

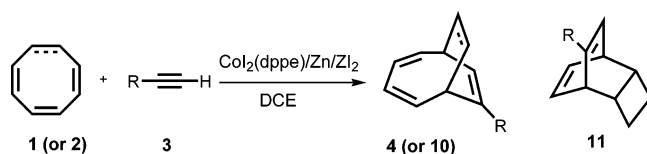
Cobalt(I)-Catalyzed [6+2] Cycloadditions of Cyclooctatetra(tri)ene with Alkynes

Mathieu Achard, Marc Mosrin, Alphonse Tenaglia, and Gérard Buono*

Laboratoire de Synthèse Asymétrique, UMR 6180 CNRS "Chirotechnologies: catalyze et biocatalyse", Université d'Aix-Marseille P. Cézanne, Faculté des Sciences et Techniques de St Jérôme, EGIM, Avenue Escadrille Normandie Niemen, 13397 Marseille Cedex 20, France

gerard.buono@univ.u-3mrs.fr

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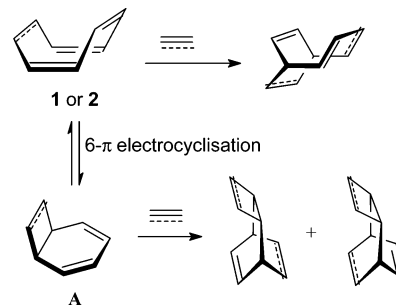


The cobalt-catalyzed [6+2] cycloaddition of cyclooctatetraene **1** with alkynes **3** affords monosubstituted bicyclo[4.2.2]deca-2,4,7,9-tetraenes **4** in fair to good yields. Due to the valence tautomerism, 1,3,5-cyclooctatriene **2**, in equilibrium with bicyclo[4.2.0]octa-2,4-diene **A**, and alkynes **3** are converted to **10** and **11** according to [6+2] and [4+2] cycloadditions, respectively.

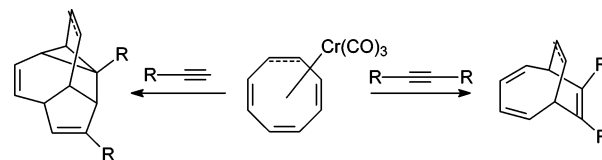
Introduction

Thermal, uncatalyzed, higher-order cycloadditions that involve polyenes as an enophile are difficult to achieve, because they suffer from a lack of periselectivity and often yield complex mixtures.¹ Due to the valence tautomerism, the cycloaddition of cyclooctatetraene (COTT) **1** or 1,3,5-cyclooctatriene (COT) **2** with alkynes or alkenes affords a mixture of tricyclic and/or bicyclic adducts resulting from the [4+2] pathway (Scheme 1).² The transition-metal-catalyzed higher-order cycloadditions of cyclooctatrienes are very useful reactions for the construction of medium-sized ring compounds.³ The [6+2] cycloaddition of the tricarbonyl(η^4 -**1**)iron(0) complex with internal alkynes was first examined by Krüerke⁴ to give metal-free adducts under thermal conditions. In contrast, the photo-

SCHEME 1. Thermal Uncatalyzed [4+2] Cycloaddition of COTT 1 or COT 2 with Alkynes or Alkenes



SCHEME 2. Cycloadditions of $[(\eta^6\text{-COTT or COT})\text{Cr}(\text{CO})_3]$ with Alkynes



induced [6+2] cycloaddition of tricarbonyl(η^4 -**1** or η^4 -**2**)iron(0) complexes afforded at once a mixture of bicyclo[4.2.2]decatetra-(tri)ene and (η^4 -bicyclo[4.2.2]decatetra(tri)ene)iron(0) complexes.⁵ A related photoinduced cycloaddition of tricarbonyl(η^6 -**1** or η^6 -**2**)chromium(0) with DMAD (Dimethyl acetylenedicarboxylate) forming metal-free adducts was reported by Rigby et al.⁶ With terminal alkynes, the chromium-promoted cycloaddition occurs through a stepwise [6+2] cycloaddition-homo[6+2] cycloaddition sequence to afford tetracyclic adducts (Scheme 2).⁷ Sporadically, such reactions with non-carbonyl complexes were reported. For instance, the stoichiometric [6+2] cycloaddition of COTT or COT with alkynes has been described with $[\text{CpMo}(\text{alkyne})_2(\text{MeCN})]$ $[\text{BF}_4]$ ⁸ or $\text{Ru}(\text{cod})(\text{cot})$.⁹

