J. Am. Chem. Soc. **1998,** *120,* 8247−8248

The First Metallacyclopentadiene(Alkyne) Complexes and Their Discrete Isomerization to η^4-Bound Arenes: The Missing Link in the Prevalent Mechanism of Transition Metal Catalyzed Alkyne Cyclotrimerizations, as Exemplified by Cyclopentadienylcobalt

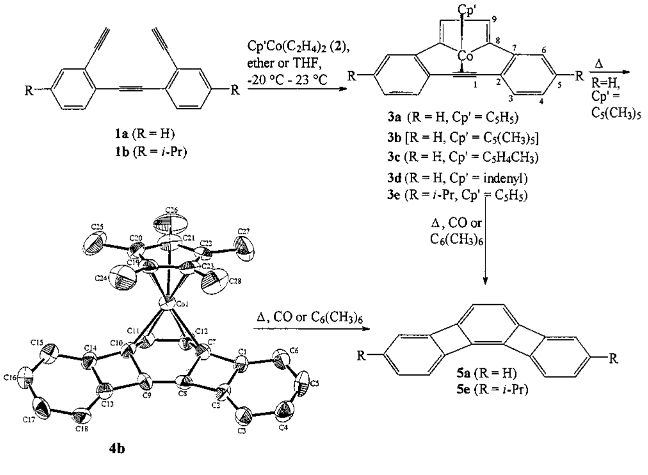
Rainer Diercks, Bruce E. Eaton, Stefan Gürtzgen,
Satish Jalisatgi, Adam J. Matzger, Rachel H. Radde, and
K. Peter C. Vollhardt*

Department of Chemistry, University of California
at Berkeley, and the Chemical Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, California 94720-1460

Received May 21, 1998

It is astounding that among the myriad of reported reactions in which alkynes have been allowed to transform in the presence of transition metal complexes, frequently in a catalytic manner leading to arenes, none has so far yielded a simple metallacyclopentadiene bearing a π-bound alkyne ligand—the crucial intermediate postulated for the “common mechanism”[1f] of such cyclotrimerizations.[1,2] The elusive nature of such a species is likely due to its facile reorganization to the (complexed) arene. We report the isolation of cobaltacyclopentadiene(alkyne) complexes **3**, in which their reactivity is attenuated by strain in the aromatic end product, the kinetics of their rearrangement, and the X-ray structural characterization of the resulting η^4-arene intermediate **4b** en route to free arene **5**. This study constitutes the most compelling confirmation to date of the “common mechanism” of such cyclizations.[3]

Scheme 1



The new metallacycles were prepared as in Scheme 1, simply by mixing $Cp'Co(C_2H_4)_2$ (**2**)[4] with triynes **1**[5] in high (quantitative by NMR) yields (isolated **3a**, 91%; **3b**, 76%; **3e**, 72%) as dark brown, microcrystalline powders, unsuitable for X-ray analysis. Their structural assignments rest on unambiguous spectral data (see Supporting Information) and subsequent transformations. Diagnostic are the metallacycle ^1H [$\delta \sim 6.5$ (H9) ppm][6] and ^{13}C NMR [$\delta \sim 195$ (C8), 142 (C9) ppm][7] absorptions, the establishment (for **3a** and **3b**) of connectivity by heteronuclear shift correlations (HMBC, HMQC) and (for **3a**) the H9−H9′ coupling ($J = 6.2$ Hz). The complexed alkyne moiety reveals ^{13}C signals ranging from $\delta = 75.8$ (**3e**) to 85.8 ppm (**3b**) and weak IR absorptions (when observable) at 1922 (**3a**) and 1979 cm^{-1} (**3b**), both types of spectroscopic data indicative of its function as a weak 2e donor with little back-bonding.[8] Apart from their novelty as organometallic intermediates, complexes **3** also represent unique examples of (metalated) dibenzodehydro[10]annulenes.[9]

