

# Cobalt-Mediated Linear 2:1 Co-oligomerization of Alkynes with Enol Ethers to Give 1-Alkoxy-1,3,5-Trienes: A Missing Mode of Reactivity

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**Abstract:** A variety of 1,6-heptadiynes and certain borylalkynes co-oligomerize with enol ethers in the presence of  $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$  (Cp=cyclopentadienyl) to furnish the hitherto elusive acyclic 2:1 products, 1,3,5-trien-1-ol ethers, in preference to or in competition with the alternative pathway that leads to the standard  $[2+2+2]$  cycloadducts, 5-alkoxy-1,3-cyclohexadienes. Minor variations, such as lengthening the diyne tether, cause reversion to the standard mechanism. The trienes, including synthetically potent borylated derivatives, are generated with excellent levels of

chemo-, regio-, and diastereoselectivity, and are obtained directly by decomplexation of the crude mixtures during chromatography. The cyclohexadienes are isolated as the corresponding dehydroalkoxylated arenes. In one example, even ethene functions as a linear cotriemerization partner. The alkoxytrienes are thermally labile with respect to  $6\pi$ -electrocyclization–elimination to give

the same arenes that are the products of cycloaddition. The latter, regardless of the mechanism of their formation, can be viewed as the result of a formal  $[2+2+2]$  cyclization of the starting alkynes with acetylene. One-pot conditions for the exclusive formation of arenes are developed. DFT computations indicate that cyclohexadiene and triene formation share a common intermediate, a cobaltacycloheptadiene, from which reductive elimination and  $\beta$ -hydride elimination compete.

**Keywords:** boron • C–H activation • cobalt • coupling reactions • electrocyclic reactions

## Introduction

1,3,5-Trienes are key subunits of a large variety of natural products, and are also synthetic precursors of cyclohexadienes through  $6\pi$ -electrocyclization of the *cis* isomers. They are usually prepared in several steps, often including a

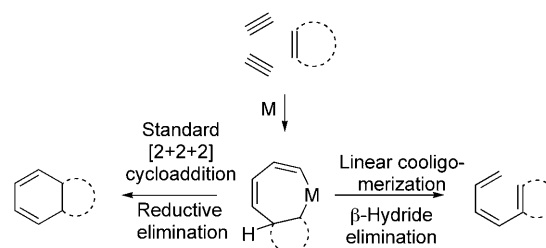
metal-catalyzed cross-coupling.<sup>[1,2]</sup> However, under specific conditions, it is possible to assemble trienes in a single operation from two alkynes and one alkene (Scheme 1). To the best of our knowledge, the first example of such a reaction was reported by Cairns and co-workers in 1952.<sup>[3]</sup> They found that a mixture of  $[\text{Ni}(\text{CO})_4]$  and  $\text{P}(\text{C}_6\text{H}_5)_3$  catalyzed the addition of acetylene to acrylic compounds to give heptatrienoic acid derivatives. In 1999, Cheng extended this reaction to substituted alkynes by employing mixtures of  $[\text{Ni}(\text{PR}_3)_2\text{X}_2]$  and Zn.<sup>[4]</sup> Ruthenium entered the scene in 1998 when Yi discovered that acetylene and acrylonitrile trans-

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Scheme 1. Generic competitive outcome of the formation of cyclic versus linear oligomers of two alkynes and one alkene.

## Results and Discussion

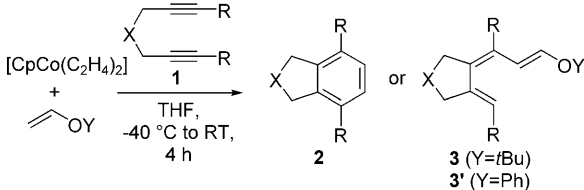
formed to heptatrienenitrile in the presence of a Cp\*ruthenacyclopentadiene catalyst (Cp\* = pentamethylcyclopentadienyl).<sup>[5]</sup> This process was synthetically exploited by Saá and co-workers in 2006, who utilized [Cp\*Ru(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub> to couple  $\alpha,\omega$ -diynes with acyclic alkenes to give trienic products.<sup>[6]</sup> With cyclic alkenes, the standard [2+2+2] cycloaddition pathway prevailed, leading to 1,3-cyclohexadienes (Scheme 1).<sup>[7]</sup> DFT calculations pinpointed a common ruthenacycloheptadiene intermediate, from which the two products arise by either  $\beta$ -hydride or reductive elimination, respectively.<sup>[6b]</sup> Very recently, a single case of a diyne-acrylamide coupling to generate a hepta-2,4,6-trienamide by using [Rh(cod)<sub>2</sub>]BF<sub>4</sub> (cod = cyclooctadiene) admixed with a chelating phosphine was reported.<sup>[8]</sup>





In view of the similarity in the chemistry of these systems to that of [CpCoL<sub>2</sub>], (Cp = cyclopentadienyl) particularly with respect to the cocyclization of alkynes with alkenes,<sup>[7]</sup> it is surprising that trienes have remained undetected in the Co series. The only exceptions are occasional dienyheterocyclic products formed in the [2+2+2] cycloaddition of alkynes to heteroaromatic double bonds.<sup>[9]</sup> However, their assembly is mechanistically distinct, and proceeds through direct electrophilic attack of the cobaltacyclopentadiene intermediate on the heterocycle and an ensuing cobalt-assisted hydrogen transfer (see below).<sup>[10]</sup> We report examples of the missing type of Co reactivity, when certain alkynes are treated with certain enol ethers in the presence of [CpCoL<sub>2</sub>] mediators to produce trienol ethers in a chemo-, regio-, and diastereoselective fashion. The reaction tolerates boryl substitution, thus enabling access to borylated alkoxytrienes. Subtle changes in the nature of the reagents reverts the outcome of this process to that of the traditional [2+2+2] pathway, as evidenced by the formation of fused arenes originating from the demetallation-dehydroalkoxylation of the corresponding 5-alkoxycyclohexadiene complexes.<sup>[11]</sup> The same type of arene is obtained on thermal 6 $\pi$ -electrocyclization of the trienol ethers.

The discovery of this new type of reactivity exhibited by [CpCoL<sub>2</sub>] was made through what appeared to be a routine extension of our work on the cobalt-mediated [2+2+2] cycloaddition of borylated monoalkynes and diynes with alkenes, including enol ethers, which, without exception, to produce the corresponding [CpCo(cyclohexadiene)] complexes.<sup>[12]</sup> It is of relevance that [CpCo(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>],<sup>[13]</sup> on its own, furnished products of ethene incorporation, whereas added alkenes outcompeted ethene in the cyclization. Moreover, variation of the tether lengths in a range of  $\alpha,\omega$ -diynes from 3 to 5 atoms did not alter the outcome of this process. However, examples featuring enol ethers were restricted to cocyclization with the monoalkyne (phenylethynyl)pinacolate. The synthetic value of the products<sup>[14]</sup> prompted the current study.

**Co-oligomerizations of  $\alpha,\omega$ -diynes with enol ethers:** This investigation began in an attempt to extend the scope of the [2+2+2] cycloaddition of enol ethers to  $\alpha,\omega$ -diynes, initially by using the previously tested *tert*-butyl,<sup>[12a]</sup> and then with other vinyl ethers such as phenyl ethenyl ether (Table 1). Operationally, the diyne was added to a solution of [CpCo(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] and the enol ether at -40 °C, and the resulting mixture was stirred at room temperature. The ensuing Co complexes were too sensitive to be isolable (see, however, Scheme 5), and therefore the crude product was subjected either to Fe<sup>III</sup> oxidation, followed by column chromatography (for **2**), or directly to the latter (for **3**). After an initial failure with the parent 1,6-heptadiyne **1a** (Table 1, entry 1), the diphenyl derivative **1b** led to a single product **3b** in 53 % yield (Table 1, entry 2). To our surprise, this compound was neither the expected cyclohexadiene complex nor the corresponding free ligand, but a new framework, formulated

Table 1. Co-oligomerization of diynes with enol ethers.



