Gold(I)-Catalyzed Synthesis of Indenes and Cyclopentadienes: Access to (±)-Laurokamurene B and the Skeletons of the Cycloaurenones and Dysiherbols

Xiang Yin, Mauro Mato, and Antonio M. Echavarren*

Abstract: *The formal (3+2) cycloaddition between terminal allenes and aryl or styryl gold(I) carbenes generated by a retro-Buchner reaction of 7-substituted 1,3,5-cycloheptatrienes led to indenes and cyclopentadienes, respectively. These cycloaddition processes have been applied to the construction of the carbon skeleton of the cycloaurenones and the dysiherbols as well as to the total synthesis of (±)-laurokamurene B.*

We previously found that cationic gold(I) complexes promote the retro-Buchner reaction of 7-substituted 1,3,5-cycloheptatrienes, such as **1** and **2**, via their norcaradiene tautomers, leading to reactive metal carbenes[1] [LAu=CHR]⁺ **3** and **4** (Scheme 1), which react with alkenes to give
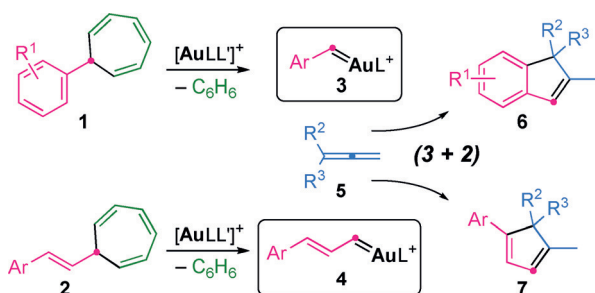
Scheme 1. Formal (3+2) cycloaddition between allenes and both aryl and styryl gold(I) carbenes generated by a retro-Buchner reaction.

cyclopropanes[2,3] or undergo intramolecular Friedel–Crafts-type reactions.[4] Cyclopentenes were obtained by the formal (4+1) cycloaddition of gold(I) carbenes **3** with cyclobutenes or methylenecyclopropanes.[5] We have now discovered that

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aryl and styryl gold(I) carbenes **3** and **4** react with allenes **5** to give highly substituted indenes[6,7] and cyclopentadienes,[8,9] respectively, by a formal (3+2) cycloaddition.

Indenes are important motifs present in many biologically relevant natural products,[10] and are building blocks in organic synthesis, organometallic chemistry, and in the field of materials science.[11] Similarly, cyclopentadienes are important substrates, mainly as reactive diene components in the Diels–Alder reaction and as ligands in organometallic chemistry.[12] To illustrate the application of the new gold(I)-catalyzed (3+2) cycloaddition reactions in the context of natural product synthesis, we have developed a route for the construction of the tetracyclic carbon skeleton common to the cycloaurenones (**8 a–c**)[13] and the dysiherbols (**9 a–c**),[14] and a total synthesis of (±)-laurokamurene B (**10**)[15] (Figure 1).
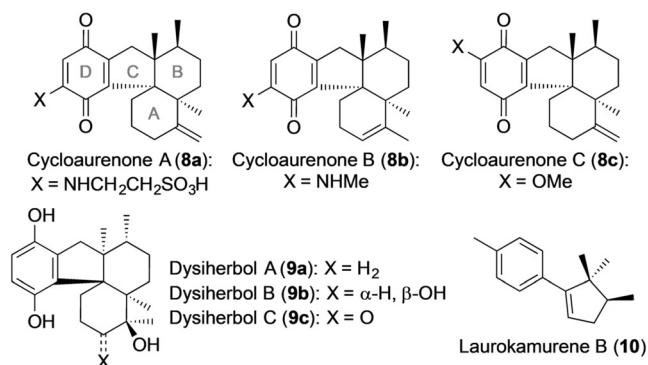

