

Gold(I) Carbenes by Retro-Buchner Reaction: Generation and Fate

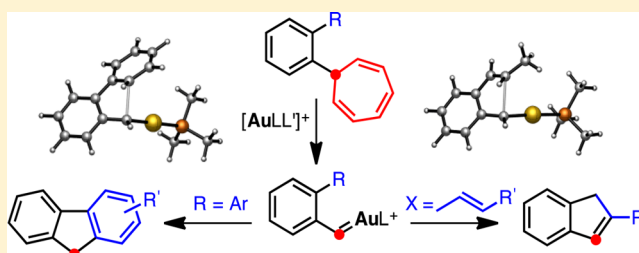
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S Supporting Information

ABSTRACT: The fate of the aryl gold(I) carbenes generated by retro-Buchner reaction of ortho-substituted 7-aryl-1,3,5-cycloheptatrienes is dependent on the constitution of the ortho substituent. Indenes and fluorenes are obtained by intramolecular reaction of highly electrophilic gold(I) carbenes with alkenes and arenes. According to density functional theory calculations, the gold-catalyzed retro-Buchner process occurs stepwise, although the two carbon–carbon cleavages occur on a rather flat potential energy surface.



1. INTRODUCTION

The Buchner reaction of metal carbenes generated from diazocarbonylates and related substrates has been observed under catalytic or stoichiometric conditions using copper(I),^{1–3} silver(I),^{4,5} gold(I),^{3,6} rhodium(II),⁷ and ruthenium complexes.⁸ Chloro(tetraphenylporphyrinato)iron has also been reported as a catalyst for the Buchner reaction.⁹ The copper- and rhodium-catalyzed processes have often been used in total synthesis.^{10,11} In contrast, we recently found that 7-substituted 1,3,5-cycloheptatrienes **1** react with cationic gold(I) complexes under catalytic conditions through their norcaradiene tautomers **2** to generate gold(I) carbenes $[LAu=CHR]^+$ (**3**) in an overall retro-Buchner process (a form of retro-cyclopropanation) (Scheme 1).¹² Our discovery of this reaction was prompted by the observation of a gold(I)-promoted retro-cyclopropanation in the context of a synthesis of 1,3-disubstituted naphthalenes.¹³ The retro-Buchner reaction proceeds readily with 7-aryl- and 7-alkenyl-1,3,5-cycloheptatrienes, whereas 7-alkynyl-1,3,5-cycloheptatrienes react differ-

ently with gold(I) or gold(III) catalysts to form indenes by a complex cycloisomerization that proceeds through gold-stabilized barbaralyl cations.¹⁴

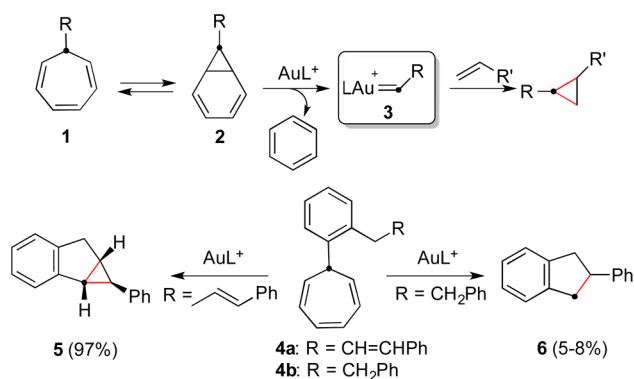
Other related gold(I)-promoted retro-cyclopropanations have also been shown to occur in the gas phase by cleavage of 1-ethoxy-2-methoxycyclopropane with $[AuIMes]^+$ $[IMes = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazol-2-ylidene}]$.^{15,16} The gold(I)-catalyzed retro-Buchner reaction obviates the use of diazo derivatives to generate reactive gold(I) carbenes. Indeed, some diazo compounds are shock-sensitive.¹⁷ Although in certain cases the use of tosylhydrazone salts offers a safer alternative for handling diazo compounds,¹⁸ the generation of the carbenes requires the use of a strong base, which is not compatible with Lewis acidic $[LAuL']X$ complexes.

Gold(I) carbenes **3** undergo inter- or intramolecular reactions with alkenes to give cyclopropanes, as shown in the formation of **5**. Insertion into a $C(sp^3)\text{-H}$ bond was also observed in the retro-Buchner reaction of **4b** to form 2-phenylindane (**6**), although with very low efficiency.¹²

Here we report new results that demonstrate the highly electrophilic character of gold(I) carbenes **3** by their reactions with alkenes and arenes. In these reactions, indenes and fluorenes are obtained by novel annulation processes. The formation of indenes involves an electrophilic addition of the gold(I) carbene to the alkene, which can be followed by an unprecedented 1,4-metallotropic shift. Significantly, the intermediates generated by the retro-Buchner reaction behave more like simple carbenes than benzylic carbocations, as demonstrated in the fluorene annulation.

The mechanism of the Buchner reaction of silver(I)⁵ and ruthenium(II)¹⁹ carbenes has been recently examined computationally. Here we also report a theoretical study of the generation of donor gold(I) carbenes **3** by retro-Buchner

Scheme 1



Received: November 14, 2013

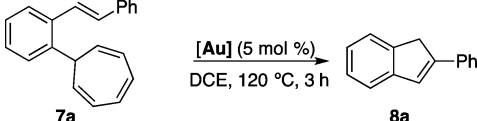
Published: December 20, 2013

reactions of 7-substituted 1,3,5-cycloheptatrienes **1** showing that the retro-cyclopropanation most probably occurs in a stepwise manner, although the barrier for the second C–C cleavage is small.

