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**Metal-Catalyzed Cycloadditions**

# Platinum-Catalyzed Intramolecular [4C+3C] Cycloaddition between Dienes and Allenes**

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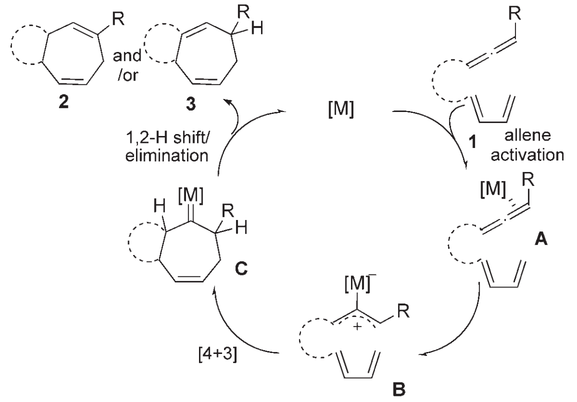
Polycyclic structures containing seven-membered carbocycles are important synthetic targets because they constitute the basic structural framework of a wide variety of biologically relevant products.[1] Among the different strategies for assembling cycloheptanoic systems, cycloaddition routes are particularly attractive because of their inherent potential for achieving a rapid increase in skeletal complexity.[2] One of the most convenient and best established cycloaddition approaches to carbocyclic seven-membered rings is the [4C+3C] annelation of dienes and allyl cation derivatives, principally oxy- and amino-allyl cations.[3–7] These cationic species are typically generated from halo, alkoxy, or sulfone carbonyl derivatives,[4] although their preparation from alkoxyallylic sulfoxides,[5] allenamides, [6] or methylene-aziridines[7] have also been described.

Despite notable advances in the implementation of these methodologies, the requirement of relatively elaborate and sometimes unstable allyl cation precursors, the need for stoichiometric activators,[8] and the frequent restriction of the success of the cycloadditions to furan and/or cyclopentadiene components, currently represent important limitations.

Recent reports on the use of Pt and Au complexes to induce reactions of allenes through allyl cation type intermediates,[9,10] led us to envisage the possibility of using allenes as three-carbon components in metal-promoted [4C+3C] cycloadditions with dienes.[11] Our mechanistic working hypothesis (Scheme 1) consists of an initial activation of the allene (**A**) to form an allylic cation–metal complex (**B**), which may react with the diene in a standard 4π(4C)-2π(3C) mode. The resulting metal–carbene intermediate **C** could then undergo a 1,2-hydrogen shift to provide the desired seven-membered carbocycles (**2** and/or **3**) with regeneration of the metal catalyst.



*Scheme 1.* Mechanistic hypothesis for a diene–allene [4C+3C] cycloaddition. [M] = Pt or Au complex.

Herein, we demonstrate the viability of the approach by reporting several examples of a platinum-catalyzed intramolecular [4C+3C] cycloaddition between dienes and allenes. The strategy provides a novel and particularly efficient way to construct bicyclic systems that contain a seven-membered carbocycle.

Initial studies to test the viability of the process were carried out on the furan-allene derivative **1a** (Table 1).[12] Treatment of **1a** with 10 mol% of the catalyst generated from [$Ph_3PAuCl$] and $AgSbF_6$[13,9b] in $CH_2Cl_2$ provided, after 24 h at room temperature, the [4C+3C] adduct **2a** in 30% yield (65% conversion, Table 1, entry 1). Poorer yields of **2a** were obtained on increasing the temperature to 40 °C or to 75 °C (using toluene instead of $CH_2Cl_2$; see the Supporting Information). Heating under reflux in toluene led to the formation of the [4+2] adducts **4** (3.5:1 *exo*/*endo* mixture) together with a small proportion of **2a** (**4**:**2a** 6.2:1, 25% combined yield; Table 1, entry 2). Control experiments confirmed that the adducts **4** can be obtained by simple thermolysis of **1a**, which suggests that the metal is not involved in their formation.[14] The use of other gold-based catalysts such as $AuCl_3$ or AuCl[15] led to poor conversions at moderate temperatures, whereas heating at 110 °C provided the Diels–Alder cycloadducts as the major products (Table 1, entries 3–5). We then turned our attention to platinum complexes, which have been recently employed in catalytic processes involving allene activation.[9a,e] The use of $PtCl_4$ and $PtCl_2$ provided mixtures of **4** and **2a**, but with higher proportions of **2a** than in the above experiments (Table 1, entries 6 and 7). As in previous cases, performing the reactions at lower temperatures led to poor conversions.