Entry	Diyne	X	R	Y	2 (Yield [%]) <sup>[a]</sup>	3/3' (Yield [%])
1	<b>1a</b>	CH <sub>2</sub>	H	<i>t</i> Bu	–	– <sup>[b]</sup>
2	<b>1b</b>	CH <sub>2</sub>	Ph	<i>t</i> Bu	–	<b>3b</b> (53)
3	<b>1c</b>	CH <sub>2</sub>	SiMe <sub>3</sub>	<i>t</i> Bu	–	– <sup>[c]</sup>
4	<b>1d</b>	CH <sub>2</sub>	BPin <sup>[d]</sup>	<i>t</i> Bu	–	<b>3d</b> (61)
5	<b>1d</b>	CH <sub>2</sub>	BPin <sup>[d]</sup>	Ph	–	<b>3'd</b> (81)
6	<b>1e</b>		Ph	<i>t</i> Bu	–	<b>3e</b> (60)
7	<b>1e</b>		Ph	Ph	–	<b>3'e</b> (60)
8	<b>1f</b>		BPin <sup>[d]</sup>	<i>t</i> Bu	–	<b>3f</b> (91)
9	<b>1f</b>		BPin <sup>[d]</sup>	Ph	–	<b>3'f</b> (75)
10	<b>1g</b>	C(CH <sub>2</sub> OMe) <sub>2</sub>	BPin <sup>[d]</sup>	<i>t</i> Bu	–	<b>3g</b> (80)
11	<b>1g</b>	C(CH <sub>2</sub> OMe) <sub>2</sub>	BPin <sup>[d]</sup>	Ph	–	<b>3'g</b> (80)
12	<b>1h</b>	NTs	Ph	Ph	–	<b>3'h</b> (51)
13	<b>1i</b>	O	Ph	<i>t</i> Bu	–	<b>3i</b> (54)
14	<b>1j</b>	O	BPin <sup>[d]</sup>	<i>t</i> Bu	–	<b>3j</b> (25)
15	<b>1k</b>	CH <sub>2</sub>	CO <sub>2</sub> Et	<i>t</i> Bu	<b>2k</b> (73)	–
16	<b>1l</b>	SiPh <sub>2</sub>	BPin <sup>[d]</sup>	<i>t</i> Bu	<b>2l</b> (62)	–
17	<b>1m</b>	C <sub>2</sub> H <sub>4</sub>	Ph	Ph	<b>2m</b> (59) <sup>[f]</sup>	–
18	<b>1n</b>	C <sub>2</sub> H <sub>4</sub>	BPin <sup>[d]</sup>	<i>t</i> Bu	<b>2n</b> (80)	–
19	<b>1n</b>	C <sub>2</sub> H <sub>4</sub>	BPin <sup>[d]</sup>	Ph	<b>2n</b> (55)	–
20	<b>1o</b>	C <sub>3</sub> H <sub>6</sub>	BPin <sup>[d]</sup>	<i>t</i> Bu	<b>2o</b> (42)	–
21	<b>1o</b>	C <sub>3</sub> H <sub>6</sub>	BPin <sup>[d]</sup>	Ph	<b>2o</b> (62)	–

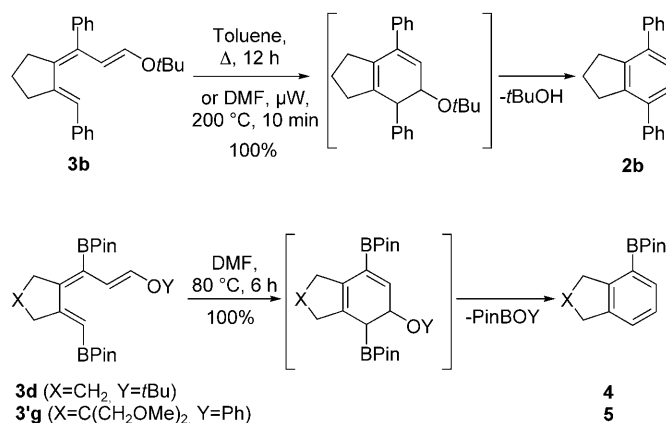
[a] The crude mixture was treated with FeCl<sub>3</sub>·6H<sub>2</sub>O (1.5 equiv) in MeCN at RT before purification. [b] Complex mixture. [c] No reaction. [d] BPin = boryl pinacolate. [e] Atom X is indicated by a C. [f] This compound is known, see the Supporting Information.

as triene **3b** on the basis of the NMR spectral data.<sup>[15]</sup> Thus, the <sup>1</sup>H NMR spectrum revealed a set of three diagnostic alkenyl signals at  $\delta=6.13$  (d), 6.68 (d), and 6.91 ppm (s), the *trans* configuration of the enol ether moiety established by  $J=12.2$  Hz. The stereochemical arrangement of the other two double bonds was confirmed by an NOE experiment, which showed a through-space interaction between the hydrogen giving rise to a singlet at  $\delta=6.91$  ppm and that associated with the doublet at  $\delta=6.13$  ppm. Conversely, irradiating the peak at  $\delta=6.68$  ppm gave no response (see also the Supporting Information). The <sup>13</sup>C NMR spectrum contained the appropriate number of CH<sub>n</sub> signals, notably the characteristically extreme chemical shifts for the sp<sup>2</sup>-hybridized carbons of the *tert*-butoxy-bearing double bond at  $\delta=113.2$  (C<sub>β</sub>) and 147.0 ppm (C<sub>α</sub>).<sup>[15]</sup>

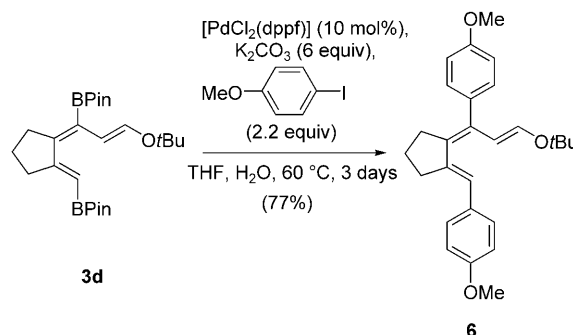
The high level of chemo-, regio-, and diastereoselectivity of the synthesis of **3b** encouraged further investigation of its scope by incremental changes in the respective starting materials. For example, switching from phenyl to trimethylsilyl substitution, as in **1c**, shut down reactivity (Table 1, entry 3). On the other hand, the arguably fairly bulky boryl pinacolate (BPin) group in **1d** is tolerated, providing the novel diborylated alkoxytriene **3d** in fairly good yield (Table 1, entry 4).<sup>[16]</sup> Notably, diyne **1d** may be regarded as a tethered analog of (phenylethynyl)pinacolborate, which engaged the *tert*-butyl enol ether only in the standard [2+2+2] cycloaddition.<sup>[12a]</sup> Phenyl vinyl ether as a new alkene component resulted in the corresponding **3'd** in 81% yield (Table 1, entry 5). Changing the three-atom tether to incorporate various functions, as in **1e–j**, gave similar results with both enol ethers, to produce trienes selectively and in modest to good yields (Table 1, entries 6–14). In no case could we detect products of cyclization, signaling a change in mechanism with  $\alpha,\omega$ -diyne substrates.

However, it became evident that this conclusion was premature on inspection of entries 15–21 of Table 1. In these cases, <sup>1</sup>H NMR inspection of the crude mixtures showed the presence of the aromatized product **2**, in addition to very sensitive CpCo complexes of 5-alkoxycyclohexadienes. To simplify this outcome operationally, the crude product was worked up with iron(III) chloride, followed by chromatography. This treatment effected the demetallation and aromatization of the ligands to create **2**, again in moderate to good yields. Specifically, entry 15 reveals that a simple substituent change on 1,6-heptadiyne from Ph (entry 2) or BPin (entry 4) to methoxycarbonyl causes mechanistic reversion of the reaction to the [2+2+2] pathway, with **2k** as the sole product in 73% yield. Similarly, elongating the tether slightly (entry 16) or more substantially (entries 17–21) leads exclusively to arenes **2l–o**. To ascertain that small amounts of trienes in the crude mixtures had not been decomposed or converted during work-up into **2**, a preparation of **3b** was subjected to Fe<sup>III</sup> treatment, without any effect. The stability of an isolated sample of **3b** toward Fe<sup>III</sup> was also checked. This experiment also rules out the occurrence of catalyzed hexatriene ring closure.<sup>[2]</sup>

