation (Scheme 4).¹² Which of these is the more dominant form depends on both the substituents and the nature of the ancillary ligand and in the present case the short Au–C1 and C2–C3 distances favour a gold-carbene formalism. This is consistent with the absence of electron-releasing groups to stabilise carbocationic character on C3.^{12a,b} Trost and Goddard have also defined a parameter *A* ($A = C1-C2/C2-C3$) as a measure of whether the

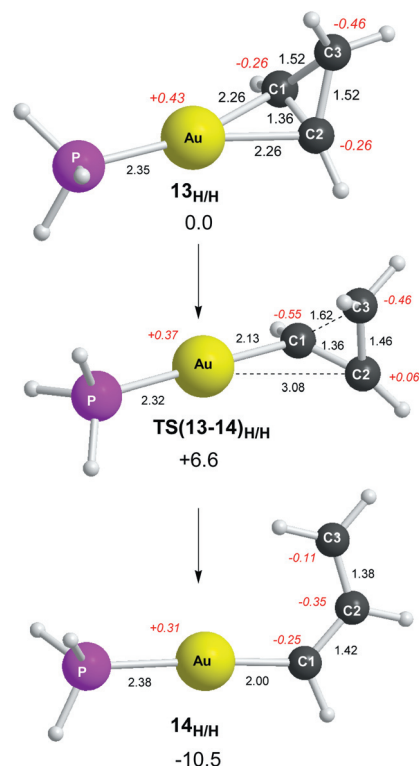
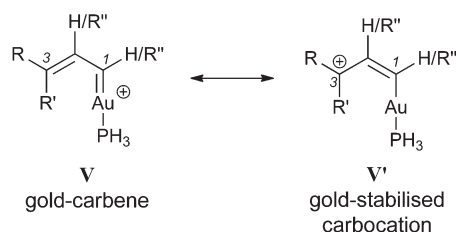


Fig. 1 Computed structures for the ring opening of $[\text{Au}(\text{PH}_3)(c\text{-C}_3\text{H}_4)]$, $\mathbf{13}_{\text{H}/\text{H}}$. Selected distances (Å) are shown in plain text and computed natural charges in italics. Relative energies are in kcal mol⁻¹.



Scheme 4 Gold-carbene and gold-stabilised carbocation extremes.

positive charge is more stabilised on C1 or C3.^{12a} Values in excess of 1.0 indicate a bias towards gold-carbene character and in $\mathbf{14}_{\text{H}/\text{H}}$ $A = 1.029$.

The calculations show that the gold-promoted ring-opening of cyclopropene is a facile process, being both kinetically accessible ($\Delta E^\ddagger = 6.6$ kcal mol⁻¹) and exothermic ($\Delta E = -10.5$ kcal mol⁻¹). Further analysis reveals considerable charge redistribution at C1 and C2 during this process. In $\text{TS}(\mathbf{13-14})_{\text{H}/\text{H}}$ the slipping of the $\{\text{Au}(\text{PH}_3)\}^+$ moiety causes considerable build-up of negative charge on C1 (from -0.26 in $\mathbf{13}_{\text{H}/\text{H}}$ to -0.55 in $\text{TS}(\mathbf{13-14})_{\text{H}/\text{H}}$) and a concomitant depletion of charge at C2 (from -0.26 to $+0.06$). In $\mathbf{14}_{\text{H}/\text{H}}$ the charge at C1 is reduced (-0.25), but C2 now adopts additional negative charge (-0.35). In contrast, the charge at C3 is unchanged in the transition state (-0.46 in both $\mathbf{13}_{\text{H}/\text{H}}$ and $\text{TS}(\mathbf{13-14})_{\text{H}/\text{H}}$) before being depleted in $\mathbf{14}_{\text{H}/\text{H}}$ (-0.11). Ring-opening is also accompanied by a steady loss in positive charge at Au ($+0.43$ in $\mathbf{13}_{\text{H}/\text{H}}$ through $+0.37$ in $\text{TS}(\mathbf{13-14})_{\text{H}/\text{H}}$).

$\mathbf{14}_{\text{H}/\text{H}}$ to $+0.31$ in $\mathbf{14}_{\text{H}/\text{H}}$). We will show below that the energetics and selectivity of ring-opening can be rationalised in terms of the abilities of different substituents to accommodate these changes in charge distribution at the C1, C2 and C3 positions during this process.