In the absence of an X-ray structure, the geometry **A** of **3a** was calculated at the B3LYP/6-311G* level (see Supporting Information),[10] revealing the expected piano stool topology around Co and details of the cobaltacyclopentadiene nucleus in excellent agreement with those experimentally determined on phosphine (instead of alkyne) ligated systems [e.g., cobaltacyclopentadiene bond lengths (Å), **A**: Co−C1 1.922, C1−C2 1.359, C2−C3 1.457; $CpCo(C_4H_4)P(C_6H_5)_3$: 1.947, 1.351, 1.447, respectively].[6a] That **A** constitutes a fairly accurate structural reflection of **3a** is also indicated by an identical calculation for **4a** that reproduces the (relevant) experimental data on **4b** (vide infra) superbly. Most remarkable in **A** is the abnormal,[3,8a,11] “perpendicular” bend from linearity of the alkyne ligand ($d_{\mathrm{C\equiv C}} = 1.242$ Å, $\alpha_{\mathrm{C\equiv CC}} = 165.97°$, dihedral angle $Co-C_{sp}-C_{sp}-C_{sp^2}$ 94.268°) relative to the complexed metal, a consequence of the requirements of the constrained dehydroannulene frame. The distance of the alkyne from the respective α-carbons in the cobaltacycle to which they become attached in the next step (vide infra) is calculated as 2.5135 Å.

---

(1) For recent reviews, see: (a) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523−596. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92. (c) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Hegedus, L. S., Volume Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 741−770. (d) Rigby, J. H.; Krueger, A. C. In *Advances in Detailed Reaction Mechanisms*; Coxon, J. M., Ed.; JAI Press: London, 1995; Vol. 4, pp 1−40. (e) Melikyan, G. G.; Nicholas, K. M. In *Modern Acetylene Chemistry*; Stang, P. J.; Diederich, F., Eds.; VCH: Weinheim, 1995; pp 99−138. (f) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119.

(2) For some, mostly higher nuclear “close calls”, see, inter alia (including the references therein): (a) Yeh, W.-Y.; Ho, C.-L.; Chiang, M. Y.; Chen, I.-T. *Organometallics* **1997**, *16*, 2698−2708. (b) Kriley, C. E.; Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2051−2058. (c) Agh-Atabay, N. M.; Davidson, J. L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1399−1401. (d) Farrugia, L. J.; Went, M. J. *J. Chem. Soc., Chem. Commun.* **1987**, 973−974. (e) Pörschke, K.-R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1288−1290. (f) Arif, A. M.; Chandler, D. J.; Jones, R. A. *Organometallics* **1987**, *6*, 506−512. (g) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806−6815. (h) Pourreau, D. B.; Whittle, R. R.; Geoffroy, G. L. *J. Organomet. Chem.* **1984**, *273*, 333−346. (i) Smart, L. E.; Browning, J.; Green, M.; Laguna, A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1777−1785. (j) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1123−1129. (k) Ferraris, G.; Gervasio, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1933−1936.

(3) A conceptually related cobaltacyclopentadiene(alkene) complex has been claimed, but its NMR spectral data and chemistry are sufficiently at odds with established science that its structural assignment appears doubtful: Okuda, J.; Zimmermann, K. H.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 430−431.

(4) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716; *Angew. Chem. Suppl.* **1983**, 1005−1016.

(5) Boese, R.; Matzger, A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2052−2053.

(6) See, inter alia: (a) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1984**, *272*, 251−263. (b) Yamazaki, H.; Yasufuku, K.; Wakatsuki, Y. *Organometallics* **1983**, *2*, 726−732.

(7) See, inter alia: (a) Brandt, L.; Green, M.; Parkins, A. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1046−1048. (b) Alt, H. G.; Engelhardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Organomet. Chem.* **1997**, *329*, 61−67.

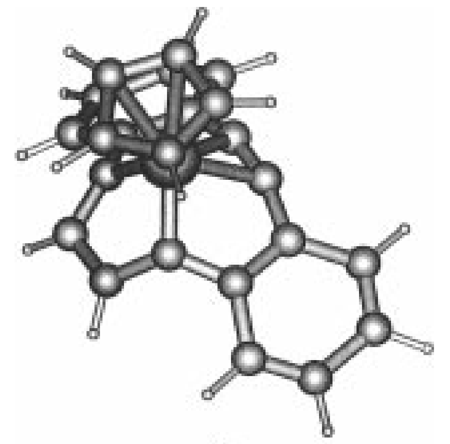
(8) For some comparative data of relevant metal alkyne complexes, see, inter alia: (a) Foerstner, J.; Kettenbach, R.; Goddard, R.; Butenschön, H. *Chem. Ber.* **1996**, *129*, 319−325. (b) Kettenbach, R. T.; Bonrath, W.; Butenschön, H. *Chem. Ber.* **1993**, *126*, 1657−1669. (c) Alt, H. G.; Engelhardt, H. E.; Filippou, A. C. *J. Organomet. Chem.* **1988**, *355*, 139−148. (d) Ball, R. G.; Burke, M. R.; Takats, J. *Organometallics* **1987**, *6*, 1918−1924. (e) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288−3290.