To our knowledge, the metal-catalyzed [6+2] cycloaddition of COTT or COT with alkynes has never been described. Recently, we reported a [6+2] cycloaddition of cycloheptatriene (CHT) with terminal alkynes catalyzed by Co(I) complexes to afford bicyclo[4.2.1]trienes.^{10a} Our interest in the development of cobalt-catalyzed cycloadditions¹⁰ prompted us to investigate

* Corresponding author. Fax: +33-491-282742.

(1) Rigby, J. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 617–643.

(2) (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebig's Ann. Chem.* **1948**, 560, 1–92. (b) Weis, C. D. *J. Org. Chem.* **1963**, 28, 74–78. (c) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1970**, 9, 751–762. (d) Huisgen, R.; Mietzsch, F. *Angew. Chem., Int. Ed. Engl.* **1964**, 3, 83–85. (e) Cope, A. C.; Haven, A. C.; Ramp, F. L.; Trumbull, E. R. *J. Am. Chem. Soc.* **1952**, 74, 4867–4871. (f) Boucher, J. L.; De Riggi, I.; Stella, L. *J. Org. Chem.* **1997**, 62, 6077–6079.

(3) (a) Schore, N. E. *Chem. Rev.* **1988**, 88, 1081–1119. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, 96, 49–92. (c) Frühauf, H. W. *Chem. Rev.* **1997**, 97, 523–596. (d) Rigby, J. H. *Tetrahedron* **1999**, 55, 4521–4538.

(4) Krüerke, U. *Angew. Chem., Int. Ed. Engl.* **1967**, 6, 79.

(5) Davis, R. E.; Dodds, T. A.; Hseu, T. H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, 96, 7562–7564.

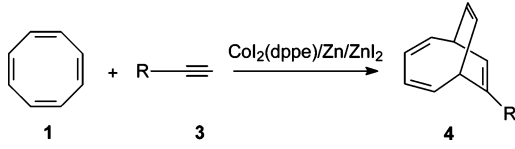
(6) Rigby, J. H.; Scribner, S.; Heeg, M. J. *Tetrahedron Lett.* **1995**, 36, 8569–8572.

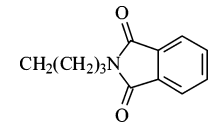
(7) (a) Kreiter, C. G.; Bolik, V. Personal communication. Bolik, V. Ph.D. Thesis, University of Kaiserslautern, 1999. (b) Related tetracyclic compounds were observed in the cycloaddition of $[(\eta^6\text{-CHT})\text{Cr}(\text{CO})_3]$ with terminal alkynes, see: Rigby, J. H.; Heap, C. R.; Warshakoon, N. C. *Tetrahedron* **2000**, 56, 2305–2311.

(8) (a) Bourner, D. G.; Brammer, L.; Green, M.; Moran, G.; Orpen, G.; Reeve, C.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1409. (b) Brammer, L.; Dunne, B. J.; Green, M.; Moran, G.; Orpen, G.; Reeve, C.; Schaverien, C. J. *J. Chem. Soc., Dalton Trans.* **1993**, 1747–1759.

(9) (a) Nagashima, H.; Matsuda, H.; Itoh, K. *J. Organomet. Chem.* **1983**, 258, C15. (b) Itoh, K.; Mukai, K.; Nagashima, H.; Nishiyama, H. *Chem. Lett.* **1983**, 499.

(10) (a) Achard, M.; Tenaglia, A.; Buono, G. *Org. Lett.* **2005**, 7, 2353–2356. (b) Pardigon, O.; Buono, G. *Tetrahedron: Asymmetry* **1993**, 4, 1977–1980. (c) Pardigon, O.; Tenaglia, A.; Buono, G. *J. Org. Chem.* **1995**, 60, 1868–1871. (d) Tenaglia, A.; Pardigon, O.; Buono, G. *J. Org. Chem.* **1996**, 61, 1129–1132. (e) Pardigon, O.; Tenaglia, A.; Buono, G. *J. Mol. Catalysis A: Chem.* **2003**, 196, 157–164.

