ORGANIC
LETTERS

2002
Vol. 4, No. 12
2075−2078

Cobalt-Mediated Synthesis of Angular [4]Phenylene: Structural Characterization of a Metallacyclopentadiene(Alkyne) Intermediate and Its Thermal and Photochemical Conversion

Peter I. Dosa, Glenn D. Whitener, and K. Peter C. Vollhardt*

Center for New Directions in Organic Synthesis, Department of Chemistry,
University of California at Berkeley, and the Chemical Sciences Division,
Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460

Andrew D. Bond

University of Cambridge, Department of Chemistry, Lensfield Road,
Cambridge, CB2 1EW, UK

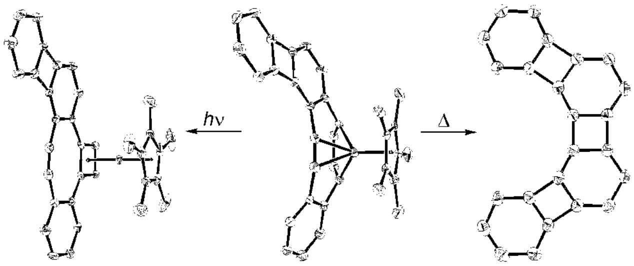
Simon J. Teat

CLRC Daresbury Laboratory, Warrington, Cheshire, WA4 4AD, UK

kpcv@uclink.berkeley.edu

Received April 1, 2002

ABSTRACT



The first X-ray crystal structure of a mononuclear metallacyclopentadiene(alkyne) complex has been obtained. This type of metallacycle is believed to be the key intermediate in the cobalt-mediated [2 + 2 + 2]cycloaddition of alkynes. Thermal treatment leads to the generation of angular [4]phenylene, the X-ray structural details of which are described. Under photochemical conditions, the cobaltacycle isomerizes to a highly strained (cyclobutadieno)dibenzocyclooctatrienyne complex.

The phenylenes have been the object of intense study by both theoretical and synthetic chemists due to their unique combination of aromatic and antiaromatic properties.[1] Although a variety have been synthesized, few X-ray crystal structures are available for phenylenes that are undistorted by substituents.[2] We report the crystal structure of angular [4]phenylene (**1**) and that of its precursor metallacycle **2**; the latter is believed to be a prototype intermediate in the cobalt-mediated [2 + 2 + 2]cycloaddition of alkynes.[3] This is the first X-ray crystal structure of a mononuclear metalla-

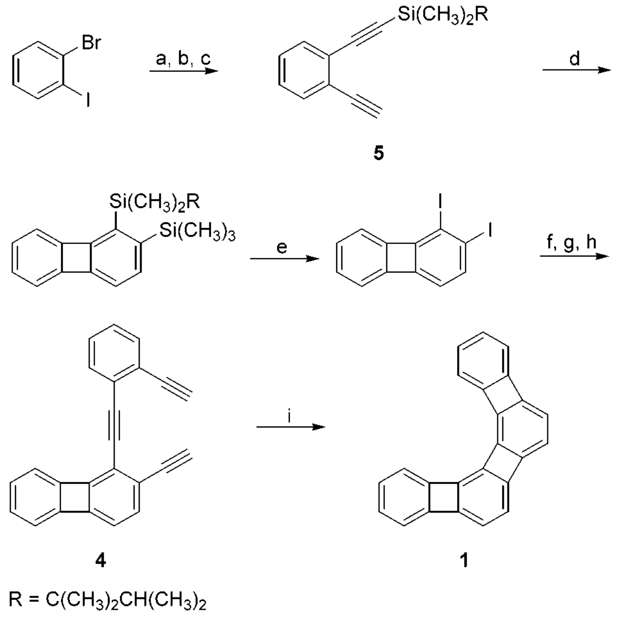
---

[1] Vollhardt, K. P. C.; Mohler, D. L. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI: London, 1996; pp 121−160.