(9) (a) Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo- Derivatives and Their Valence Isomers*; CRC Press: Boca Raton, 1987; Vol. 2, p 149. (b) Haley, M. M. *Synlett* **1998**, 556.

(10) For more approximative molecular orbital calculations of metallacyclopentadienes see: Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M.-L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010−2023 and the references therein.

(11) For a compilation of data, see: Gervasio, G.; Rosetti, R.; Stanghellini, P. L. *Organometallics* **1985**, *4*, 1612−1619.

S0002-7863(98)01766-1 CCC: $15.00



A

With compounds **3** in hand, their relevance with respect to the mechanism of the CpCo-catalyzed cyclization of **1** to angular [3]-phenylene **5**[12] was scrutinized. Thus, thermal decomposition (100−130 °C) of **3** gave the corresponding angular phenylenes **5a** and **5e**, respectively, in variable yields. Cleanest conversions (quantitative by ^{1}H NMR for **3a**) were achieved in the presence of external ligands [CO, $C_6(CH_3)_6$], which serve to trap the Cp′Co unit. Moreover, complexes **3** are catalytically about as effective as $CpCo(CO)_2$ for the conversion of **1** to **5**. Kinetic analysis of the transformation of **3a** to **5a** in the presence of CO (1−5 atm) at 55−85 °C followed a first-order rate law, independent of CO pressure, with $\Delta H^{\ddagger} = 26(2)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 11$ (1) eu. We suggest that these parameters are associated with the reorganization of the ligands around CpCo to a reactive η^4-arene complex,[1,10b] by a probably concerted "double vinyl shift" (topologically equivalent to an intramolecular Diels−Alder reaction). The slightly positive (rather than negative) $\Delta S^{\ddagger}$ value might be a reflection of the relative rigidity of the framework in **3** in which the reacting centers are already perfectly aligned to enter into the next step. The alternative "single vinyl shift" (equivalent to insertion of the alkyne unit to furnish a metallacycloheptatriene) is sterically prohibitive for **3** (but is, of course, not ruled out for other systems). Corroboration of the suggested nature of the rate determining step is obtained with **3b**, which rearranges by very similar, added ligand independent kinetics at 85 °C [$\Delta H^{\ddagger} = 27(3)$ kcal mol^{-1}, $\Delta S^{\ddagger} = 5(7)$ eu] to the very heat- and air-sensitive, dark red complex **4b** that could be characterized by X-ray crystallography.[13] Unlike that in the corresponding η^6-Cr complex,[14] the metal is clearly tetrahapto-bound, with the characteristic leveling of the bound diene C−C bond distances and a boat-shaped benzene nucleus.[13] The value of the dihedral angle between the two benzene planes (32.3°) is at the low end of the range reported for complexes most closely related to **4b** (35.4−47.9°).[13] The calculated structure (vide supra) of **4a** reproduces all the pertinent features of **4b** (nearly) within experimental error, including the boat deformation of the ligating cyclohexatriene (dihedral angle 33.28°).

It is interesting to note that the metal prefers to coordinate in such a way as to minimize benzocyclobutadienoid resonance in the angular [3]phenylene frame,[12,15] perhaps of thermodynamic origin, considering the fluxionality of the systems CpM(η^4-C_6R_6) (M = Co, Rh, Ir).[16] The site of attachment of CpCo to the angular phenylene frame contrasts with that observed for its (higher) linear counterparts, where it prefers cyclobutadiene ligation.[17] Another noteworthy feature is the almost identical activation parameters for the conversion of **3a** and **3b**. It is possible that the expected greater stabilization[18] of the (formally) higher valent Co(III) in **3b** relative to **3a** is attenuated by steric activation due to the bulkier ligand. Finally, curious, albeit possibly fortuitous, are the rather similar kinetic data observed for the topologically related rearrangement of Cp−cobaltacyclopentadiene(phosphite) complexes to their alkoxyphospholoxide counterparts ($\Delta H^{\ddagger} \sim 19-22$ kcal mol^{-1}, $\Delta S^{\ddagger} \sim -4$ eu).[19]

While the simplest pathway from **3** to **4** is the one postulated, we cannot rule out a rate determining retrocyclization[20] of the cobaltacycle followed by oxidative coupling of one of the terminal alkyne units with its internal neighbor to furnish an isomeric benzocyclobutacobole[21] which is then trapped by the appended other terminal triple bond by either double or single "vinyl shifts" to eventually provide **4**. This and other intricacies of the mechanism of the reaction may be studied with appropriately substituted versions of **3**, now readily accessible.