Ring closure is nevertheless attainable by thermal means, a process that is accompanied by aromatization. Thus, **3b** transformed quantitatively into **2b** in boiling toluene (12 h), or in hot DMF (10 min) under microwave irradiation, by electrocyclic–dehydroalkoxylation. Similarly, **3d** and **3'g** were converted to **4** and **5**, respectively, for which the deboroalkoxylation occurred spontaneously (Scheme 2). The onset of this cascade is sufficiently slow below 80 °C that other useful transformations can be executed on these systems. For example, **3d** underwent successful double Suzuki cross-coupling with *p*-iodoanisole, giving **6** in 77% yield (Scheme 3).<sup>[17]</sup>

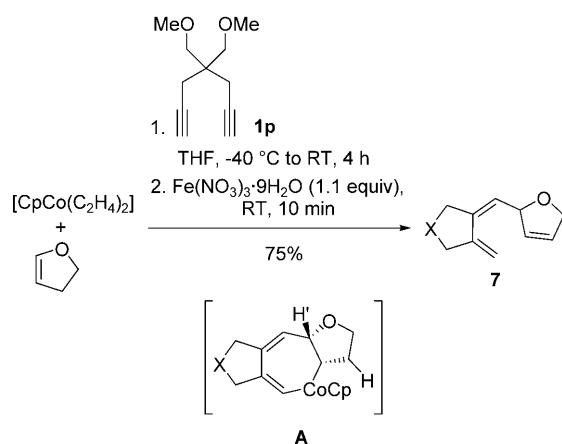


Scheme 2. Thermal electrocyclic–elimination of trienol ethers. BPin = boryl pinacolate.



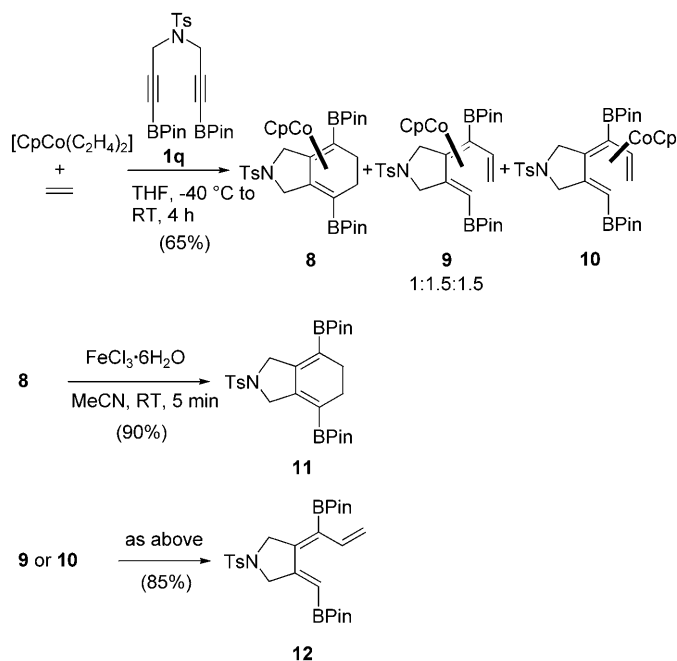
Scheme 3. Double Suzuki coupling of **3d**.

Two further experiments attest to the possibility that the scope of the 2:1 linear co-oligomerization of diynes extends beyond the examples in Table 1. The first featured the cyclic ether 2,3-dihydrofuran, which, on exposure to **1p**, generated **7** (Scheme 4). The unconjugated nature of its triene array is evident from the NMR spectral data and implicates the occurrence of a  $\beta$ -hydride elimination from the cobaltacycloheptadiene intermediate **A** (see also the mechanistic section). Notably, there was no evidence for the formation of the isomeric phenylethanol of type **2**, as observed in a related reaction that used Ir catalysis.<sup>[11d]</sup>



Scheme 4. Co-oligomerization of **1p** with 2,3-dihydrofuran (X=C(CH<sub>2</sub>OMe)<sub>2</sub>).

The second case is more far-reaching, and involved simply ethene as the alkene partner, again a substrate that had previously only given cyclohexadiene products, including those derived from cocyclizations with a variety of diborylated  $\alpha,\omega$ -diynes.<sup>[12]</sup> Remarkably, the diyne **1q**, not tested previously, transformed in the presence of [CpCo(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] not only to the expected **8** (16%), but also to triene complexes **9** (24%) and **10** (24%). These complexes were separable by chromatography and fully characterizable, an exercise greatly aided by their relative stability. Interestingly, the formation of **10** is of kinetic origin, as it isomerizes to **9** quantitatively by a “CpCo-walk”<sup>[18]</sup> on prolonged standing in solution. Further structural proof rested on oxidative demetallation of **8** to furnish the free ligand **11** (Scheme 5), displaying



Scheme 5. Co-oligomerization of **1q** with ethene.

unambiguous NMR data. Upon the same oxidative treatment, the regioisomeric complexes **9** and **10** delivered an identical product, the triene **12**, which could also be readily characterized. Thus, it appears that the linear co-oligomerization pathway is energetically competitive with the standard cyclization without alkoxy substitution of the ene component.

**Intermolecular co-oligomerizations of borylalkynes with enol ethers:** The results of the previous section raised the question of whether monoalkynes could be induced to enter into the linear 2:1 co-oligomerization. Again extending prior work,<sup>[12]</sup> the initial focus was on the use of alkynyl borates. The results re-emphasize the energetic closeness of the three regiochemical pathways for alkyne oxidative coupling, and the ensuing competition toward cyclic versus acyclic products (Table 2). The starting point was a repetition of the

Table 2. Co-oligomerization of borylated alkynes with enol ethers. BPin = boryl pinacolate.

Entry	Alkyne	R	Y	Yield [%] of <b>14</b>	Yield [%] of <b>14'</b>	Yield [%] of <b>15/15'</b>	Yield [%] of <b>16/16'</b>
1	<b>13a</b>	Ph	<i>t</i> Bu	59 <sup>[a]</sup>	–	–	–
2	<b>13a</b>	Ph	Ph	–	–	–	55 <sup>[a]</sup>
3	<b>13b</b>	CH <sub>2</sub> OMe	<i>t</i> Bu	88 <sup>[a]</sup>	–	–	–
4	<b>13b</b>	CH <sub>2</sub> OMe	Ph	55 <sup>[a]</sup>	–	–	31 <sup>[a]</sup>
5	<b>13c</b>	Pr	<i>t</i> Bu	–	33	– <sup>[b]</sup>	–
6	<b>13c</b>	Pr	Ph	–	71	– <sup>[b]</sup>	–
7	<b>13d</b>	<i>i</i> Bu	<i>t</i> Bu	–	–	59	–
8	<b>13d</b>	<i>i</i> Bu	Ph	–	–	72	–

[a] The crude mixture was treated with FeCl<sub>3</sub>·6H<sub>2</sub>O (1.5 equiv) in MeCN at RT before purification. [b] Observed but unstable (see text).

reaction of **13a** with *tert*-butyl vinyl ether, which had produced selectively the 1,3-diboryl-2,4-diphenyl-5-*tert*-butoxycyclohexa-1,3-diene CpCo complex in 65% yield.<sup>[12a]</sup> Under the conditions of work-up described in Table 1, this experiment rendered the unsymmetrical **14a** in 59% yield, as expected (Table 2, entry 1). However, by using phenyl vinyl ether instead, a dramatic change in the reaction outcome ensued: trienol ether **16'a**, displaying a 1,4 arrangement of the boron atoms, was obtained, as evidenced by the presence of the characteristically shielded vinyl boron hydrogen (Table 2, entry 2).<sup>[19]</sup> A similar, if attenuated, switchover occurred in the case of methoxymethylated **13b**: the *tert*-butoxyalkene led to arene **14b** only (Table 2, entry 3), whereas the phenoxy analog gave substantial amounts of triene **16'b**, in addition to **14b** (Table 2, entry 4). In contrast, the alkyl derivatives **13c** and **13d** assembled alkoxytrienes irrespective of the vinyl ether employed, but now in the regioiso-

meric form **15**, which is associated with protodeborylation at the 4-position.<sup>[20]</sup> Moreover, the propyl-substituted trienes **15c** and **15'c**, although clearly observable in the <sup>1</sup>H NMR spectra of the crude reaction mixtures, were prone to remarkably rapid electrocyclization–dehydroalkoxylation during purification, and could be isolated only as the corresponding arene **14'c** (Table 2, entries 5 and 6). This problem was circumvented with the bulkier isobutyl group (Table 2, entries 7 and 8). Although more work is required to delineate the scope and utility of this reaction, it is phenomenologically clear that certain constellations of monoalkynes and enol ethers will produce 2:1 co-oligomerization products.

