fluxing glyme (10 h) to provide a mixture (3:1) of **12e** and **12f** (72%). Once again, the diastereomeric alcohols **11b–f** exhibited no tendency toward either an anionic [3,3] or [1,3][17] rearrangement under the conditions identical with those required for the transformation of **10b–f** → **12b–f**.

Thus, we have unveiled a useful variant of the anionic oxy-Cope rearrangement which allows ready access to the bicyclo[5.3.1]undec-7-ene ring system. The application of this process to the total synthesis of the taxane diterpenes via intermediates related to **2** and **3** is the subject of present investigations and will be reported in due course.

Acknowledgment. We thank the Robert A. Welch Foundation and the National Cancer Institute (CA 21860) for their generous support of this research.

Registry No. 4, 38231-60-6; **5**, 66921-89-9; **6**, 82281-04-7; **7**, 82281-05-8; **8**, 82281-06-9; **9**, 82281-07-0; **10a**, 82281-08-1; **10b**, 82281-09-2; **10c**, 82281-10-5; **10d**, 82281-11-6; **10e**, 82281-12-7; **10f**, 82335-17-9; **11a**, 82335-18-0; **11b**, 82335-19-1; **11c**, 82335-20-4; **11d**, 82335-21-5; **11e**, 82335-22-6; **11f**, 82335-23-7; **12a**, 82281-13-8; **12b**, 82281-14-9; **12c**, 82281-15-0; **12d**, 82281-16-1; **12e**, 82281-17-2; **12f**, 82281-18-3; **13**, 82281-19-4; 2-propenyl bromide, 106-95-6; 1-cyclohexenyllithium, 37609-34-0; ethylidenetriphenylphosphorane, 1754-88-7; (methoxymethylene)triphenylphosphorane, 20763-19-3; methylenetriphenylphosphorane, 3487-44-3.

---

[17] For example, see: (a) Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Bowlin, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 1241–1247. (b) Thies, R. W.; Seitz, E. P. *J. Chem. Soc., Chem. Commun.* **1976**, 846–847. (c) Wilson, S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* **1978**, 479–480. (d) Danheiser, R. L.; Martinez-Davila, C.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2443–2446. (e) Danheiser, R. L.; Martinez-Davila, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943–3950. (f) Zoeckler, M. T.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 7661–7663.

[18] Recipient of National Institutes of Health (National Cancer Institute) Research Career Development Award (1980–1985).

Stephen F. Martin,*[18] James B. White, Rolf Wagner
Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

Received April 13, 1982

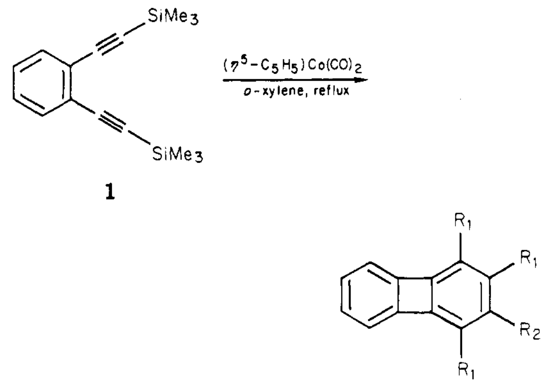
A New Route to Biphenylene via "Vollhardt Cyclization" from *o*-Bis[(trimethylsilyl)ethynyl]benzene

Summary: Reaction of *o*-bis[(trimethylsilyl)ethynyl)]-benzene with cyclopentadienyldicarbonylcobalt as catalyst and reagent is described, yielding biphenylene derivatives and cobalt complexes bearing novel organic ligands, respectively.

Sir: In the last decade, cobalt-catalyzed intra- and intermolecular acetylene and olefin cooligomerizations have been investigated intensively,[1,2] yielding a number of natural products[3] and species of theoretical interest.[4] 3-Hexene-1,5-diyne derivatives, however, have not played a role, hitherto, although interesting strained molecules might be synthesized.

