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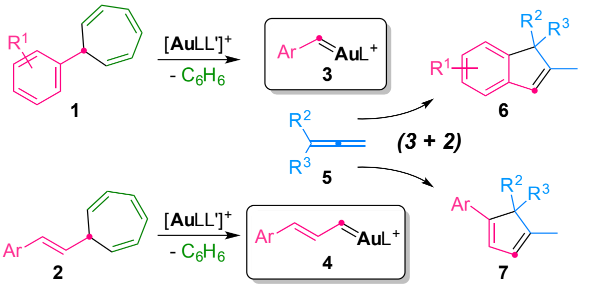
Gold(I)-Catalyzed Synthesis of Indenes and Cyclopentadienes: Access to (±)-Laurokamurene B and the Skeletons of Cycloaurenones and Dysiherbols

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

Abstract: *The formal (3 + 2) cycloaddition between terminal allenes with aryl or styryl gold(I) carbenes generated by retro-Buchner reaction of 7-substituted 1,3,5-cycloheptatrienes leads to indenes and cyclopentadienes, respectively. These cycloadditions 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 found that cationic gold(I) complexes promote the retro-Buchner reaction of 7-substituted 1,3,5-cycloheptatrienes, such as **1** and **2**, through their norcaradiene tautomers, leading to relatively simple reactive metal carbenes[1] $[LAu{=}CHR]^+$ **3** and **4** (Scheme 1), which react with alkenes to give cyclopropanes [2,3] or undergo intramolecular Friedel–Crafts-type reactions.[4] Cyclopentenes were obtained by formal (4 + 1) cycloaddition of gold(I) carbenes **3** with cyclobutenes or methylenecyclopropanes.[5] We have now discovered that aryl and styryl gold(I) carbenes **3** and **4** react with allenes **5** giving rise to highly substituted indenes[6,7] and cyclopentadienes,[8,9] respectively, by a formal (3 + 2) cycloaddition.



Scheme 1. Formal (3 + 2) cycloaddition between allenes and both aryl and styryl gold(I) carbenes generated by retro-Buchner reaction.

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) cycloadditions in the context of natural product synthesis, we have developed a route for the construction of the tetracyclic carbon skeleton common to the cycloaurenones (**8a-c**)[13] and the dysiherbols (**9a-c**),[14] and a total synthesis of (±)-laurokamurene B (**10**)[15] (Figure 1).

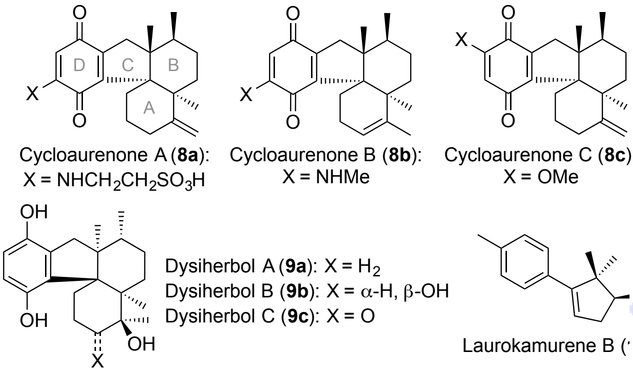
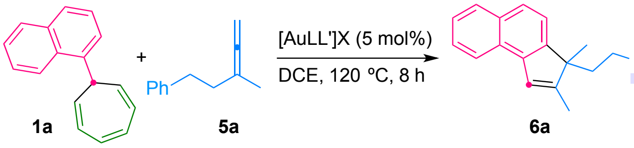


Figure 1. Cycloaurenones (**8a-c**), dysiherbols (**9a-c**) a laurokamurene B (**10**).