10.1021/ol025956o CCC: $22.00

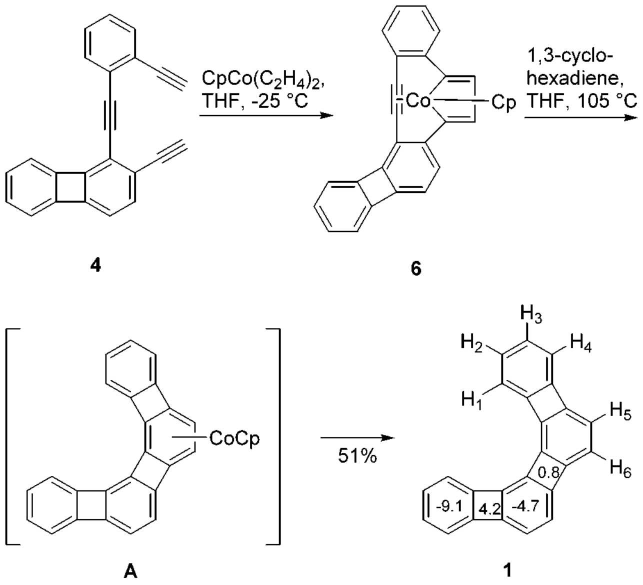
cyclopentadiene bearing a π-bound alkyne ligand.[4] The unusual photoconversion of **2** to the highly strained cyclobutadiene cobalt complex **3** is also described.

Scheme 1[a]



[a] Reaction Conditions: (a) $(CH_3)_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, NEt_3, 93%; (b) $(CH_3)_2CHC(CH_3)_2Si(CH_3)_2C{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, azacyclohexane, toluene, Δ, 79%; (c) K_2CO_3, MeOH, ether, 100%; (d) $(CH_3)_3Si{-}C{\equiv}CH$; $CpCo(CO)_2$, *m*-xylene, *hν*, Δ, 19%; (e) ICl, CH_2Cl_2, 0 °C, 56%; (f) $(CH_3)_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, NEt_3, 64%; (g) **5**, $PdCl_2(PPh_3)_2$, CuI, NEt_3, 76%; (h) $Bu_4N^+F^-$, THF, 96%; (i) $CpCo(CO)_2$, *m*-xylene, *hν*, Δ, 30%.

Scheme 2[a]



[a] Reference 7.

Phenylene **1** can be synthesized in nine steps from 1-bromo-2-iodobenzene (Scheme 1).[5] In a modification of this approach, the final step, cyclotrimerization of triyne **4** using $CpCo(CO)_2$, was replaced by a two-step protocol employing $CpCo(C_2H_4)_2$, thus increasing the overall yield of **1** from 30 to 51% (Scheme 2). In this sequence, metallacycle **6** was generated first in the cold and subsequently decomposed at high temperatures in the presence of 1,3-cyclohexadiene to trap CpCo as it evolved from intermediate A.[4,6] Previous attempts to obtain an X-ray crystal structure of **1** had been frustrated by its tendency to form thin needlelike crystals too small for conventional X-ray analysis. This difficulty was overcome by using synchrotron radiation (Station 9.8, SRS Daresbury, UK).

The crystal structure of **1** (Figure 1) reveals a significant amount of bond alternation,[8] especially in the internal benzene rings of the molecule, which are 52% bond fixed.[9] This phenomenon is less pronounced (25%) in the terminal

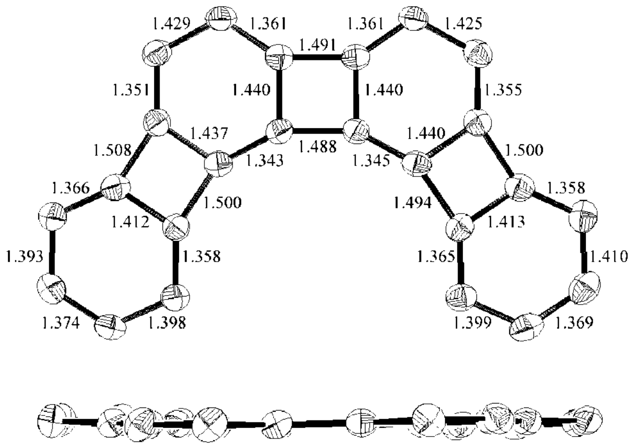


Figure 1. Crystal structure of **1**: views from above (top) and the side (bottom). Bond lengths (Å; ±0.004).

---

(2) (a) For biphenylene, see: Fawcett, J. K.; Trotter, J. *Acta Crystallogr.* **1966**, *20*, 87. (b) For angular [3]phenylene, see: Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266. (c) For linear [3]phenylene, see: Schleifenbaum, A.; Feeder, N.; Vollhardt, K. P. C. *Tetrahedron Lett.* **2001**, *42*, 7329. (d) For triangular [4]phenylene, see: Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem. Eur. J.* **1999**, *5*, 3399.