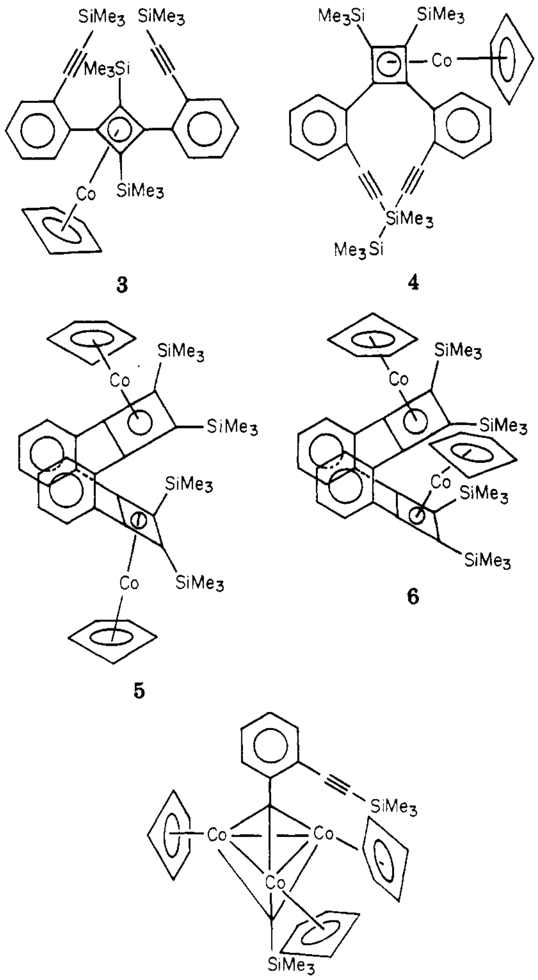
With use of syringe-pump techniques 1,2-bis[(trimethylsilyl)ethynyl]benzene (**1**)[5] dimerizes in refluxing *o*-xylene in the presence of catalytic amounts of (η^5-cyclopentadienyl)dicarbonylcobalt to yield biphenylene derivative **2** in 72% (Scheme I).[6,7]

Scheme I



2, R_1 = SiMe$_3$; R_2 = (o-Me$_3$SiC≡C)C$_6$H$_4$

Chart I



Under the same reaction conditions in a cobalt-mediated cyclization (ratio of **1** and CpCo(CO)$_2$ = 1:1) **2** was obtained in 8% yield in addition to a variety of cobalt complexes

---

[1] (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Gesing, E. R. F.; Sinclair, J. A.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1980**, 286.

[2] Croudace, M. C.; Schore, N. E. *J. Org. Chem.* **1981**, *46*, 5357.

[3] Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5253 and references therein.

[4] (a) Saward, C. J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1975**, 4539. (b) Duclos, R. I., Jr.; Vollhardt, K. P. C.; Yee, L. S. *J. Organomet. Chem.* **1979**, *174*, 109.

[5] Gesing, E. R. F. *J. Chem. Soc., Chem. Commun.*, **1982**, 426.

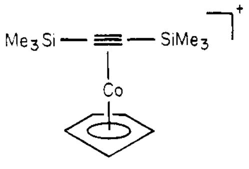
[6] Mass spectrum, m/e 540 (M$^+$, 12); ^{1}H NMR (90 MHz, acetone-d_6) δ 7.50–7.17 (m, 4 H), 6.83 (s, 4 H), 0.47 (s, 9 H), 0.07 (s, 9 H), −0.10 (s, 18 H); ^{1}H NMR (90 MHz, CCl$_4$) δ 7.43–7.10 (m, 4 H), 6.67 (s, 4 H), 0.40 (s, 9 H), 0.03 (s, 9 H), −0.17 (s, 9 H), −0.18 (s, 9 H); IR (CH$_2$Cl$_2$) 2960 (s), 2900 (s), 2160 (s), 1240 (s) cm^{-1}.

[7] All new compounds gave satisfactory analytical data and/or high-resolution mass spectral data.

0022-3263/82/1947-3192$01.25/0

(**3-6**)[7,8] bearing novel organic ligands[9] and a new biscarbyne cobalt cluster (**7**;[7,10] Chart I), the separation of which was achieved by careful alumina gravity column chromatography, using pentane-ether mixtures as eluants. The total mass balance was excellent (86%) and structural assignments of compounds **3-7** rest mainly on mass spectra which reveal the basic composition, ^{1}H NMR data which indicate the symmetry of the structures, particularly by the number of cyclopentadienyl and trimethylsilyl peaks, and characteristic infrared absorptions.

The diastereoisomers **3** and **4** are derived from intermolecular dimerization of two acetylene units in the coordination sphere of cyclopentadienylcobalt, leaving two unreacted acetylene groups. Differentiation between **3** and **4** was achieved by inspection of the mass spectral data, as only **4** may show fragment **8** (*m/e* 294).[8] **4** is a possible intermediate en route to bis(cyclobutadiene) complexes **5** and **6**, which might show interesting chemical behavior on decomplexation. This is a subject of continuing investigation. The structures of **5** and **6** are in accordance with spectral measurements. Their relative configuration was tentatively assigned syn for **5** and anti for **6** on the basis of the appearance of the ^{1}H NMR spectra. Both trimethylsilyl groups (δ 0.33 and 0.27) and cyclopentadienyl ligands (δ 4.83 and 4.73) are nonequivalent in **6**, whereas in **5** cyclopentadienyl protons and trimethylsilyl protons, respectively, are isochronous. Interestingly, cluster **7** is formed by alkyne cleavage, a reaction which seems to be general.[10] Another set of four still unknown complexes (19%) was isolated, three of which containing complexed cyclopentadienone moieties and (trimethylsilyl)acetylene units (ν_{CO} 1580 cm^{-1}, $\nu_{C\equiv C}$ 2150 cm^{-1}). Their ^{1}H NMR spectra, however, are very complex and do not allow a final structural elucidation. The fourth, a purple complex whose basic composition was indicated by its mass spectrum and elemental analysis, arises from the reaction of one diyne molecule **1** with three cyclopentadienylcobalt units and one carbon monoxide molecule ($C_{32}H_{37}OSi_2Co_3$). An X-ray study is under investigation.