2. RESULTS AND DISCUSSION

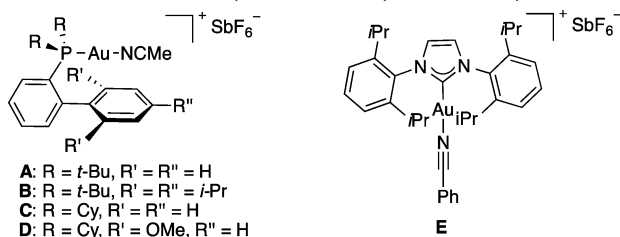
Annulation of *o*-Styrene Derivatives. (*E*)-7-(2-Styrylphenyl)cyclohepta-1,3,5-triene (**7a**) reacted with cationic gold(I) complexes to give 2-phenyl-1*H*-indene (**8a**) (Table 1).

Table 1. Gold(I)-Catalyzed Synthesis of Indene **8a via Retro-Buchner Reaction^a**



entry	[Au]	yield (%) ^b
1	A	86 (74 ^c)
2	B	86
3	C	67
4	D	8
5	E	85

^aReaction at 120 °C (0.1 M in 1,2-dichloroethane), catalyst (5 mol %), 3 h. ^bYields determined by ¹H NMR analysis. ^cIsolated yield.

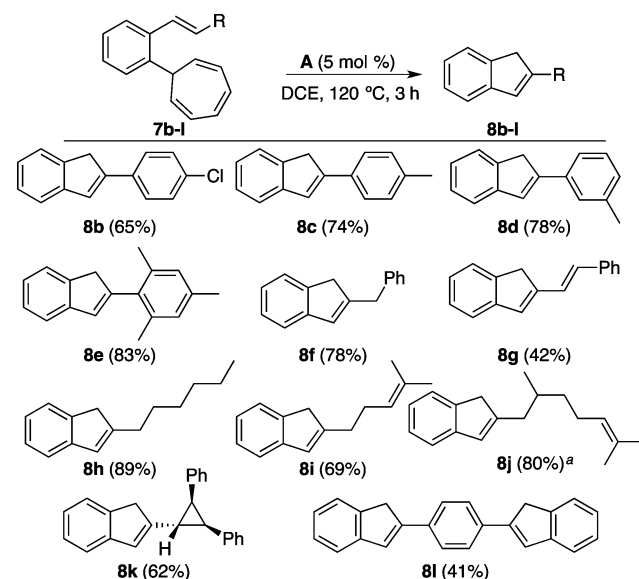


Nearly identical good yields were obtained using cationic phosphine–gold(I) complexes **A** and **B** and carbene complex **E** (Table 1, entries 1, 2, and 5), whereas catalyst **D** led to poor results (entry 4). We identified JohnPhos–gold(I) complex **A** as the catalyst of choice because of its ready availability and robustness for the synthesis of 2-substituted indenenes from *o*-alkenyl cycloheptatrienes (Scheme 2). This reaction proceeds in a rather general manner with substrates substituted with alkyl, alkenyl, or aryl substituents at C2 to give indenenes **8a–l** in moderate to good yields.

Other cationic gold(I) complexes **B–E** were also active as catalysts but usually led to lower yields, although for the synthesis of indene **8j** *i*Pr–gold(I) catalyst **E** was used. In this case, only the closest double bond reacted with the carbene intermediate. The cyclopropyl group in **7k** did not suffer ring expansion. 1,4-Bis(1*H*-inden-2-yl)benzene (**8l**) could also be obtained in moderate yield in a double annulation reaction.

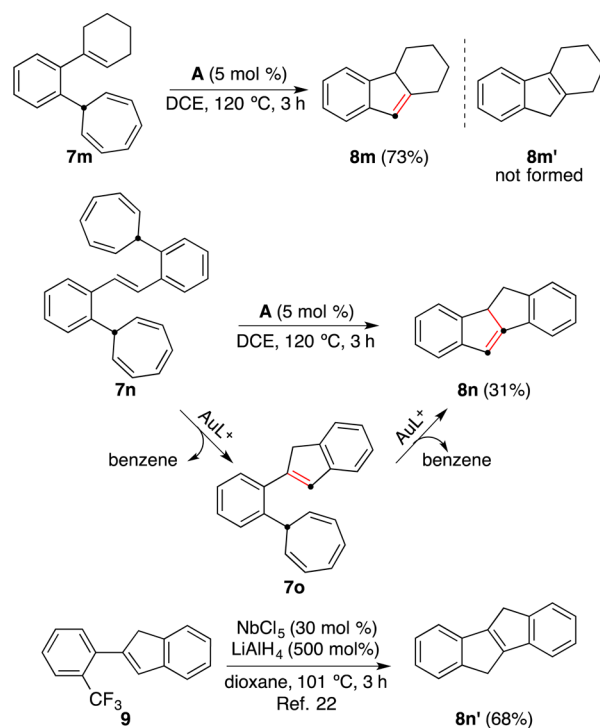
The annulation of *o*-cyclohexenyl derivative **7m** under the standard conditions gave exclusively 2,3,4,4a-tetrahydro-1*H*-fluorene (**8m**), which has not been reported before (Scheme 3). The known and more stable isomer²⁰ 2,3,4,9-tetrahydro-1*H*-fluorene (**8m'**), which would have been formed by C–H insertion, was not observed. The symmetrical derivative **7n** reacted by a double retro-Buchner reaction via **7o** to give 4b,5-dihydroindeno[2,1-*a*]indene (**8n**), a member of a class of compounds that have attracted certain attention lately (Scheme 3).²¹ This method is thus complementary to the synthesis of indenenes by annulation of 2-alkenyl-2-(trifluoromethyl)benzenes

Scheme 2



^aReaction with catalyst **E** (5 mol %), 12 h.

