

# Rhodium(I)-Catalyzed Intramolecular Carbonylative [2+2+1] Cycloaddition of Bis(allene)s: Bicyclo[6.3.0]undecadienones and Bicyclo[5.3.0]decadienones

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The  $[\text{Co}_2(\text{CO})_8]$ -mediated [2+2+1] cycloaddition involving an alkyne  $\pi$  bond, an alkene  $\pi$  bond, and carbon monoxide (CO) is known as the Pauson–Khand reaction,<sup>[1]</sup> and the intramolecular Pauson–Khand reaction of enynes (alkyne/alkene derivatives) can generally be applied to the formation of bicyclo[3.3.0]octenones and bicyclo[4.3.0]nonenones in good to high yields. However, the application of this protocol to the construction of larger systems, bicyclo[5.3.0]decenones, could not be achieved except for a few specific substrates, which have, for example, an aromatic ring as the template.<sup>[2]</sup> The Rh<sup>I</sup>-catalyzed carbonylative [2+2+1] cycloaddition<sup>[3,4]</sup> of allenynes (alkyne/allene derivatives)<sup>[5–7]</sup> or allenenes (alkene/allene),<sup>[8]</sup> however, has been described by us<sup>[5,8]</sup> and Brummond et al.,<sup>[6]</sup> to afford the corresponding bicyclo[5.3.0] compounds in satisfactory yields.<sup>[9]</sup> Described herein are the preliminary results of the  $[\{\text{RhCl}(\text{CO})_2\}_2]$ - and  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$ -catalyzed carbonylative ring-closing reaction of bis(allene)s to effect the preparation of the medium-sized bicyclo[*m*.3.0] skeletons (*m* = 5, 6).<sup>[10]</sup>

Our initial evaluation of the Rh<sup>I</sup>-catalyzed carbonylative [2+2+1] cycloaddition of a bis(allene) focused on the preparation of bicyclo[5.3.0]decadienones which would require the participation of the two allenic terminal double bonds of compounds **1**. Indeed, the reaction of 5,5-bis(methoxycarbonyl)-1,2,7,8-nonatetraene (**1a**)<sup>[11]</sup> was first submitted to several ring-closing reaction conditions, but only an intractable mixture was obtained. We then turned to examining phenylsulfonyl-substituted derivatives, which have been utilized as substrates for most of our allenyne and allenene cyclometalation reactions because of their ready availability as well as their ability to selectively react at the terminal double bonds.<sup>[5,8]</sup> After several reaction conditions were screened, we found that treatment of the malonate derivative **1b** with 5 mol % of  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$  in toluene at 80 °C under an atmosphere of CO produced two carbonylative [2+2+1] cycloaddition products **2b** and **4**, each in 15 % yield, along with the [2+2] cycloaddition product **3b** (14 % yield;