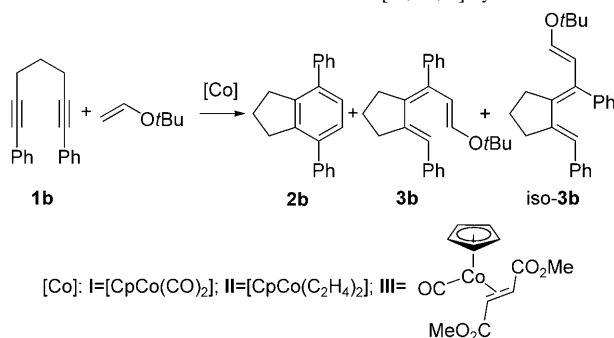
**One-pot preparation of fused arenes by co-oligomerization of 1,6-diyne with enol ethers:** Regardless of their mechanism of formation, arenes **2** (and **14**) are the result of a formal CpCo-catalyzed [2+2+2] cycloaddition of the respective alkynes with acetylene, a strategy that has been used previously with other metals to circumvent the drawbacks associated with acetylene itself.<sup>[11]</sup> Considering the sensitivity of the Co complexes generated under the low-temperature conditions employed above and the electrocyclization–aromatization cascade traversed by the triene products at elevated temperatures, it seemed possible that executing the co-oligomerization reaction above 110 °C would channel it toward exclusive arene formation. Initial tests of the feasibility of this notion were carried out with **1b** and *tert*-butyl vinyl ether, by using the three cobalt complexes [CpCo(CO)<sub>2</sub>] (**I**), [CpCo(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (**II**), and the recently reported air-stable catalyst **III**<sup>[21]</sup> (Table 3). Gratifyingly, already in boiling toluene (12 h), **I** gave rise exclusively to

**2b**, albeit in poor yield (Table 3, entry 1). On the other hand, incomplete decomposition of the triene complexes and/or incomplete ring closure of **3b** was signaled when using **II** as the cobalt source (Table 3, entry 2), again in poor yield. Surprisingly, this run revealed, in addition to **2b** and **3b**, the formation of another isomer of the latter, *iso-3b*. Its NMR spectra are very similar to those of **3b** (including the *trans* coupling of the enol ether group), with one marked exception: the singlet for the styrenyl hydrogen at the triene terminus is shifted upfield by almost 1 ppm, a result of shielding by the other, now proximal, phenyl ring. This proximity was confirmed by NOE experiments, and was further supported by the recording of an NOE between the hydrogen giving rise to the doublet at  $\delta=6.22$  ppm (the enol ether hydrogen next to the alkoxy group) and the allylic methylene hydrogen atoms resonating at  $\delta=2.62$ – $2.69$  ppm (see the Supporting Information). The mechanism of the isomerization of **3b** is obscure, although a number of species in the thermolysis mixture could be invoked as acting as catalysts for such. Fortunately with respect to the goal of this line of investigation, pure *iso-3b*, although more resilient than **3b**, also transformed thermally to **2b** (200 °C,  $\mu$ W, 10 min). Complex **III** gave the best mass recovery under these initial conditions, but still substantial quantities of *iso-3b* (Table 3, entry 3).

Because boiling toluene was not sufficient to convert all triene products to **2b**, the reaction temperature was increased to 200 °C (DMF, microwave reactor). This change had the desired effect, even though yields were still moderate (Table 3, entries 4–6). We next engaged substoichiometric amounts of metal (Table 3, entries 7–9). This change was most successful in the case of complex **III**: with 0.4 equivalents, the isolated yield of **2b**

was essentially quantitative (Table 3, entry 9). Unfortunately, lesser Co loading was detrimental (Table 3, entry 10). Therefore, the conditions of Table 3, entry 9 were chosen in order to explore further the scope and limitations of this one-pot process (Table 4). First, several enol ethers other than *tert*-butyl were tested as surrogates for acetylene in the reaction of **1b**. However, none of them proved comparable (Table 4, entries 1–5). Next, substituents on the three-carbon tether of the diyne (Table 4, entries 6 and 9), the tether length (Table 4, entries 8 and 10), and the terminal alkyne groups (Table 4, entry 7) were altered. In all cases moderate to good yields of the fused arene **2** were obtained.

Table 3. Optimization of the reaction conditions for a formal [2+2+2] cycloaddition of diynes to acetylene.



Entry	[Co] ([mol %]) <sup>[a]</sup>	Conditions <sup>[b]</sup>	Yield [%] ( <b>2b</b> : <b>3b</b> : <i>iso-3b</i> ) <sup>[c]</sup>
1	<b>I</b> (100)	toluene, reflux, 12 h	32 (1:0:0)
2	<b>II</b> (100)	toluene, reflux, 12 h	37 (0.3:1:0.4)
3	<b>III</b> (100)	toluene, reflux, 12 h	68 (0.6:0:1)
4	<b>I</b> (100)	DMF, $\mu$ W, 200 °C, 10 min	18 (1:0:0)
5	<b>II</b> (100)	DMF, $\mu$ W, 200 °C, 10 min	51 (1:0:0)
6	<b>III</b> (100)	DMF, $\mu$ W, 200 °C, 10 min	38 (1:0:0)
7	<b>I</b> (40)	DMF, $\mu$ W, 200 °C, 20 min	28 (1:0:0)
8	<b>II</b> (40)	DMF, $\mu$ W, 200 °C, 20 min	28 (1:0:0)
9	<b>III</b> (40)	DMF, $\mu$ W, 200 °C, 20 min	96 (1:0:0)
10	<b>III</b> (20)	DMF, $\mu$ W, 200 °C, 20 min	58 (1:0:0)

[a] Based on diyne. [b] The diyne (2 equiv), enol ether (5 equiv), and Co species were mixed prior to heating. [c] Products obtained directly after chromatography on silica gel.



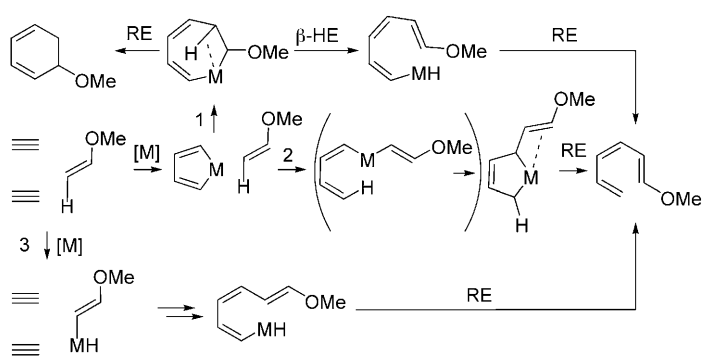
Table 4. Scope and limitations of the formal [2+2+2] cycloaddition of diynes to acetylene.

Entry	Diyne	R	X	Y	Product	Yield [%]
1	<b>1b</b>	Ph	CH <sub>2</sub>	Ph	<b>2b</b>	53
2	<b>1b</b>	Ph	CH <sub>2</sub>	Et	<b>2b</b>	44
3	<b>1b</b>	Ph	CH <sub>2</sub>	Bu	<b>2b</b>	64
4	<b>1b</b>	Ph	CH <sub>2</sub>	<i>n</i> -C <sub>12</sub> H <sub>25</sub>	<b>2b</b>	23
5	<b>1b</b>	Ph	CH <sub>2</sub>	Ac	<b>2b</b>	32
6	<b>1e</b>	Ph		<i>t</i> Bu	<b>2e</b> <sup>[b]</sup>	41
7	<b>1k</b>	CO <sub>2</sub> Et	CH <sub>2</sub>	<i>t</i> Bu	<b>2k</b>	41
8	<b>1m</b>	Ph	(CH <sub>2</sub> ) <sub>2</sub>	<i>t</i> Bu	<b>2m</b>	67
9	<b>1r</b>	Ph	C(CO <sub>2</sub> Me) <sub>2</sub>	<i>t</i> Bu	<b>2r</b>	74
10	<b>1s</b> <sup>[c]</sup>	Ph	OC(CH <sub>2</sub> ) <sub>2</sub> CO	<i>t</i> Bu	<b>2s</b>	53 <sup>[d]</sup>

[a] Atom X is indicated by a C. [b] This compound is known, see Supporting Information. [c] 1,8-Diphenylocta-1,7-diyne-3,6-dione. [d] Yield of 5,8-diphenylnaphthalene-1,4-dione, the product of air oxidation.