TABLE 1. Cobalt-Catalyzed [6+2] Cycloaddition of Cyclooctatetraene with Terminal Alkynes^a


entry	alkyne	R	product	yield ^b (%)
1	3a	Ph	4a	70
2	3b	<i>n</i> -Bu	4b	61
3	3c	SiMe ₃	4c	89
4	3d	CH ₂ SO ₂ Ph	4d	71
5	3e	CH ₂ CH(CO ₂ Me) ₂	4e	79
6	3f	CH ₂ C(Me) ₂ CH ₂ Ac	4f	75
7 ^c	3g	CH ₂ OH	4g	69
8 ^c	3h	CH ₂ CH ₂ OH	4h	76
9	3i	CH ₂ CH ₂ OAc	4i	56
10	3j	CH ₂ CH ₂ OTs	4j	63
11	3k		4k	94
12	3l	(CH ₂) ₃ CN	4l	88

^a All reactions were carried out with COTT **1**/alkyne **3**/Co₂(dppe)/Zn/ZnI₂ in a 1.2/1/0.05/0.15/0.1 molar ratio in DCE at 40 °C for 20 h. ^b Yields of isolated products by column chromatography. ^c TFE as solvent.

the behavior of COTT or COT as enophiles. Herein, we report the first cobalt-catalyzed [6+2] cycloaddition of COTT or COT as the partner of the reaction with alkynes.

Results and Discussion

The reaction of phenylethyne **3a** and COTT **1** in the presence of Co₂(dppe)¹¹ and a Lewis acid/reducing agent couple, namely, ZnI₂/Zn¹² in DCE at 40 °C for 20 h, afforded the desired 7-phenylbicyclo[4.2.2]deca-2,4,7,9-tetraene **4a** in 70% yield (Table 1, entry 1). A similar result was observed combining Co₂(dppe) and Bu₄NBH₄/ZnI₂¹³ in 66% yield. However, the first catalytic system was preferred for its compatibility with the functional group of the trienophile.

The scope and limitations of the [6+2] cycloaddition with regard to the terminal alkynes are summarized in Table 1. The reaction appeared to be quite general, with various alkynes bearing functional groups such as ketone, sulfone, ester, imide, sulfonate, and nitrile (entries 4–6, 9–12) and trimethylsilyl substituent (entry 3), affording the [6+2] cycloadducts in moderate to good yields (56–94%).

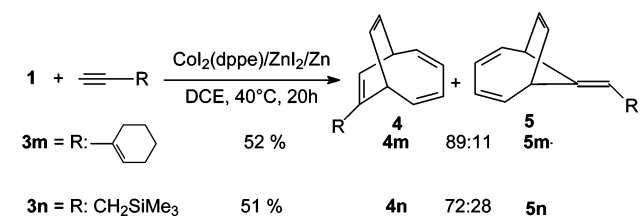
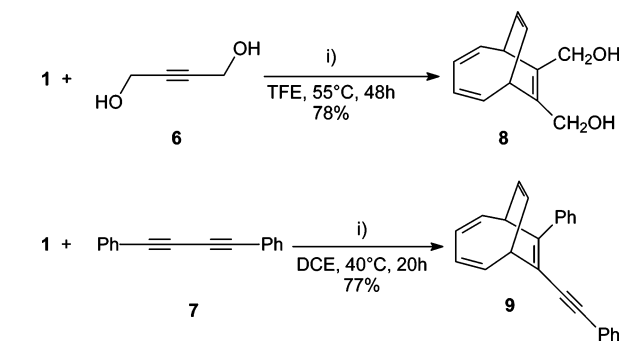
Cycloadducts resulting from the valence tautomerism of the COTT were not formed. The only byproducts observed (≤5%) by ¹H NMR of the crude reaction mixture were aromatic cyclotrimers from alkynes **3a**, **3b**, or **3d**.¹⁴ As previously observed, the choice of the solvent was crucial for the reactions involving alkynols, and TFE (trifluoroethanol) proved to be the

(11) Cotton, F. A.; Faut, O. D.; Goodgame, M. L.; Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 1780–1785.