(3) For a recent theoretical study of this mechanism as it pertains to CpCo, see: Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 6055.

(4) See: Diercks, R.; Eaton, B. E.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247 and references therein.

(5) Schmidt-Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1992**, *114*, 9713.

(6) Dosa, P. I.; Schleifenbaum, A.; Vollhardt, K. P. C. *Org. Lett.* **2001**, *3*, 1017.

(7) NICS(1) values from: Schulman, J. M.; Disch, R. L.; Jiao, H.; Schleyer, P. v. R. *J. Phys. Chem. A* **1998**, *102*, 8051. For additional theoretical studies of the phenylenes, see: Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1996**, *118*, 8470; *J. Phys. Chem. A* **1997**, *101*, 5596 and references therein.

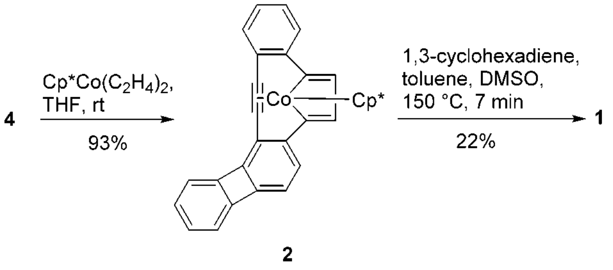
rings, classifying them as more aromatic by this criterion. This difference in aromatic character can also be observed in the ^{1}H NMR spectrum of **1**: H_5 and H_6 ($\delta = 6.31$ ppm, CD_2Cl_2) are shielded relative to H_1−H_4 ($\delta_{avg} = 6.89$ ppm),[1,5] consistent with a more cyclohexatrienic environment for the former.

It is instructive to compare **1** with its lower analogue, angular [3]phenylene (**7**),[2b] in which the respective extent of bond alternation is 62 and 22% and the central ring protons are shielded ($\delta = 6.18$ ppm) relative to those in **1**, in agreement with nucleus-independent chemical shift (NICS) calculations (Scheme 2).[7] These trends can be understood if one views **1** as the result of benzocyclobutadienofusion of **7**. In **7**, the terminal rings maximize their aromaticity by acting in concert to induce bond alternation in their central neighbor. Alteration of **7** to **1** induces increased bond alternation in one of the formerly terminal rings, thus relieving the "pressure" to bond fixation in the opposing internal ring. Because of symmetry, the net result is a smaller reduction in the aromatic character of the inside benzenes in **1** relative to that in **7**.

The geometry of **1** is unusually flat (Figure 1), with a median angle of 0.7° between the least-squares planes of each ring, ranging from 0.1 to 1.1°. In contrast, most phenylenes show significantly larger deviations from planarity, a testament to their ready deformability.[2d] For example, in triangular [4]phenylene, an isomer of **1**, the corresponding median angle between planes is 2.0°, ranging from 0.7 to 3.5°.[2d]

The ready generation of metallacycle **6**, formed in analogy to its debenzocyclobutadieno relatives on route to **7**,[4] spurred renewed efforts to obtain crystals suitable for an X-ray analysis, a task that had proven impossible with several previous derivatives. While **6** was again unsuitable, crystallization of the Cp* analogue **2**, prepared as in Scheme 3, was successful (Figure 2).

Scheme 3



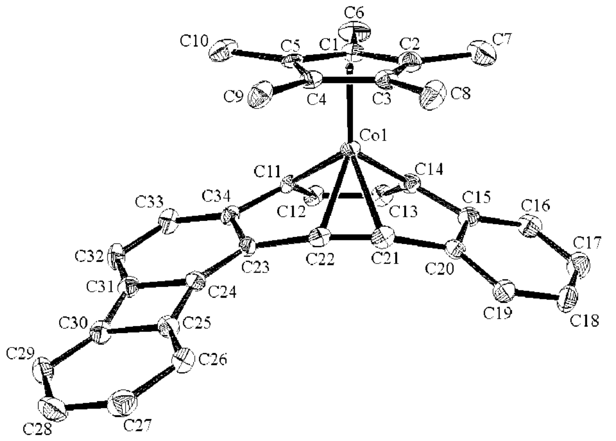
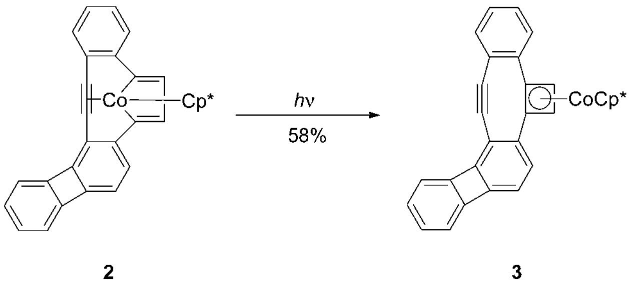