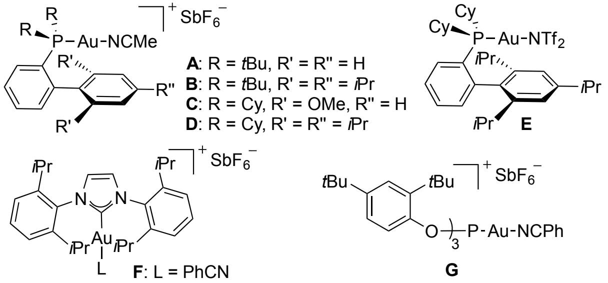
We first studied the reaction of 7-(1-napthyl)-1,3 cycloheptatriene (**1a**) with allene **5a** with different gold(I) cataly (Table 1). Reaction of **1a** with 2.0 equiv of **5a** in the presence o mol% of gold(I) complex $[(JohnPhos)Au(MeCN)]SbF_6$ (**A**) in 1 dichloroethane at 120 ºC for 8 h gave indene **6a** in 66% isolated yi (Table 1, entry 1). Other gold(I) complexes (**B**-**F**) could also be u in the reaction (Table 1, entries 2-6), although none of th outperformed catalyst **A**. Complex **G** bearing a phosphite lig failed to promote this transformation.

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 of **1a** (0.1 M in 1,2-dichloroethane) with 2.0 equiv of **5a**, 5 mol of catalyst at 120 ºC for 8 h. [b] Yields determined by ^1H NMR using 1,3,5 trimethoxybenzene as internal standard. [c] (Isolated yield). [d] Not detecte



Indenes **6b-v** were obtained under the standard conditions in 41-72% yield by reaction of 1,1-disubstituted allenes **5a-g** with *ortho*-, *para*-substituted and *ortho*,*meta*-disubstituted aryl (**1b-j**), 1- and 2-naphtyl (**1a** and **1k**), and 9-phenanthryl (**1l**) cycloheptatrienes (Table

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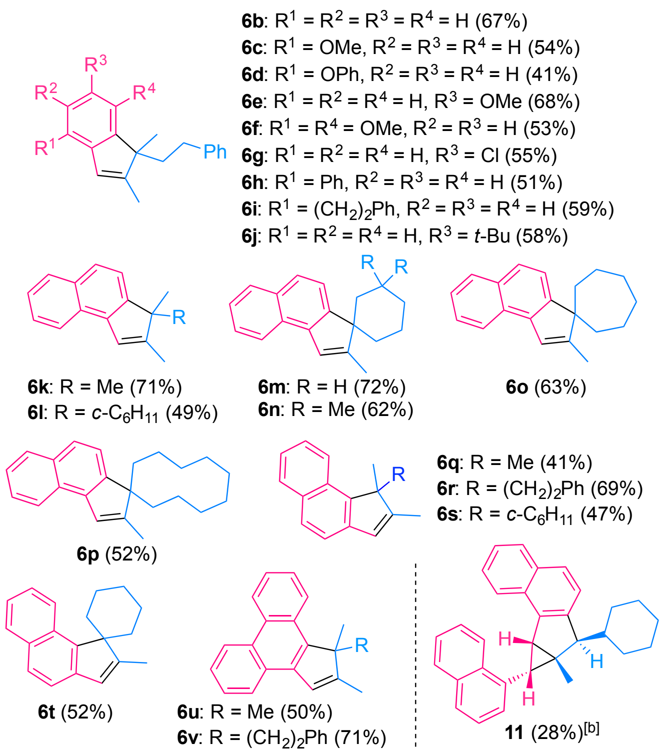
2). This reaction is perfectly suited for the preparation of spiro compounds such as **6m-p** and **6t**. The structure of indenes **6d**, **6t** and **6u** was confirmed by single crystal X-ray diffraction.[16] Although the resulting indenes have a reactive double bond, 2:1 adducts were only observed 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]

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



6b: $R^1 = R^2 = R^3 = R^4 = H$ (67%)
6c: R^1 = OMe, $R^2 = R^3 = R^4 = H$ (54%)
6d: R^1 = OPh, $R^2 = R^3 = R^4 = H$ (41%)
6e: $R^1 = R^2 = R^4 = H$, R^3 = OMe (68%)
6f: $R^1 = R^4$ = OMe, $R^2 = R^3 = H$ (53%)
6g: $R^1 = R^2 = R^4 = H$, R^3 = Cl (55%)
6h: R^1 = Ph, $R^2 = R^3 = R^4 = H$ (51%)
6i: $R^1 = (CH_2)_2Ph$, $R^2 = R^3 = R^4 = H$ (59%)
6j: $R^1 = R^2 = R^4 = H$, R^3 = *t*-Bu (58%)

6k: R = Me (71%)
6l: R = *c*-C_6H_{11} (49%)

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

6o (63%)

6p (52%)