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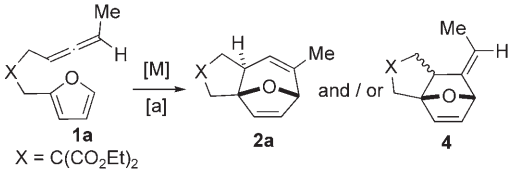
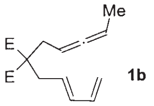
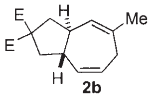
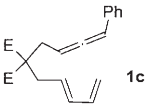
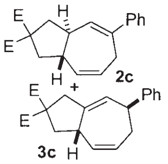
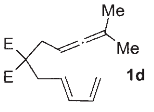
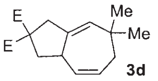
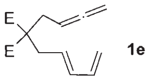
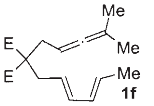
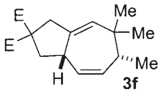
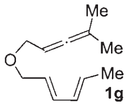
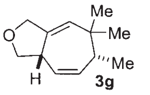
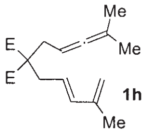
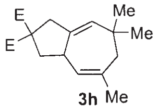
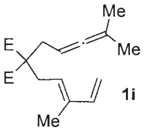
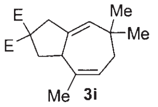
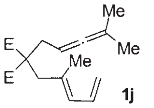
***Table 1:*** Optimization of the [4C+3C] cycloaddition of **1a**.[a]



| Entry | [M] | Products (ratio)[b] | $T$ [°C] | Yield [%][c] |
|---|---|---|---|---|
| 1 | [Ph$_3$PAuCl]/AgSbF$_6$ | **2a** | 23 | 30[d] |
| 2 | [Ph$_3$PAuCl]/AgSbF$_6$ | **4**:**2a** (6.2:1) | 110 | 25 |
| 3 | AuCl$_3$ | **2a** | 40 | 26[e] |
| 4 | AuCl$_3$ | **4**:**2a** (6.1:1) | 110 | 57 |
| 5 | AuCl | **4**:**2a** (19:1) | 110 | 89[f] |
| 6 | PtCl$_4$ | **4**:**2a** (4.4:1) | 110 | 57 |
| 7 | PtCl$_2$ | **4**:**2a** (3.4:1) | 110 | 73 |
| 8 | PtCl$_2$/CO (1 atm) | **2a** | 110 | 45[f] |

[a] Conditions: **1a** (0.2 M), 10 mol% [M]. Reactions at 23 or 40 °C were carried out in CH$_2$Cl$_2$, otherwise toluene was employed. Conversions are >99% unless otherwise noted. [b] Ratios determined by $^1$H NMR spectroscopy of the crude mixtures. [c] Determined by $^1$H NMR spectroscopy against an internal standard (1,2,3-trimethoxybenzene), unless otherwise stated. [d] 65% conversion. [e] 66% conversion. [f] Yield of isolated product.

***Table 2:*** Platinum-catalyzed [4C+3C] cycloaddition of acyclic dienes to allenes.[a]

| Entry | Substrate[12] | Product | $T$ [°C] | $t$ [h] | Yield[b] |
|---|---|---|---|---|---|
| 1 |  **1b** |  **2b** | 110 | 5 | 62 |
| 2 |  **1c** |  **2c** + **3c** | 110 | 5 | 95[c] |
| 3 | **1c** | **2c**:**3c** | 65 | 12 | 87[d] |
| 4 |  **1d** |  **3d** | 110 | 2 | 92 |
| 5 | **1d** | **3d** | 110 | 12 | 90[e] |
| 6 | **1d** | **3d** | 23 | 18 | 95 |
| 7 | **1d** | **3d** | 23 | 2 | 98[f] |
| 8 |  **1e** | – | 110 | 12 | – |
| 9 |  **1f** |  **3f** | 110 | 2 | 81 |
| 10 |  **1g** |  **3g** | 110 | 3 | 62 |
| 11 |  **1h** |  **3h** | 110 | 12 | 72 |
| 12 |  **1i** |  **3i** | 110 | 12 | 73 |
| 13 |  **1j** | – | 110 | 24 | –[g] |