Scheme 3

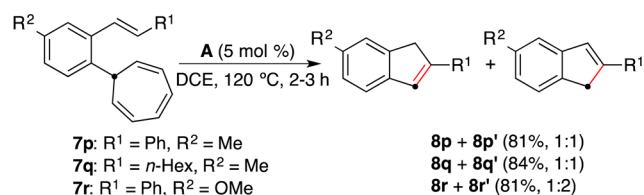


with NbCl_5 and LiAlH_4 , since 2-arylidene **9** leads exclusively to 5,10-dihydroindeno[2,1-*a*]indene (**8n'**).²²

Although at first glance indenenes **8a–l** appear to have been formed by a $\text{C}(\text{sp}^2)\text{--H}$ insertion of a gold(I) carbene intermediate, the formation of **8m** and **8n** strongly suggests that electrophilic addition of a gold(I) carbene operates in these systems.

The exclusive formation of **8m** and **8n** from **7m** and **7n** contrasts with the observed reactivity of substrates **7p–r** (Scheme 4). The reactions of substrates **7p** and **7q** bearing a *p*-Me substituent led to 1:1 mixtures of indenenes **8p/8p'** and **8q/8q'**, respectively. A 1:1 regioisomeric ratio was also obtained

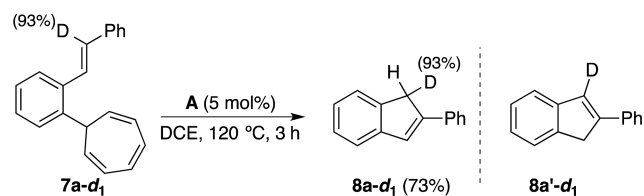
Scheme 4



when the reaction was performed at 100 °C for 3 h (57% conversion as determined by ¹H NMR analysis). Even more surprising was the result obtained in the cyclization of **7r** bearing a *p*-MeO substituent, which led to a 1:2 mixture of **8r** and **8r'**.

Regioisomeric indenenes **8p'**, **8q'**, and **8r'** could have arisen by isomerization of **8p**, **8q**, and **8r** by two consecutive [1,5]-H sigmatropic migrations.²³ However, the reaction of **7a-d**₁ with catalyst **A** led exclusively to **8a-d**₁ with the deuterium label at the methylene, which is not consistent with an isomerization via [1,5]-H sigmatropic migrations, which would have also formed **8a'-d**₁ (Scheme 5). Additionally, no deuterium incorporation

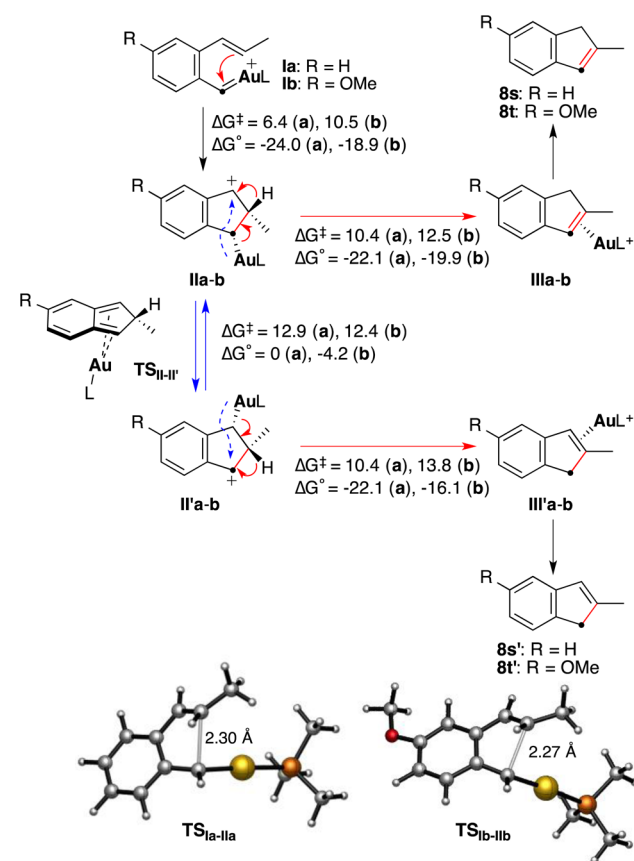
Scheme 5



was observed when the reaction of **7a** was performed in 1,2-dichloroethane saturated with D₂O. Finally, no kinetic isotope effect was observed in the reaction of a 1:1 mixture of **7a** and **7a-d**₁ with gold(I) complex **A** at 100 °C.²⁴

A closer mechanistic inspection of these puzzling results suggested that an unexpected 1,4-gold(I) migration could be involved in the formation of mixtures of regioisomers in some of the indene syntheses. First, we studied computationally the formation of model indenenes **8s** and **8t** from the corresponding gold(I) carbenes using density functional theory (DFT) at the M06 level including solvent effects for 1,2-dichloroethane (Scheme 6). After the retro-Buchner reaction, highly electrophilic gold(I) carbenes **Ia** and **Ib** (L = PMe₃) react intramolecularly with the alkene through TS_{Ia-IIa} and TS_{Ib-IIb} in highly exothermic processes to form benzylic carbocations **IIa** and **IIb**, respectively. Despite being formally a 5-endo-trig cyclization from the perspective of the alkene,²⁵ this process is rendered kinetically and thermodynamically favorable by the high electrophilicity of the gold(I) carbenes. As expected, the *p*-OMe group in **Ib** attenuates the electrophilicity of the gold(I) carbene, raising the energy of TS_{Ib-IIb} and resulting in a less exothermic cyclization. Carbocationic intermediates **IIa** and **IIb** can then evolve by a 1,2-H shift to form directly the indenenes η²-coordinated to AuPMe₃⁺ (**IIIa** and **IIIb**, respectively).^{26,27} Mechanistically, the cyclization of **Ia/Ib** to **IIa/IIb** is formally related to the intramolecular reaction of rhodium nitrenes with alkenes in the rhodium-catalyzed synthesis of indoles from *o*-alkenylaryl azides.²⁸

