

**Intermolecular Cobalt-mediated [2+2+2]Cycloadditions: Regiospecific  
One-step Construction of Bicyclic Dienes from  
 $\alpha,\omega$ -Enynes and Alkynes**

By CHU-AN CHANG, JOSEPH A. KING, JR., and K. PETER C. VOLLHARDT\*

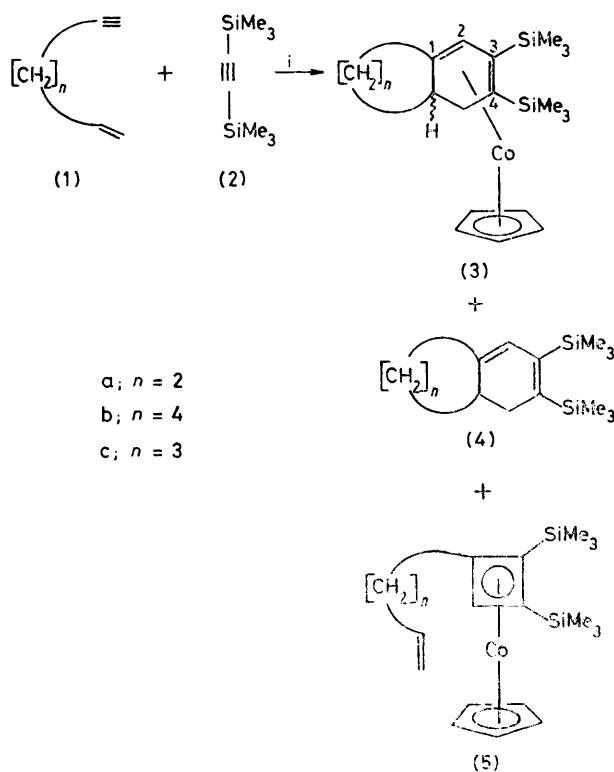
*(Department of Chemistry, University of California, and the Materials and Molecular Research Division  
Lawrence Berkeley Laboratory, Berkeley, California 94720)*

*Summary*  $\alpha,\omega$ -Enynes are co-cyclised with alkynes and stoichiometric amounts of dicarbonyl(cyclopentadienyl)cobalt to furnish bicyclic-diene cobalt complexes and their free ligands regiospecifically, the former being convertible into the latter by oxidative demetallation.

WE have recently shown that acyclic enediynes cyclise intramolecularly in the co-ordination sphere of  $\eta^5$ -cyclopentadienyl (Cp) cobalt to give tricyclic diene complexes from which the ligands could be liberated by oxidative demetallation.<sup>1</sup> We report here the application of the intermolecular variant of this method to the regiospecific

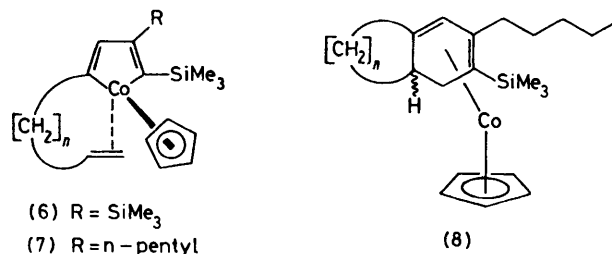
construction of bicyclic dienes, including a new strained molecule of synthetic potential: 3,4-bis(trimethylsilyl)-bicyclo[4.2.0]octa-1,3-diene (**4a**). Although under present conditions only moderate yields have been achieved, the work described establishes the basic feasibility of the approach.