Figure 1. Cycloaurenones (**8 a–c**), dysiherbols (**9 a–c**), and laurokamurene B (**10**).
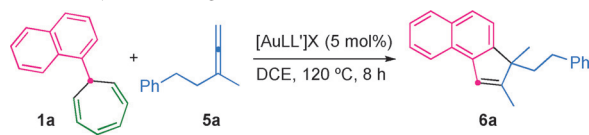
We first studied the reaction of 7-(1-napthyl)-1,3,5-cyclo-heptatriene (**1a**) with allene **5a** with different gold(I) catalysts (Table 1). The reaction of **1a** with **5a** (2.0 equiv) in the presence of the gold(I) complex [(JohnPhos)Au(MeCN)]SbF₆ (**A**; 5 mol%) in 1,2-dichloroethane at 120°C for 8 h gave indene **6a** in 66% yield for the isolated product (Table 1, entry 1). Other gold(I) complexes **B–F** could also be used in the reaction (Table 1, entries 2–6), although none of them outperformed catalyst **A**. Complex **G** bearing a phosphite ligand failed to promote this transformation.

Indenes **6b–v** were obtained under the standard conditions in 41–72% yield by the reaction of 1,1-disubstituted allenes **5a–g** (see the Supporting Information for structures) with cycloheptatrienes with an unsubstituted, *ortho-* or *para-* substituted, or *ortho,meta-*disubstituted aryl group (substrates **1b–j**), a 1- or 2-naphthyl group (substrates **1a** and **1k**), or a 9-phenanthryl group (substrate **1l**; Table 2). This reaction is

Table 1: Catalyst screening for the reaction of **1a** with allene **5a**.[a]

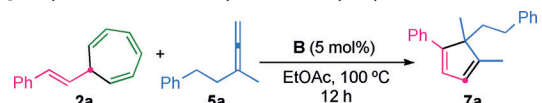| Entry	Catalyst	6a Yield [%][b]
1	A	74 (66)[c]
2	B	55
3	C	61
4	D	55
5	E	31
6	F	57
7	G	—[d]

[a] Reaction conditions: **1a** (0.1 M in DCE), **5a** (2.0 equiv), catalyst (5 mol%), 120°C, 8 h. [b] The yield was determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. [c] The yield of the isolated product is given in parentheses. [d] Not detected. Cy = cyclohexyl, DCE = 1,2-dichloroethane, Tf = trifluoromethanesulfonyl.

A: R = tBu, R' = R" = H
B: R = tBu, R' = R" = iPr
C: R = Cy, R' = OMe, R" = H
D: R = Cy, R' = R" = iPr

E

F: L = PhCN

G
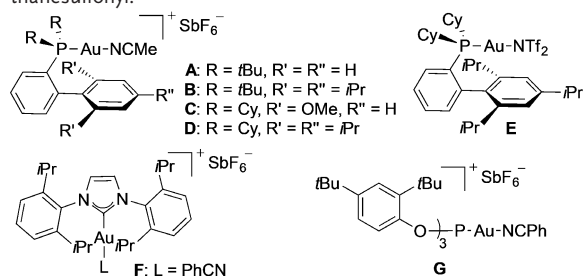
Table 2: Scope of the gold(I)-catalyzed synthesis of indenes.[a]

6b: R¹ = R² = R³ = R⁴ = H (67%)
6c: R¹ = OMe, R² = R³ = R⁴ = H (54%)
6d: R¹ = OPh, R² = R³ = R⁴ = H (41%)
6e: R¹ = R² = R⁴ = H, R³ = OMe (68%)
6f: R¹ = R⁴ = OMe, R² = R³ = H (53%)
6g: R¹ = R² = R⁴ = H, R³ = Cl (55%)
6h: R¹ = Ph, R² = R³ = R⁴ = H (51%)
6i: R¹ = (CH₂)₂Ph, R² = R³ = R⁴ = H (59%)
6j: R¹ = R² = R⁴ = H, R³ = t-Bu (58%)

6k: R = Me (71%)
6l: R = c-C₆H₁₁ (49%)

6m: R = H (72%)
6n: R = Me (62%)

6o (63%)

6p (52%)

6q: R = Me (41%)
6r: R = (CH₂)₂Ph (69%)
6s: R = c-C₆H₁₁ (47%)