(12) (a) Ma, B.; Snyder, J. K. *Organometallics* **2002**, *21*, 4688–4695. (b) Chen, Y.; Kiattansakul, R.; Ma, B.; Snyder, J. K. *J. Org. Chem.* **2001**, *66*, 6932–6942.

(13) Hilt, G.; Lüers, S.; Schmidt, F. *Synthesis* **2003**, *4*, 634–638.

(14) (a) For a recent report on the cobalt-catalyzed trimerization of alkyne, see: Hilt, G.; Hess, W.; Vogler, T.; Hengst, C. *J. Organomet. Chem.* **2005**, *690*, 5170–5181. (b) For a recent microreview, see: Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741–4767.

SCHEME 3. Cobalt-Catalyzed Formation of **4** and **5**

SCHEME 4. Cobalt-Catalyzed [6+2] Cycloaddition of Cyclooctatetraene with Internal Alkynes


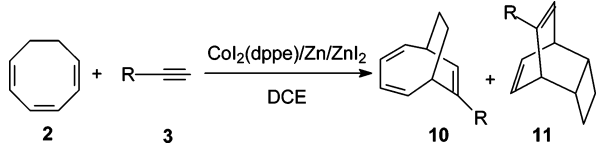
(i) COTT **1**/alkyne **6** or **7**/Co₂(dppe)/Zn/ZnI₂: 1.2/1/0.05/0.15/0.1.

best solvent, allowing the formation of cycloadducts in good yields (entries 7 and 8). Unexpectedly, the reaction with ethynylcyclohexene **3m** and propargyl trimethylsilane **3n** afforded, along with the [6+2] cycloadducts **4**, a byproduct **5** featuring the 9-methylene-bicyclo[4.2.1]nona-2,4-diene framework (Scheme 3). The structure of this newly formed cycloadduct **5** was firmly established by a ¹H–¹H COSY experiment. Interestingly, the formation of **5** can be viewed as a formal [6+1] cycloaddition probably as a result of the electronic effects of the TMS or vinyl substituents. This reaction was briefly examined, with COTT **1** and symmetrical internal alkynes or 1,3-diyne affording the expected [6+2] cycloadducts in good yields (Scheme 4). For unknown reasons, the reactions with diphenylethyne or 3-hexyne failed even at increased temperatures. The cobalt-catalyzed [6+2] cycloaddition was further examined with COT **2**. In the presence of the cobalt catalyst at 40 °C, COT **2** and phenylethyne **3a** afforded the desired 7-phenylbicyclo[4.2.2]deca-2,4,7-triene **10a** along with the tricyclic adduct **11a** in approximately 1/1 ratio and 38% global yield (Table 2, entry 2).

The structure of **11a** was established by a NOESY experiment, which revealed the featuring cyclobutane ring anti to the phenyl-substituted bridge. The absence of the cycloadducts **12** and/or **13** (Scheme 5) in the crude reaction mixture rules out a [4+2] pathway for the cycloaddition of COTT or COT with alkynes leading to **4** or **10**, respectively. In a control experiment, no adduct was observed in the absence of catalyst.

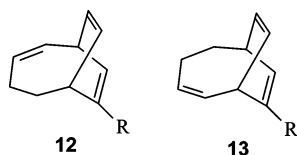
Similar results were obtained with alkynes **3c** and **3e** (entries 8 and 9). The allowed disrotatory ring closure of **2** to bicyclo[4.2.0]octa-2,4-diene **A** (Scheme 1) precedes the cobalt-catalyzed [4+2] cycloaddition. At 35 °C, the ratio COT/A in equilibrium¹⁵ is about 80/20. As shown in Table 2, the ratio

(15) (a) Cope, A. C.; Haven, A. C.; Ramp, F. L.; Trumbull, E. R. *J. Am. Chem. Soc.* **1952**, *74*, 4867. (b) Kröner, M. *Chem. Ber.* **1967**, *100*, 3172. (c) Huisgen, R.; Boche, G.; Dahmen, A.; Hecht, W. *Tetrahedron Lett.* **1968**, 5215. (d) Adam, W.; Gretzke, N.; Hasemann, L.; Klug, G.; Peters, E. M.; Peters, K.; von Schnering, H. G.; Will, B. *Chem. Ber.* **1985**, *118*, 3357.