[a] E = CO$_2$Et; conditions: Toluene 110 °C, **1** (0.1–0.2 M), 10 mol% PtCl$_2$ unless otherwise stated. Conversion >99% (determined by $^1$H NMR spectroscopy). [b] Yield of isolated product. [c] Combined yield of the mixture of **2c** and **3c** (6:4). Ratio of products determined by $^1$H NMR spectroscopy in the crude reaction mixtures. [d] Ratio **2c**/**3c** = 7:3. [e] 2 mol% of PtCl$_2$. [f] Reaction carried out under CO (1 atm). [g] The starting material was recovered unaltered. The use of CO (1 atm) gave the same results.

On the assumption that the [4C+3C] cycloaddition process might be favored by increasing the electrophility of the Pt$^{II}$ center, we carried out the reaction with PtCl$_2$ under an atmosphere of CO.[16] Interestingly, complete disappearance of **1a** was observed after just one hour, and **2a** was the only cycloadduct detected, although it was obtained in a moderate yield of 45% (Table 1, entry 8).[17]

Envisaging that the presence of the furan unit could be detrimental for the desired [4+3] annulation by favoring the competitive Diels–Alder reaction as well as metal-induced secondary processes, we decided to test the behavior of substrate **1b**, which features a simple, acyclic diene. Remarkably, **1b** underwent the desired cycloaddition when heated under reflux in toluene in the presence of PtCl$_2$ (10 mol%), and provided **2b** in 62% yield (Table 2, entry 1).[18,19] It is worth highlighting the complete diastereoselectivity of the process, which provided exclusively the *trans*-fused 5,7-system **2b**. The reaction is also completely regioselective: the formation of regioisomers of type **3** was not detected. The use of an atmosphere of CO did not bring about any significant improvement in the yield of **2a**, it just led to slightly faster reaction rates. Therefore, further experiments addressing the scope of the transformation were carried out using the operationally safer standard inert atmosphere. It can be seen from the results in Table 2 that substrate **1c**, which includes an allene with a terminal phenyl substituent instead of the methyl group, underwent a very efficient [4+3] cycloaddition (Table 2, entry 2). In this case, the reaction provided both regioisomers **2c** and **3c** (in a 6:4 ratio) in 95% combined yield. Decreasing the reaction temperature to 65 °C led to a slight increase in the regioselectivity (Table 2, entry 3). Further lowering of the temperature gave incomplete conversions.

Trisubstituted allenes are excellent partners for the cycloaddition. Thus, reaction of **1d** with PtCl$_2$ (10 mol%) provided the cycloadduct **3d** in excellent yield (92%) after only 2 h at 110 °C (Table 2, entry 4).[20] It is noteworthy that the catalyst loading could be reduced to 2 mol% without affecting the efficiency of the process (Table 2, entry 5). The cycloaddition of **1d** could also be carried out at room temperature to give the desired cycloadduct as the only detectable product and in equally excellent yield (Table 2, entries 6 and 7). The superior performance of **1c** and **1d** than **1b** in the cycloaddition reaction might be related to the higher stability of the hypothetical allylic cation generated upon activation of the allene with $PtCl_2$ (**B**, Scheme 1). Consistent with this hypothesis, substrate **1e**, which contains a monosubstituted allene, failed to undergo the [4+3] cycloaddition when heated under standard conditions. The reaction gave rise to a mixture of oligomers together with a small amount of a [4+2] adduct.[21]

We next analyzed the influence of the diene substitution on the reaction. The introduction of a methyl substituent at the terminal position of the diene is well tolerated, as evident from the efficient conversion of **1f** into the [4C+3C] adduct **3f** with complete stereoselectivity (Table 2, entry 9). Reaction of the oxygen analogue **1g**, which lacks the geminal diester moiety of the tether, also proceeded smoothly to afford **3g** in 62% yield (Table 2, entry 10). Finally, allenedienes **1h** and **1i**, which are substituted at internal positions of the diene fragment, provided the corresponding cycloadducts **3h** and **3i** in satisfactory yields (Table 2, entries 11 and 12).