Table 1, entry 2). The formation of **2b** can be interpreted in terms of the intermediacy of the initially formed 1,3-diene derivative **2b'** and subsequent isomerization to the  $\alpha,\beta$ -unsaturated ketone **2b**. The bicyclo[4.3.0] derivative **4**, having the exo-methylene moiety, must have been obtained through the reaction between the terminal and internal double bonds of the two allenyl groups. In the case of the methylene tethered mono-phenylsulfonyl derivative **1c**, the corresponding bicyclo[5.3.0] derivative **2c** became the sole isolable product in 45 % yield. Neither the bicyclo[4.3.0] derivative nor the [2+2] cycloadduct could be detected (Table 1, entry 3). Increasing the amount of the catalyst used led to an increase in the total yield of the [2+2+1] cycloaddition products (63 % yield), including isomer **2c'** (Table 1, entry 4).<sup>[12]</sup> Gratifyingly, the bis(phenylsulfonylallene) derivative **1d** was shown to be a suitable substrate affording 2,6-bis(phenylsulfonyl)bicyclo[5.3.0]deca-1,7-dien-9-one (**2d**) in a quantitative yield under the influence of 5 mol % of  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$  for one hour (Table 1, entry 5). An alternative catalyst,  $[\{\text{RhCl}(\text{CO})_2\}_2]$ , also gave the ring-closing product **2d** in 85 % yield, although a longer reaction time (6 h) was necessary (Table 1, entry 6). Increasing the amount of  $[\{\text{RhCl}(\text{CO})_2\}_2]$  from 5 to 10 mol % provided **2d** in a better yield and within a shorter reaction time (Table 1, entry 7). Notably, a lower reaction temperature (80 °C), compared to the cases of allenynes and allenenes which required refluxing toluene or xylene, was sufficient to complete this ring-closing reaction. No [2+2] cycloaddition products could be detected under either set of reaction conditions, presumably because of the low reaction temperature (Table 1, entries 5 and 6). The malonate derivative **1e** in the presence of 5 mol % of  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$  however, unexpectedly furnished **2e** in a low yield along with the predominant production of the [2+2] cycloaddition product **3e** in 70 % yield (Table 1, entry 8). Increasing the amount of  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$  used did not improve the yield of **2e** (Table 1, entry 9). A satisfactory yield (83 or 89 %) of **2e** was realized by using  $[\{\text{RhCl}(\text{CO})_2\}_2]$  instead of  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$  (Table 1, entries 10 and 11). The nitrogen-atom-containing substrate **1f** reacted with  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$  to afford the corresponding azabicyclo[5.3.0]decadienone **2f** in 98 % yield (Table 1, entry 12), whereas **2f** was formed in a low yield (44 %) when treated with  $[\{\text{RhCl}(\text{CO})_2\}_2]$  and the [2+2] cycloaddition product **3f** was obtained as a by-product (Table 1, entry 13). The oxo congener **2g** could also be synthesized from **1g** in the presence of  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$  in a satisfactory yield (Table 1, entry 14). Again,  $[\{\text{RhCl}(\text{CO})_2\}_2]$  provided **2g** in a

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**Table 1:** Rhodium(I)-catalyzed synthesis of bicyclo[5.3.0] compounds by a carbonylative [2+2+1] cycloaddition of bis(allene)s.<sup>[a]</sup>

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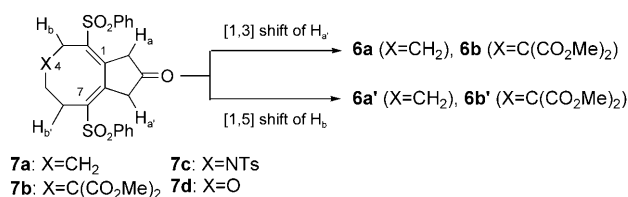
[a] Reaction conditions: A solution of bis(allene) **1** (0.1 mmol) and Rh<sup>I</sup> catalyst (5 mol %) in toluene (1 mL) was stirred at 80 °C under CO atmosphere.[b] Yields of isolated products. [c] Used 10 mol % of the catalyst. dppp = 1,3-bis(diphenylphosphino)propane. Ts = *p*-toluenesulfonyl.

rather low yield (Table 1, entries 15 and 16). Therefore the results in Table 1 indicate that [{RhCl(CO)dppp}<sub>2</sub>] is superior to [{RhCl(CO)<sub>2</sub>]<sub>2</sub>] in the carbonylative [2+2+1] cycloaddition of the bis(allene) derivatives **1**, except for the malonate derivative **1e** (Table 1, entries 8–11).

The results in Table 1 imply that the introduction of two phenylsulfonyl groups on both allenyl functionalities makes the intramolecular carbonylative [2+2+1] cycloaddition between the terminal double bonds of the two allenyl groups extremely smooth. The bulky phenylsulfonyl groups

might not only suppress the cyclometalation between the two internal double bonds<sup>[11d]</sup> or between a terminal and an internal double bond of two allenyl groups,<sup>[11c,f,g]</sup> but might also orient the two terminal double bonds of the allenyl moieties such that they can react. An unexpectedly easy formation of the bicyclo[5.3.0]decadienone framework from bis(allene)s, particularly from bis(phenylsulfonylallene) derivatives, under mild reaction conditions (5 mol % of  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$ , 1 atm CO, toluene 80 °C, 1 h) encouraged us to apply this new method to the construction of the bicyclo[6.3.0] ring system based on the Pauson–Khand-type [2+2+1] cycloaddition was previously reported by us, in which allenynes were used as substrates and a template effect was necessary to attain high yields.<sup>[5e]</sup>