TABLE 2. Cobalt-Catalyzed [6+2] vs [4+2] Cycloaddition of COT with Terminal Alkynes^a


entry	alkyne	T °C	time (h)	10/11 ^b	yield ^c (%)
1	3a	20	72	53/47	29
2	3a	40	20	47/53	38
3	3a	54	20	33/67	55
4	3a	58	20	30/70	53
5	3a	60	20	25/75	60
7	3a	64	20	14/86	71
8	3c	40	20	31/69	67
9	3e	40	20	40/60	46

^a All reactions were carried out with COT **2**/alkyne **3**/CoI₂(dppe)/Zn/ZnI₂ in a 1.2/1/0.05/0.15/0.1 molar ratio in DCE. ^b Ratio determined by ¹H NMR. ^c Yields of isolated products by column chromatography.

SCHEME 5. Undetected [4+2] Cycloadducts

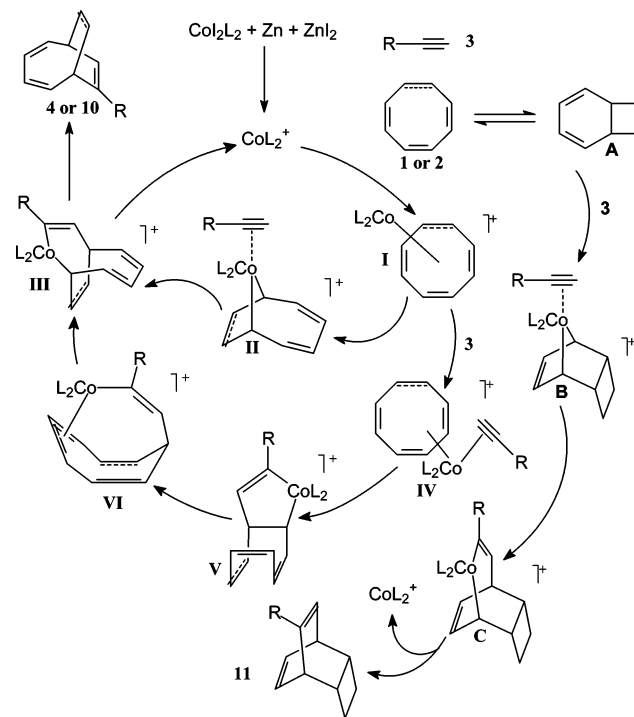
10/11 depends on the temperature (entries 1–7) and the nature of the acetylenic compounds (entries 2, 8, and 9) but not on the initial equilibrium. According to the Curtin–Hammett principle, the discrepancy in the formation of adducts **10** versus **11** shows that the rate-controlling step is related to the relative reactivity of COT and **A** (Scheme 1).

The mechanism for the cycloaddition is not yet clear, but on the basis of the known cobalt chemistry, two pathways can be proposed (Scheme 6).¹⁶ According to Snyder et al., reduction of Co(II) to cationic Co(I) by zinc is accelerated by ZnI₂.¹² Coordination of the cyclic polyene with [Co(I)L₂]⁺ complex¹³ forms [η^6 -(COT or COTT)Co(I)L₂]⁺ complex **I**.¹⁷

According to the first path, oxidative cyclometalation of complex **I**, followed by coordination of the alkyne, leads to cobaltacycle **II**. Insertion of the alkyne on the Co–C bond affords the cobaltabicyclo **III**, and subsequent reductive elimination of cobalt releases the cycloadduct and regenerates the active species [Co(I)L₂]⁺.

In the second path, we suggest that the oxidative cyclometalation of complex **IV** is initiated by a change of hapticity of the triene from η^6 (**I**) to η^4 (**IV**), allowing the coordination of the alkyne to afford the η^4 – η^2 complex **IV**. The complex **V**, resulting from the oxidative cyclometalation of **IV**, undergoes a 1,5 migration of the Co–C(sp³) bond through σ – π –allyl complexes to form the cobaltabicyclo adduct **III**.