8 (*m/e* 294)

The described reaction of diyne **1** with catalytic amounts of $CpCo(CO)_2$ demonstrates a new entry to biphenylene derivatives which are not accessible by other routes. With equimolar amounts of the same transition-metal complex no intramolecular condensation occurs probably due to strain-related factors, but intermolecular mono- and biscondensation products are formed which are stabilized by complexation to cyclopentadienylcobalt. Further reactions of 3-hexene-1,5-diyne derivatives with different transition metals are in progress.

Acknowledgment. I thank the Department of Organic Chemistry of the University of Zürich-Irchel, the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, and especially Professor A. S. Dreiding for financial support. Furthermore, I am grateful for a fellowship of the Deutsche Forschungsgemeinschaft (1981-1983).

Registry No. 1, 73392-23-1; 2, 82190-52-1; 3, 82190-53-2; 4, 82190-54-3; 5, 82190-55-4; 6, 82228-16-8; 7, 82190-56-5; $(\eta^5\text{-}C_5H_5)Co(CO)_2$, 12078-25-0.

Ernst Rudolf F. Gesing
Organisch-Chemisches Institut der
Universität Zürich-Irchel
Winterthurerstrasse 190
CH-8057 Zürich, Switzerland

Received March 10, 1982

---

(8) **3**: 2%; yellow plates (from ether); mp 159 °C; IR (CH_2Cl_2) 2950 (m), 2895 (m), 2145 (s), 1240 (m), 865 (s), 845 (s) cm^{-1}: mass spectrum, *m/e* 664 (84, M$^+$), 649 (2, M$^+$ - CH$_3$), 599 (7, M$^+$ - C$_5$H$_5$), 591 (12, M$^+$ - Me$_3$Si), 394 (100, M$^+$ - C$_5$H$_5$Co - 2Me$_3$Si), 329 (92), 73 (51, Me$_3$Si); ^{1}H NMR (CDCl$_3$) δ 7.63-7.30 (m, 4 H), 7.27-7.07 (m, 4 H), 5.15 (s, 5 H), 0.23 (s, 18 H), 0.00 (s, 18 H). **4**: 7%; yellow needles (from ether); mp 164 °C; IR (CH_2Cl_2) 2945 (m), 2895 (m), 2140 (m), 1240 (m), 860 (s), 840 (s) cm^{-1}; mass spectrum *m/e* 664 (100, M$^+$), 649 (2, M$^+$ - CH$_3$), 599 (6, M$^+$ - C$_5$H$_5$), 591 (26, M$^+$ - Me$_3$Si), 394 (97, M$^+$ - C$_5$H$_5$Co - 2Me$_3$Si), 329 (87), 294 (54, Me$_3$SiCCSiMe$_3$CoC$_5$H$_5$), 73 (50, Me$_3$Si); ^{1}H NMR (CDCl$_3$) δ 7.68-7.48 (m, 4 H), 7.47-7.15 (m, 4 H), 5.22 (s, 5 H), 0.28 (s, 18 H), 0.22 (s, 18 H). **5**: 32%; yellow plates (from acetone); mp >300 °C; IR (CHCl$_3$) 3100 (w), 3050 (w), 2960 (m), 2900 (w), 1245 (s), 1005 (s), 860 (s), 840 (s) cm^{-1}; mass spectrum, *m/e* 788 (53, M$^+$), 773 (1, M$^+$ - CH$_3$), 716 (2, M$^+$ - Me$_2$SiCH$_2$), 644 (8, M$^+$ - 2Me$_2$SiCH$_2$), 617 (22), 429 (43), 294 (22, Me$_3$SiCCSiMe$_3$CoC$_5$H$_5$), 189 (46, (C$_5$H$_5$)$_2$Co), 73 (100, Me$_3$Si); ^{1}H NMR (CDCl$_3$) δ 7.70-7.47 (m, 4 H), 7.10-6.97 (m, 4 H), 4.90 (s, 10 H), 0.03 (s, 36 H). **6**: 11%; yellow plates (from acetone); mp 224 °C; IR (CH_2Cl_2) 2950 (m), 2895 (m), 1245 (m), 1005 (m), 855 (s), 840 (s), 810 (s) cm^{-1}; mass spectrum, *m/e* 788 (100, M$^+$), 773 (2, M$^+$ - CH$_3$), 618 (44), 294 (16, Me$_3$SiCCSiMe$_3$CoC$_5$H$_5$), 189 (52, (C$_5$H$_5$)$_2$Co), 124 (6, C$_5$H$_5$Co), 72 (44, Me$_3$Si); ^{1}H NMR (CDCl$_3$) δ 7.93-7.67 (m, 2 H), 7.23-6.83 (m, 6 H), 4.83 (s, 5 H), 4.73 (s, 5 H), 0.33 (s, 18 H), 0.27 (s, 18 H). **7**: 7%; purple needles (from ether/pentane); mp 58 °C; IR (CH_2Cl_2) 2955 (m), 2920 (m), 2900 (m), 2850 (w), 2140 (m), 1240 (m), 1115 (m), 1010 (m), 860 (s), 840 (s), 800 (s), 645 (m) cm^{-1}; mass spectrum, *m/e* 642 (40, M$^+$), 189 (100, (C$_5$H$_5$)$_2$Co), 124 (2, C$_5$H$_5$Co), 73 (13, Me$_3$Si); ^{1}H NMR (CDCl$_3$) δ 7.87-7.33 (m, 4 H), 4.57 (s, 15 H), 0.93 (s, 9 H), 0.20 (s, 18 H).