Thus, this method constitutes a viable and possibly more general alternative to those based on Rh and Ir.<sup>[11]</sup>

**Mechanistic considerations and DFT calculations:** It is tempting to interpret our experimental results as mimicking mechanistically the trails computed previously for Co<sup>[10a]</sup> and Ru<sup>[6b]</sup> (Scheme 1), in which alkynes are exposed to normal (i.e., nonalkoxylated) alkenes. However, the discovery of a different channel, featuring direct electrophilic attack of the cobaltacyclopentadiene intermediate coupled with a cobalt-assisted hydrogen transfer in the case of heterocycle dienylation (see the Introduction),<sup>[10]</sup> and consideration of the relatively electron-rich nature of the enol ether double bond, made the occurrence of such a pathway a reasonable alternative to the  $\beta$ -hydride elimination route. Three generic routes were addressed in the following investigation (Scheme 7). The most likely is the initial oxidative coupling of the two alkyne units, leading to a metallacyclopentadiene intermediate. The standard mechanism would then proceed by alkene insertion, giving rise to a seven-membered metallacycle (Scheme 6, pathway 1). Its direct reductive elimination would generate the 1,3-cyclohexadiene core, whereas  $\beta$ -hydride elimination followed by reductive elimination would result in the triene framework. The viable alternative to (Scheme 6, pathway 1) is metathesis of the C–H bond of the alkene moiety (Scheme 6, pathway 2), either in a stepwise fashion via a vinyl dienyl metal intermediate (oxidative hydrogen migration),<sup>[22]</sup> or in a concerted manner leading directly to a metallacyclopentene, the reductive elimination of which furnishes the triene system. Unlikely, but included in our considerations for calibration, is early C–H activation at the alkene (Scheme 6, pathway 3), followed by two carbometallations of the triple bonds and reductive elimination (RE). Previous calculations suggested

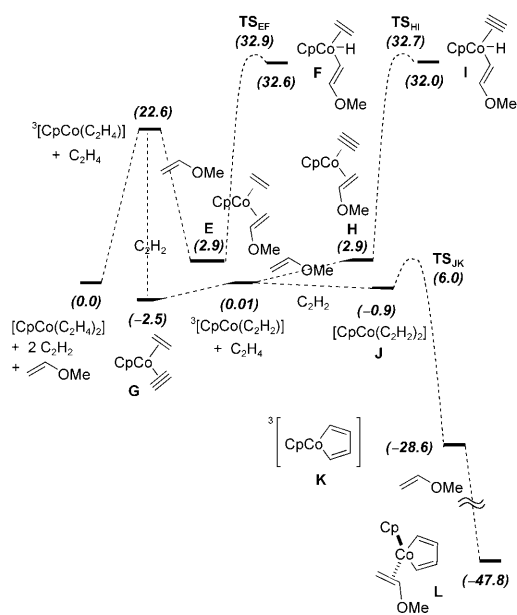


Scheme 6. Mechanistic pathways of the co-oligomerization of enol ethers with alkynes subjected to computational scrutiny. RE = reductive elimination;  $\beta$ -HE =  $\beta$ -hydride elimination.

that although pathway 1 prevails with ethene, pathway 2 (stepwise) becomes competitive with aromatics, such as benzene, furan, thiophene,<sup>[10a]</sup> and pyridones.<sup>[10b]</sup>

To deduce the relative likelihood of the options represented in Scheme 6, DFT computations were carried out. All geometries of molecules and transition states were optimized fully without symmetry constraints by using the Gaussian 03 program.<sup>[23]</sup> Calculations were carried out with the BP86 functional as implemented and the LACVP(d,p) basis set. The cobalt atom was described by a double- $\zeta$  basis set with the effective core potential of Hay and Wadt (LANL2DZ),<sup>[24]</sup> and the 6-31G(d,p) basis set<sup>[25]</sup> was used for the other elements. Frequency calculations were performed to confirm the nature of the stationary points and to obtain zero-point energies (ZPE). The connectivity between stationary points was established by intrinsic reaction coordinate calculations (IRC). The energy values (kcal mol<sup>-1</sup>) refer to enthalpies ( $\Delta H_{298}$  and  $\Delta H_{298}^\ddagger$ ). Taking the free energies into account proved inconsequential with respect to the conclusions reached. Methyl vinyl ether and acetylene were chosen as model substrates.

We had established previously that ligand substitution on CpCo is dissociative, that the ground states of 16-electron species are triplets, whereas those of their 18-electron counterparts are singlets, and that the oxidative coupling of two alkynes is energetically more favorable than the coupling of one alkyne with one alkene.<sup>[10a,12a,26]</sup> At the level of theory employed, the removal of ethene from [CpCo(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] leads to the triplet species <sup>3</sup>[CpCo(C<sub>2</sub>H<sub>4</sub>)] at an enthalpic cost of 22.6 kcal mol<sup>-1</sup> (Scheme 7). Complexation of the enol ether gives rise to the singlet complex **E**, lying 2.9 kcal mol<sup>-1</sup> above the reactants.<sup>[27]</sup> Activation of any C–H bond of the enol ether ligand to give a cobalt hydride such as **F** requires a prohibitive enthalpy of activation above 30 kcal mol<sup>-1</sup> (see for instance **TS<sub>EF</sub>**) and is strongly endothermic. On the other hand, complexation of acetylene to <sup>3</sup>[CpCo(C<sub>2</sub>H<sub>4</sub>)] to give **G** is exothermic. Dissociation of the second ethene ligand requires 2.51 kcal mol<sup>-1</sup>, and the resulting triplet species may either coordinate the enol ether to furnish **H** endothermally, or coordinate acetylene to provide **J**, which lies 0.9 kcal mol<sup>-1</sup> below the reactants. Transformation of **H** into

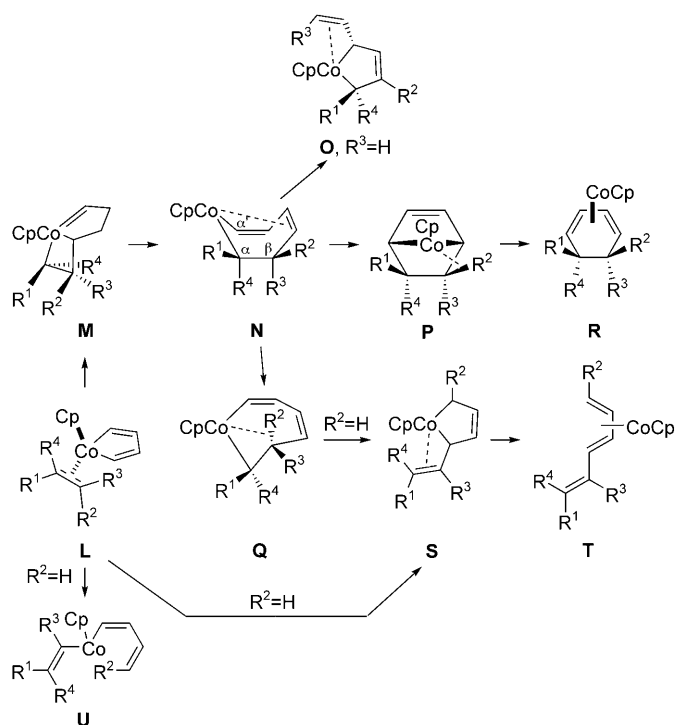


Scheme 7. Competition between alkyne coupling and vinyl C–H activation pathways in the coordination sphere of CpCo (enthalpies, kcal mol<sup>-1</sup>).

the cobalt hydride **I** or any other regioisomer again requires a very high enthalpy of activation (e.g., **TS<sub>HI</sub>**) and is strongly endothermic, whereas the transformation of **J** into cobaltacyclopentadiene **K** is realized at an enthalpic cost of only 6.9 kcal mol<sup>-1</sup>, and is exothermic by 27.7 kcal mol<sup>-1</sup>. Barrierless complexation of the enol ether may give various regio- and diastereomers **L** with close-lying energies in the range of 2.6 kcal mol<sup>-1</sup>,<sup>[28]</sup> the most stable located at -47.8 kcal mol<sup>-1</sup>. The upshot of this initial set of computations is that early vinyl-H activations according to pathway 3 depicted in Scheme 6 are very unlikely. Our focus therefore turned to species **L** and its various options of isomerization, summarized in Scheme 8 and Table 4.

