standardized hydrochloric acid in methanol, and methanol-deionized water (to bring the final water concentration to 5%) were thermostated prior to mixing. After the reaction solution was mixed, it was transferred to a cuvette and the absorbance read as a function of time in a Beckman DU-Gilford with a thermostated cell compartment. Most substrates were run under second-order conditions (nearly equal concentrations of tin compound and acid in the range of 10^{-3} M) at least at one temperature and also under pseudo-first-order conditions with a 50-fold excess of acid. Second-order rate constants and activation parameters were obtained from a standard least-squares plot.

Reaction of Triphenylvinyltin (12) with 2,4-Dinitrobenzenesulfenyl Chloride. A solution of 0.620 g (2.65×10^{-3} mol) of 2,4-dinitrobenzenesulfenyl chloride in 5 mL of methylene chloride was added dropwise with stirring to 1.00 g (2.65×10^{-3} mol) of triphenylvinyltin (12) in 5 mL of methylene chloride. The reaction mixture was allowed to stir overnight. The solution was washed twice with water, dried over magnesium sulfate, and evaporated to dryness. The residue was dissolved in hot ethanol. On cooling, 0.49 g (67%) of yellow crystals was formed. A second recrystallization gave crystals of 2,4-dinitrophenyl phenyl sulfide **16**, mp 118–119 °C [lit.[27] 119.5–120.5 °C]. The NMR spectrum showed only aromatic protons.

Acknowledgment. We wish to thank Professor H.G. Kuivila for helpful discussions during the preparation of this paper. The research was supported by several grants from the Colgate University Research Council which are gratefully acknowledged. Also we wish to thank M & T Chemicals for their gift of chemicals and Norwich Pharmical for recording some of the NMR spectra.

Registry No. 1, 754-06-3; 2, 2117-47-7; 3, 20474-38-8; 4, 7486-35-3; 5, 4964-07-2; 6, 4964-06-1; 7, 762-73-2; 8, 66680-88-4; 9, 7330-43-0; 10, 1112-56-7; 11, 7422-28-8; 12, 2117-48-8; 13, 7532-85-6; 14, 4109-84-6; 15, 1426-65-9.

(27) Bost, R. W.; Turner, J. O.; Norton, R. D. *J. Am. Chem. Soc.* **1932**, *54*, 1985.

The Diethynylcyclobutadiene Rearrangement: A Degenerate Ligand Reorganization in the Coordination Sphere of (η^5-Cyclopentadienyl)cobalt[1]

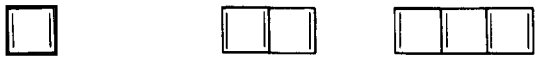
John R. Fritch[2] and K. Peter C. Vollhardt*[3]

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

Received November 16, 1981

Reaction of $CpCo(CO)_2$ with bis(trimethylsilyl)butadiyne leads to small amounts of silylated 1,2- and 1,3-diethynylcyclobutadiene complexes **13** and **18** among other products. Alternatively, cocyclization of bis(trimethylsilyl)hexatriyne with bis(trimethylsilyl)acetylene furnishes **13** in 64.2% yield. These compounds may be protodesilylated with alcoholic KOH or fluoride. Flash vacuum thermolysis of the 1,2-diethynylcyclobutadiene complexes **9**, **19**, and **49** induces a clean rearrangement in which the four sp carbons of the ethynyl groups cyclize to form a new cyclobutadiene ring and the original cyclobutadiene ring retrocyclizes to generate two new alkyne groups. In this way **9** undergoes a degenerate rearrangement, whereas **19** converts to **30**, and **49** equilibrates with **50**. Mechanistic speculation is offered which suggests a CpCo-complexed cycloocta-3,7-diene-1,5-diyne (**11**) or cycloocta-1,2,3,5,6,7-hexaene (**12**) as a likely intermediate. A topologically equivalent alternative, (η^4-tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene)(η^5-cyclopentadienyl)cobalt (**10**), appears less favored on theoretical grounds.

Polycyclic benzenoid hydrocarbons have played an important part in the development of the theory of π-electronic cycles. They have received renewed recent attention in connection with diverse areas such as those concerned with the mechanism of carcinogenicity induced by environmentally abundant polycyclic benzenoids[4] and the conversion of coal to liquid and gaseous fuels.[5] These compounds are conceptually derived by linear and angular fusion of benzene rings, the latter constituting the prototype aromatic molecule.[6] One might conceive of nonbenzenoid analogs of the benzenoid aromatics formed by fusion of the prototype "antiaromatic"[7] molecule: cyclobutadiene.[8] The first three members of such a series (which can only be linear) are cyclobutadiene (1), butalene



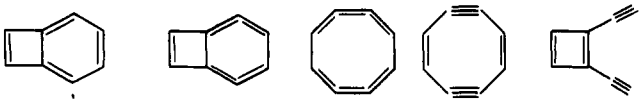
1 2 3

(bicyclo[2.2.0]hexa-1,3,5-triene) (**2**), and tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene (**3**), for which in analogy with the trivial naming of biphenylene, the name bicyclobutadienylene may be proposed. Interestingly, and in contrast to the benzenoid series, only the first member, cyclobutadiene, has been studied relatively thoroughly.[8] Compound **2** has been invoked as a reactive intermediate,[9]

(1) Taken in part from the Ph.D. Thesis of J. R. Fritch, University of California, Berkeley, 1980.
(2) Regents' Predoctoral Fellow (1977–1978) and Gulf Oil Fellow (1978–1979).
(3) Alfred P. Sloan Foundation Fellow (1976–1980), Camille and Henry Dreyfus Teacher-Scholar (1978–1983).
(4) R. Freudenthal and P. W. Jones, "Carcinogenesis—A Comprehensive Survey", Vol. 1, Raven Press, New York, 1976. H. V. Gelboin and P. O. P. Ts'o, Eds., "Polycyclic Hydrocarbons and Cancer", Vol. 2, Academic Press, New York, 1978.
(5) J. Falbe, "Chemierohstoffe aus Kohle", G. Thieme Verlag, Stuttgart, 1977.
(6) P. Garratt and P. Vollhardt, "Aromatizität", G. Thieme Verlag, Stuttgart, 1973.
(7) For a recent critical exposé: N. L. Bauld, T. L. Welsher, J. Cessac, and R. L. Holloway, *J. Am. Chem. Soc.*, **100**, 6920 (1978).
(8) S. Masamune, F. A. Souto-Bachiller, T. Machiguchi, and J. E. Bertie, *J. Am. Chem. Soc.*, **100**, 4889 (1978); D. W. Whitman and B. K. Carpenter, *ibid.*, **102**, 4272 (1980), and the references therein.
(9) R. Breslow, J. Napierski, and T. C. Clarke, *J. Am. Chem. Soc.*, **97**, 6275 (1975); R. Breslow and P. L. Khanna, *Tetrahedron Lett.*, 3429 (1977); R. G. Bergman, *Acc. Chem. Res.*, **6**, 25 (1973); R. R. Jones and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 660 (1972).

0276-7333/82/2301-0590$01.25/0 © 1982 American Chemical Society

and one of its interesting features is its potential to exist as the isomeric cyclic bisallene or *p*-benzyne biradical.[10] The 8π-system **3** has similar and additional structural possibilities which it might be inclined to adopt in an effort to alleviate strain related and electronically induced destabilizing features. These are shown in **4**–**8**.



4 **5** **6** **7** **8**

The literature reveals that some theoretical thought has been devoted to **3**.[10] This is of interest particularly with respect to estimates of its relative stability in comparison with **1** and **2**. In most treatments the stability of **3** is calculated to lie inbetween that of **1** and **2**,[10c] all three compounds being destabilized by conjugation ("antiaromatic"). For example, a structure–resonance theory approach suggests negative resonance energies (REs) of −0.65, −0.31, and −0.52 eV for **1**, **2**, and **3**.[10c] A perturbational molecular orbital estimate[10b] similarly places the stability of **3** (RE = 2.45 β) lower than that of **2** (RE = 2.83 β). A graph theoretical approach to this problem is particularly instructive because it is based on the enumeration of so-called conjugated circuits related to the presence and relative importance of classical Kekulé structures.[11] Thus, in the five possible resonance structures of **3**, one may detect four benzene-like circuits, but ten cyclobutadiene and two cyclooctatetraene circuits. The resulting calculated resonance energy value is in accord with the other treatments portraying **3** to be more antiaromatic (AA = −65.88%) than **2** (AA = −57.24%).