(ii) Ring-opening of $c\text{-C}_3\text{H}_3\text{-3-R}$ (R = substituent, R' = R'' = H in $\mathbf{12}$)

Introduction of a substituent in the 3-position of cyclopropene means that two η^2 -reactants are possible, in which the R group is either *anti* ($\mathbf{13}_{\text{H}/\text{R}}$) or *syn* ($\mathbf{13}_{\text{R}/\text{H}}$) to the $\{\text{Au}(\text{PH}_3)\}^+$ fragment. The computed energetics for ring-opening when R = Me, Ph and CO₂Me are summarised in Table 2, where in each case energies are quoted relative to the most stable η^2 -cyclopropene adduct. For both R = Me and Ph the *anti* form is slightly lower in energy and leads to more stable transition states and intermediates. For these species the trends in computed structure and charge distribution are similar to those shown in Fig. 1 with cyclopropene. The biggest substituent effect is in the overall energy change for ring-opening, which is more exothermic (by 10 kcal mol⁻¹ for $\mathbf{13}_{\text{H}/\text{Me}}$ and by 20 kcal mol⁻¹ for $\mathbf{13}_{\text{H}/\text{Ph}}$) than from $\mathbf{13}_{\text{H}/\text{H}}$. The enhanced stability of these $\mathbf{14}_{\text{H}/\text{R}}$ intermediates reflects the significant reduction in charge at C3 in these species and the ability of the Me and Ph substituents to accommodate this. The computed trend in the A parameter ($A = 1.014$ in $\mathbf{14}_{\text{H}/\text{Me}}$ and 0.986 in $\mathbf{14}_{\text{H}/\text{Ph}}$) is also indicative of increasingly efficient stabilisation of positive (or reduced negative) charge at C3 in these species. In contrast, the charge at C3 changes little between the η^2 -reactants and the transition states and as a consequence activation barriers are less sensitive to the substituent at that position.

Ring-opening of the *syn* isomers produces intermediates $\mathbf{14}_{\text{Me}/\text{H}}$ and $\mathbf{14}_{\text{Ph}/\text{H}}$ in which the R groups are *cis* to the metal centre. This reaction is somewhat less favourable than with the *anti* isomers (entry 3 vs. 2 and entry 5 vs. 4) and this may simply reflect the more strained geometry of the $\{\text{AuC}_3\text{H}_3\text{R}\}$ moiety being formed. For example, in $\mathbf{14}_{\text{Ph}/\text{H}}$ the C₃H₃Ph moiety must twist to accommodate the neighbouring Ph and $\{\text{Au}(\text{PH}_3)\}$ groups, whereas $\mathbf{14}_{\text{H}/\text{Ph}}$ displays perfect mirror-symmetry which allows for maximum delocalisation along the C1–C2–C3 backbone into the Ph ring. This effect is also seen in the parent allylic cations, with *cis*-C₃H₄Me⁺ being 3.2 kcal mol⁻¹ less

Table 2 Computed energies (kcal mol⁻¹) for ring-opening of $[\text{Au}(\text{PH}_3)(c\text{-C}_3\text{H}_3\text{-3-R})]$ (R = Me, Ph, CO₂Me). In naming the cyclopropenes the first-named substituent is *syn* to the metal centre in the $\mathbf{13}_{\text{R}/\text{R}'}$ precursor

Entry	R/R'	E($\mathbf{13}_{\text{R}/\text{R}'}$)	E($\text{TS}(\mathbf{13-14})_{\text{R}/\text{R}'}$)	E($\mathbf{14}_{\text{R}/\text{R}'}$)
1	H/H	0.0	+6.6	-10.5
2	H/Me	0.0	+5.4	-20.3
3	Me/H	+0.2	+7.5	-16.0
4	H/Ph	0.0	+2.9	-30.8
5	Ph/H	+0.9	+8.4	-23.4
6	H/CO ₂ Me	+0.0	+6.4	-11.1
7	CO ₂ Me/H	-11.8	+5.6	-9.2
8	Ph/CO ₂ Me	0.0	+7.3	-20.6
9	CO ₂ Me/Ph	-6.5	+1.8	-24.1

stable than its *trans* isomer while the difference is 5.4 kcal mol⁻¹ between *cis*- and *trans*-C₃H₄Ph⁺.