Although the more direct oxidative hydrogen migration (pathway 2 in Scheme 6) to dienylnyl vinylcobalt intermediates **U**, and metathesis to metallacyclopentenes of type **S**, could be modeled, they appear to be noncompetitive. Thus, the former are substantially endothermic and require appreciable activation (**TS<sub>LU</sub>** ≈ 17–21 kcal mol<sup>-1</sup>). The latter are exothermic but still require more than 23 kcal mol<sup>-1</sup> of activation. In contrast, insertion of the enol ether ligand into a Co–C bond to give seven-membered complexes **N**, either in stepwise fashion via the cobalt carbene **M** or concertedly, is straightforward, with enthalpies of activation between 3.8 and 5.6 kcal mol<sup>-1</sup>. The respective formation of both **M** and **N** is reasonably exothermic by approximately 3–10 kcal mol<sup>-1</sup>. Thus, insertion remains the preference of the bound alkene in **L**, regardless of the presence of the alkoxy group (Table 5).

Having ascertained the intermediacy of **N**, the next task was to quantify the bifurcation toward products **R** and **T**. Before considering the traditional intermediates **P** and **Q**, inspection of the rigid and severely bent structure of **N**, a



Scheme 8. Computed possible isomerizations of **L**.

Table 5. Enthalpies of species **L–U** and associated transition states relative to the most stable isomer of **L** [kcal mol<sup>-1</sup>].

Species	R <sup>1</sup> = OMe <sup>[a]</sup>	R <sup>2</sup> = OMe <sup>[a]</sup>	R <sup>3</sup> = OMe <sup>[a]</sup>	R <sup>4</sup> = OMe <sup>[a]</sup>
<b>L</b>	0.1	0.0	2.6	1.7
<b>M</b>	–	–3.3	–5.3	–
<b>N</b>	–9.3	–9.3	–5.9	–9.7
<b>O</b>	–25.5	–35.9	–	–
<b>P</b>	–11.8	–11.8	–12.6	–12.6
<b>Q</b>	–10.3	–7.2	–13.4	–8.9
<b>R</b>	–54.8	–54.8	–53.9	–53.9
<b>S</b>	–30.8	–	–31.2	–21.3
<b>T</b>	–37.1	–	–36.1	–36.7
<b>U</b>	13.4	–	8.5	10.8
<b>TS<sub>LS</sub></b>	24.3	–	32.9	23.1
<b>TS<sub>LU</sub></b>	17.5	–	20.9	17.2
<b>TS<sub>LM</sub></b>	5.3	3.8	4.9	5.6
<b>TS<sub>MN</sub></b>	–	–1.1	–0.6	–
<b>TS<sub>NO</sub></b>	15.0	16.2	–	–
<b>TS<sub>NP</sub></b>	4.6	3.8	–1.6	8.5
<b>TS<sub>NQ</sub></b>	3.0	6.4	8.1	5.0
<b>TS<sub>PR</sub></b>	–3.8	–3.8	–5.3	–5.3
<b>TS<sub>QS</sub></b>	–8.7	–	–13.0	–8.4
<b>TS<sub>ST</sub></b>	–1.8	–	–2.6	1.3

[a] Position of the OMe group in the respective complexes. The other R groups in each case represent H. [b] Collapses to **N**. [c] Not applicable (R<sup>3</sup> = H). [d] Not computed, as the corresponding TS could not be located. [e] Not applicable (R<sup>2</sup> = H). [f] Not computed, as species **M** collapses to **N** in this case. [g] Not found.

consequence of the η<sup>2</sup>-bonding of the metal to the distal double bond, revealed that R<sup>3</sup> is positioned quite close to the α' carbon. This finding, in turn, suggested the possibility of a hitherto unrecognized 1,5-shift (R<sup>3</sup> = H), which would assemble **O**, from which triene complexes would emerge by

valence tautomerization. Indeed, such a rearrangement could be computed for two isomers of **N**, but at a prohibitively high enthalpic cost ( $\text{TS}_{\text{No}}$ ). Returning to the established mechanisms,<sup>[10a]</sup> but now as potentially modified by methoxy substitution, the energies connected to the isomerization of **N** to **R** via **P**, and of **N** to **T** via **Q** and **S** were computed (Table 5). Both processes traverse through relatively low-lying transition states, and no pronounced energetic predilection for either pathway can be discerned, as observed experimentally. Interestingly, with the methoxy group at  $\text{R}^1$  or  $\text{R}^4$ , the formation of **Q** appears kinetically favored over that of **P**. Moreover,  $\text{TS}_{\text{No}}$  ( $\text{R}^3 = \text{OMe}$ ) is relatively large, providing a tentative explanation for the emergence of the alkoxy groups at the termini of the product trienes. Similarly, the trajectory for  $\text{R}^1 = \text{OMe}$ , leading to the *trans* stereochemistry observed, appears slightly favored. Evidently, however, structural factors must influence this outcome strongly, as indicated by the results of Scheme 4. These processes do not stop at a cobalt hydride of the type shown in Scheme 6, but the  $\beta\text{H}$  atoms are transferred directly to the  $\alpha'$  carbons to give cobaltacyclopentenes of type **S**. Reductive elimination of these species provides the triene complexes **T**.

Overall, the calculations suggest that trienes and cyclohexadienes share a common intermediate, and that the formation of trienes follows the  $\beta$ -hydride elimination pathway 1 depicted in Scheme 6. This result is in consonance with those obtained for the isoelectronic CpRu systems.

## Conclusion

Long overdue, the competitive occurrence of  $\beta$ -hydride elimination from a cobaltacycloheptadiene in the co-oligomerization of alkynes with alkenes by stoichiometric CpCo has been established experimentally. It surfaces when the alkene is an enol ether with certain alkadiyne and -monoyne substrates. In these cases it is generally completely chemo-, regio-, and stereospecific, with the resulting free alkoxyhexatrienes emerging exclusively with a terminal ether function in the *trans* configuration after column chromatography. Particularly promising synthetically are cases involving borylated alkynes, which furnish borylated alkoxytrienes. The potential further generality of this reaction channel is indicated by the observation that ethene itself can be a co-oligomerization partner. The trienes undergo  $6\pi$ -electrocyclization followed by dehydroalkoxylation, giving rise to benzene derivatives formally arising from  $[2+2+2]$  cycloaddition of alkynes to acetylene. The same type of arene is accessed from the regular cocyclization channel by oxidative demetalation–dehydroalkoxylation of the resulting alkoxyhexadiene complexes. By using high-temperature conditions for the co-oligomerization reaction, both pathways converge to the same arene products, providing a one-step protocol for using enol ethers as acetylene surrogates. DFT calculations confirm the energetic closeness of the  $[2+2+2]$  reductive

and  $\beta$ -hydride elimination pathways, and rule out alternative vinyl hydrogen activation routes toward the triene products.