Inspection of **6** and **7** and comparison with **3** suggests the interesting possibility that all of these molecules might be resonance structures. This suggestion is deemed unlikely on the basis of the results of ab initio SCF LCAO-MO calculations revealing distinct energy minima on the D_{2h} C_8H_4 potential energy surface.[12]

Intuitively, **7** might be deemed the lowest energy isomer in the series. It also constitutes an attractive synthetic target since it would represent the first unsubstituted planar cyclooctatetraene derivative, a molecule of considerable current theoretical interest.[18] The anticipated strain in such a system, although appreciable, should not be prohibitive, on the basis of literature analogies,[18,19] particularly the remarkable stability of cycloocta-1,5-diyne.[19a]

The equally interesting cycloocta-1,2,3,5,6,7-hexaene (**6**) is similar to **7** in that it also contains a planar, monocyclic eight π-electron system. 1,2,4,5,7-Cyclooctapentaene, a dihydro derivative of **6**, has been suggested as an intermediate in the thermal rearrangement of *cis,cis*-octa-3,5-diene-1,7-diyne to benzocyclobutadiene.[20]

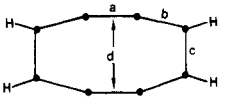
Potential synthetic approaches to the C_8H_4 manifold symbolized by structures **3**–**7** will have to take into account the likely lability and sensitivity of any of the target molecules. Transition metals have frequently been used as stabilizing appendages to otherwise reactive or thermally labile π systems.[21] It occurred to us that this might be applicable also in this case. In particular, rather than attempting to trap one of the reactive species **3**, **6**, and **7** by using an added metal complex, a strategy we considered fraught with experimental difficulties, we felt that incorporating the metal into a suitable precursor from which one of the theoretically interesting ligands might be accessible by unimolecular rearrangement was a more promising proposition.

Stabilization of cyclobutadienes by complexation to a transition metal has been firmly established experimentally[22] after having been predicted theoretically.[23] In particular, (η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt complexes are air-stable and, in the absence of reactive substituents, can be heated in condensed phases to well

(10) (a) H. E. Simmons and A. G. Anastassiou in M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, 1967, p 396. (b) M. J. S. Dewar, M. C. Kohn, and N. Trinajstić, *J. Am. Chem. Soc.*, **93**, 3437 (1971); (c) W. C. Herndon and M. L. Ellzey, *ibid.*, **96**, 6631 (1974); (d) C. F. Wilcox, Jr., *Tetrahedron Lett.*, 795 (1968).

(11) M. Randić, *J. Am. Chem. Soc.*, **99**, 444 (1977); *Tetrahedron*, **23**, 1905 (1977); see also J. A. N. F. Gomes, *Croat. Chem. Acta*, **53**, 561 (1980).

(12) Single-determinant SCF LCAO-MO Hartree–Fock calculations[13] were performed with the Gaussian 70 computer program series[14] using the minimal STO-3G basis set and the recommended standard exponents.[15] The only C_8H_4 geometries considered were those that have D_{2h} configurations. In each geometry, the hydrogen atoms were positioned such that the C–H bond lengths were their standard value[16] of 1.08 Å and such that all eight C–C–H bond angles were equal. Starting with the geometry for **3** in which all ten C–C bond lengths were set to their standard value[16] of 1.4 Å, the dimensions *a*, *b*, *c*, and *d* shown were



simultaneously optimized by using the modified Davidon–Fletcher–Powell gradient search technique[17] to obtain the minimum-energy geometry for **3**: a = 1.3464 Å, b = 1.4861 Å, c = 1.3635 Å, d = 1.5014 Å; total energy = −301.091 062 hartrees. Successive increases in parameter d from the optimized geometry for **3** suggested the presence of a second energy minimum in the D_{2h} C_8H_4 potential surface. Simultaneous optimization[17] of dimensions a, b, c, and d then gave the minimum-energy geometry for **7**: a = 1.1800 Å, b = 1.4719 Å, c = 1.3340 Å, d = 2.5863 Å; total energy = −301.284 705 hartrees. An attempt to find the transition state for a possible **3** ⇌ **7** rearrangement led to the discovery of a third energy minimum. After simultaneous optimization[17] of parameters a, b, c, and d, the minimum-energy geometry for **6** resulted: a = 1.3081 Å, b = 1.3764 Å, c = 1.4053 Å, d = 2.0226 Å; total energy = −300.990 194 hartrees. Although we do not have much confidence in the quantitative accuracy of the method or even the relative energy ordering when applied to our system, we do attach some significance to the theoretical distinction between **3**, **6**, and **7**.

(13) C. C. J. Roothan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(14) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

(15) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(16) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

(17) J. B. Collins, P. von R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

(18) For some benzoderivatives, see: C. F. Wilcox, Jr., J. P. Uetrecht, G. D. Grantham, and K. G. Grohmann, *J. Am. Chem. Soc.*, **97**, 1914 (1975); H. N. C. Wong, P. J. Garratt, and F. Sondheimer, *ibid.* **96**, 5604 (1974); H. N. C. Wong and F. Sondheimer, *Angew. Chem.*, **88**, 126 (1976); *Angew. Chem., Int. Ed. Engl.*, **15**, 117 (1976); F. Gerson, W. B. Martin, G. Plattner, F. Sondheimer, and H. N. C. Wong, *Helv. Chim. Acta*, **59**, 2038 (1976); R. Destro, T. Pilati, and M. Simonetta, *Acta Crystallogr., Sect. B*, **B33**, 447 (1977); T.-L. Chan, Y.-S. Lam, and T. C. W. Mak, *ibid.*, **B35**, 218 (1979); M.-K. Au, T.-W. Siu, T. C. W. Mak, and T.-L. Chan, *Tetrahedron Lett.*, 4269 (1978); H. N. C. Wong and F. Sondheimer, *ibid.*, 983 (1980); *J. Org. Chem.*, **45**, 2438 (1980); H. Gugel and H. Meier, *Chem. Ber.*, **113**, 1431 (1980); R. A. G. de Graaff, S. Gorter, C. Romers, H. N. C. Wong, and F. Sondheimer, *J. Chem. Soc., Perkin Trans. 2*, 478 (1981). A planar perfluorotetrakis(cyclobutacyclooctatetraene) has recently been reported: F. W. B. Einstein, A. C. Willis, W. R. Cullen, and R. L. Soulen, *J. Chem. Soc., Chem. Commun.*, 526 (1981).

(19) For some less unsaturated derivatives, see: (a) E. Kloster-Jensen and J. Wirz, *Helv. Chim. Acta*, **58**, 162 (1975); (b) H. Maier and H. Petersen, *Synthesis*, 596 (1978); H. Petersen, H. Kolshorn, and H. Meier, *Angew. Chem.*, **90**, 483 (1978); *Angew. Chem., Int. Ed. Engl.*, **17**, 461 (1978); W. Leupin and J. Wirz, *Helv. Chim. Acta*, **61**, 1663 (1978); H. Petersen and H. Meier, *Chem. Ber.*, **113**, 2383 (1980); H. Meier, H. Petersen, and H. Kolshorn, *ibid.*, **113**, 2398 (1980).