6q: R = Me (41%)
6r: R = $(CH_2)_2Ph$ (69%)
6s: R = *c*-C_6H_{11} (47%)

6t (52%)

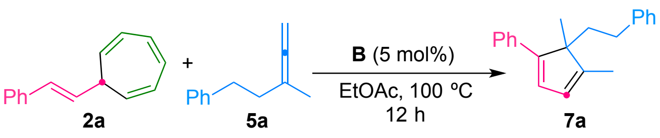
6u: R = Me (50%)
6v: R = $(CH_2)_2Ph$ (71%)

11 (28%)[b]

[a] Reaction of **1** (0.1 M in 1,2-dichloroethane) with 2.0 equiv of allene **5**, 5 mol% of catalyst **A** at 120 ºC for 8 h. Yields are for isolated products. [b] 16 h.

Styryl cycloheptatriene **2a** reacts with allene **5a** to give cyclopentadiene **7a** in 50% yield in the presence of 5 mol% of gold(I) complex **B** in EtOAc at 100 ºC (Table 3). Less bulky catalyst **A** performs 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]

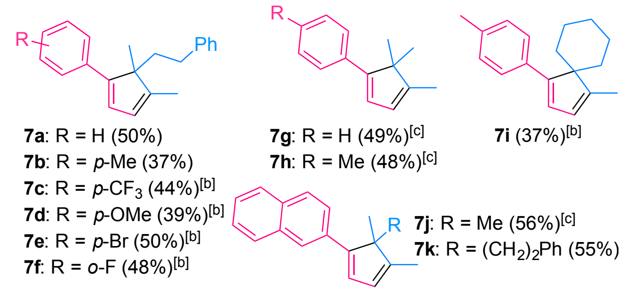


Entry	Deviation from above[a]	7a Yield [%][b]
1	None	52 (50)[c]
2	Catalyst **A** instead of **B**	45
3	Catalyst **D** instead of **B**	-[d]
4	Catalyst **F** instead of **B**	17
5	DCE instead of EtOAc	25
6	90 ºC	33
7	120 ºC	40

[a] Reaction of **2a** (0.1 M in EtOAc) with 1.5 equiv of **5a**, 5 mol% of catalyst **B** at 100 ºC for 12 h. [b] Yields determined by GC-FID using diphenylmethane as internal standard. [c] (Isolated yield). [d] Not detected.

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

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



7a: R = H (50%)
7b: R = *p*-Me (37%)
7c: R = *p*-CF_3 (44%)[b]
7d: R = *p*-OMe (39%)[b]
7e: R = *p*-Br (50%)[b]
7f: R = *o*-F (48%)[b]

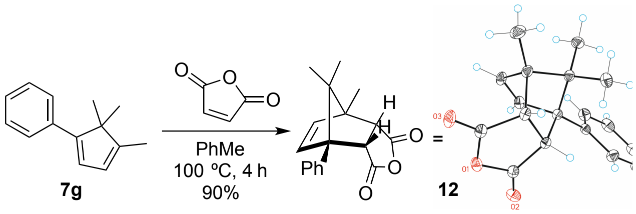
7g: R = H (49%)[c]
7h: R = Me (48%)[c]

7i (37%)[b]

7j: R = Me (56%)[c]
7k: R = $(CH_2)_2Ph$ (55%)

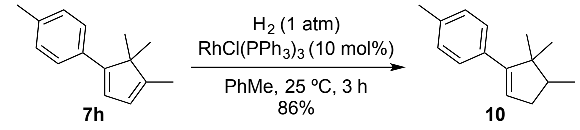
[a] Reaction of **2** (0.1 M in EtOAc) with 1.5 equiv of allene **5**, 5 mol% of cata
B at 100 ºC for 12 h. Yields are for isolated products. [b] 2.0 equiv of allene
3.0 equiv of allene.

A Diels–Alder reaction between **7g** and maleic anhydride lec crystalline *endo* adduct **12** in excellent yield, whose X-ray diffract structure[16] allowed confirming those assigned for **7a-k** (Table 4)



Scheme 2. Diels–Alder reaction of **7g** with maleic anhydride.