The data in Table 2 indicate that **13**_{H/CO₂Me} (entry 6) behaves in a similar fashion to [Au(PH₃)(*c*-C₃H₄)]⁺ and this is underlined by the same *A* values of 1.029 being computed for **14**_{H/H} and **14**_{H/CO₂Me}. However, the alternative *syn*-isomer in this case (**13**_{CO₂Me/H}, entry 7) exhibits a far more stable *O*-bound reactant (*E* = -11.8 kcal mol⁻¹, see Fig. 2). Ring-opening therefore requires this additional Au–O interaction to be broken, leading to a much higher activation barrier of 17.4 kcal mol⁻¹ in this case. Ring-opening is also slightly endothermic (ΔE = +2.6 kcal mol⁻¹) relative to this *O*-bound form.

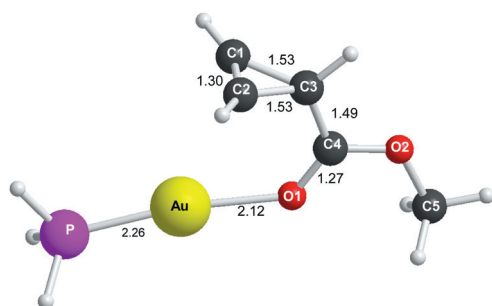


Fig. 2 Computed structure of [Au(PH₃)(κ-*O*-*c*-C₃H₃-3-CO₂Me)], **13**_{CO₂Me/H}, with selected distances (Å).

We have also considered the ring-opening of **4** at the simple {Au(PH₃)}⁺ fragment (entries 8 and 9). Comparison of data in Table 2 suggests that the effects of the two substituents are approximately additive. Thus the presence of the CO₂Me group means that an *O*-bound form, **13**_{CO₂Me/Ph} is the more stable precursor complex, 6.5 kcal mol⁻¹ below the η²-bound **13**_{Ph/CO₂Me}. However, the Ph substituent lowers the barrier to ring-opening to only 8.3 kcal mol⁻¹ (*cf.* 17.4 kcal mol⁻¹ for **13**_{CO₂Me/H}) and also ensures this process is still significantly exothermic (ΔE = -17.6 kcal mol⁻¹). *A* ≈ 0.98 for both **14**_{PhCO₂Me} and **14**_{CO₂MePh}, suggesting enhanced gold-stabilised carbocation character. Further details of this process will be given below, where the reaction with the {Au(PPh₃)}⁺ fragment is considered.

(iii) Ring-opening of *c*-C₃H₃-1-R'' (R = R' = H, R'' = substituent in 12)

Computed data for [Au(PH₃)(*c*-C₃H₃-1-R'')] ⁺ species (R'' = Me, vinyl and Ph) are given in Table 3 and key structural data are given in Fig. 3 for **13**_{Ph} where R'' = Ph. The discussion will focus on this species, the behaviour of which is representative of

Table 3 Computed energies (kcal mol⁻¹) for ring-opening of [Au(PH₃)(*c*-C₃H₃-1-R'')] ⁺ (R'' = Me, C₂H₃, Ph)

R''	13 _{R''}	TS(13-14) _{R''} ^α	14 _{IR''} ^α	TS(13-14) _{R''} ^β	14 _{R''} ^β
Me	0.0	+14.0	-12.2	+1.9	-4.6
C ₂ H ₃	0.0	+17.2	-13.3	+2.6	-0.6
Ph	0.0	+20.8	-12.1	+6.4	+5.8

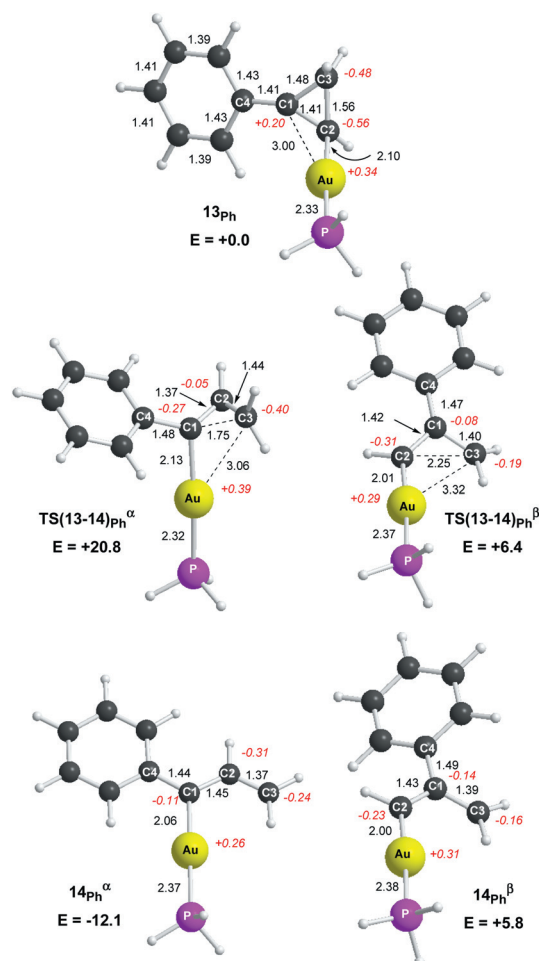


Fig. 3 Computed structures for the ring opening of [Au(PH₃)(*c*-C₃H₃-2-Ph)], **13**_{Ph}. Selected distances (Å) are shown in plain text and computed natural charges in italics. Relative energies are in kcal mol⁻¹.