6t (52%)

6u: R = Me (50%)
6v: R = (CH₂)₂Ph (71%)

11 (28%)[b]
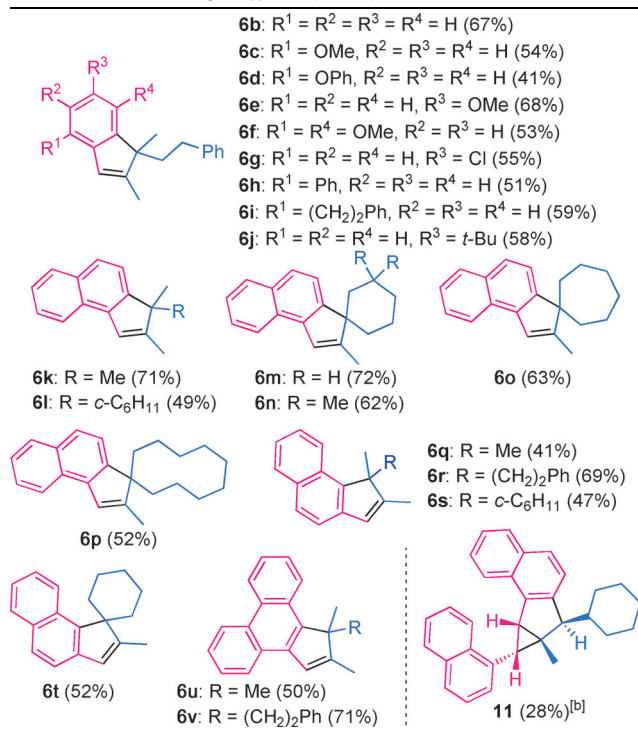
[a] Reaction conditions: **1** (0.1 M in 1,2-dichloroethane), allene **5** (2.0 equiv), catalyst **A** (5 mol%), 120°C, 8 h. Yields are for the isolated product. [b] Reaction time: 16 h.

perfectly suited for the preparation of spiro compounds, such as **6m**–**p** and **6t**. The structure of indenes **6d**, **6t**, and **6u** was confirmed by single-crystal X-ray diffraction.[16] Although the resulting indenes have a reactive double bond, 2:1 adducts were only observed as very minor products in the crude reaction mixtures. In contrast, a 2:1 adduct was obtained in the reaction of 1-cyclohexylallene **5h**, a monosubstituted allene, with **1a** to form **11**, whose relative configuration was determined by X-ray diffraction.[16]

Styryl cycloheptatriene **2a** reacted with allene **5a** to give cyclopentadiene **7a** in 50% yield in the presence of gold(I) complex **B** (5 mol%) in EtOAc at 100°C (Table 3). The less bulky catalyst **A** performed similarly (Table 3, entry 2), whereas NHC gold(I) complexes, such as **F**, were less reactive (Table 3, entry 4).
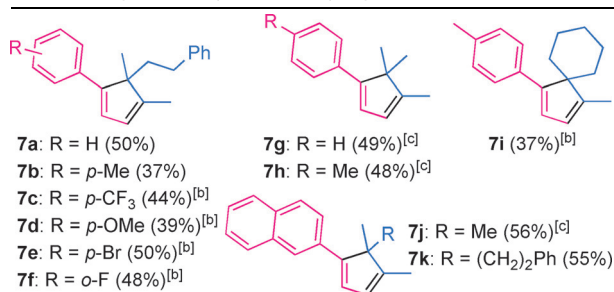
Table 3: Optimization of the synthesis of cyclopentadienes.[a]

| Entry	Deviation from above[a]	Yield [%][b]
1	none	52 (50)[c]
2	catalyst A instead of B	45
3	catalyst D instead of B	—[d]
4	catalyst F instead of B	17
5	DCE instead of EtOAc	25
6	90°C	33
7	120°C	40

[a] Reaction conditions: **2a** (0.1 M in EtOAc), **5a** (1.5 equiv), catalyst **B** (5 mol%), 100°C, 12 h. [b] The yield was determined by GC–FID with diphenylmethane as an internal standard. [c] The yield of the isolated product is given in parentheses. [d] Not detected. FID = flame ionization detection.