Laurokamurene B (**10**), isolated from the red algae *Lauren okamurae*, is a member of a small family of natural compou displaying antifungal and cytotoxic activity.[15] (±)-Laurokamuren (**10**) was easily synthesized in good yield by simple hydrogenatio cyclopentadiene **7h** using Wilkinson's catalyst (Scheme Considering that (*E*)-7-(4-methylstyryl)cyclohepta-1,3,5-triene (**2** the cycloheptatriene required for the preparation of **7h**, can be eas obtained by reaction of potassium (*E*)-(4-methylstyryl)trifluorobor with tropylium tetrafluoroborate in almost quantitative yield,[3] total synthesis requires just three steps and provides (±)-**10** in 3 overall yield from commercially available starting materials, wh compares favorably with previous syntheses of (±)-**10**.[17]



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

Cycloaurenones A-C (**8a-c**) feature a *cis*-decalin, whereas dysiherbols (**9a-c**) show a *trans*-fusion for the A/B rings (Figure 1). They also differ in their absolute configurations. These compounds are biogenetically related to other natural products isolated from sponges, such as (+)-smenoqualone,[18] ilimaquinone,[19] and smenospongin,[20] displaying antimicrobial, anti-HIV, anti-inflamatory, antiproliferative, and antisecretory activities, which 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 for the synthesis of these natural products, we considered applying the (3 + 2) cycloaddition together

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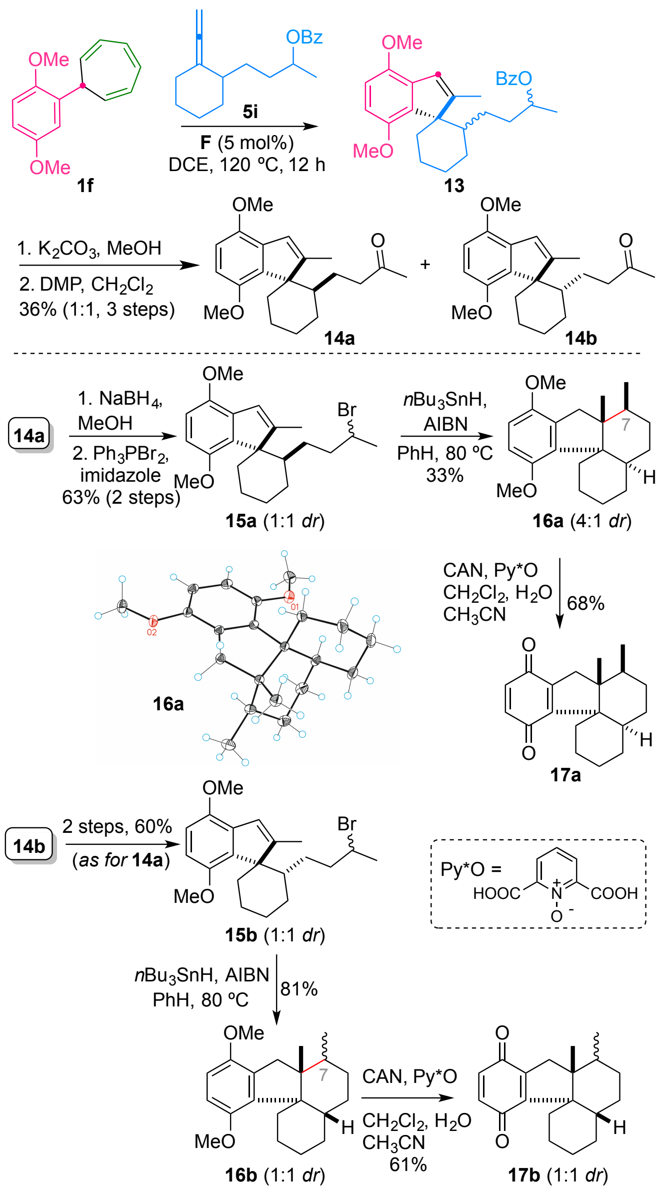
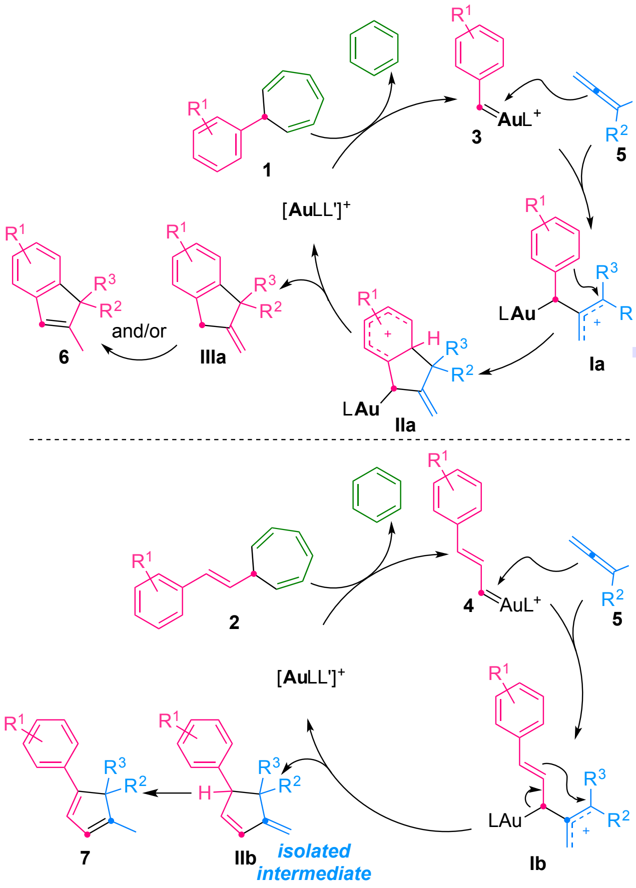
with an intramolecular radical cyclization to build up the carbocyclic core structure of **8a-c** and **9a-c** (Scheme 4).