The DFT calculations show that intermediates **II** can evolve into **II'** by a formal metal migration from C1 to C3, which actually corresponds to a suprafacial 1,4-metallotropic migration.²⁹ Another type of gold(I) migration has also been

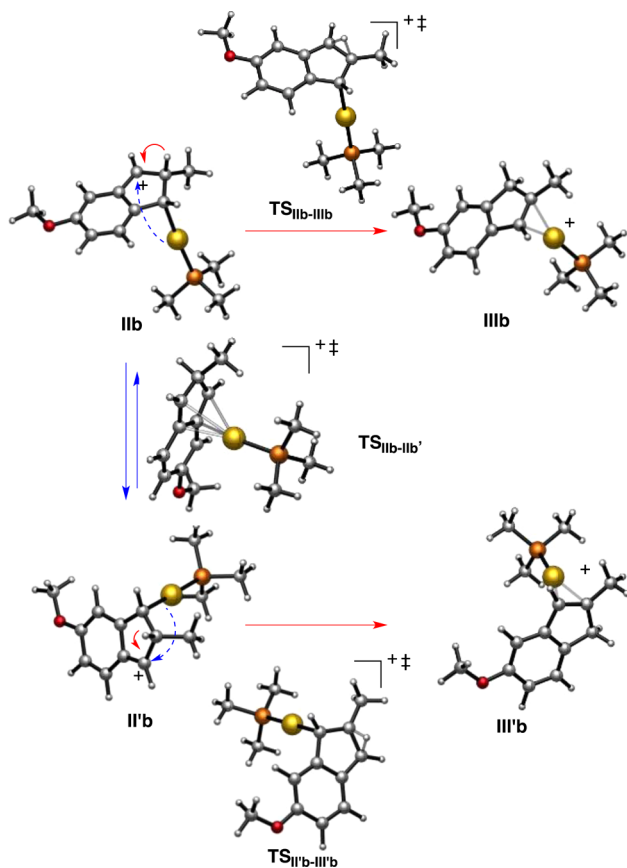
Scheme 6. DFT Calculations on the Cyclization of **Ia** and **Ib** (Free Energies in kcal mol⁻¹)

proposed in a metathesis-type process occurring in competition with the cyclopropanation of enol ethers by gold(I) carbenes generated in the gas phase.^{15c} Whereas for intermediate **IIa** this migration is degenerate, the *p*-OMe-substituted substrate **II'b** is 4.2 kcal mol⁻¹ more stable than **IIb** as a result of the stabilization of the benzylic carbocation by the *p*-MeO group (Scheme 6). The transition states TS_{II-II'} for the 1,4-metallotropic migration show an η⁴-(2*H*-indene)Au(I) structure, with shorter distances from the metal center to the internal carbons C4a–C7a (2.51–2.54 Å) than to C1 and C3 (2.86–2.88 Å).

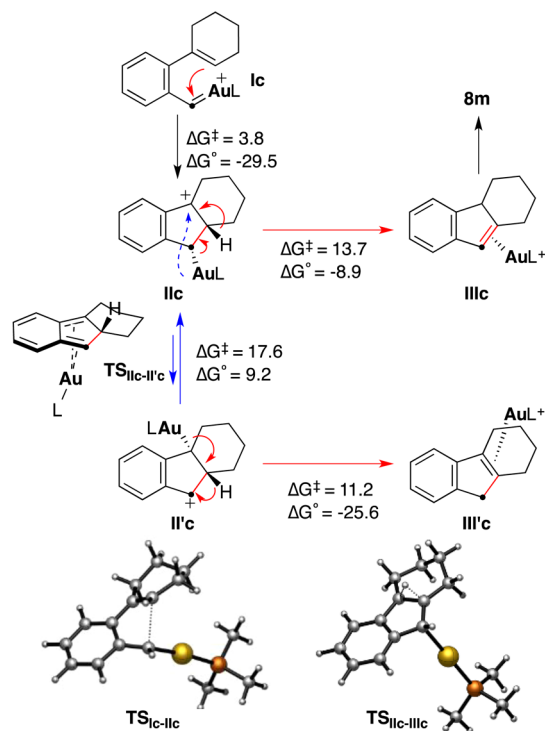
The 1,4-migration of AuPMe₃ in **IIb** requires almost the same activation energy (12.4 vs 12.5 kcal mol⁻¹) as the competitive 1,2-H shift to form **IIIb** (Scheme 7). The difference in activation energies is higher for the unsubstituted system **IIa/IIIa** (2.5 kcal mol⁻¹). The computed tendencies are in close agreement with those found experimentally in the cyclizations of **7p–r**, which led to 1:1 mixtures in the first two cases (*p*-Me as the donor substituent), whereas substrate **7r** (*p*-MeO substituent) gave **8r'** preferentially as a result of a more favorable migration of **IIb** to **II'b**.³⁰