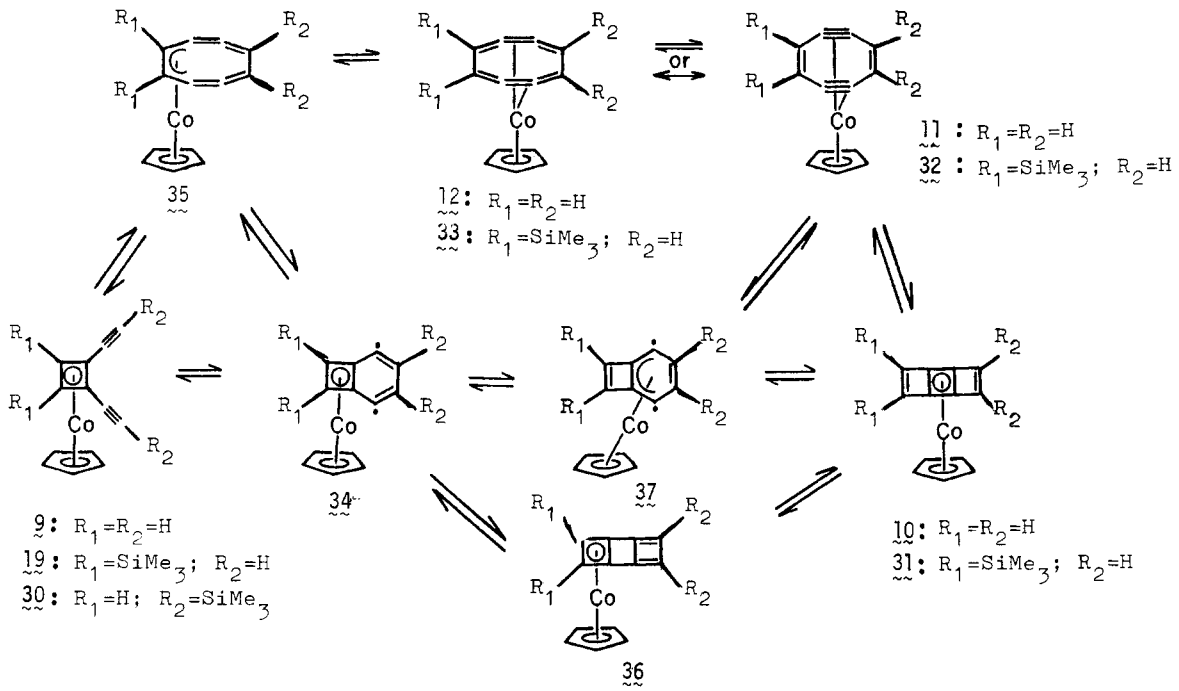
(20) G. H. Mitchell and F. Sondheimer, *J. Am. Chem. Soc.*, **91**, 7520 (1969).

(21) J. P. Collman and L. S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry", University Science Books, Menlo Park, Ca., 1980.

(22) (a) A. Efraty, *Chem. Rev.*, **77**, 691 (1977), and the references therein; (b) P. M. Maitlis and K. W. Eberius, "Nonbenzenoid Aromatics", J. P. Synder, Ed., Academic Press, New York, 1971, Chapter 6.

(23) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

Scheme I



over 200 °C without detectable decomposition.[22] Given these considerations, a practical approach to the synthesis of at least liganded **3**, **6**, or **7** might be to start with (η^4-1,2-diethynylcyclobutadiene)(η^5-cyclopentadienyl)cobalt (CpCo) (**9**), which should be sufficiently stable to be isolated, characterized, and exposed to thermal rearrangement conditions. (η^4-cyclobutadiene)CpCo complexes can often be prepared by direct reaction of $CpCo(CO)_2$ with the corresponding alkynes.[22,24] Thermolysis or photolysis of **9** would then hopefully generate **10**, **11**, or **12**, the CpCo complexes of **3**, **7**, and **6**, respectively (Scheme I).

It is not clear to what extent complexation will change the order of thermodynamic stability of **3**, **6**, and **7**. However, one might anticipate the electronically most destabilized ligand to be the most strongly bound.[25] If **10**, **11**, or **12** resulted from rearrangement of **9**, the corresponding free ligands might be obtained by oxidative[22] or ligand displacement[26] techniques.

CpCo complex **9** has an important advantage over other possible metal complexes of **8** (for example, the iron tricarbonyl complex). The (η^5-cyclopentadienyl)cobalt bond strength, 64 kcal mol^{-1} (from cobaltocene), is substantially greater than the ligand–metal bond energies for carbon monoxide, phosphine, isocyanide, olefin, alkyl, and butadiene ligands.[27] Consequently, the cyclopentadienyl moiety is expected to serve as a relatively inert blocking group for the three cobalt coordination sites not occupied by the respective ligands **3**, **6**, **7**, and **8**. The potential reactivity of other ligands that might be used to complete the metal's coordination shell could result in undesired reactions that would obscure or prevent the desired rearrangement of ligand **8**. The following is a full account of the preparation of 1,2-diethynylcyclobutadiene complexes of the type **9** and their thermal and other chemistry which has led to the discovery of a novel transformation in the coordination sphere of cobalt, the 1,2-diethynylcyclobutadiene rearrangement.[28]

Results and Discussion

Preparation of (Diethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt Complexes. The 1,2-diethynylcyclobutadiene ligand of CpCo complex **9** can be conceptually dissected into component alkynes in two different ways. One dissection gives two molecules of butadiyne; the other dissection yields acetylene and hexatriyne. Reaction of either pair of component alkynes with $CpCo(CO)_2$ could, in principle, provide **9**.[22,24]

However, butadiyne[29] and hexatriyne[30] polymerize at temperatures much lower than those required for the cyclization reaction. This problem might be circumvented by using either bis(trimethylsilyl)butadiyne[34] or bis(trimethylsilyl)acetylene and bis(trimethylsilyl)hexatriyne[33] to prepare **13** (Scheme II). Protodesilylation would then yield the desired **9**. Alcoholic KOH is known to protodesilylate ethynyl trimethylsilyl groups,[31] and removal of aromatic trimethylsilyl substituents has been achieved with fluoride ion,[32] under conditions which might be effective on the cyclobutadiene nucleus.

Unfortunately, reaction of $CpCo(CO)_2$ with 2 equiv of bis(trimethylsilyl)butadiyne in refluxing *n*-octane followed by chromatographic separation of the products on silica

(24) (a) R. L. Hillard and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **99**, 4058 (1977); (b) J. R. Fritch and K. P. C. Vollhardt, *Angew. Chem.*, **91**, 439 (1979); *Angew Chem., Int. Ed. Engl.*, **18**, 409 (1979); (c) R. I. Duclos, K. P. C. Vollhardt, and L. S. Yee, *J. Organomet. Chem.*, **174**, 109 (1979); (d) J. R. Fritch, K. P. C. Vollhardt, M. R. Thompson, and V. W. Day, *J. Am. Chem. Soc.*, **101**, 2768 (1979); (e) E. R. F. Gesing and K. P. C. Vollhardt, *J. Organomet. Chem.*, **217**, 105 (1981); (f) G. Ville, K. P. C. Vollhardt, and M. J. Winter, *J. Am. Chem. Soc.*, **103**, 5267 (1981).

(25) M. J. S. Dewar, *Angew. Chem.*, **83**, 859 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

(26) A. Krebs, H. Kimling, and R. Kemper, *Justus Liebigs Ann. Chem.*, 431 (1978).

(27) J. A. Connor, *Top. Curr. Chem.*, **71**, 71 (1977); V. I. Tel'noi and I. B. Rabinovich, *Russ. Chem. Rev. (Engl. Transl.)* **46**, 689 (1977); J. R. Chipperfield, J. C. R. Sneyd, and D. E. Webster, *J. Organomet. Chem.*, **178**, 177 (1979).

(28) A preliminary report has been published: J. R. Fritch and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **100**, 3643 (1978).

(29) J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 44 (1951).

(30) J. B. Armitage, C. L. Cook, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2010 (1952).

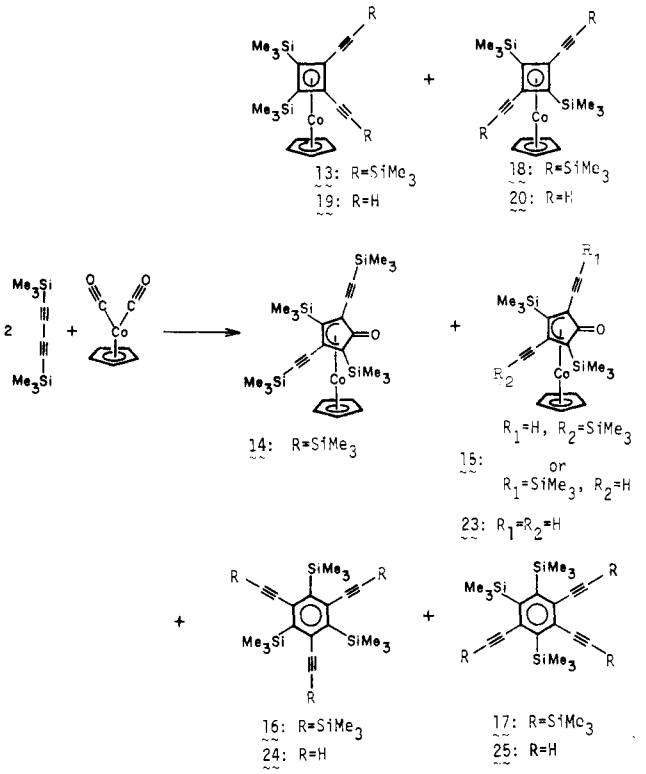
(31) D. A. Ben-Efrain "The Chemistry of the Carbon-Carbon Triple Bond", S. Patai, Ed., Part 2, Wiley, New York, 1978, Chapter 18.