Figure 2. Crystal structure of metallacycle **2**. Selected bond lengths (Å; ±0.007): Co1−C11 1.920, Co1−C14 1.923, Co1−C21 2.039, Co1−C22 2.042, C11−C12 1.358, C12−C13 1.455, C13−C14 1.353, C14−C15 1.483, C15−C20 1.417, C20−C21 1.469, C21−C22 1.232, C22−C23 1.451, C23−C34 1.460, C11−C34 1.467, Co1−Ct 1.721. Selected bond angles (deg): C20−C21−C22 164.7, C21−C22−C23 165.7.

The geometry of the ligating triple bond in **2** closely resembles that calculated for the analogous (CpCo) organometallic precursor to angular [3]phenylene (C≡C 1.242 Å, Co−C≡ 2.097 Å, C≡CC 165.97°),[4,10] as well as the parent $CpCo(C_4H_4)(C_2H_2)$.[3] Significantly, all the Co−C_{alkyne} bond distances in **2** are large in comparison with other alkyne−cobalt complexes,[11] in agreement with the notion of an intrinsically weak cobalt−alkyne bond.[3]

During attempts to improve yields of **1**, complex **2** was irradiated with a slide projector lamp. Surprisingly, the product obtained from this reaction was not **1** but rather the bright orange cyclobutadiene (Cb) complex **3** (Scheme 4). While CbCo complexes are common byproducts of cobalt-mediated alkyne oligomerizations, no such species has ever been observed during the synthesis of angular phenylenes.

Scheme 4



---

(8) The structure is in excellent agreement with calculations at the B3LYP/6-31G* level: Professor P. von Ragué Schleyer and Dr. H. Jiao, private communication. The maximum deviation of the calculated from the experimental bond lengths is 0.025 Å, and the average deviation is 0.012 Å.

(9) The formula [Σ single-bond lengths − Σ double-bond lengths]/3 provides a quantitative measure of bond alternation in each ring. This number was normalized using the exocyclic diene portion of 3,4-dimethylenecyclobutene (1.497, 1.338 Å) as a 100% standard. See: Beckhaus, H.-D.; Faust, R.; Matzger, A. J.; Mohler, D. L.; Rogers, D. W.; Rüchardt, C.; Sawhney, A. K.; Verevkin, S. P.; Vollhardt, K. P. C.; Wolff, S. *J. Am. Chem. Soc.* **2000**, *122*, 7819 and references therein.

(10) Alkyl substitution has a negligible effect on the Co−C_{alkyne} bond distances in a series of R_xCpCo(CO)(alkyne) systems: Benisch, C.; Chávez, J.; Gleiter, R.; Nuber, B.; Irngartinger, H.; Oeser, T.; Pritzkow, H.; Rominger, F. *Eur. J. Inorg. Chem.* **1998**, *629*, 9.

Reductive elimination may occur from a coordinatively unsaturated cobaltacyclopentadiene to furnish the four-membered ring.[3] In the case of **2**, light may cause dissociation of the alkyne ligand as a first step toward the formation of **3**, although a direct photoisomerization is entirely possible.