Acknowledgment. This work was supported by the NSF (CHE 9202152 and 9610430). R.D. was a NATO Science Fellow, S.G. a Feodor Lynen Fellow, and A.J.M. a Syntex predoctoral and an ACS Division of Organic Chemistry Graduate Fellow (sponsored by Rohm and Haas Co.).

Supporting Information Available: Experimental and spectral details of the synthesis of **3a**−**e**, **4b**, and **5e**, calculated theoretical structural parameters for **3a** and **4a**, and experimental X-ray structural data for **4b** (65 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA981766Q

---

[12] Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266−268.

[13] This appears to be the first reported CpCo(η^4-arene) structure,[4] although related complexes of other metals, including Rh and Ir,[10b] have been analyzed by X-ray, see also: (a) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J. *Chem. Rev.* **1982**, *82*, 499−525. (b) Müller, J.; Escarpa Gaede, P.; Hirsch, C.; Qiao, K. *J. Organomet. Chem.* **1994**, *472*, 329−335. (c) Bell, T. W.; Helliwell, M.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1992**, *11*, 1911−1918. (d) Bowyer, W. J.; Merkert, J. W.; Geiger, W. E.; Rheingold, A. *Organometallics* **1989**, *8*, 191−198.

[14] Nambu, M.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 369−371.

[15] Mohler, D. L.; Vollhardt, K. P. C. in *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press: London, 1996; Vol. 5, pp 121−160.

[16] (a) Kang, J. W.; Childs, R. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 720−722. (b) Kölle, U.; Fuss, B. *Chem. Ber.* **1986**, *119*, 116−128.

[17] (a) Hirthammer, M.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 2481−2482. (b) Blanco, L.; Helson, H. E.; Hirthammer, M.; Mestdagh, H.; Spyroudis, S.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1246−1247.

[18] For a compilation of references, see: (a) Gassman, P. G.; Mickelson, J. W.; Sowa, J. R., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6942−6944. For a comparison of the two ligands in Co- and Rh-catalyzed alkyne cyclooligomerizations, see: (b) Diversi, P.; Ingrosso, G.; Lucherini, A.; Vanacore, D. *J. Mol. Catal.* **1987**, *40*, 261−270. (c) Cioni, P.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Ronca, P. *J. Mol. Catal.* **1987**, *40*, 337−357. (d) Abdulla, K.; Booth, B. L.; Stacey, C. *J. Organomet. Chem.* **1985**, *293*, 103−114.

[19] Yasufuku, K.; Hamada, A.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1980**, *102*, 4363−4372.

[20] See, inter alia: (a) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 1491−1496. (b) Hiller, J.; Thewalt, U.; Polášek, M.; Petrusová, L.; Varga, V.; Sedmera, P.; Mach, K. *Organometallics* **1996**, *15*, 3752−3759. (c) Lefeber, C.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1995**, *501*, 179−188. (d) Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275−1288. (e) Ohkubo, A.; Fujita, T.; Ohba, S.; Aramaki, K.; Nishihara, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1553−1555.

[21] Strained ring fused metallacyclopentadienes are accessible via alkyne coupling reactions; see, inter alia: (a) Mahieu, A.; Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J.-P. *Organometallics* **1997**, *16*, 3086−3088. (b) Xi, Z.; Fischer, R.; Hara, R.; Sun, W.-H.; Obora, Y.; Suzuki, N.; Nakajima, K.; Takahashi, T. *J. Am. Chem. Soc.* **1997**, *119*, 12842−12848. (c) Tillack, A.; Baumann, W.; Ohff, A.; Lefeber, C.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *J. Organomet. Chem.* **1996**, *520*, 187−193. (d) Dickson, R. S.; Mok, C.; Connor, G. *Aust. J. Chem.* **1977**, *30*, 2143-2151. See also, however: (e) Warner, B. P.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5471−5472.