(32) (a) N. Ishikawa and K. Isobe, *Chem. Lett.*, 435 (1972); (b) R. F. Cunico and E. M. Dexheimer, *J. Organomet. Chem.*, **59**, 153 (1973).

(33) H. Bock and H. Seidl, *J. Chem. Soc. B*, 1158 (1968).

(34) D. R. M. Walton and F. Waugh, *J. Organomet. Chem.*, **37**, 45 (1972).

Scheme II



gel afforded primarily the (2,4-diethynyl-η^4-cyclopentadienone)CpCo complexes **14** (24% yield) and **15** (27%), smaller amounts of diyne cyclotrimers **16** (6.4%) and **17** (4.0%), and only trace amounts of the (diethynyl-η^4-cyclobutadiene)CpCo complexes **13** (0.5%) and **18** (0.8%) (Scheme II). Formation of substituted (η^4-cyclopentadienone)CpCo complexes from the reaction of $CpCo(CO)_2$ and alkynes is well-known.[35] Triethynylbenzenes **16** and **17** were previously reported as products from the $Hg[Co(CO)_4]_2$-catalyzed trimerization of bis(trimethylsilyl)butadiyne.[36]

Complex **15**, which was obtained as a single, pure isomer having one of the two possible structures shown in Scheme II, probably resulted from protodesilylation of **14** during chromatography on silica gel. In fact, silica gel chromatography frequently converted a substantial fraction of all trimethylsilylethynyl groups, including those of **13** and **18**, into terminal ethynyl or acetyl groups. Consequently, silica gel chromatography of mixtures containing trimethylsilylethynyl groups was avoided whenever possible.

Alcoholic KOH protodesilylated the ethynyl positions of complex **13** to provide the thermally unstable complex **19** in 94% yield. Similarly, complex **18** was converted to **20**. The trimethylsilyl substituents on the cyclobutadiene rings of **19** and **20** are evidently inert to alcoholic KOH, even though the carbon to which they are bound is between sp^1 and sp^2 hybridized[37] constituting a potentially good leaving group.

The cyclobutadiene ring positions can also be protodesilylated but only with a stronger desilylating agent such as fluoride ion. For example, (1,3-diethynyl-η^4-cyclobutadiene)CpCo (**21**) resulted in 94% yield from **20**, or in 100% yield from **18**, by reaction with tetramethylammonium fluoride and H_2O in Me_2SO.

Treatment of a THF solution of **21** with 2 equiv of *n*-butyllithium followed by 2 equiv of chlorotrimethylsilane provided (1,3-bis((trimethylsilyl)ethynyl)-η^4-cyclobutadiene)CpCo (**22**) in 97% yield. The synthesis of **22** was required in order to establish the identity of the products obtained from the flash vacuum pyrolyses discussed later.

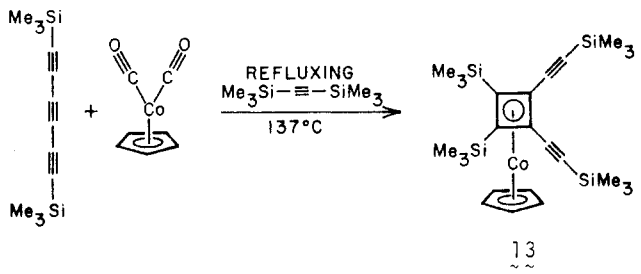
It was found that the yield of **19** could be increased by slow syringe pump addition of the reactants to nitrogen-flushed, refluxing *n*-decane (bp 174 °C), removal of solvent, and protodesilylation of the resulting residue with alcoholic KOH. The latter treatment greatly improved the chromatographic separation of products. In this way, **19** (2% yield), **20** (51%), **24** (11%), **25** (2%), and **23** (7%), in addition to a new complex **26** (4%), (2,4-diethynyl-5-(trimethylsilyl)-η^4-cyclopentadienone)CpCo, were isolated after chromatography on neutral alumina. The structures of all new compounds are in accord with their spectral and analytical characteristics (see Experimental Section). The relative assignment of the 1,2- vs. the 1,3-diethynyl substitution pattern in the cyclobutadiene complexes is based on the characteristic mass spectral fragmentation patterns[39] with prominent molecular ion peaks due to retro [2 + 2] cyclization of the four-ring, ^{13}C satellite NMR spectra (vide infra), chemical correlations (vide infra), and ultimately an unambiguous synthesis of **13** (vide infra). The substitution pattern in **26** was established by spectral comparison with model compounds.[40]

The observed product distribution in Scheme II is clearly indicative of preferential oxidative coupling of two complexed diynes to furnish a 2,4-bis trimethylsilylated cobaltacyclopentadiene.[14] This is surprising since the trimethylsilyl group ordinarily prefers the α-position in cobaltacycles of this type.[24a,40,41,42] Bis(trimethylsilyl)butadiyne and other 1,3-diynes react with iron carbonyls to form metallacycles and cyclopentadienone complexes in which the ethynyl groups are located in all possible positions.[43]

In larger scale preparations of **13** and **18**, particularly when using a large excess of bis(trimethylsilyl)butadiyne, a small quantity of a new compound, **27**, was isolated which gave spectral data consistent with 1,2,4,5-tetrakis((trimethylsilyl)ethynyl)-3,6-bis(trimethylsilyl)benzene (**27**). This structural assignment was subsequently ascertained by conversion to the known[44] 1,2,4,5-tetraethylbenzene by protodesilylation (KOH, ethanol) to give 1,2,4,5-tetraethynyl-3,6-bis(trimethylsilyl)benzene (**28**), hydrogenation (Wilkinson's catalyst) to 1,2,4,5-tetraethyl-3,6-bis(trimethylsilyl)benzene (**29**), and protodesilylation (CF_3CO-OH) to give 1,2,4,5-tetraethylbenzene, identical with an authentic sample and distinct from the independently prepared other two isomers.[44] Compound **27** is formally the product of a cocyclization of two bis(trimethylsilyl)-butadiyne units with one bis(trimethylsilyl)hexatriyne

(35) R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, **14**, 245 (1974).
(36) W. Hübel and R. Merényi, *Chem. Ber.*, **96**, 930 (1963).
(37) $J_{(^{13}C-H)}$ for the cyclobutadiene protons in **30** is 190.7 Hz, possibly implying hybridization of sp ~1.6 for the corresponding carbon orbitals.[38]
(38) J. B. Stothers, "Carbon-13 NMR-Spectroscopy", Academic Press, New York, 1972.
(39) M. D. Rausch, I. Bernal, B. R. Davies, A. Siegel, F. A. Higbie, and G. F. Westover, *J. Coord. Chem.*, **3**, 149 (1973).
(40) E. R. F. Gesing, J. P. Tane, and K. P. C. Vollhardt, *Angew. Chem.*, **92**, 1057 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 1023 (1980).
(41) K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977).
(42) C. Chang, J. A. King, and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, 53 (1981). See also: A. Stockis and R. Hoffmann, *J. Am. Chem. Soc.*, **102**, 2952 (1980).
(43) G. G. Cash and R. C. Pettersen, *Inorg. Chem.*, **17**, 650 (1978); F. R. Young, D. H. O'Brien, R. C. Pettersen, R. A. Levenson, and D. L. von Minden, *J. Organomet. Chem.*, **114**, 157 (1976); K. H. Pannell and G. M. Crawford, *J. Coord. Chem.*, **2**, 251 (1973); W. Hübel and R. G. Merényi, *Chem. Ber.*, **96**, 930 (1963).
(44) L. I. Smith and C. O. Guss, *J. Am. Chem. Soc.*, **62**, 2625, 2631 (1940).

Scheme III



molecule. Indeed, the latter was subsequently detected by GC–mass spectroscopy as a 3% impurity in our bis(trimethylsilyl)butadiyne. This suggested that the triyne might function as an efficient cocyclizing agent with bis(trimethylsilyl)acetylene (BTMSA)[41] to provide an alternative and selective route to **13**.