all three systems. In **13**_{Ph} *c*-C₃H₃-1-Ph binds in a highly unsymmetrical fashion through the unsubstituted carbon (Au–C2 = 2.10 Å, Au...C1 = 3.00 Å). As a result the cyclopropene ring is already significantly activated, with C2–C3 elongated to 1.56 Å and a short C1–C3 distance of 1.48 Å. This is also reflected in the charge distribution around the ring (C1: +0.20; C2: -0.56); the short C1–C4 bond of 1.41 Å and bond alternation around the phenyl ring also suggest a stabilisation of the positive charge at C1. Cleavage of the C2–C3 bond in **13**_{Ph} readily occurs *via* TS (**13-14**)_{Ph}^β (so-called as the Ph substituent is destined for the β-position in the ring-opened species, **14**_{Ph}^β) and has a barrier of only 6.4 kcal mol⁻¹. TS(**13-14**)_{Ph}^β however exhibits a late, product-like geometry with long C2–C3 and Au...C3 distances of 2.25 Å and 3.22 Å respectively and this is consistent with formation of **14**_{Ph}^β being endothermic (ΔE = +5.8 kcal mol⁻¹). In contrast, the alternative C1–C3 bond cleavage entails a much higher barrier of 20.8 kcal mol⁻¹. This primarily reflects the large movement required of the {Au(PH₃)} moiety onto C1 to form TS(**13-14**)_{Ph}^α. The geometry of TS(**13-14**)_{Ph}^α is, however, earlier than TS(**13-14**)_{Ph}^β in terms of the breaking C1–C3 bond (1.75 Å) and the Au...C3 distance (3.06 Å). Accordingly, ring-opening is exothermic in this case (ΔE = -12.1 kcal mol⁻¹).

The above results contrast a kinetic preference for cleavage of the C2–C3 bond of the cyclopropene with a thermodynamic preference for the alternative C1–C3 bond cleavage. Similar trends are also seen for $R'' = C_2H_3$ and Me (see Table 3) and can again be understood through the ability of these electron-releasing substituents to stabilise the more electron deficient carbons as they arise during the ring-opening process. As the ring cleavage transition states involve removal of charge from what will be the β -position of the ring-opened species, $TS(13-14)_{R''}^{\beta}$ is naturally more stable than $TS(13-14)_{R''}^{\alpha}$. For the intermediates, however, the β -carbon experiences a significant build up of negative charge and so the preferred form avoids having R'' located at the β -position, *i.e.* $14_{R''}^{\alpha}$ is more stable than $14_{R''}^{\beta}$. In all these intermediates the A parameters are in excess of 1.0, indicating enhanced gold carbene character. Interestingly these are higher for $14_{R''}^{\alpha}$ ($A \approx 1.05$) than for $14_{R''}^{\beta}$ ($A \approx 1.03$), despite the fact that the Au–C distances are longer in $14_{R''}^{\alpha}$. This suggests that

the substituents at the α -position are more effective at stabilising positive charge than the Au centre.

(iv) Ring-opening and rearrangement of **4** at $\{Au(PPh_3)\}^+$

Computed reaction profiles for the key steps in the formation of butenolide **5** and indene **6** are shown in Fig. 4. The initial ring-opening processes retain the basic features seen with the $\{Au(PH_3)\}^+$ model. Thus the *O*-bound form, $15_{CO_2Me/Ph}$, is the most stable precursor¹³ and ring-opening proceeds through $TS(15-16)_{CO_2Me/Ph}$ at +12.0 kcal mol⁻¹ to give $16_{CO_2Me/Ph}$ at -13.2 kcal mol⁻¹. In comparison the stationary points derived from the η^2 -bound precursor are all less stable, by 5.0 kcal mol⁻¹ for $15_{Ph/CO_2Me}$, 3.0 kcal mol⁻¹ for $TS(15-16)_{Ph/CO_2Me}$ and 2.6 kcal mol⁻¹ for $16_{Ph/CO_2Me}$. Comparison of the data in Fig. 4 and Table 2 suggests the effect of the larger PPh₃ ligand is