## Experimental Section

**General methods:** Reactions were carried out under argon. Except for the  $[2+2+2]$  cycloaddition reactions involving **III**, which were carried out without pretreatment, solvents were purified as follows:  $\text{CH}_2\text{Cl}_2$  was distilled from calcium hydride, toluene and xylenes from  $\text{NaK}_{2.8}$ , and THF and  $\text{Et}_2\text{O}$  from sodium benzophenone ketyl. Solvents were degassed (Ar) prior to the use of  $[\text{CpCo}(\text{CO})_2]$  and  $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$ .  $[\text{CpCo}(\text{CO})_2]$  was purchased from Aldrich and used as received.  $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$  was prepared according to the known procedure.<sup>[13]</sup> Reaction mixtures employing  $[\text{CpCo}(\text{CO})_2]$  were irradiated (visible light) by using a 300 W halogen lamp. Microwave heating was carried out in a Biotage microwave synthesizer (400 W max). Thin layer chromatography (TLC) was performed on Merck 60  $\text{F}_{254}$  silica gel. Merck Gerudan SI 60 Å silica gel (35–70  $\mu\text{m}$ ) was used for column chromatography.  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR spectra were recorded at 20 °C at 400, 377, 128, and 100 MHz, respectively, on a Bruker AVANCE400 spectrometer.  $^{13}\text{C}$  NMR signals of carbon atoms attached to boron are very broad and were not observed. Chemical shifts ( $\delta$ ) are given in ppm, for  $^1\text{H}$  NMR referenced to the residual proton resonance of the solvents ( $\delta = 7.26$  for  $\text{CDCl}_3$ ;  $\delta = 7.16$  for  $\text{C}_6\text{D}_6$ ), and for  $^{13}\text{C}$  NMR to the corresponding carbon resonance ( $\delta = 77.16$  for  $\text{CDCl}_3$ ;  $\delta = 128.06$  for  $\text{C}_6\text{D}_6$ ). Coupling constants ( $J$ ) are given in Hertz (Hz). The terms m, s, d, t, q, and quin refer to multiplet, singlet, doublet, triplet, quartet, quintet, respectively; br stands for broad. When possible, NMR signals were assigned on the basis of NOE, DEPT (Distortionless Enhancement by Polarization Transfer), and 2D-NMR (COSY, HMBC) experiments. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer. High resolution mass spectral data (HRMS) were obtained by ESI. Melting points were measured with an SMP3 Stuart Scientific melting point apparatus and were not corrected. Starting materials were either commercial or prepared according to the literature.<sup>[29]</sup>

**Procedure for preparation of products 3, 3', 14, and 14' (Tables 1 and 2):**  $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$  (360 mg, 2 mmol) was dissolved in THF (8 mL). The enol ether (5 equiv) was added neat and the mixture was allowed to stir for 4 h at RT. The alkyne (4 mmol) or the diyne (2 mmol) in THF (2 mL) was transferred by using a cannula into the mixture at  $-40^\circ\text{C}$ . The cold bath was removed and the mixture was stirred at room temperature for 4 h. After evaporation of the solvent, the residue was purified with flash column chromatography by using gradient mixtures of pentane and diethyl ether.

**Procedure for preparation of products 2, 14, and 16' (Tables 1 and 2):**  $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$  (360 mg, 2 mmol), the enol ether (5 equiv), and the monoalkyne (4 mmol) or diyne (2 mmol) were reacted as above. The solvent was removed with a rotary evaporator. Acetonitrile (25 mL) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (810 mg, 3 mmol) were added in one portion at RT. The red color turned violet instantaneously. The mixture was promptly evaporated and the residue was submitted to flash column chromatography over silica gel by using gradient mixtures of pentane and diethyl ether.

**Procedure for direct arene formation from diynes and *tert*-butyl vinyl ether (Table 3, entry 9, and Table 4):** In a microwave vial, a solution of diyne (0.68 mmol), *tert*-butyl vinyl ether (3.4 mmol), and **III** (0.06 mmol) in DMF (4 mL) was heated to 200 °C for 20 min. After cooling to RT, water and  $\text{Et}_2\text{O}$  were added, and the aqueous layer was extracted with  $\text{Et}_2\text{O}$ . The combined organic extracts were washed with water, dried over  $\text{MgSO}_4$ , and concentrated. The residue was purified by flash column chromatography by using gradient mixtures of pentane and diethyl ether.

**2k:** Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.40$  (t,  $J = 7.2$  Hz, 6H), 2.09 (quin,  $J = 7.2$  Hz, 2H), 3.29 (t,  $J = 7.6$  Hz, 4H), 4.37 (q,  $J = 7.1$  Hz, 4H), 7.85 ppm (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 14.4$  ( $\text{CH}_3$ ), 24.8 ( $\text{CH}_2$ ), 33.7 ( $\text{CH}_2$ ), 61.1 ( $\text{CH}_2$ ), 128.0 (CH), 130.1 (C), 148.3 (C), 166.8 ppm (C); IR (neat):  $\tilde{\nu}_{\text{max}} = 1025, 1124, 1268, 1713, 2978 \text{ cm}^{-1}$ ; HRMS: calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_4\text{Na}$ : 285.1097; found: 285.1096.



**2o**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.33 (s, 24H), 1.68–1.81 (m, 2H), 2.12–2.27 (m, 4H), 3.08–3.19 (m, 4H), 7.47 ppm (s, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 22.3 ( $\text{CH}_3$ ), 24.8 ( $\text{CH}_3$ ), 27.7 ( $\text{CH}_2$ ), 33.1 ( $\text{CH}_2$ ), 83.4 (C), 131.8 (CH), 149.2 ppm (C), C-B not observed; IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1108, 1212, 1270, 1315, 1369, 2858, 2930, 2975  $\text{cm}^{-1}$ ; HRMS: calcd for  $\text{C}_{25}\text{H}_{36}\text{B}_2\text{O}_4\text{Na}$ : 421.2697; found: 421.2700.

**3b**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.18 (s, 9H), 1.66 (quin,  $J$  = 7.5 Hz, 2H), 2.16 (t,  $J$  = 7.5 Hz, 2H), 2.73 (t,  $J$  = 7.5 Hz, 2H), 6.13 (d,  $J$  = 12.2 Hz, 1H), 6.68 (d,  $J$  = 12.2 Hz, 1H), 6.91 (s, 1H), 7.21–7.30 (m, 4H), 7.34–7.42 ppm (m, 6H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 23.5 ( $\text{CH}_2$ ), 28.1 ( $\text{CH}_3$ ), 32.3 ( $\text{CH}_2$ ), 32.4 ( $\text{CH}_2$ ), 84.4 (C), 113.2 (CH), 126.0 (CH), 126.1 (CH), 126.5 (CH), 128.0 (CH), 128.1 (CH), 128.9 (CH), 129.7 (CH), 133.1 (C), 137.8 (C), 139.0 (C), 142.7 (C), 143.6 (C), 147.0 ppm (CH); IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1156, 1628, 3054  $\text{cm}^{-1}$ ; HRMS: calcd for  $\text{C}_{25}\text{H}_{28}\text{ONa}$ : 367.2024; found: 367.2034.

**iso-3b**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.15 (s, 9H), 1.77 (quin,  $J$  = 7.3 Hz, 2H), 2.64 (t,  $J$  = 7.3 Hz, 2H), 2.69 (t,  $J$  = 7.3 Hz, 2H), 5.48 (s, 1H), 5.96 (d,  $J$  = 11.8 Hz, 1H), 6.22 (d,  $J$  = 11.8 Hz, 1H), 6.93–7.06 (m, 3H), 7.15–7.22 (m, 3H), 7.26–7.39 ppm (m, 4H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 24.1 ( $\text{CH}_2$ ), 28.1 ( $\text{CH}_3$ ), 32.1 ( $\text{CH}_2$ ), 34.0 ( $\text{CH}_2$ ), 84.1 (C), 113.7 (CH), 125.0 (CH), 125.7 (CH), 126.8 (CH), 127.9 (CH), 128.7 (CH), 128.9 (CH), 129.8 (CH), 132.4 (C), 135.2 (C), 139.3 (C), 141.0 (C), 142.7 (C), 146.2 ppm (CH); IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1155, 1625, 3022  $\text{cm}^{-1}$ .

**3d**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.26 (s, 9H), 1.27 (s, 12H), 1.33 (s, 12H), 1.62–1.67 (m, 2H), 2.50 (t,  $J$  = 7.1 Hz, 2H), 2.64 (t,  $J$  = 7.9 Hz, 2H), 5.75 (s, 1H), 6.43 (d,  $J$  = 12.9 Hz, 1H), 6.86 ppm (d,  $J$  = 12.9 Hz, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 23.6 ( $\text{CH}_2$ ), 24.9 (2 C,  $\text{CH}_3$ ), 28.1 ( $\text{CH}_3$ ), 34.2 ( $\text{CH}_2$ ), 34.5 ( $\text{CH}_2$ ), 76.5 (C), 82.6 (C), 83.3 (C), 111.3 (CH), 146.1 (CH), 147.2 (C), 163.7 ppm (C), C-B not observed; IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1111, 1164, 1264, 1426, 1732, 2930, 3053  $\text{cm}^{-1}$ ; HRMS: calcd for  $\text{C}_{25}\text{H}_{42}\text{B}_2\text{O}_5\text{Na}$ : 461.3116; found: 467.3118.