Scheme 4. Assembly of the tetracyclic carbon skeleton of cycloaurenones (**17a**) and the dysiherbols (**16b**).

The synthesis of allene **5i** was performed in gram scale in seven steps from cyclohexanone, starting by the Michael addition of its cyclohexylimine to acrylonitrile[22,23] The gold(I) catalyzed reaction between **5i** and cycloheptatriene **1f** was better performed using [(IPr)Au(PhCN)]SbF$_6$ (**F**) as catalyst to give 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 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 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 delivering the corresponding tetracyclic product **16a** in 33% yield (4:1 mixture of epimers at C-7). The major isomer displays the configuration of cycloaurenones, as shown by X-ray diffraction.[16] Finally, oxidative deprotection of the methoxy groups with cerium ammonium nitrate and 2,6-pyridinedicarboxylic acid *N*-oxide[24] led to quinone **17a**. Following the same scheme, **16b**, corresponding to the tetracyclic carbon skeleton of the dysiherbols, was obtained as a 1:1 mixture of epimers via a remarkably efficient radical cyclization of **15b** (81% yield).[23] Oxidation of **16b** as before provided **17b**.

Both (3 + 2) cycloadditions start by the gold(I)-promoted retro-Buchner reaction of **1** or **2**, releasing benzene and generating gold(I) carbenes **3** and **4**, respectively, which undergo electrophilic attack to the central carbon of allenes **5** giving rise to allyl cationic species **Ia** or **Ib** (Scheme 5). In the first case, an intramolecular electrophilic aromatic substitution gives intermediate **IIa**, which could undergo rearomatization and protonolysis of the Au-C bond to form **II** which would undergo isomerization to give indene **6**. Alternative protonation at the exocyclic double bond of **IIa** with concomit deauration would furnish directly **6**. For the cyclopentadi synthesis, the cyclization of **Ib** would give **IIb**, which gives rise the **7** after isomerization. Indeed, monitoring the reaction by GC- allowed observing the rapid formation of **IIb** (as a mixture of *a* and syn-**IIb** when R^2 ≠ R^3), which slowly undergoes isomerizat into **7**. Intermediates **IIb** were also observed by ^{1}H NMR and th isomerization into **7** was found to be catalyzed by gold(I).[23]



Scheme 5. Proposed mechanisms for the formal (3 + 2) cycloaddition between allenes and aryl or styryl gold(I) carbenes.

In summary, two new gold(I)-catalyzed formal (3 + 2) cycloaddition reactions have been developed by reaction of allenes with aryl or styryl gold(I) carbenes generated by retro-Buchner reaction of 7-substituted cycloheptatrienes, 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 is underway.

Acknowledgements

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Keywords: Gold catalysis · cycloaddition · indenes · cyclopentadienes · total synthesis

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