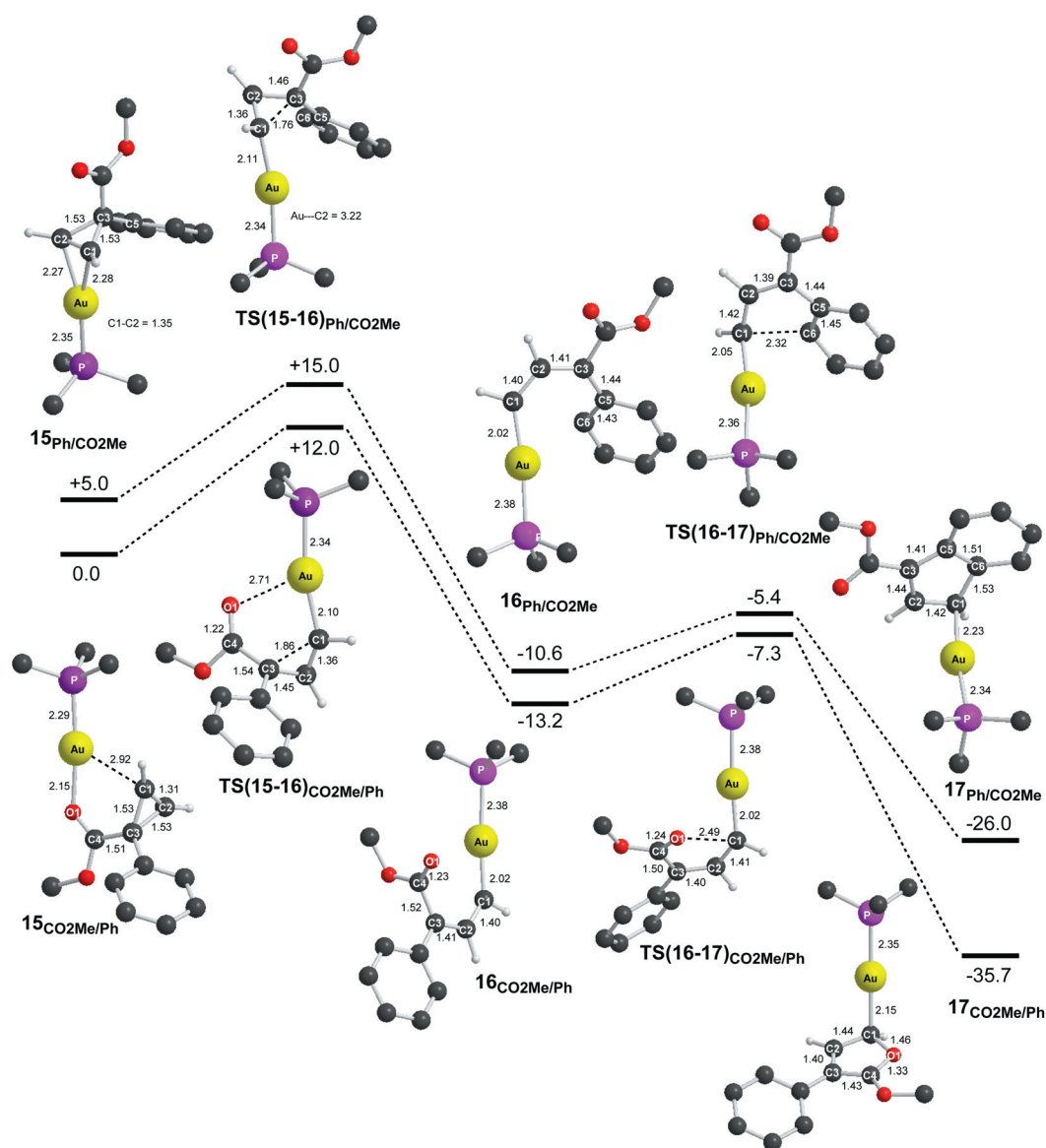


Fig. 4 Computed reaction profiles (kcal mol⁻¹) with selected distances (Å) for the rearrangement of **4** at $\{Au(PPh_3)\}^+$. Phosphine phenyl substituents are truncated at the *ipso* carbon for clarity.