Bis(trimethylsilyl)hexatriyne was prepared by a modification of the literature procedure[33,45] (see Experimental Section) in improved yield. Gratifyingly, syringe pump addition of $CpCo(CO)_2$ and 1 equiv of bis(trimethylsilyl)hexatriyne to refluxing, nitrogen-flushed BTMSA provided the desired **13** in 64.2% yield (Scheme III). Several other compounds were formed in small amounts including a mixture of isomeric bis(cyclobutadiene) complexes derived by further cocyclization of one of the ethynyl groups in **13**, cyclobutadiene complexes generated by cocyclization of 1-(trimethylsilyl)-3-methylbut-1-yn-3-ol, an impurity in commercial BTMSA, and tetrakis(trimethylsilyl)butatriene[24d] (see Experimental Section).

The Diethynylcyclobutadiene Rearrangement. The rearrangement of (1,2-diethynyl-η^4-cyclobutadiene)CpCo (**9**) to **10**, **11**, or **12** (Scheme I) was attempted by flash vacuum pyrolysis (FVP). Although as a result of the very short contact times, the temperature required for a FVP reaction is several hundred degrees centigrade higher than that required for the same reaction carried out in solution, the exclusion of intermolecular gas phase collisions permits thermal unimolecular rearrangements (or fragmentations) to be performed without interfering bimolecular reactions of reactive intermediates with starting material, final products, solvents, or oxygen.[46] Consequently, FVP has proven to be an extremely valuable tool for the preparation and chemical investigation of unstable species[46] and, although uncommon with organometallic compounds, appears to be the method of choice for attempting the rearrangement of **9**, or its derivatives, such as **19**.

Surprisingly, sublimation of **19** through a hot quartz tube at 525 °C (10^{-4} torr) resulted in the unprecedented clean rearrangement to its isomer **30**! The isolated yield was 63%, but since **30** was the only compound detected in the pyrolysate and since the FVP left no trace of any decomposition products inside the quartz FVP tube, the yield of **30** based on **19** that actually sublimed was probably quantitative.[56] A small amount of intractable material was left unsublimed due to decomposition of the sensitive **19**. Protodesilylation of the ethynyl positions of the rearrangement product **30** was effected with alcoholic KOH to produce (1,2-diethynyl-η^4-cyclobutadiene)CpCo (**9**) quantitatively. The spectral data for **30** and its reaction with alcoholic KOH confirmed the presence of two (trimethylsilyl)ethynyl groups. The close similarity (but nonequivalence) of the spectral data for **30** and **22** and of the spectral data for **9** and **21** then provided convincing evidence for the structural assignments. The ^{13}C-satellite peaks in the ^1H NMR spectrum of **30** showed that the coupling constant between the two cyclobutadiene hydrogens is less than 0.35 Hz, which is also consistent with 1,2 but not 1,3 substitution of the cyclobutadiene ring. For (η^4-cyclobutadiene)iron tricarbonyl, the coupling constant between 1,2 hydrogens was found to be zero and that between 1,3- hydrogens was 8.9 Hz.[47]

Complex **30** is evidently thermodynamically more stable than **19**. This may be ascribed to two factors. First, the steric strain between the two trimethylsilyl groups of **19** is not present in **30**. Second, the electropositive trimethylsilyl group has a likely electronic preference for the more electronegative sp-hybridized ethynyl carbons over the less electronegative, formally sp^2-hybridized cyclobutadiene ring carbons, and this preference is probably greater than that of a hydrogen atom.[48]

There are several mechanisms which may be formulated in order to explain the observed rearrangement. Scheme I outlines the mechanistic possibilities that have as key intermediates the (η^4-tricyclo[4.2.0.0^{2,5}]octa-1,3,5,7-tetraene)CpCo complex **31**, the (η^4-cycloocta-1,5-diene-3,7-diyne)CpCo complex **32**, or the (η^4-cycloocta-1,2,3,5,6,7-hexaene)CpCo complex **33**. All of these species have the symmetry appropriate of a molecule which would provide the mechanistic connection between **19** and **30**. These intermediates may be kinetically accessible in a variety of ways. For example, *cis*-hex-3-ene-1,5-diyne rearranges to benzene-1,4-diyl (*p*-benzyne) with an activation free energy of 32 kcal mol^{-1}.[9] This might indicate that the rearrangement of **19** is initiated by a similar ring closure to generate (η^4-benzocyclobutadiene-3,6-diyl)CpCo complex **34**. The antisymmetric combination of the two formally singly occupied, nonbonded sp^2-hybridized carbon orbitals of **34** mixes with the antibonding σ molecular orbital between the bridgehead carbons. Although this "through-bond" interaction stabilizes the antisymmetric combination of the two nonbonded, sp^2-hybridized carbon orbitals and also lowers the total energy of diradical **34**, it does so only by populating the antibonding σ molecular orbital between the bridgehead carbons.[49]

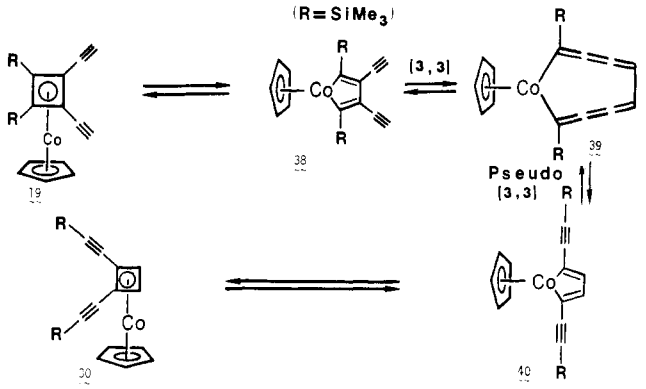
Cleavage of the weakened bond would provide (η^4-cycloocta-1,2,3,5,6,7-hexaene)CpCo complex **35**. Alternatively, **35** could be formed directly from **19** by a Cope-type process. Migration of CpCo to the center position of the cycloocta-1,2,3,5,6,7-hexaene ligand would then give complex **33**, which presumably is separated from (η^4-cycloocta-1,5-diene-3,7-diyne)CpCo complex **32** by only a very small activation barrier, if any.

An alternative pathway involves radical coupling of **34** to generate complex **36**. Migration of CpCo to the center cyclobutadiene ring would then yield tricyclooctatetraene complex **31**. If migration were to precede coupling, **37** would become an intermediate which might collapse to **31** or directly open to **32**. The observed rearrangement product would then result from **31**, **32**, or **33** by a corresponding set of reverse transformations.

CpCo participates only passively in the carbon skeleton rearrangements shown in Scheme I. Migration of CpCo between the cyclobutadiene rings of a tricyclo[4.2.0.0^{2,5}]-octa-1,3,5,7-tetraene ligand (e.g., **36** → **31**) is predicted to be thermally "forbidden" by orbital symmetry considerations,[50] increasing the likelihood that one of the other

(45) F. Bohlmann, *Chem. Ber.*, **84**, 785 (1951).
(46) G. Seybold, *Angew. Chem.*, **89**, 377 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 365 (1977).
(47) H. A. Brune, H. P. Wolff, and H. Hüther, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.*, **23B**, 1184 (1968).
(48) L. H. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw-Hill, New York, 1965.
(49) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).

Scheme IV



intermediates in Scheme I is present. Intramolecular migration of a transition metal between two rings of a coordinated bi- or tricyclic π system has been well established experimentally.[51]

Scheme IV shows an alternative mechanism for the diethynylcyclobutadiene rearrangement, one in which cobalt participates actively. Oxidative insertion of cobalt into the most sterically strained σ bond of the cyclobutadiene ring of **19** would yield cobaltacyclopentadiene complex **38**. This proposed transformation is essentially the reverse process of the well-known thermal conversion of (triphenylphosphine)(η^5-cyclopentadienyl)cobaltacyclopentadiene complexes into their corresponding CpCo(cyclobutadiene) complexes.[24f,52] Subsequent expansion of the cobaltacyclopentadiene ring by a [3,3] sigmatropic shift would provide cobaltacyclonona-2,3,4,6,7,8-hexaene complex **39**. Complex **40** could then conveivably result via a "pseudo [3,3] sigmatropic shift". This rearrangement would be interesting because it would involve apparently simultaneous [1,3] shifts of two cobalt–carbon bonds; sequential [1,3] shifts would require an intermediate that probably would be prohibitively strained. Consequently, the proposed pseudo [3,3] sigmatropic shift would differ from a normal [3,3] sigmatropic shift only by insertion of a cobalt atom into the migrating bond. Finally, reductive coupling would afford the observed rearrangement product **30**. This mechanism is topologically equivalent to those depicted in Scheme I and is not distinguishable from it by any labeling experiments (unless the cobalt configuration in **38–40** is invertible[24f]).