A range of styryl cycloheptatrienes gave rise to 1,1,2,5-tetrasubstituted cyclopentadienes bearing both electron-rich (products **7b**, **7d**) and electron-poor substituents (products **7c**, **7e**, **7f**) in the aryl moiety in 37–56% yield (Table 4).

A Diels–Alder reaction between **7g** and maleic anhydride led to the crystalline *endo* adduct **12** (Scheme 2). The X-ray diffraction structure of **12**[16] allowed confirmation of the structures assigned to **7a**–**k** (Table 4).

Table 4: Scope of the synthesis of cyclopentadienes.[a]

7a: R = H (50%)
7b: R = p-Me (37%)
7c: R = p-CF₃ (44%)[b]
7d: R = p-OMe (39%)[b]
7e: R = p-Br (50%)[b]
7f: R = o-F (48%)[b]

7g: R = H (49%)[c]
7h: R = Me (48%)[c]

7i (37%)[b]

7j: R = Me (56%)[c]
7k: R = (CH₂)₂Ph (55%)

[a] Reaction conditions: **2** (0.1 M in EtOAc), allene **5** (1.5 equiv), catalyst **B** (5 mol%), 100°C, 12 h. Yields are for the isolated product. [b] The reaction was carried out with 2.0 equivalents of the allene. [c] The reaction was carried out with 3.0 equivalents of the allene.
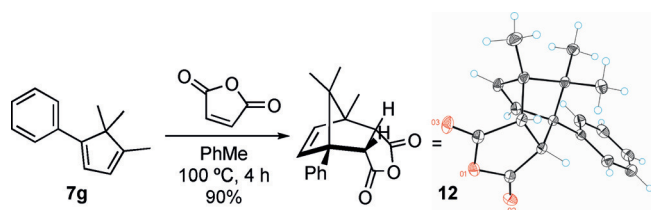
Scheme 2. Diels–Alder reaction of **7g** with maleic anhydride.

Laurokamurene B (**10**), isolated from the red algae *Laurencia okamurae*, is a member of a small family of natural compounds displaying antifungal and cytotoxic activity.[15] (±)-Laurokamurene B (**10**) was readily synthesized in good yield by simple hydrogenation of cyclopentadiene **7h** in the presence of the Wilkinson catalyst (Scheme 3). Considering
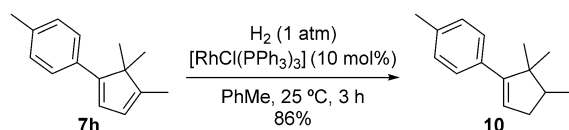

Scheme 3. Total synthesis of (±)-laurokamurene B (**10**).

that (*E*)-7-(4-methylstyryl)cyclohepta-1,3,5-triene (**2b**), the cycloheptatriene required for the preparation of **7h**, can be readily obtained by the treatment of potassium (*E*)-(4-methylstyryl)trifluoroborate with tropylium tetrafluoroborate in almost quantitative yield,[3] this total synthesis requires just three steps and provides (±)-**10** in 39% overall yield from commercially available starting materials, which compares favorably with previous syntheses of (±)-**10**.[17]

Cycloaurenones A–C (**8a–c**) feature a *cis*-decalin moiety, whereas the dysiherbols (**9a–c**) show *trans* fusion of the A/B rings (Figure 1). They also differ in their absolute configuration. These compounds are biogenetically related to other natural products isolated from sponges, such as (+)-smenoqualone,[18] ilimaquinone,[19] and smenospongin.[20] Many of these natural products display antimicrobial, anti-HIV, anti-inflamatory, antiproliferative, and antisecretory activities and have attracted the interest of synthetic chemists.[21] However, no approach towards the synthesis of the cycloaurenones and the dysiherbols has been reported. As a first approach to the synthesis of these natural products, we considered applying the (3+2) cycloaddition together with an intramolecular radical cyclization to build up the carbocyclic core structure of **8a–c** and **9a–c** (Scheme 4).