The exposure of the 3,8-bis(phenylsulfonyl)-1,2,8,9-decetraene (**5a**) to the standard ring-closing conditions (5 mol % of  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$ , 1 atm CO, 80 °C in toluene) for three hours afforded the bicyclo[6.3.0]undecadienone derivative **6a** in 70 % yield together with its isomer **6a'** in 23 % yield (Table 2, entry 1). Interconversion between **6a** and **6a'** could not be observed under the standard reaction conditions. Therefore, the production of these two eight-membered ring products could be rationalized by having the common intermediate **7a**; **7a** could undergo a 1,3-hydrogen shift ( $\text{H}_a$ ) to provide **6a**, or a 1,5-hydrogen shift ( $\text{H}_b$ )<sup>[13]</sup> to give **6a'** (Scheme 1). Under similar conditions, the malonate deriva-



**Scheme 1.** Hydrogen shift within intermediate **7**.

tive **5b** afforded a mixture of **6b** and **6b'** in 75 % yield in a ratio of 1:6 (Table 2, entry 2). Interestingly, the carbonylative [2+2+1] cycloaddition of the nitrogen congener **5c** and the oxygen congener **5d** led to the formation of the eight-membered ring products **6c** (87 % yield) and **6d** (86 % yield), respectively, through an exclusive 1,3-hydrogen ( $\text{H}_a$ ) shift on the side nearest to the heteroatom of **7c** and **d** (Table 2, entries 3 and 4). In the case of the diaza derivative **5e**, the desired carbonylative [2+2+1] cycloaddition product **6e** was formed in 27 % yield as a minor product after a prolonged reaction time. Instead, the corresponding [2+2] cycloaddition product **8e** was obtained as a major product (Table 2, entry 5). The data in entry 6 of Table 2 indicate a significant improvement in the yield of **6e** by using 10 mol % of the catalyst. Thus, it might be concluded that the carbonylative [2+2+1] cycloaddition reaction of bis(allene) derivatives can consistently and efficiently be applied to the preparation of both bicyclo[5.3.0]decadienone and bicyclo[6.3.0]undecadienone skeletons.

To extend the scope of this method, we examined some bis(allene)s that would lead to bicyclo[4.3.0]nonadienone derivatives. The bis(allene) **9**, prepared from L-tartrate, was

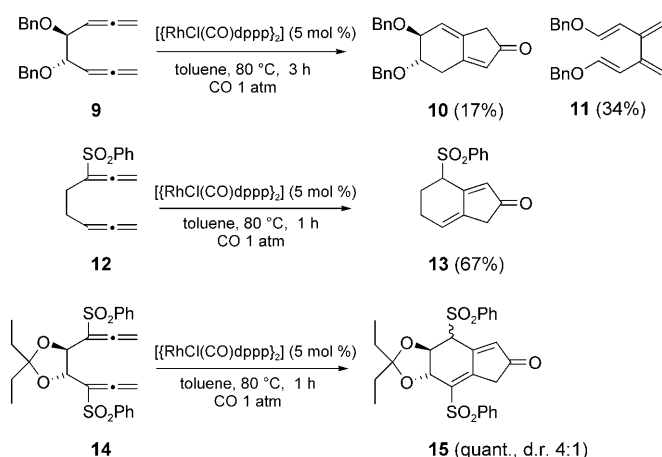
**Table 2:** Rhodium(I)-catalyzed synthesis of bicyclo[6.3.0] compounds by a carbonylative [2+2+1] cycloaddition of bis(allene)s.<sup>[a]</sup>