The  $\alpha,\omega$ -enyne (**1**) (1 equiv.) and  $\text{CpCo}(\text{CO})_2$  (1 equiv.) in bis(trimethylsilyl)acetylene (BTMSA) (**2**) were added to BTMSA solvent at reflux under  $\text{N}_2$  over a period of 2–3 days to give the bicyclic-diene complexes (**3**) in ca. 20–30% yield in addition to the free ligand (**4**) [ca. 12% of (**4a**), <5% of (**4b**)].<sup>†</sup> The major reaction product was the cyclobutadiene complex (**5**) (ca. 50%), its formation providing a rationale for the diminished efficiency of the process: the presumed intermediate metallacycle (**6**)<sup>2</sup> evidently prefers valence tautomerization to (**5**) over incorporation of the appended alkene unit.



SCHEME. Cocyclisation of enynes (**1**) with BTMSA (**2**): i,  $\text{CpCo}(\text{CO})_2$ , 1 equiv.

Purification of all new compounds was achieved by reverse-phase high performance liquid chromatography using argon-saturated acetonitrile-dioxan (ca. 95:5) as eluant.<sup>3</sup> This technique also allowed a clean separation of the two diastereomers of (**3b**) formed (ratio = 1:1). The reaction leading to (**3a**) gave only one isomer in which the relative configuration of the  $\text{C-H}_{\text{tert}}$  hydrogen with respect to the  $\text{CpCo}$ -unit was assigned to be *endo* by 250 MHz  $^1\text{H}$  n.m.r. spectroscopy. Such protons in ( $\eta^4$ -cyclohexadiene)-( $\eta^5$ -cyclopentadienyl)cobalt complexes have been found to



be relatively deshielded, and their *exo*-counterparts relatively shielded.<sup>1,4</sup> Moreover, models indicate that when the cobalt nucleus and the tertiary cyclohexadiene proton are on the same side of the molecule, the *exo*-methylene proton adjacent to the latter is positioned distinctly axially, well within the shielding cone of the metal. Consistent with this finding, the *endo*-isomers exhibit a double doublet, at higher field than the  $\text{Me}_4\text{Si}$  resonance, assigned to this proton, the corresponding *endo*-proton absorbing as a double doublet below  $\delta = 1$ , and the tertiary hydrogen as a multiplet at even lower field. In contrast, the *exo*-isomers ( $\text{CpCo}$  and  $\text{C-H}_{\text{tert}}$  *exo* with respect to each other) exhibit a higher field (ca.  $\delta$  0.5–0.8) multiplet for the *exo*-tertiary proton and two lower field double doublets for the neighbouring methylene hydrogens. Decoupling experiments corroborate these assignments.

Since the structures of (**3a**) and (**4a**) incorporate the new strained diene framework of a bicyclo[4.2.0]octa-1,3-diene<sup>5</sup> the spectral characteristics of these compounds are reported here: (**3a**) [red oil;  $m/e$  374 ( $M^+$ , 78%), 372 ( $M-2\text{H}$ , 16%), 301 ( $M-\text{SiMe}_3$ , 32%), and 73 ( $\text{SiMe}_3$ , 100%);  $^1\text{H}$  n.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.69 (s, 5H), 4.37 (s, 1H, 2-H), 2.64 (m, 1H,  $\text{C-H}_{\text{tert}}$ ), 2.50 (m, 1H), 2.09 (m, 2H), 1.76 (ddd,  $J$  7.9, 9.8, 17.6 Hz, 1H), 1.18 (dd,  $J$  7.5, 11.2 Hz, 1H, *endo*- $\text{CH}_2$ ), 0.51 (s, 9H), 0.29 (s, 9H), and  $-0.78$  (dd,  $J$  8.2, 11.2 Hz, 1H, *exo*- $\text{CH}_2$ );  $^{13}\text{C}$  n.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  82.8, 79.8 (Cp), 79.5, 75.2 (C-2), 63.0 (C-4), 55.8 (C-6), 35.2, 33.8, 26.2 (C-7), 1.92, and 0.88 p.p.m.]; (**4a**) [colourless oil;  $m/e$  250 ( $M^+$ , 2%), 235 ( $M^+ - \text{CH}_3$ , 9%), 162 (33%), and 73 (100%);  $^1\text{H}$  n.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.05 (s, 1H, 2-H), 2.9 (m, 1H), 2.79 (m, 1H), 2.56 (m, 2H), 2.18 (m, 1H), 1.85 (m, 1H), 1.50 (m, 1H), 0.38 (s, 9H), and 0.34 (s, 9H);  $^{13}\text{C}$  n.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  147.5, 146.6, 141.8, 118.9 (C-2), 36.1, 35.5, 32.2 (C-5), 28.0 (C-7), 2.55, and 2.24 p.p.m.]. The ligand (**4a**), evidently not a 'Bredt compound',<sup>6</sup> may be quantitatively liberated from (**3a**) by treatment with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (3 equiv.) in acetonitrile containing  $\text{NEt}_3$  (1.5 equiv.), and is moderately stable.