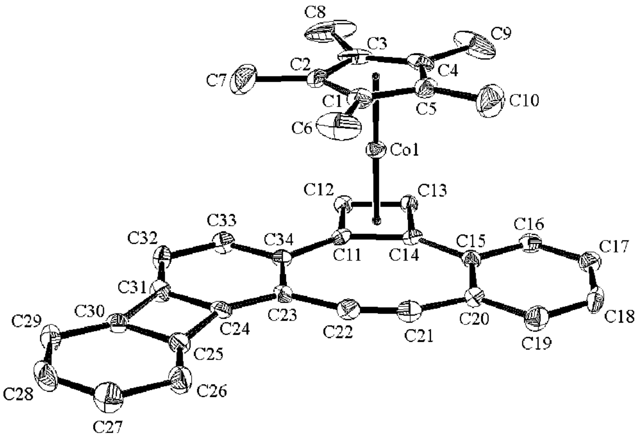
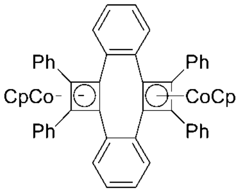


Figure 3. Crystal structure of **3**. Selected bond lengths (Å; ±0.005): C11−C12 1.455, C12−C13 1.421, C13−C14 1.461, C11−C14 1.500, C21−C22 1.196. Selected bond angles (deg): C20−C21−C22 157.6, C21−C22−C23 156.3, C12−C11−C14 88.9, C11−C14−C13 88.0, C11−C12−C13 91.3, C12−C13−C14 91.8.

The structure of **3** was confirmed by X-ray crystallography (Figure 3). Constraining the triple bond into an eight-membered ring leads to bond angles (C21−C22−C23 156.3°, C20−C21−C22 157.6°) that deviate significantly from linearity. Similar distortions are found in related cyclynes[12a] such as 1,2,5,6-dibenzocyclooct-3-en-7-yne, which has acetylenic bond angles of 154°.[12b] The strain inherent in the molecule also causes the cyclobutadiene ring to distort into a trapezoidal configuration: the bond of fusion (C11−C14) is significantly longer and C12−C13 shorter than normal (~1.46 Å).[13] This distortion is not present in **8**, a closely related complex lacking a triple bond.[14] In this molecule, the carbon−carbon bond distances in the four-membered rings all fall in a narrow normal range (1.460−1.477 Å).



8

In conclusion, the crystal structures of angular [4]phenylene and two mechanistically relevant organometallic complexes have been obtained. These structures further understanding of the phenylenes and the cobalt-mediated [2 + 2 + 2]cycloaddition that produces them.

Acknowledgment. The NSF (CHE-0071887) funded this work. The Center for New Directions in Organic Synthesis is supported by Bristol-Myers Squibb as a Sponsoring Member and Novartis as a Supporting Member. G.D.W. thanks the NSF and Bayer-Miles for predoctoral fellowships. A.D.B. thanks the Engineering and Physical Sciences Research Council (EPSRC, U.K.) (Grant GR/R08919) and The Biotechnology and Biological Sciences Research Council (BBSRC, U.K.) (Grant 8/B11586) for funding access to the synchrotron. We are indebted to Professor P. von R. Schleyer for the communication of unpublished data and to Personal Chemistry, Inc., for access to their Smith SynthesizerTM.

Supporting Information Available: Detailed experimental procedures, full characterization of all new compounds, and crystallographic data for **1**, **2**·0.5(toluene), and **3**·0.5(THF). This material is available free of charge via the Internet at http://pubs.acs.org.

OL025956O

---

(11) A search of the Cambridge Structural Database failed to uncover a structurally characterized Co(III)−alkyne complex. For examples of Co(I) complexes with shorter Co−alkyne bonds, see: (a) ref 10. (b) Foerstner, J.; Kettenbach, R.; Goddard, R.; Butenschön, H. *Chem. Ber.* **1996**, *129*, 319. (c) Okuda, J.; Zimmermann, K. H.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 430. For a discussion of how bond distances may vary with an oxidation state, see: Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717.

(12) (a) Gleiter, R.; Merger, R. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, Germany, 1995; pp 285−319. (b) De Graaff, R. A. G.; Gorter, S.; Romers, C.; Wong, H. N. C.; Sondheimer, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 478.

(13) For a tabulation, see: Benisch, C.; Gleiter, R.; Staeb, T. H.; Nuber, B.; Oeser, T.; Pritzkow, H.; Rominger, F. *J. Organomet. Chem.* **2002**, *641*, 102.

(14) Rausch, M. D.; Tokas, E. F.; Gardner, S. A.; Clearfield, A.; Chinn, J. W., Jr.; Bernal, I. *J. Organomet. Chem.* **1981**, *212*, 247.