The synthesis of allene **5i** was performed on a gram scale in seven steps from cyclohexanone, starting with the Michael addition of its cyclohexylimine to acrylonitrile.[22,23] The gold(I)-catalyzed reaction between **5i** and cycloheptatriene **1f** was most efficient with [(IPr)Au(PhCN)]SbF$_6$ (**F**) as the catalyst and gave spiroindene **13** as a mixture of four stereoisomers (Scheme 4).[23] Cleavage of the benzoate and oxidation of the secondary alcohols with Dess–Martin periodinane (DMP) delivered ketones **14a** and **14b** in a 1:1 ratio and 36% yield over three steps, after only one chromatographic purification. Ketone **14a** was reduced to the corresponding
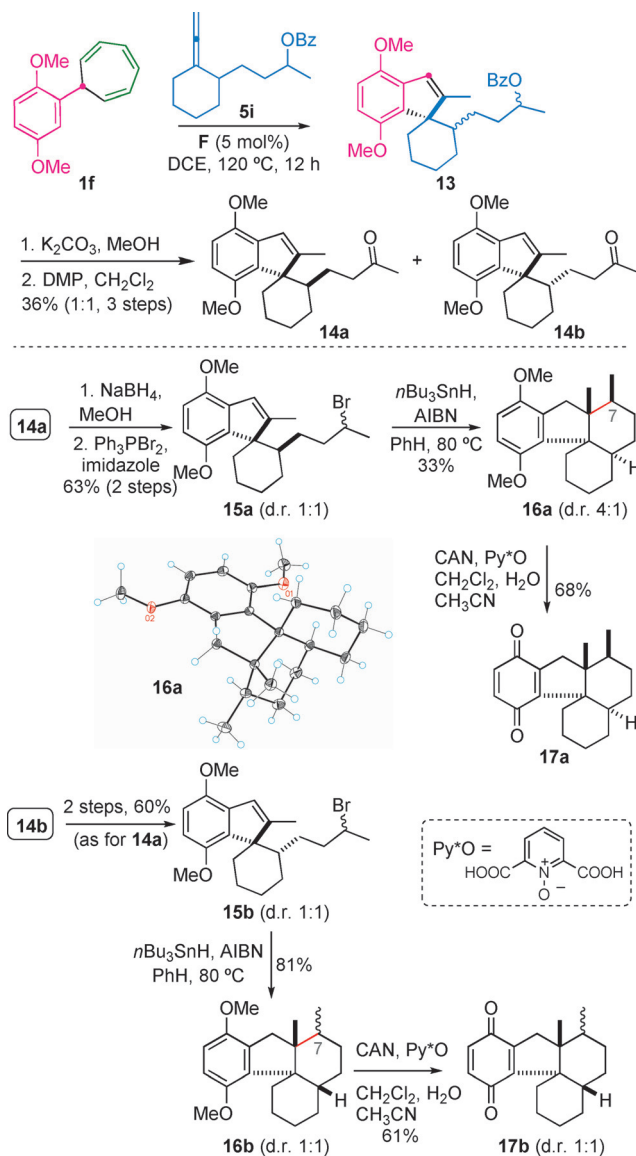
Scheme 4. Assembly of the tetracyclic carbon skeleton of the cycloaurenones (structure **17a**) and dysiherbols (structure **16b**). AIBN = azobisisobutyronitrile, Bz = benzoyl.

alcohol and then treated with triphenylphosphine dibromide to give alkyl bromide **15a** in 63% yield over two steps. Treatment of **15a** with *n*Bu$_3$SnH in the presence of AIBN triggered a radical cyclization, which delivered the corresponding tetracyclic product **16a** in 33% yield (4:1 mixture of epimers at C7). The major isomer displayed the configuration of cycloaurenones, as shown by X-ray diffraction.[16] Finally, oxidative deprotection of the methoxy groups with cerium ammonium nitrate (CAN) and pyridine-2,6-dicarboxylic acid *N*-oxide (Py*O)[24] led to quinone **17a**. By the same sequence of reactions, **16b**, corresponding to the tetracyclic carbon skeleton of the dysiherbols, was obtained as a 1:1 mixture of epimers through a remarkably efficient radical cyclization of **15b** (81% yield).[23] Oxidation of **16b** as before provided **17b**.