(9) See also: Gesing, E. R. F.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1981**, *217*, 105.

(10) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem.* **1980**, *92*, 570; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559.

A Short Synthesis of the 4-Demethoxy-11-deoxyanthracycline Skeleton. Regiospecific Enolate C-Carboxylation with Carbon Oxysulfide

Summary: Regiospecific C-carboxylation of enolate **2** and COS followed by methylation (CH$_3$I) and cuprous triflate cyclization results in a tetracyclic product **9** which can be converted into 11-deoxyanthracyclines.

Sir: We have been interested in an approach to 4-demethoxy-11-deoxyanthracyclines[1] which takes advantage of the remarkably efficient 1,4-addition of the benzyl anion **1** to cyclohexenone. The adduct enolate **2** can be trapped by protonation or by silylation to give **3** (75-85%) or **4** (ca. 90%), respectively. This reaction proceeds smoothly when HMPA is present (1.5 equiv). In THF alone, the yield of **3** isolated after enolate quenching drops to 10% and complex side products are formed

---

(1) 4-Demethoxy-11-deoxy derivatives: Tatsuta, K.; Takeuchi, T. *J. Antibiot.* **1980**, *33*, 1581. 11-Deoxy derivatives: Gesson, J. P.; Jacquesy, J. C.; Mondon, N. *Tetrahedron Lett.* **1980**, 3551. Bauman, J. G.; Barber, R. B.; Gless, R. D.; Rapoport, H. *Ibid.* **1980**, 4777. Krohn, K. *Justus Liebigs Ann. Chem.* **1981**, 2285. Yadav, J.; Corey, P.; Hsu, C.-T.; Perlman, K.; Sih, C. J. *Tetrahedron Lett.* **1981**, 811. Kende, A. S.; Rizzi, J. P. *Ibid.* **1981**, 1779; *J. Am. Chem. Soc.* **1981**, *103*, 4347. Kende, A. S.; Boettger, S. D. *J. Org. Chem.* **1981**, *46*, 2799. Ahmed, Z.; Cava, M. P. *Tetrahedron Lett.* **1981**, 5239. Lit, T.-t.; Wu, Y. L. *J. Am. Chem. Soc.* **1981**, *103*, 7007. Confalone, P. N.; Pizzolato, G. *Ibid.* **1981**, *103*, 4251. Pearlman, B. A.; McNamara, J. M.; Hasan, I.; Hatakeyama, S.; Sekizaki, H.; Kishi, Y. *Ibid.* **1981**, *103*, 4348. Kimball, S. D.; Walt, D. R.; Johnson, F. *Ibid.* **1981**, *103*, 1561. Jung, M. E.; Node, M.; Pfluger, R. W.; Lyster, M. A.; Lowe, J. A. *J. Org. Chem.* **1982**, *47*, 1150. Ramakao, A. V.; Deshpande, V. H.; Reddy, N. L. *Tetrahedron Lett.* **1982**, 775. Gesson, J. P.; Mondon, M. *Chem. Commun.* **1982**, 421.

0022-3263/82/1947-3193$01.25/0