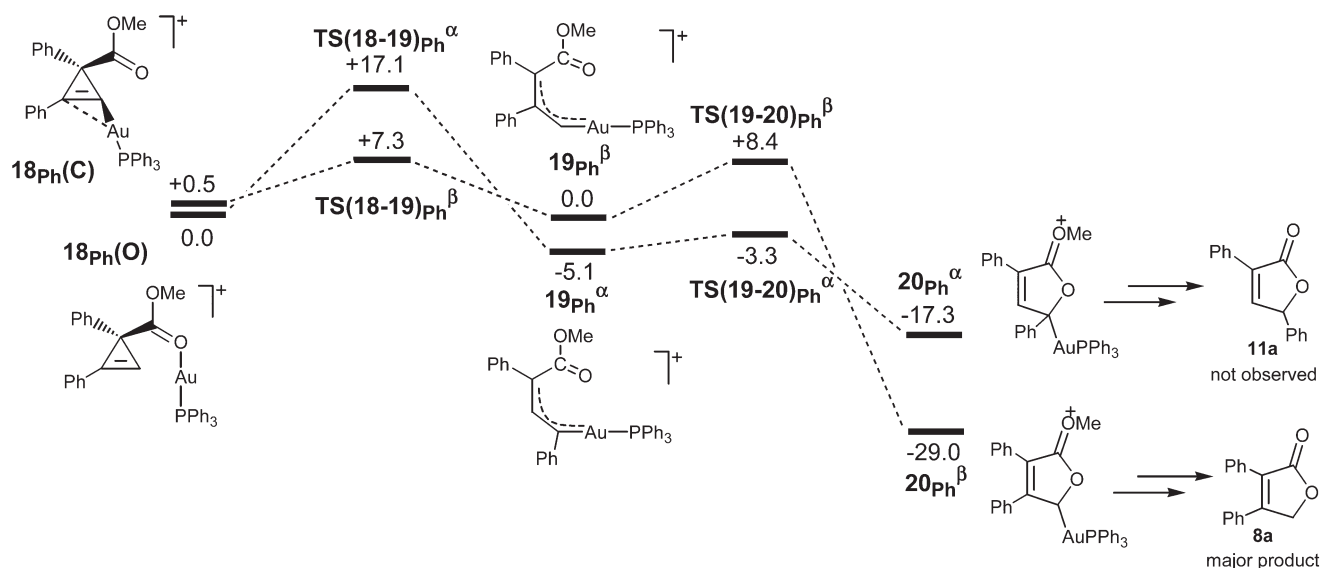


Fig. 5 Computed reaction profiles (kcal mol^{-1}) for the rearrangement of **7a** at $\{\text{Au}(\text{PPh}_3)\}^+$.

to increase the activation barriers and reduce the exothermicity associated with ring-opening, and presumably this reflects the increased steric bulk of the PPh_3 ligand. A values for $\mathbf{16}_{\text{CO}_2\text{Me}/\text{Ph}}$ (0.985) and $\mathbf{16}_{\text{Ph}/\text{CO}_2\text{Me}}$ (0.989) are slightly higher than with the PH_3 models, but the selectivity of ring-opening is unaffected by the nature of the phosphine.

In $\mathbf{16}_{\text{CO}_2\text{Me}/\text{Ph}}$ the ester moiety is *cis* to the Au centre allowing carbonyl group attack at the C^α , the next step in the formation of butenolide **5**. This proceeds with a barrier of only $5.9 \text{ kcal mol}^{-1}$ through $\text{TS}(\mathbf{16-17})_{\text{CO}_2\text{Me}/\text{Ph}}$ ($E = -7.3 \text{ kcal mol}^{-1}$, $\text{C1}\cdots\text{O1} = 2.49 \text{ \AA}$) and forms the very stable intermediate $\mathbf{17}_{\text{CO}_2\text{Me}/\text{Ph}}$ ($E = -35.7 \text{ kcal mol}^{-1}$, $\text{C1-O1} = 1.46 \text{ \AA}$). An equivalent process occurs from $\mathbf{16}_{\text{Ph}/\text{CO}_2\text{Me}}$ to form the new C-C bond in $\mathbf{17}_{\text{Ph}/\text{CO}_2\text{Me}}$, en route to the formation of indene **6**. The barrier of $5.2 \text{ kcal mol}^{-1}$ is actually lower than that for C-O bond formation, however, the higher energy of $\mathbf{16}_{\text{Ph}/\text{CO}_2\text{Me}}$ means that the C-C bond forming transition state, $\text{TS}(\mathbf{16-17})_{\text{Ph}/\text{CO}_2\text{Me}}$, remains $1.9 \text{ kcal mol}^{-1}$ above $\text{TS}(\mathbf{16-17})_{\text{CO}_2\text{Me}/\text{Ph}}$. The $\text{C1}\cdots\text{C6}$ distance is 2.32 \AA in $\text{TS}(\mathbf{16-17})_{\text{CO}_2\text{Me}/\text{Ph}}$ and shortens to 1.53 \AA in $\mathbf{17}_{\text{Ph}/\text{CO}_2\text{Me}}$. $\mathbf{17}_{\text{Ph}/\text{CO}_2\text{Me}}$ is also $9.7 \text{ kcal mol}^{-1}$ less stable than butenolide precursor $\mathbf{17}_{\text{CO}_2\text{Me}/\text{Ph}}$.