Scheme V outlines yet another possible mechanism for the diethynylcyclobutadiene rearrangement. Retrocyclization of the cyclobutadiene ligand of complex **19** could generate bis(diacetylene)CpCo complex **41**, presumably (but not necessarily)[24f] via the intermediacy of a cobaltacyclopentadiene complex. We have observed such retrocyclizations in specifically (1,2-bis(silyl)-3-alkyl-)-substituted cyclobutadiene–CpCo systems, albeit occurring much more slowly.[24f] Nevertheless, the rather special substitution pattern in **19** makes consideration of this alternative advisable. Once formed, bis(diacetylene)CpCo complexes such as **41** might rearrange by "diacetylene shifts", i.e., migration of CpCo between the two triple bonds of a diacetylene ligand. For example, two such diacetylene shifts would provide bis(diacetylene)CpCo complex **42** from **41**. The observed rearrangement product would then result from subsequent recyclization of the diacetylene ligands.[24f] However, as the scheme indicates, random alkyne rotations and recyclizations should compete with the **19** → **30** transformation, generating product mixtures. Although such rotations may be slow in some complexes,[53] they appear to be fast for CpCo systems (with the exception of bulky ligands).[24b,f] Thus, complexes **43** and **44** should be accessible from **41** and **42**, respectively. The former pair would then be interconverted by two diacetylene shifts, and recyclization would yield **20** and **22**, respectively. Alternatively, a single diacetylene shift of either **43** or **44** could generate **45**, which would subsequently provide either **46** by recyclization or complex **47** by ligand rotation. The latter could also result directly from either **41** or **42** by a single diacetylene shift without the intervention of any alkyne ligand rotations. Recyclization of **47** would then afford complex **48**.

The failure to observe any of the complexes **20**, **22**, **46**, and **48** in the rearrangement of **19** might be ascribed to the greater thermodynamic stability of the observed product, **30**. This would lead to the prediction that exposure of any of the other isomers to the pyrolysis conditions would also convert them to **30**. However, this is not the case. Complexes **20** and **22** are inert at temperatures up to 600 °C. Above that limit one observes retrocyclization of the four-ring complex and mainly extrusion of the resulting (trimethylsilyl)butadiyne ligands, in addition to small amounts of ligand rotation–recyclization products, but no alkyne shifts.[24b]

To rigorously exclude the mechanism depicted in Scheme V, a deuterium-labeling experiment was performed employing **49** as the substrate in the rearrangement. Scheme V predicts the formation of **49**, **51**, and **50** in a statistical (1:2:1) ratio on pyrolysis. Scheme I, on the other hand, should give only pairwise deuterium exchange and avoid the formation of **51**.

Deuteriodesilylation of **30** with a CH_3OD solution of CH_3OK followed by D_2O workup afforded **49** containing deuterium in the ethynyl positions (Scheme VI). Subsequent 520 °C (1×10^{-4} torr) FVP yielded a 1:1 mixture of **49** and **50**. The absence of **51** in the pyrolysate was ascertained by exchanging all acetylenic deuterium in the mixture for proton (methanolic KOH). ^{1}H NMR and IR spectra of the resulting mixture showed equal amounts of **9** and **50**. Furthermore, the mass spectrum showed peaks of equal intensity at m/e 224 and 226 (corresponding to **9** and **50**, respectively) and the absence of m/e 225 (corresponding to **52**) in any significant amount exceeding that calculated on the basis of the fragmentation of **50**, natural abundance isotope concentrations, and the degree of deuterium incorporation in the pyrolysis mixture. Thus,

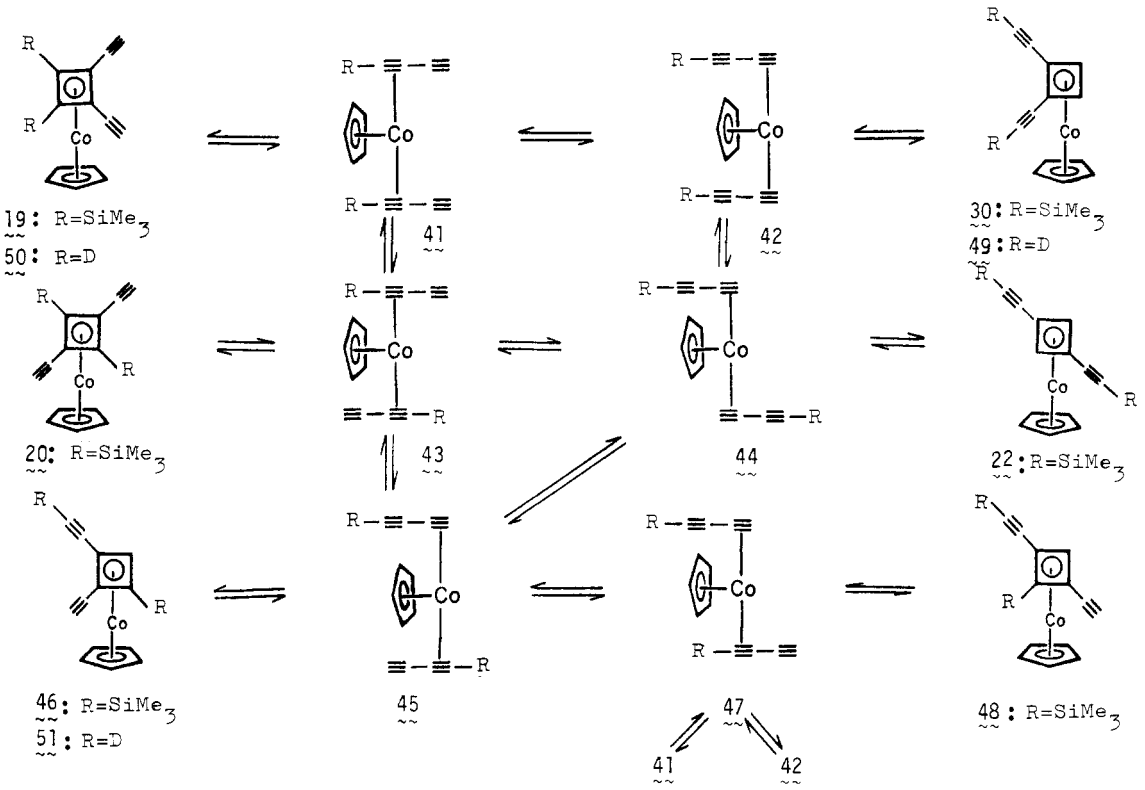
(50) P. Hofmann and T. A. Albright, *Angew. Chem.*, **92**, 747 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 728 (1980).

(51) C. C. Lee, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1071 (1971); P. M. Treichel and J. W. Johnson, *J. Organomet. Chem.*, **88**, 207 (1975); K. M. Nicholas, R. C. Kerber, and E. I. Stiefel, *Inorg. Chem.*, **10**, 1519 (1971); A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, and S. Andre, *J. Organomet. Chem.*, **154**, 45 (1978); A. N. Nesmeyanov, N. A. Ustynyuk, L. N. Novikova, T. N. Rybina, Yu. A. Ustynyuk, Yu. F. Oprunenko, and O. I. Trifonova, *ibid.*, **184**, 63 (1980); N. A. Ustynyuk, B. V. Lokshin, Yu. F. Oprunenko, V. A. Roznyatovsky, Yu. N. Luzikov, and Yu. A. Ustynyuk, *ibid.*, **202**, 279 (1980); C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1654 (1977); J. W. Johnson and P. M. Treichel, *J. Chem. Soc., Chem. Commun.*, 688 (1976); P. M. Treichel and J. W. Johnson, *Inorg. Chem.*, **16**, 749 (1977); J. W. Johnson and P. M. Treichel, *J. Am. Chem. Soc.*, **99**, 1427 (1977); M. Magon and G. Schröder, *Liebigs Ann. Chem.*, 1379 (1978); J. Müller, P. Göser, and M. Elian, *Angew. Chem.*, **81**, 332 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 374 (1969).