It was of mechanistic interest to determine the regiochemical outcome of the described intermolecular cocyclisation reaction. To this end 1-trimethylsilylhept-1-yne (1 equiv.) was cocyclised with (**1b**) or (**1c**) (1 equiv.) and  $\text{CpCo}(\text{CO})_2$  (1 equiv.) in *n*-octane to give, regioselectively compounds (**8**) as 1:1 mixtures of diastereoisomers.<sup>†</sup> This was indicated by  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectroscopy and comparison with molecular models.<sup>1</sup> This suggests that during the course of the reaction the intermediate metallacycle (**7**), with the silicon substituent next to cobalt, is formed selectively. Evidence for such a preference by the trimethylsilyl substituent has been observed previously<sup>7</sup> and is in accord with theoretical predictions.<sup>8</sup>

<sup>†</sup> All compounds have been fully characterised.

We thank N.I.H. and N.S.F. for financial, and P.C.R. a Camille and Henry Dreyfus Teacher-Scholar (1978—1983). Research Chemicals for material, support. K. P. C. V. is a Fellow of the Alfred P. Sloan Foundation (1976—1980) and

(Received, 29th September 1980; Com. 1064.)

<sup>1</sup> E. D. Sternberg and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1980, **102**, 4839; C. Chang, C. G. Francisco, T. R. Gadek, J. A. King, Jr., E. D. Sternberg, and K. P. C. Vollhardt, *Pure Appl. Chem.*, in the press.

<sup>2</sup> R. L. Funk and K. P. C. Vollhardt, *Chem. Soc. Rev.*, 1980, **9**, 41; K. P. C. Vollhardt, *Ann. N.Y. Acad. Sci.*, 1980, **333**, 241; Y. Wakatsuki, K. Aoki, and H. Yamazaki, *J. Am. Chem. Soc.*, 1979, **101**, 1123; C. E. Dean, R. D. W. Kemmit, D. R. Russell, and M. D. Schilling, *J. Organomet. Chem.*, 1980, **187**, C1; L. D. Brown, K. Itoh, H. Suzuki, K. Hirai, and J. A. Ibers, *J. Am. Chem. Soc.*, 1978, **100**, 8232 and references therein.

<sup>3</sup> J. H. Huggins, J. A. King, Jr., K. P. C. Vollhardt, and M. J. Winter, *J. Organomet. Chem.*, in the press.

<sup>4</sup> R. I. Duclos, Jr., K. P. C. Vollhardt, and L. S. Yee, *J. Organomet. Chem.*, 1979, **174**, 109.

<sup>5</sup> A. Greenberg and F. R. Liebman, 'Strained Organic Molecules,' Academic Press, New York, 1978, p.126.

<sup>6</sup> G. Köbrich, *Angew. Chem.*, 1973, **85**, 494; *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 464.

<sup>7</sup> R. L. Hillard and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1977, **99**, 4058; E. R. F. Gesing, J. P. Tane, and K. P. C. Vollhardt, *Angew. Chem.*, in the press.

<sup>8</sup> A. Stockis and R. Hoffman, *J. Am. Chem. Soc.*, 1980, **102**, 2952.