The final formation of butenolide **6** and indene **7** will both involve further reactions of their respective precursors, $\mathbf{17}_{\text{CO}_2\text{Me}/\text{Ph}}$ and $\mathbf{17}_{\text{Ph}/\text{CO}_2\text{Me}}$ (*i.e.* hydrolysis and protodemetalation/rearomatization, see Scheme 2). We have not attempted to model these processes, but assume they will readily occur. More importantly, Fig. 4 already contains the origin of the selectivity for butenolide over indene formation. Both processes are computed to be feasible, however, the computed pathway for butenolide formation is more accessible kinetically and thermodynamically. The calculations are therefore consistent with butenolide **5** being the dominant product observed upon the ring opening and rearrangement of **4**. However, the differences in energy along the two reaction profiles are relatively small, especially for the selectivity-determining ring-opening step ($\Delta\Delta E^\ddagger = 3.0 \text{ kcal mol}^{-1}$).^{14,15} Indene formation may therefore also occur as a minor side product. In the absence of an ester substituent the

computed profile suggests indene formation can readily occur, as has been seen experimentally on several occasions.^{4a,b}

(v) Ring-opening and rearrangement of **7a** at $\{\text{Au}(\text{PPh}_3)\}^+$

Computed reaction profiles for the key steps in the formation of butenolides **8a** and **11a** from cyclopropene **7a** are shown schematically in Fig. 5. The *O*-bound reactant, $\mathbf{18}_{\text{Ph}}(\text{O})$, is again the most stable form, although an η^1 C-bound isomer ($\mathbf{18}_{\text{Ph}}(\text{C})$, similar to $\mathbf{13}_{\text{Ph}}$, Fig. 3) is only $0.5 \text{ kcal mol}^{-1}$ higher in energy. A ring-opening transition state for the formation of $\mathbf{19}_{\text{Ph}}^\alpha$ was located from $\mathbf{18}_{\text{Ph}}(\text{O})$ ($\text{TS}(\mathbf{18-19})_{\text{Ph}}^\alpha$, $E = +17.1 \text{ kcal mol}^{-1}$). The pathway for formation of butenolide **8a** proceeds from $\mathbf{18}_{\text{Ph}}(\text{C})$ via $\text{TS}(\mathbf{18-19})_{\text{Ph}}^\beta$ ($E = +7.3 \text{ kcal mol}^{-1}$). In this case the intermediate formed, $\mathbf{19}_{\text{Ph}}^\beta$, has the CO_2Me group positioned correctly for subsequent nucleophilic attack at C^α . In contrast, the transition state for cleavage of the C1-C3 bond derived from $\mathbf{18}_{\text{Ph}}(\text{O})$, although appearing very similar to $\text{TS}(\mathbf{15-16})_{\text{CO}_2\text{Me}/\text{Ph}}$ in Fig. 4, leads to rotation about the $\text{C}^\beta\text{-C}^\gamma$ bond that moves the ester group away from the metal in the intermediate formed.