Allenediene **1j**, which has a methyl substituent at the most internal position of the diene, failed to undergo the cycloaddition reaction when heated in the presence of $PtCl_2$ or $PtCl_2$/CO (1 atm); the starting material was recovered after 24 h under reflux (Table 2, entry 13). The failure of this reaction could be related to the high energetic cost associated with the *S-cis* conformation of this diene, a conformation that is required if the cycloaddition involves a concerted $[4\pi + 2\pi]$ process.

The stereochemical course of the reported cycloadditions, which are completely diastereoselective, is consistent with a concerted annulation process involving an *exo*-like or extended transition state such as those depicted in Figure 1.[3] This model explains the observed diastereoselectivity for the cycloaddition of **1b**, **1c**, **1f**, and **1g**.

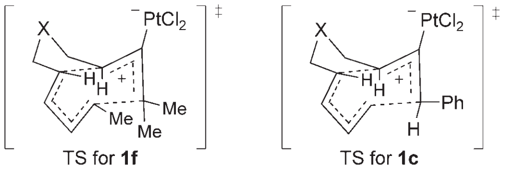
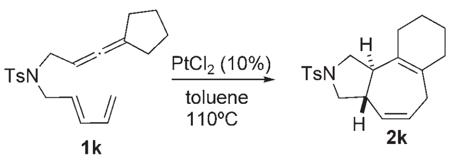


***Figure 1.*** Proposed extended (*exo*-like) transition state (TS) for the [4C+3C] cycloadditions of **1f** and **1c** ($X = C(CO_2Et)_2$).

According to the working mechanism depicted in Scheme 1, the metal-regeneration step requires a hydrogen migration process; however, the required turnover could also be hypothetically achieved by an alternative process, such as a 1,2-alkyl shift.[9a,10] Although we did not observe products arising from a 1,2-methyl shift in the cycloaddition of substrates bearing the dimethylallenyl moiety (**1d** and **1f**–**1i**), we were intrigued to know the outcome in the cases of allenes bearing a fused cycle.

Remarkably, treatment of allenediene **1k** with $PtCl_2$ (10 mol%) in refluxing toluene for 2 h afforded, in a completely diastereo- and regioselective fashion, the tricyclic product **2k** in 75% yield (Scheme 2). This transformation, in addition to validating a cycloaddition mechanism involving a 1,2-shift on a platinum–carbene intermediate of type **C** (Scheme 1), opens up an interesting alternative to constructing 5-7-6-tricyclic systems, a type of skeleton present in a wide variety of natural products.[22]



***Scheme 2.*** Cycloaddition/ring expansion of substrate **1k**.

In conclusion, we have developed a novel [4C+3C] cycloaddition process involving a platinum-catalyzed reaction of allenes and dienes. The method represents the first use of allenes as three-carbon components in any type of [4+3] catalytic cycloaddition. The excellent atom economy and stereoselectivity of the process, together with its operational simplicity, allows this method to be ranked among the most practical and rapid alternatives to construct cycloheptane-containing polycycles. Further studies on the scope, including an enantioselective version, and the mechanism of the process are underway.

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**Keywords:** carbocycles · cycloaddition · homogeneous catalysis · platinum · polycycles

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[19] Other platinum salts (PtCl$_4$, PtBr$_2$) led to considerably lower conversions, whereas the use of [Ph$_3$PAuCl]/AgSbF$_6$ in CH$_2$Cl$_2$ led to mixtures of products even at lower temperatures. See the Supporting Information for details.

[20] Besides extensive NMR experiments, definitive confirmation of the structure of **3d** was obtained by X-ray crystallography of an immediate derivative, see the Supporting Information. CCDC 661923 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] This [4+2] cycloaddition must be a PtCl$_2$-catalyzed process as thermolysis of **1e** does not give the cycloadduct.

[22] An alternative mechanism for the cycloadditions of allenedienes **1** involving deprotonation of **C** and protonation of the resulting vinyl platinum intermediate could be proposed. However, performing the cycloaddition of **1c** in toluene saturated with D$_2$O provided nondeuterated cycloadducts (**2c**:**3c** = 6:4, 82 % yield), thus making this pathway very unlikely.