Both (3+2) cycloaddition reactions start with the gold(I)-promoted retro-Buchner reaction of **1** or **2** to release benzene and generate the gold(I) carbene **3** or **4**, respectively, which
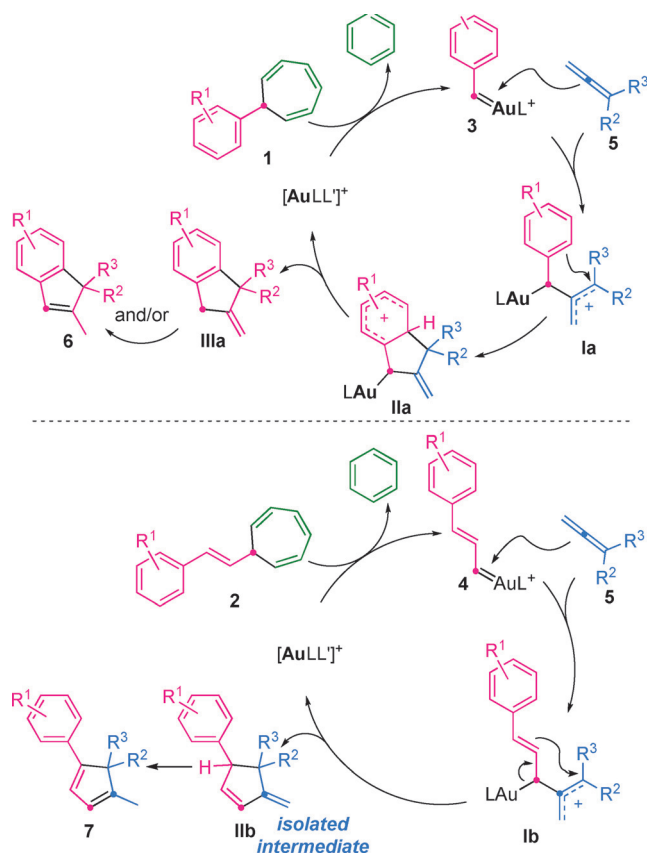
Scheme 5. Proposed mechanisms for the formal (3+2) cycloaddition between allenes and aryl or styryl gold(I) carbenes.

undergoes electrophilic attack at the central carbon atom of allenes **5** to give an allyl cationic species **Ia** or **Ib** (Scheme 5). In the first case, intramolecular electrophilic aromatic substitution gives intermediate **IIa**, which can undergo rearomatization and protonolysis of the Au–C bond to form **IIIa**, which can undergo isomerization to give indene **6**. Alternatively, protonation at the exocyclic double bond of **IIa** with concomitant deauration would directly furnish **6**. For the cyclopentadiene synthesis, the cyclization of **Ib** would give **IIb**, which is converted into **7** by isomerization. Indeed, monitoring of the reaction by GC–MS allowed observation of the rapid formation of **IIb** (as a mixture of *anti*- and *syn*-**IIb** when R$^2 \neq$ R^3), which slowly underwent isomerization to **7**. Intermediates **IIb** were also observed by ^{1}H NMR spectroscopy, and their isomerization to **7** was found to be catalyzed by gold(I).[23]

In summary, two new gold(I)-catalyzed formal (3+2) cycloaddition reactions have been developed between allenes and aryl or styryl gold(I) carbenes generated by a retro-Buchner reaction of 7-substituted cycloheptatrienes, thus leading to highly substituted indenes and cyclopentadienes, respectively. The usefulness of these new methods has been demonstrated by the shortest total synthesis of laurokamurene B reported to date and by the ready construction of the carbon skeleton of the cycloaurenones and the dysiherbols. Efforts directed towards the synthesis of these natural products are under way.

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