Overall, the energetics of ring-opening from $\mathbf{18}_{\text{Ph}}(\text{C})/\mathbf{18}_{\text{Ph}}(\text{O})$ are similar to those computed from $\mathbf{13}_{\text{Ph}}$, *i.e.* the presence of the Ph substituent at the 1-position of the cyclopropene dominates. Ring-opening to form $\mathbf{19}_{\text{Ph}}^\beta$ is therefore kinetically more accessible ($\Delta E^\ddagger = 7.3 \text{ kcal mol}^{-1}$ *cf.* $17.1 \text{ kcal mol}^{-1}$ via $\text{TS}(\mathbf{18-19})_{\text{Ph}}^\alpha$), while intermediate $\mathbf{19}_{\text{Ph}}^\alpha$ is more stable ($-5.1 \text{ kcal mol}^{-1}$ *cf.* $\mathbf{19}_{\text{Ph}}^\beta$ at $0.0 \text{ kcal mol}^{-1}$).¹⁶ The presence of a Ph substituent in either the α - or β -position means that both intermediates exhibit enhanced gold-carbene character ($A > 1.0$). The subsequent cyclisation via carbonyl attack in $\mathbf{19}_{\text{Ph}}^\beta$ is actually less accessible than that in $\mathbf{19}_{\text{Ph}}^\alpha$; moreover the transition state for this process ($\text{TS}(\mathbf{19-20})_{\text{Ph}}^\beta$, $E = +8.4 \text{ kcal mol}^{-1}$) is higher in energy than the previous ring-opening transition state $\text{TS}(\mathbf{18-19})_{\text{Ph}}^\beta$. C-O bond formation is therefore the rate determining process along the pathway to the butenolide precursor $\mathbf{20}_{\text{Ph}}^\beta$. Despite this, the overall barrier of $8.4 \text{ kcal mol}^{-1}$ is still

significantly lower than that for formation of 20_{Ph}^{α} (17.1 kcal mol⁻¹). 20_{Ph}^{β} is also 11.7 kcal mol⁻¹ more stable than 20_{Ph}^{α} . Overall the computed profiles suggest that the observed formation of butenolide **8a** over **11a** is primarily a result of kinetic selectivity in the rearrangement process, reinforced by a thermodynamic preference for butenolide precursor 20_{Ph}^{β} .

Experimentally, the reactions of **8a** also result in the formation of indene products and computation of the relevant pathways located a barrier of 9.8 kcal mol⁻¹ equating to ring opening en route to the formation of **9a** (see ESI†). This process can therefore again compete with butenolide formation, although the latter has a slightly lower barrier and so should dominate. Finally, rearrangement of **7a** to form **8a** has a lower barrier (8.4 kcal mol⁻¹) than that for the rearrangement of **4** to give **5** (+12.0 kcal mol⁻¹) and this is consistent with the former process being accessible under milder reaction conditions.

Conclusions

Density functional theory calculations have been employed to define the mechanism of the Au-catalysed intramolecular rearrangement of cyclopropenes. With 3-phenylcyclopropene-3-methylcarboxylate, **4**, the selectivity for butenolide **5** formation seen experimentally derives from the initial ring-opening step. The reaction involves an *O*-bound adduct and ring-opening to form a gold-stabilised carbocation/gold-carbene intermediate in which the carboxylate group is adjacent to the reactive C^α position ($\Delta E^{\ddagger} = 12.0$ kcal mol⁻¹; $\Delta E = -13.2$ kcal mol⁻¹). Facile nucleophilic attack and cyclisation leads to butenolide formation. With 1,3-diphenylcyclopropene-3-methylcarboxylate, **7a**, the kinetically preferred pathway ($\Delta E^{\ddagger} = 7.3$ kcal mol⁻¹) places the additional Ph substituent at the β -position in the intermediate and so accounts for the formation of butenolide **8a** experimentally. For both reactions the alternative indene pathways have only slightly higher barriers, accounting for the experimental observation of such species as side-products. Model calculations show that significant changes in charge occur during the ring-opening process, in particular a loss of electron density at C^β. Phenyl (and also vinyl and methyl) substituents therefore favour this site. The nature of the gold-stabilised carbocation/gold-carbene ring-opened intermediates also varies depending on the nature and position of the substituents present.

Computational details

Calculations were run with Gaussian 03¹⁷ with geometry optimisations using the BP86 functional.¹⁸ Au and P centers were described with the Stuttgart RECPs and associated basis sets,¹⁹ with added d-orbital polarisation on P ($\zeta = 0.387$).²⁰ 6-31G** basis sets were used for all other atoms.²¹ All stationary points were fully characterized *via* analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue) and IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. Energies quoted in the text include a correction for zero-point energy. For the reaction of 3-phenylcyclopropene-3-methylcarboxylate at {Au(PPh₃)⁺} solvent effects (toluene and dichloromethane) were tested for

key stationary points *via* PCM calculations. No significant changes to the trends reported in the main text were seen.

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- while use of hexane as solvent produced no reaction. Cyclopropene **4** can also undergo the gold(i)-catalysed rearrangement to **5** and **6** at room temperature in DCM, but longer reaction times are required (16 h) and the yields of **5** and **6** are only 36% and 15% respectively.
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