The formation of **11** is likely to occur from the well-documented cobalt-catalyzed [4+2] cycloaddition of dienes with alkynes.¹⁸ The successive oxidative cyclometalation, alkyne

SCHEME 6. Postulate Mechanism of the Cobalt-Catalyzed [6+2] Cycloaddition of **1** or **2** with Alkynes

insertion, and reductive elimination steps give rise to **B**, **C**, and **11** respectively.

Conclusion

In summary, we have demonstrated the first catalyzed [6+2] cycloaddition of COTT with alkynes promoted with CoI₂(dppe)/Zn/ZnI₂ that affords 7-alkyl-bicyclo[4.2.2]deca-2,4,7,9-tetraenes. The reaction with COT gives both [6+2] and [4+2] adducts as a result of the valence tautomerism of COT. The enantioselective version of this cycloaddition is underway in our laboratories.

Experimental Section

General Procedure for the [6+2] Cycloaddition of Cyclooctatetraene. Preparation of 4a–l, 8 and 9. 7-Phenylbicyclo[4.2.2]deca-2,4,7,9-tetraene, **4a**, as a Representative Example with a Terminal Alkyne. Zinc powder (8.2 mg, 0.125 mmol, 15 mol %) was added to a solution of CoI₂(dppe) (30 mg, 4.22 × 10^{−2} mmol, 5 mol %) in DCE (1.5 mL) in a 15 mL Schlenk tube, and the mixture was stirred at room temperature for two minutes. Then COTT **1** (105 mg, 1.0 mmol) in DCE (0.75 mL), phenylethyne **2a** (86 mg, 0.843 mmol) in DCE (0.75 mL), and dry zinc iodide (27 mg, 8.43 × 10^{−2} mmol, 10 mol %) were successively added, and the resultant mixture was stirred at 40 °C for 20 h. The reaction was stopped by the addition of pentane or petroleum ether and by stirring in air for 10 minutes to deactivate the catalyst. After filtration on a short pad of silica and concentration in vacuo, the crude product was purified by flash chromatography (silica gel, petroleum ether) to afford 121 mg (70%) of **4a** as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.52–7.49 (m, 2H), 7.43–7.38 (m, 2H), 7.33–7.31 (m, 1H), 6.52–6.34 (m, 2H), 6.15 (dd, *J* = 6.0, 0.7 Hz, 1H), 5.98–5.89 (m, 3H), 5.82 (dd, *J* = 5.8, 8.6 Hz, 1H), 3.93 (dd, *J* = 6.0, 8.6 Hz, 1H), 3.45 (dt, *J* = 8.6, 6.0 Hz, 1H); ¹³C

(16) For mechanism proposals of cobalt-catalyzed HDA and [4+2+2] cycloadditions, see: Lautens, M.; Lautens, J. C.; Smith, A. C. *J. Am. Chem. Soc.* **1990**, *112*, 5627–5628. See also, ref 12.

(17) For a recent report on the similar (η^6 -arene)L₂Co(I) complexes, see: Grossheimann, G.; Holle, S.; Jolly, P. W. *J. Organomet. Chem.* **1998**, *568*, 205–211.

(18) (a) Hilt, G.; Mesnil, F. X. D. *Tetrahedron Lett.* **2000**, *41*, 6757–67561. (b) Hilt, G.; Korn, T. *Tetrahedron Lett.* **2001**, *42*, 2783–2785. (c) Hilt, G.; Smolko, K. I. *Angew. Chem., Int. Ed.* **2003**, *42*, 2795–2797.

NMR (50 MHz, CDCl_3) δ 141.8 (d), 140.9 (d), 139.7 (s), 135.0 (s), 128.3 (d, 2C), 126.6 (d), 126.4 (d, 2C), 124.7 (d), 124.6 (d), 121.4 (d), 120.3 (d), 119.6 (d), 38.2 (d), 35.3 (d). IR (neat): ν 3026, 3013, 2922, 1596, 1487, 1441 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{14}$: C, 93.16; H, 6.84. Found: C, 93.29; H, 6.64.