According to DFT calculations, the formation of 2,3,4,4a-tetrahydro-1*H*-fluorene (**8m**) followed a similar pathway involving intramolecular electrophilic attack of the gold(I) carbene on the alkene in **Ic** to form intermediate **IIc**, which undergoes 1,2-H shift to give (η²-alkene)Au(I) complex **IIIc** (Scheme 8). In this case, however, the transition state required for the suprafacial 1,4-metallotropic migration (**IIc** to **II'c**) was found to lie 3.9 kcal mol⁻¹ higher than that of the 1,2-H shift, and moreover, **II'c** is destabilized with respect to **IIc**, which

Scheme 7. Details of 1,4-Metallotropic Migration versus Formation of (η^2 -Indene)gold(I) Complexes in the Formation of IIIb/IIIb'



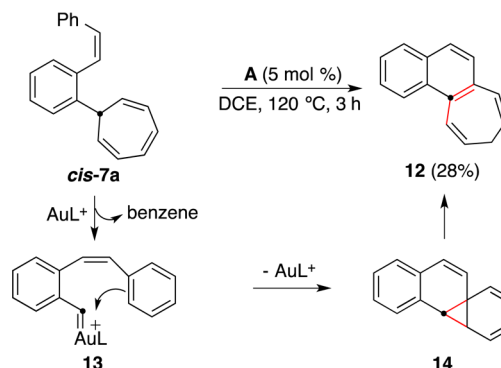
Scheme 8. DFT Calculations on the Formation of 8m (Free Energies in kcal mol⁻¹)



explains the selective formation of 8m over the more stable 8m' from 7m (Scheme 3).

Surprisingly, *cis*-7a did not behave in the same manner as its *trans* isomer in the presence of catalyst A (Scheme 9).

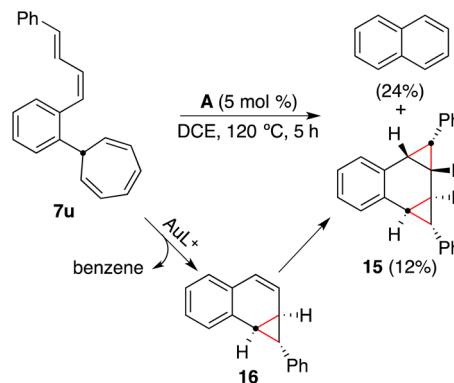
Scheme 9



Presumably as a result of the proximity of the phenyl ring to the gold carbene in intermediate 13, an intramolecular Buchner reaction takes place to form 14, which then undergoes disrotatory norcaradiene-to-cycloheptatriene opening followed by a 1,5-H shift to give 12. A similar transformation had been observed in the thermal decomposition of diazo compounds to form naphtho[*a*]cycloheptenes of type 12.³¹

An even more elaborate cascade of retro-cyclopropanation/cyclopropanation reactions was observed starting from diene 7u (Scheme 10). The initially formed intermediate 16, resulting

Scheme 10

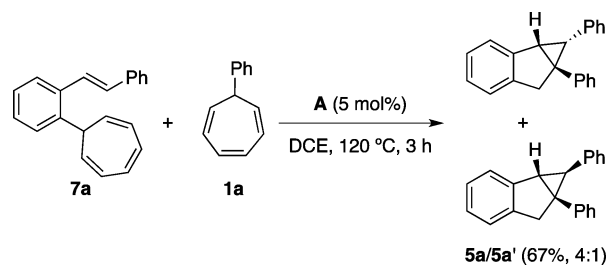


from a gold-catalyzed retro-Buchner reaction followed by intramolecular cyclopropanation, evolves by a second retro-cyclopropanation to form naphthalene with the concomitant generation of the reactive gold carbene [LAu=CHPh]⁺,¹³ which reacts with 16 to give 15.

In our previous study,¹² we found that indenenes are suitable substrates for intermolecular cyclopropanation by gold carbenes generated in a retro-Buchner reaction. An efficient tandem transformation can be achieved by combining indene formation and intermolecular cyclopropanation with [LAu=CHPh]⁺ by reacting 7a with 1a to give 5a and 5a' in a 4:1 ratio (67% yield) (Scheme 11).

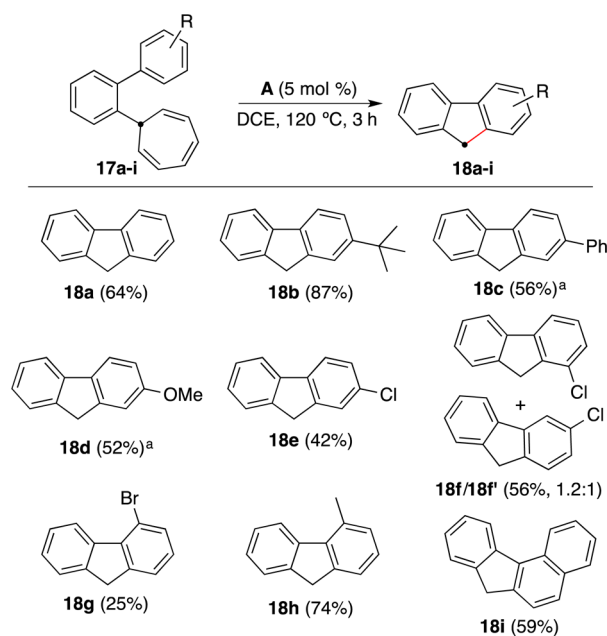
Annulation of *o*-Biphenyl Derivatives. Free *o*-biphenylcarbene has been demonstrated to undergo cyclization to form fluorene,^{32,33,40c} whereas *o*-phenylbenzyl carbocation failed to undergo a similar cyclization.³⁴ *o*-Biphenyl gold(I) carbenes

Scheme 11



generated by retro-Buchner reactions behave like free carbenes, leading to fluorenes. Thus, reaction of 2-cycloheptatrienyl biphenyls **17a–i** with catalyst **A** or **E** gave fluorenes **18a–i** in moderate to good yields by a Friedel–Crafts-type methylenation reaction (Scheme 12). The annulation proceeded

Scheme 12



^aReaction with catalyst **E** (5 mol %), 3 h.