**3'd**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.28 (s, 12H), 1.33 (s, 12H), 1.65 (quin,  $J$  = 7.9 Hz, 2H), 2.60 (t,  $J$  = 7.9 Hz, 2H), 2.67 (dt,  $J$  = 7.9, 2.1 Hz, 2H), 5.75 (br s, 1H), 6.71 (d,  $J$  = 12.9 Hz, 1H), 6.98–7.05 (m, 4H), 7.27–7.34 ppm (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 21.1 ( $\text{CH}_2$ ), 24.5 ( $\text{CH}_3$ ), 24.9 ( $\text{CH}_3$ ), 32.7 ( $\text{CH}_2$ ), 33.9 ( $\text{CH}_2$ ), 83.2 (C), 83.4 (C), 115.3 (CH), 120.5 (CH), 125.8 (CH), 129.6 (CH), 133.0 (CH), 143.5 (C), 150.7 (C), 169.5 ppm (C), C-B not observed; IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1120, 1264, 1357, 1717, 2980  $\text{cm}^{-1}$ .

**3g**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.26 (s, 12H), 1.27 (s, 9H), 1.32 (s, 12H), 2.39 (s, 2H), 2.53 (s, 2H), 3.21 (s, 4H), 3.31 (s, 6H), 5.74 (s, 1H), 6.39 (d,  $J$  = 12.9 Hz, 1H), 6.86 ppm (d,  $J$  = 12.9 Hz, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 24.9 ( $\text{CH}_3$ ), 25.0 ( $\text{CH}_3$ ), 28.1 ( $\text{CH}_3$ ), 39.7 ( $\text{CH}_2$ ), 39.8 ( $\text{CH}_2$ ), 44.3 (C), 59.3 ( $\text{CH}_3$ ), 75.8 ( $\text{CH}_2$ ), 76.6 (C), 82.7 (C), 83.4 (C), 111.1 (CH), 145.8 (C), 146.2 (CH), 161.9 ppm (C), C-B not observed; IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1107, 1371, 1457, 1716, 2924  $\text{cm}^{-1}$ ; HRMS: calcd for  $\text{C}_{30}\text{H}_{50}\text{B}_2\text{O}_5\text{Na}$ : 567.3640; found: 567.3642.

**3'g**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 1.27 (s, 12H), 1.32 (s, 12H), 2.50 (s, 2H), 2.57 (s, 2H), 3.23 (s, 4H), 3.28 (s, 6H), 5.74 (s, 1H), 6.67 (d,  $J$  = 12.9 Hz, 1H), 6.98–7.03 (m, 3H), 7.27–7.34 ppm (m, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 24.5 ( $\text{CH}_3$ ), 24.9 ( $\text{CH}_3$ ), 38.6 ( $\text{CH}_2$ ), 40.2 ( $\text{CH}_2$ ), 47.4 (C), 59.3 ( $\text{CH}_3$ ), 76.3 ( $\text{CH}_2$ ), 83.2 (C), 83.4 (C), 115.3 (CH), 120.5 (CH), 125.6 (CH), 127.7 (CH), 129.6 (CH), 133.4 (CH), 141.4 (C), 149.2 (C), 155.7 ppm (C), C-B not observed.

**14a**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 0.79 (s, 12H), 1.10 (s, 12H), 7.25–7.52 (m, 11H), 7.72 ppm (d,  $J$  = 7.9 Hz, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 24.5 ( $\text{CH}_3$ ), 24.6 ( $\text{CH}_3$ ), 83.3 (C), 83.5 (C), 126.3 (CH), 126.6 (CH), 127.0 (CH), 127.9 (CH), 129.2 (CH), 130.2 (CH), 134.2 (CH), 143.3 (C), 143.8 (C), 147.4 (C) 151.5 ppm (C), 1 CH peak is accidentally isochronous with another, C-B not observed; IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1140, 1267, 2926, 2978  $\text{cm}^{-1}$ ; HRMS: calcd for  $\text{C}_{30}\text{H}_{36}\text{B}_2\text{O}_4\text{Na}$ : 505.2697; found: 505.2701.

**15d**: Colorless oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 0.85 (d,  $J$  = 6.8 Hz, 6H), 0.88 (d,  $J$  = 6.8 Hz, 6H), 1.26 (s, 9H), 1.29 (s, 12H), 1.68 (non,  $J$  = 6.8 Hz, 1H), 1.82 (non,  $J$  = 6.8 Hz, 1H), 2.02 (d,  $J$  = 7.2 Hz, 2H), 2.33 (d,  $J$  = 7.2 Hz, 2H), 5.33 (s, 1H), 5.50 (s, 1H), 6.15 (d,  $J$  = 12.4 Hz, 1H), 6.65 ppm (d,  $J$  = 12.4 Hz, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 22.5 ( $\text{CH}_3$ ), 22.6 ( $\text{CH}_3$ ), 24.6 ( $\text{CH}_3$ ), 24.9 ( $\text{CH}_3$ ), 27.2 (CH), 27.3 (CH), 44.9 ( $\text{CH}_2$ ), 45.6 ( $\text{CH}_2$ ), 80.2 (C), 83.2

(C), 125.7 (CH), 131.1 (CH), 135.9 (CH), 144.2 (C), 148.7 ppm (C), C-B not observed;  $^{11}\text{B NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 32 ppm; IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1209, 1349, 1612, 1679, 3078  $\text{cm}^{-1}$ ; HRMS: calcd for  $\text{C}_{24}\text{H}_{43}\text{BO}_3\text{Na}$ : 413.3197; found: 413.3194.

**15'd**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 0.88 (d,  $J$  = 8.3 Hz, 6H), 0.91 (d,  $J$  = 8.3 Hz, 6H), 1.28 (s, 12H), 1.60–1.70 (m, 1H), 1.80–1.90 (m, 1H), 2.09 (d,  $J$  = 7.5 Hz, 2H), 2.37 (d,  $J$  = 7.5 Hz, 2H), 5.35 (s, 1H), 5.70 (s, 1H), 6.53 (d,  $J$  = 12.9 Hz, 1H), 6.80 (d,  $J$  = 12.9 Hz, 1H), 6.97–7.03 (m, 2H), 7.06–7.12 (m, 1H), 7.33 ppm (t,  $J$  = 9.2 Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 22.4 ( $\text{CH}_3$ ), 24.5 ( $\text{CH}_3$ ), 24.8 ( $\text{CH}_3$ ), 30.2 (CH), 30.3 (CH), 45.3 ( $\text{CH}_2$ ), 45.4 ( $\text{CH}_2$ ), 83.0 (C), 115.3 (CH), 120.1 (CH), 126.4 (CH), 127.7 (CH), 129.5 (CH), 130.0 (CH), 141.3 (C), 155.5 ppm (C), C-B not observed; IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1216, 1269, 1368, 1381, 1500, 1607, 1718, 2869, 2928  $\text{cm}^{-1}$ .

**16'a**: Yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 0.70 (s, 12H), 1.21 (s, 12H), 5.71 (s, 1H), 6.42 (d,  $J$  = 7.7 Hz, 1H), 6.83–6.89 (m, 3H), 6.99–7.04 (m, 1H), 7.23–7.37 ppm (m, 12H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 24.0 ( $\text{CH}_3$ ), 24.7 ( $\text{CH}_3$ ), 82.9 (C), 83.0 (C), 115.4 (CH), 116.9 (CH), 123.1 (CH), 127.3 (CH), 127.6 (CH), 128.0 (CH), 129.3 (CH), 129.5 (CH), 129.6 (CH), 129.9 (CH), 141.8 (C), 141.9 (C), 146.8 (C), 149.6 (CH), 156.9 (C), 159.5 ppm (C), C-B not observed; IR (neat):  $\tilde{\nu}_{\text{max}}$  = 1143, 1264, 1421, 1735, 2927, 3054  $\text{cm}^{-1}$ ; HRMS: calcd for  $\text{C}_{36}\text{H}_{42}\text{B}_2\text{O}_5\text{Na}$ : 599.3116; found: 599.3118.

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