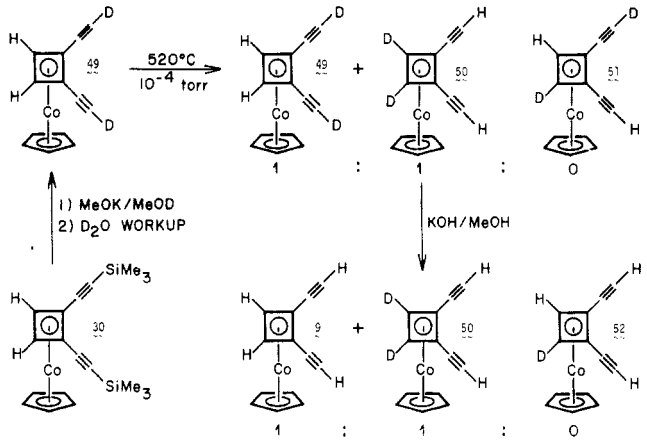
(52) H. Yamazaki and Y. Wakatsuki, *J. Organomet. Chem.*, **149**, 377 (1978); H. Yamazaki and N. Hagihara, *ibid.*, **21**, 431 (1970).

(53) For unhindered rotation in CpM (alkyne) complexes: B. E. Schilling, R. Hoffmann, and D. Lichtenberger, *J. Am. Chem. Soc.*, **101**, 585 (1979); J. L. Davidson, M. Green, J. Z. Nyathi, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2246 (1977); M. Bottrill and M. Green, *ibid.*, 2365 (1977); B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.*, **102**, 1532 (1979); D. L. Reger and C. J. Coleman, *Inorg. Chem.*, **18**, 3270 (1979); M. L. H. Green. J. Knight, and J. Segal, *J. Chem. Soc., Dalton Trans.*, 2189 (1977), and the references therein.

Scheme V



Scheme VI



51 is not formed within experimental error in the FVP of 49. This rules out Scheme V as a likely mechanistic rationale for the 1,2-diethynylcyclobutadiene rearrangement.

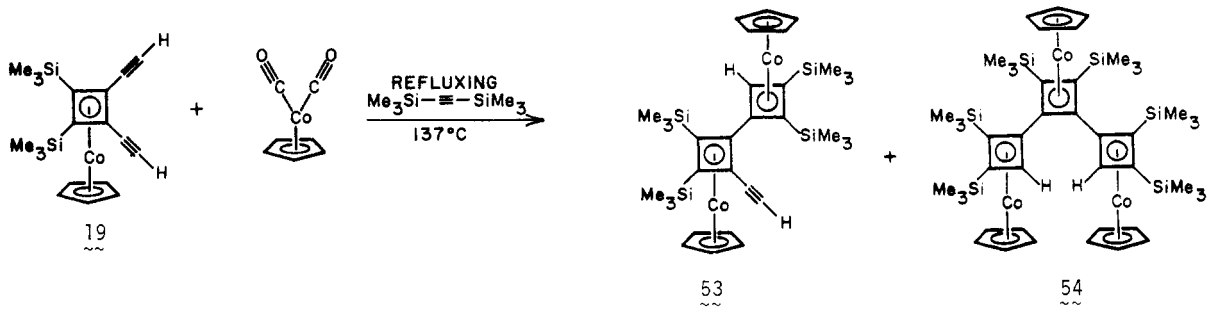
To demonstrate the feasibility of one of the pathways outlined in Scheme I, we considered trapping one of the proposed intermediates. For example, evidence for the diradical character of benzene-1,4-diyl was obtained by radical trapping experiments.[9] Similarly, formation of the known (η^4-1,2-bis(trimethylsilyl)benzocyclobutadiene)(η^5-cyclopentadienyl)cobalt[24c] from thermolysis of complex **19** in alkane solvent would constitute evidence for the intermediacy of diradical **34** in the diethynylcyclobutadiene rearrangement of **19** to **30**. However, thermolysis of **19** in refluxing 2,6,10,14-tetramethylpentadecane (pristane, bp 300 °C) provided only **30** (in 12% yield), in addition to (1-(trimethylsilyl)ethynyl-2-ethynyl-η^4-cyclobutadiene)CpCo (in about 10% yield), probably resulting by protomonodesilylation of **30** due to adventitious moisture.

An attempt to observe any of the intermediates or products in Scheme I by irradiation (Pyrex) of **9** and **50** led only to recovered starting material.

Finally, an additional strategy was attempted in an effort to stabilize one of the suggested intermediates in Scheme I. This was based on the anticipation that the two alkyne units in **19** might be induced to close to a cyclobutadiene in the coordination sphere of added cobalt. However, slow syringe pump addition of an equimolar mixture of **19** and $CpCo(CO)_2$ to refluxing, nitrogen-flushed cyclooctane (bp 151 °C) yielded only intractable products.

When an equimolar mixture of **19** and $CpCo(CO)_2$ was added slowly by syringe pump to refluxing, nitrogen-

Scheme VII



flushed BTMSA, the resulting reaction proceeded along an entirely different course (Scheme VII). After removal of the unreacted BTMSA, alumina chromatography of the resulting nonvolatile residue separated the two possible diastereomers of **53** (57% and 4.6% yields based on starting **19**), the two possible meso diastereomers of **54** (2.5% and 0.28%, three Me_3Si resonances), and also the only other possible diastereomer of **54** (0.44%, six Me_3Si resonances). No evidence could be found for any cocyclotrimerized derivatives.

The preparation of **53** and **54** indicates that either one or both of the ethynyl groups of **19** can individually cocyclize with BTMSA and $CpCo(CO)_2$ to produce either one or two new CpCo-complexed cyclobutadiene rings. The metallacycle precursor to **53** is evidently incapable of incorporating the appended second alkyne group. Interestingly, since the two diastereomers of **53** were isolated in 12:1 ratio, the stereospecificity of this cocyclization is high (about 92%). Even if all of the isolated **54** had resulted from completely stereoselective cocyclization of only the minor diastereomer of **53**, the stereospecificity of the first cocyclization would still be 88%.

In conclusion, we have observed a novel degenerate rearrangement in the coordination sphere of (η^5-cyclopentadienyl)cobalt, termed the 1,2-diethynylcyclobutadiene rearrangement, which most likely proceeds through the intermediacy of a theoretically interesting metal complexed C_8H_4 isomer such as **11** or **12**. Attempts to prove its presence have failed so far. Current investigations are directed at the independent synthesis of complexes of the type **11** or **12**. Their thermal chemistry should prove interesting in connection with our current mechanistic thinking.

Experimental Section

General Considerations and Procedures. $CpCo(CO)_2$, (trimethylsilyl)acetylene,[54] bis(trimethylsilyl)butadiyne,[34] and 1,6-dichlorohexa-2,4-diyne[55] were prepared according to previously published procedures. Other starting materials were purchased from commercial sources. BTMSA is available from PCR Research Chemicals. High boiling hydrocarbons were purified by two concentrated H_2SO_4 washings followed by distillation from CaH_2. Diethyl ether and tetrahydrofuran (THF) were distilled from $LiAlH_4$, *o*-xylene and hexane from CaH_2, methylene chloride from P_2O_5, and 1-heptene from sodium metal, all under N_2. Dimethyl sulfoxide (Me_2SO) was distilled at 75 °C from CaH_2 under 10 torr of N_2. The distilled solvents were stored over 3A molecular sieves under a positive pressure of nitrogen.

Solvents and solutions were degassed either by bubbling a stream of nitrogen through the (preferably refluxing) liquid or by subjecting the liquid to several freeze–evacuation–thaw cycles on a vacuum line.

All column chromatography was performed either on 70-230 mesh silica gel (E.M. Reagents) or on 70-290 mesh neutral alumina (Woelm) activity II. Preparative thin-layer chromatography (TLC) was carried out on plates prepared from silica gel (E.M. Reagents PF-254) containing $CaSO_4$ binder and a fluorescent indicator. Melting points and decomposition points are uncorrected and were determined with a Thomas Hoover Uni-Melt apparatus. Unless indicated otherwise, melting points and decomposition points were obtained from samples that had been sealed inside capillary tubes under nitrogen.