Entry	Bis(allene)	t [h]	Products (yield) <sup>[b]</sup>
1		3	 <b>6a</b> (70%)  <b>6a'</b> (23%)
2		5	 <b>6b</b> 75% (1:6)  <b>6b'</b>
3		1	 <b>6c</b> (87%)
4		1	 <b>6d</b> (86%)
5		22	 <b>6e</b> (27%)  <b>8e</b> (39%)
6 <sup>[c]</sup>		18	 <b>6e</b> (54%)  <b>8e</b> (22%)

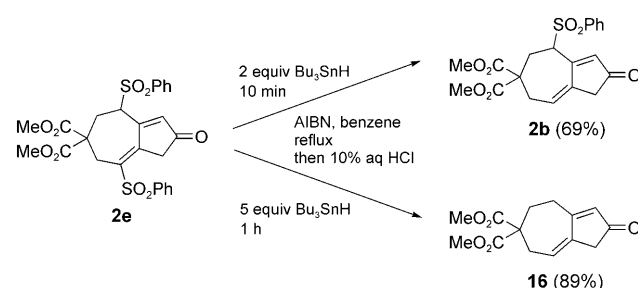
[a] Reaction conditions: A solution of bis(allene) **5** (0.1 mmol) and  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$  (5 mol %) in toluene (1 mL) was stirred at 80 °C under CO atmosphere. [b] Yields of isolated products. [c] Used 10 mol % of the catalyst.

submitted to the standard reaction conditions to give the carbonylative product **10** in 17 % yield along with the tetraene derivative **11** (34 % yield); **11** may have arisen from a thermal [3,3]-sigmatropic rearrangement of the starting material (Scheme 2).<sup>[14]</sup> The mono-phenylsulfonyl substrate **12** afforded the desired product **13** in 67 % yield. These results are in good agreement with the prediction based on the aforementioned results in Table 1. Upon treatment with 5 mol %  $[\{\text{RhCl}(\text{CO})\text{dppp}\}_2]$  in toluene under an atmosphere of CO, bis(phenylsulfonylallene) derivative **14** produced **15** in a quantitative yield as expected.

The sulfonyl group is known to be easily transformed into various functional groups.<sup>[15]</sup> For example, a phenylsulfonyl group can be regarded as a surrogate for a hydrogen atom, and can be easily converted into a hydrogen atom by conventional means. In fact, we examined the selective desulfonylation of one of the two phenylsulfonyl groups of the [2+2+1] cycloaddition products (Scheme 3). The removal of a vinylic sulfone of **2e** was realized in a highly selective manner by using of two equivalents of tributyltin hydride in the presence of AIBN<sup>[16]</sup> and the subsequent acidic workup. Exposure of **2e** to an excess of tributyltin hydride led to the desulfonylation of both vinylic and allylic positions.



**Scheme 2.** Formation of bicyclo[4.3.0]nonadienones by rhodium(I)-catalyzed carbonylative [2+2+1] cycloaddition of bis(phenylsulfonylallene) derivatives **9**, **12**, and **14**.



**Scheme 3.** Desulfonylation of **2e**. AIBN = 2,2'-azobis(isobutyronitrile).

In summary, we developed a novel  $[[\text{RhCl}(\text{CO})\text{dppp}]_2]$ -catalyzed intramolecular [2+2+1] cycloaddition of bis(phenylsulfonylallene) derivatives under mild conditions leading to the facile formation of the 2,7-bis(phenylsulfonyl)bicyclo[6.3.0]undecadien-10-one framework, in which the terminal double bonds of both allenyl moieties exclusively served as the two  $\pi$  components. This method is superior to that previously reported, which took advantage of the carbonylative [2+2+1] cycloaddition of allenyne derivatives possessing a suitable template functionality. The newly developed method was also shown to be applicable to the construction of 2,6-bis(phenylsulfonyl)bicyclo[5.3.0]decadien-9-one and 2,5-bis(phenylsulfonyl)bicyclo[4.3.0]nonadien-8-one skeletons in high yields. We have demonstrated the usefulness of a bis(allene) functionality in the carbonylative [2+2+1] cycloaddition reaction. The additional scope and limitations of this method, as well as application to the synthesis of natural products are now being investigated.

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