7,8-Dihydroxymethylbicyclo[4.2.2]deca-2,4,7,9-tetraene, 8, as a Representative Example with an Internal Alkyne. Prepared from but-2-yne-1,4-diol **6** (72.6 mg, 0.84 mmol) and COTT **1** (105 mg, 1.0 mmol) at 55 °C for 2 days with TFE as solvent. Chromatography (silica gel, petroleum ether/AcOEt, 70/30 \rightarrow 50/50) afforded 125 mg (78%) of **8** as a colorless viscous oil: ^1H NMR (200 MHz, CDCl_3) δ 6.40–6.10 (m, 2H), 5.85–5.63 (m, 4H), 4.25 (m, 4H), 4.02 (br s, 2H), 3.44 (dd, $J = 5.8, 8.5$ Hz, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 141.5 (d, 2C), 132.3 (s, 2C), 124.8 (d, 2C), 121.1 (d, 2C), 59.4 (t, 2C), 37.5 (d, 2C). IR (CCl_4): ν 3480, 3019, 2914, 2866, 1335 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: C, 75.76; H, 7.42; O, 16.82. Found: C, 75.60; H, 7.65.

[6+2] Cycloaddition of 1,3,5-Cyclooctatriene. Preparation of 10a,c,e/11a,c,e. 7-Phenylbicyclo[4.2.2]deca-2,4,7-triene, 10a, and exo-7-Phenyltricyclo[4.2.2.0^{2,5}]deca-7,9-diene, 11a, as a Representative Example. Using the same procedure described for the cyclooctatetraene, the reaction of phenylethyne **3a** (43 mg, 0.42 mmol) and COT **2** (53 mg, 0.50 mmol) at 54 °C with DCE as solvent afforded, after chromatography (silica gel, petroleum ether), 49 mg (55%) of **10a/11a** in a 33:67 ratio, determined by ^1H NMR, as a colorless oil. Further chromatography (silica gel, petroleum ether) allowed the separation of the isomers. **7-Phenylbicyclo[4.2.2]-deca-2,4,7-triene, 10a:** ^1H NMR (200 MHz, CDCl_3) δ 7.40–7.27

(m, 4H), 7.19 (tt, $J = 1.5, 8.1$ Hz, 1H), 6.24 (d, $J = 7.1$ Hz, 1H), 6.16 (dd, $J = 8.6, 12.4$ Hz, 1H), 6.13 (dd, $J = 8.8, 11.7$ Hz, 1H), 5.77 (dd, $J = 7.7, 12.4$ Hz, 1H), 5.61 (dd, $J = 7.7, 11.7$ Hz, 1H), 3.31–3.25 (m, 1H), 2.88 (dtd, $J = 8.6, 6.9, 2.0$ Hz, 1H), 2.35–2.26 (m, 1H), 2.17–2.07 (m, 1H), 1.92–1.70 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 141.5 (s), 139.9 (d), 139.0 (d), 136.8 (s), 128.3 (d, 2C), 126.3 (d), 126.2 (d, 2C), 126.0 (d), 124.1 (d), 123.3 (d), 36.7 (d), 32.6 (d), 31.6 (t), 27.0 (t). IR (neat): ν 3025, 2922, 2845, 1596, 1492 cm^{-1} . **exo-7-Phenyltricyclo[4.2.2.0^{2,5}]deca-7,9-diene, 11a:** ^1H NMR (200 MHz, CDCl_3) δ 7.40–7.27 (m, 4H), 7.19 (tt, $J = 1.3, 7.1$ Hz, 1H), 6.55 (m, 2H), 6.47 (ddd, $J = 0.2, 1.8, 6.4$ Hz, 1H), 4.06 (ddd, $J = 1.8, 3.9, 5.6$ Hz, 1H), 3.70–3.64 (m, 1H), 2.39–2.27 (m, 2H), 1.94–1.85 (m, 2H), 1.28–1.21 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 145.9 (s), 138.6 (s), 134.1 (d), 133.7 (d), 128.9 (d), 128.4 (d, 2C), 126.6 (d), 124.7 (d, 2C), 43.9 (d), 42.0 (d), 38.1 (d), 37.8 (d), 20.1 (t), 19.9 (t). IR (CCl_4): ν 3065, 2968, 2930, 1603, 1494, 1442 cm^{-1} .

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Supporting Information Available: Experimental procedures and characterization data for all unknown compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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