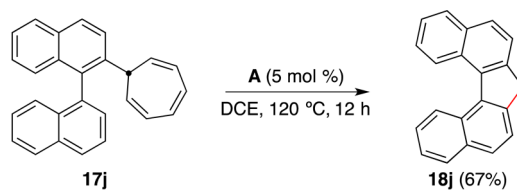
satisfactorily with substituents at different positions, although fluorene **18g** was obtained in low yield. As expected, in the case of *m*-ClC₆H₄ derivative **17f**, a mixture of two regioisomers **18f** and **18f'** was obtained.

This new fluorene synthesis complements other recently developed methods based on transition-metal-catalyzed annulations.^{35–37} Interestingly, related rhodium- or copper-catalyzed annulation of biaryl diazoacetates leads to fluorene carboxylates,³⁸ which emphasizes the similar reactivity of rhodium, copper, and gold carbenes.

With this method, 2-binaphthylcycloheptatriene (**17j**), prepared in one step from commercially available 2-bromo-1,1'-binaphthalene,³⁹ was converted into nonplanar 7*H*-dibenzo[*c,g*]fluorene (**18j**) (Scheme 13).⁴⁰ This is the shortest synthesis of **18j**, whose anion, dibenzo[*c,g*]fluorenyl, has attracted recent interest for its particular aromatic character⁴¹ and as a six- π -electron donor ligand in organometallic chemistry.⁴²

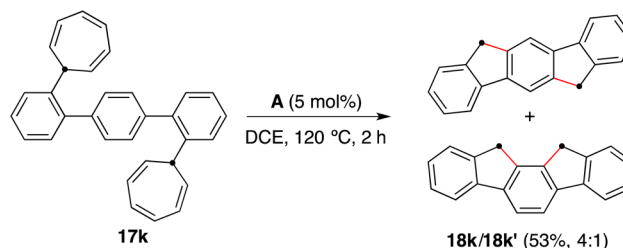
Indenofluorenes (IFs) have found various applications in organic electronics on account of the conjugation along their

Scheme 13



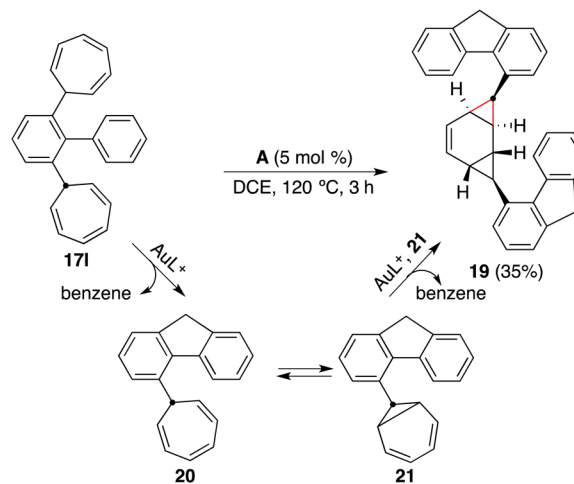
aromatic framework and their high rigidity, which stems from the methylene bridging unit of their biphenyl core.⁴³ By extending our new method to a double annulation, we prepared indeno[1,2-*b*]fluorene (**18k**) as a mixture with indeno[2,1-*a*]fluorene (**18k'**) in 53% isolated yield from **17k** (Scheme 14).

Scheme 14



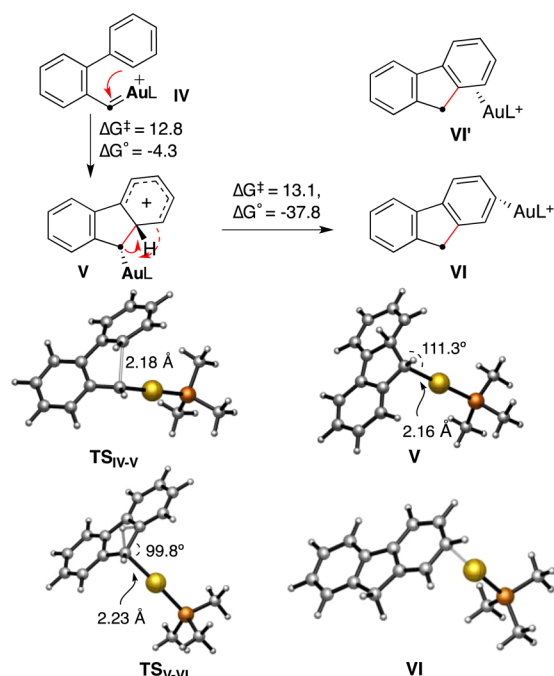
During our attempts to form 4,8-dihydrocyclopenta[*def*]fluorene by generating two gold(I) carbenes on the same aromatic ring, we found that the rigidity of the fluorene backbone makes the second annulation unfavorable. Instead, intermolecular dimerization to give **19** occurred, with no indication of other diastereoisomers (Scheme 15). The reaction

Scheme 15



proceeds by retro-Buchner reaction of **17l** to form **20** followed by a second retro-Buchner reaction of its tautomer **21** to form a fluorenyl gold(I) carbene intermediate that cyclopropanates one of the double bonds of **21**.

For the reactions leading to fluorenes by retro-Buchner reactions of 2-cycloheptatrienyl biphenyls **17**, DFT calculations (M06 level, 1,2-dichloroethane) are consistent with a Friedel–Crafts-type reaction of gold(I) carbene **IV** (L = PMe₃) through transition state **TS_{IV–V}** in a moderately exothermic process to form Wheland intermediate **V** (Scheme 16). Intermediate **V** evolves by a 1,2-H shift via transition state **TS_{V–VI}** to form (η^1 -

Scheme 16. DFT Calculations on Intermediates IV–VI (Free Energies in kcal mol⁻¹)

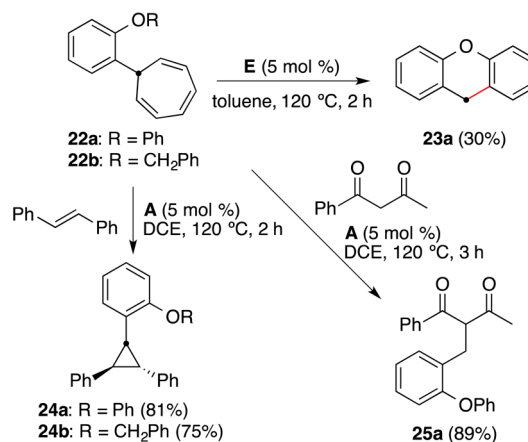
fluorene)gold(I) complex **VI** instead of **VI'** with gold(I) coordinated to the C1–C9a bond. All of the calculations led directly to **VI** as the global minimum by a further shift of [Au(PMe₃)⁺ toward C2, which suggests that a very low barrier exists for the isomerization of **VI'** into **V**. In this process, the [Au(PMe₃)⁺ fragment migrates toward the aryl ring in a concerted but highly asynchronous diatropic-type transformation. The calculated shortest Au–C bond distance of 2.30 Å with C2 in **VI** is very similar to the shortest contacts determined by X-ray diffraction in complexes [LAu(ArH)]SbF₆ (ArH = toluene, *p*-xylene).⁴⁴

Aryl carbenes generated by pyrolysis of aryl diazomethanes undergo formal insertion into the adjacent ortho position of the XC₆H₅ ring to form dihydroanthracenes (X = CH₂) and dihydroacridines (X = NH), whereas substrates with X = O or S lead to products of the Buchner reaction.⁴⁵ In our case, the reaction of cycloheptatrienyl derivative **22a** gave 9*H*-xanthene (**23a**), the product of a formal insertion into the ortho position of the phenyl group, albeit in low yield (Scheme 17). Despite the steric hindrance introduced by the ortho OR substituents, the ortho-substituted aryl gold(I) carbenes generated from **22a** and **22b** could be trapped efficiently with *trans*-stilbene to form the corresponding cyclopropanes **24a** and **24b**. Similarly, **25a** could be obtained by trapping with 1-phenylbutane-1,3-dione.

Mechanism of the Retro-Buchner Reaction. Cleavage of cyclopropanes to form metal carbenes had only been achieved electrophilically by using a mixture of highly electrophilic PhWCl₃ and RAlCl₂ (R = Et, Cl).⁴⁶ On the other hand, highly strained bicyclo[1.1.0]butanes undergo ring opening by oxidative addition to Ni(0) or Rh(I) complexes.⁴⁷

Prior to our initial report,¹² the metal-catalyzed retro-Buchner reaction was unknown, although the reverse process, formation of cycloheptatrienes, is a minor reaction in the gold(I)-catalyzed reaction between ethyl diazoacetate and arenes.⁴⁸ In contrast to the cleavage of substituted cycloheptatriene derivatives observed in the presence of Au(I), strong

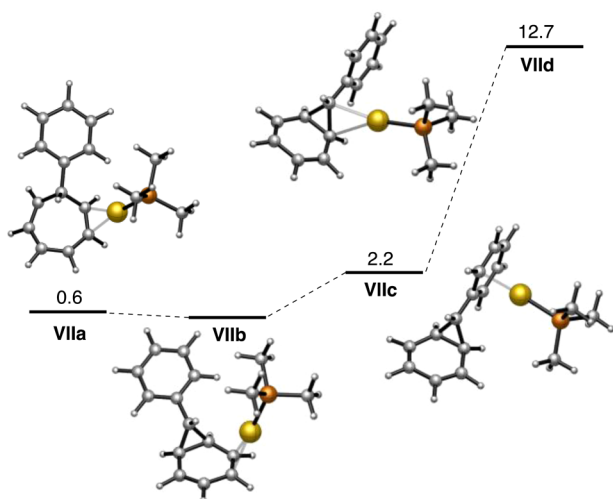
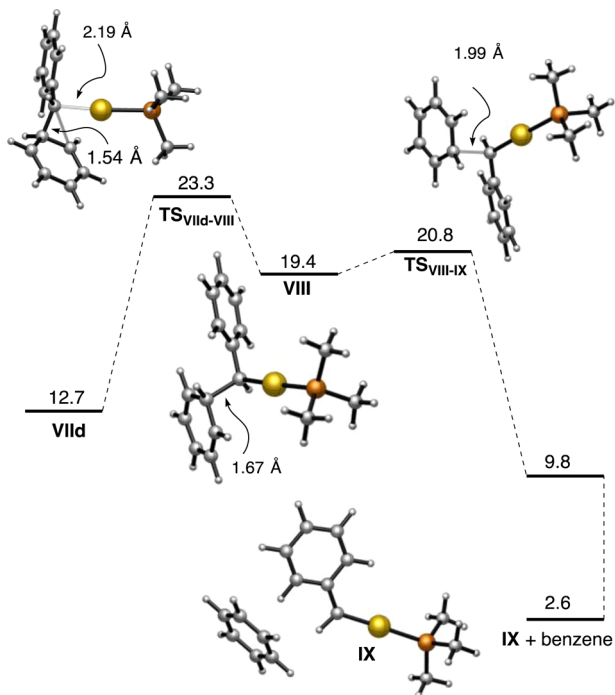
Scheme 17



electrophiles such as TeCl₄ lead to the cleavage of a single C–C bond to form benzylic chlorides.⁴⁹ The reaction of 7-ethynylcyclohepta-1,3,5-triene with trifluoroacetic acid leads to phenylallene by protonation of the alkyne in the norcaradiene tautomer followed by cyclopropane cleavage to form the arenium cation.⁵⁰ The reaction of 7-ethoxycarbonyl-1,3,5-cycloheptatriene with an equimolar amount of Pd(OAc)₂ at 80 °C in MeCN had been reported to give ethyl 2- and 4-formylbenzoate (8% each) by cleavage of one cyclopropane C–C bond of the corresponding norcaradienes.⁵¹ In addition, diethyl maleate (14% yield) was formed, presumably by a dimetization of a Pd(II) carbene formed by a retro-Buchner process.⁵² Formation of benzyl-Rh(II) from cycloheptatrienyl-Rh(I) occurs by a metalloradical process. Cycloheptatriene has also been found to react on the metal carbide W(100)-(5 × 1)-C surface to generate benzene at 600 K,⁵³ whereas (tricarbonyl)(tropylium)chromium perchlorate forms benzene-(tricarbonyl)chromium by reaction with sodium cyclopentadienide or diethyl sodium malonates by an unknown mechanism.⁵⁴ Carbenes have been generated by photochemical cleavage of a cyclopropanated phenanthrene.⁵⁵

Our DFT computational study of the gold-catalyzed retro-Buchner reaction (M06 level, 1,2-dichloroethane) was complicated by the likely existence of several η²-coordinated gold(I) species in solution. Thus, in addition to η²-coordinated cycloheptatriene (**VIIa**) and norcaradiene (**VIIb**), the (η¹-arene)gold(I) complex **VIIc** was also found as a local minimum (Scheme 18). An intermediate norcaradiene in which gold(I) is η²-coordinated to the cyclopropane C–C bond (**VIIId**) was also found at a free energy 12.7 kcal mol⁻¹ higher than that of **VIIb**. Previously, on the basis of related DFT calculations, we proposed the formation of related edge- or corner-metalated cyclopropanes as products in intra- and intermolecular gold(I)-catalyzed cyclopropanations of alkenes with 1,6-enynes⁵⁶ and intramolecular cyclopropanation of 1,5-enynes.⁵⁷

A transition state (**TS_{VIIId-VIII}**) was found for the electrophilic cleavage of intermediate **VIIId** (Scheme 19), which lies 23.3 kcal mol⁻¹ higher than the most stable initial complex **VIIb**. This value for the activation energy of the retro-Buchner reaction is consistent with the range of temperatures required for these reactions (100–120 °C). Transition state **TS_{VIIId-VIII}** leads to Wheland-type intermediate **VIII**, which is in a shallow minimum that smoothly evolves through **TS_{VIII-IX}** to form phenyl gold(I) carbene **IX** and benzene. Although the overall process of the retro-Buchner reaction is moderately endother-

Scheme 18. DFT Calculations on η^2 -Coordinated Gold(I) Species (Free Energies in kcal mol⁻¹)Scheme 19. DFT Calculations on the Mechanism (Free Energies in kcal mol⁻¹)

mic, further reactions of gold(I) carbene IX with alkenes (including intermolecular cyclopropanations⁵⁶) or arenes are highly exothermic processes.

3. CONCLUSIONS

In summary, gold(I) carbenes generated by the retro-Buchner reaction of 1,3,5-cycloheptatrienes catalyzed by cationic gold(I) complexes can be trapped intramolecularly by alkenes or arenes to form indenenes or fluorenes. This methodology provides a new synthetic approach to indenenes and fluorenes and may be applied to the synthesis of indenofluorenes used in organic electronics. These reactions proceed via intramolecular Friedel–Crafts-type attack of the highly electrophilic gold(I) carbenes to the alkenes and arenes. The reactivity displayed by

the cationic intermediates generated by the retro-Buchner reaction is more similar to that of metal carbenes of rhodium or copper or even free carbenes than that of carbocations.

Closer scrutiny of the mechanisms of these reactions has revealed some intriguing details. Thus, in the indene synthesis, we have found that a novel 1,4-metallotropic migration competes with the primary pathway for the formation of the (η^2 -indene)gold(I) complexes by a concerted 1,2-H migration/gold(I) elimination. The formation of fluorenes involves a diatropic-type process in the formation of an (η^1 -fluorene)-gold(I) complex. Finally, the mechanism of the gold(I)-catalyzed retro-Buchner reaction of substituted cycloheptatrienes proceeds by electrophilic cleavage of two C–C bonds of the norcaradiene tautomers. Although the cleavage occurs stepwise, the potential energy surface connecting the two transition states is rather shallow.

■ ASSOCIATED CONTENT

Supporting Information

Additional data, experimental details, and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank MEC (Project CTQ2010-16088/BQU), the European Research Council (Advanced Grant 321066), EU Project ICT (ATMOL, Contract FP7-270028), the AGAUR (Project 2009 SGR 47), and the ICIQ Foundation for financial support.

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