Analytical gas chromatography was carried out with a Hewlett-Packard Model 5710A gas chromatograph equipped with a flame ionization detector (FID). A nitrogen carrier gas flow rate of 60 mL·min^{-1} through a $^1/_4$-in. o.d. × 10-ft length stainless-steel column containing 20% UCW 98 on 60-80 mesh Chromosorb W-DMCS-AW was used to analyze for components having retention times comparable to or less than that of bis(trimethylsilyl)hexatriyne. A nitrogen carrier gas flow rate of 20 mL·min^{-1} through a $^1/_8$-in. o.d. × 20-in. length stainless-steel column containing 10% UCW 98 on 80-100 mesh Chromosorb WAW-DMCB was used to analyze for components having retention times comparable to or greater than that of bis(trimethylsilyl)hexatriyne. After the sample had been injected, the column temperature was held constant at 60 °C for 2 min and was then increased to 270 °C at 4 °C·min^{-1}. These FID GC conditions permitted quantitative analysis of the mononuclear CpCo(cyclobutadiene) complexes.

GC/mass spectral analyses were carried out on a Finnigan Model 4023 GC/mass spectrometer. A helium carrier gas flow rate of 20 mL·min^{-1} through a 2-mm i.d. × 2-m length glass column containing 3% OV 225 on 100-120 mesh Chromosorb WHP was used to analyze the flash vacuum pyrolysates of the CpCo(cyclobutadiene complexes. The other samples were analyzed with a SP 2100-coated glass capillary column that was temperature-programmed from 40 to 280 °C at 4 °C·min^{-1}.

^{1}H NMR spectra were recorded on Varian T-60 and EM-390 spectrometers and a home-built 180-MHz pulsed-Fourier transform instrument. ^{13}C NMR spectra were obtained on a Nicolet TT-23 25.14 MHz pulsed-Fourier transform instrument and, unless indicated otherwise, were proton decoupled. Data are reported in the following format: (solvent/internal chemical shift reference compound, if not $SiMe_4$) chemical shift in parts per million (ppm) downfield from internal tetramethylsilane (multiplicity, coupling constant(s); number of protons or relative peak height). Standard abbreviations are used. The following ^{1}H NMR chemical shifts (in ppm downfield from internal tetramethylsilane) were measured and then used to reference those ^{1}H NMR spectra that did not use tetramethylsilane as the internal standard: benzene-d_5 in benzene-d_6, 7.093; benzene in CCl_4, 7.20; benzene in CS_2, 7.16; $CHCl_3$ in $CDCl_3$, 7.19. The following ^{13}C NMR chemical shifts (in ppm downfield from internal tetramethylsilane) were used to reference those ^{13}C NMR spectra that did not use tetramethylsilane as the internal standard: center peak of solvent benzene-d_6 triplet, 128.35; center peak of solvent $CDCl_3$ triplet, 77.10. Whenever chromium tris(acetylacetonate) [Cr(acac)$_3$] was used as a spin relaxation agent in ^{13}C NMR samples, its concentration was about 6 mg·mL^{-1}.

Infrared absorption spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer and were referenced to polystyrene absorptions (usually 1601.4 and 1028.0 cm^{-1}). Only selected IR data are presented in the following format: (solvent) ν_{max} in cm^{-1}.

Satisfactory mass spectra and elemental analyses for all new compounds were provided by the Analytical Laboratory of the Chemistry Department of the University of California, Berkeley. The complete mass spectral, infrared, and analytical data, including occasional high-resolution masses, are given in the supplementary material.

Flash Vacuum Pyrolysis (FVP) Apparatus and Procedure. The flash vacuum pyrolyses were performed by subliming the starting materials at low pressure (~10^{-4} torr, measured at a point outside the reactor system) into one end of a hot (350–1000 °C) quartz tube while collecting the resulting FVP products in a liquid-nitrogen-cooled trap connected to the other end of the hot quartz tube. The residence (or contact) times of individual molecules inside the hot zone were estimated to lie between 1 and 20 ms and were typically about 5 ms.[46,56]

(54) M. Krüerke, *J. Organomet. Chem.*, **21**, 83 (1970).
(55) J. B. Armitage and M. C. Whiting, *J. Chem. Soc.*, 2005 (1952).

(56) FVP of **19** at 451 °C gave a mixture of **30** and **19** in a 7:3 ratio. An approximate E_a for the reaction (36 kcal mol^{-1}) may be calculated from this figure and an estimate of the contact time of the molecule.[46] The latter was obtained empirically by calibrating to tube parameters using known unimolecular reactions (cyclopentadiene from its dimer, cyclopentadiene from norbornene, toluene from cycloheptatriene).[57] This approach may not be valid since at the measured pressures the clearly unimolecular character of these processes is doubtful.[58] This "fall off" effect may be calculated according to the RRK theory[59] and was found appreciable. However, the pressure in the pyrolysis zone is likely to be considerably higher than measured (10^{-4} torr) at a point beyond the product trap. Thus, the above figure provides at least a rough estimate of the barrier of activation.
(57) S. W. Benson, "Kinetic Data on Gas Phase Unimolecular Reactions", United States Department of Commerce, 1970.
(58) K. J. Laidler, "Chemical Kinetics", 2nd ed., McGraw-Hill, New York, 1965.

The cold trap consisted essentially of a 1.5-cm o.d. Pyrex tube bent into the shape of a "V". One end of the V-shaped cold trap was connected to the quartz FVP tube with an outer 14/20 ground glass joint and was also connected to a solvent reservoir through a vacuum stopcock. The other end of the V-shaped cold trap was connected through vacuum stopcocks to a diffusion pump and to a nitrogen line vented to atmospheric pressure through a mercury bubbler. An NMR tube was attached to the bottom of the V-shaped cold trap. The quartz FVP tube was heated with a Hoskins Type FD303A electric furnace. A pentane solution of the starting material was evaporated under aspirator vacuum on a rotary evaporator to a thin crystalline film coating the inside surface of a 25-mL round-bottom flask. The flask was then attached to one end of a quartz FVP tube that consisted of a 1.8-cm o.d. × 36.5-cm length quartz section connected to two inner 14/20 standard taper ground quartz joints, one at each end. (The joints and their stems brought the total length of the quartz FVP tube to 52 cm.) To be sublimed at a sufficiently rapid rate, the starting material usually had to be warmed. This was accomplished by enclosing the 25-mL flask containing the starting material inside a metal can lined with an electrically heated cord. After the sublimation was complete, the products were washed into the attached NMR tube with solvent that had been vacuum transferred into the system.

The Reaction of $CpCo(CO)_2$ with Bis(trimethylsilyl)butadiyne. $CpCo(CO)_2$ (0.864 g, 4.80 mmol) was added by syringe in one portion over 1 min to a degassed, magnetically stirred solution of bis(trimethylsilyl)butadiyne (1.944 g, 10.00 mmol) in *n*-octane (100 mL) refluxing under nitrogen. After 11 h of continued refluxing, the initially reddish orange reaction mixture had turned brown, 97% of the starting bis(trimethylsilyl)butadiyne had been consumed (GC), and the reaction mixture was cooled to room temperature. The solvent was vacuum transferred off the reaction mixture at room temperature (10^{-3} torr), and the resulting nonvolatile dark brown solid residue was chromatographed on silica gel. The first colorless band was eluted from the column with pentane to yield a small amount of unreacted bis(trimethylsilyl)butadiyne.

A second colorless band was then collected with pentane eluent to provide 1,3,5-tris((trimethylsilyl)ethynyl)-2,4,6-tris(trimethylsilyl)benzene[36] (**16**, 125 mg, 0.21 mmol, 6.4% yield). Recrystallization from diethyl ether/methanol and sublimation (95 °C (1×10^{-3} torr)) gave colorless crystals: mp 117.5–118.5 °C; *m/e* (relative intensity) 582 (M^+, 39.37), 568 (63.85), 73 (100); NMR (CCl_4) δ 0.47 (s, 27 H), 0.22 (s, 27 H); IR ($CHCl_3$) 2146 (C≡C), 1248 ($SiMe_3$) cm^{-1}.

A third colorless band was then eluted off the column with pentane to afford 1,2,4-tris((trimethylsilyl)ethynyl)-3,5,6-tris(trimethylsilyl)benzene[36] (**17**, 78 mg, 0.13 mmol, 4.0% yield). Recrystallization from diethyl ether/methanol and sublimation (120 °C (1×10^{-3} torr)) gave colorless crystals: mp 124–124.5 °C; *m/e* (relative intensity) 582 (M^+, 18.67), 73 (100); NMR (CCl_4) δ 0.48 (s, 9 H), 0.44 (s, 9 H), 0.40 (s, 9 H), 0.245 (s, 27 H); IR ($CHCl_3$) 2146 (C≡C), 1248 ($SiMe_3$) cm^{-1}.

A first yellow band was then eluted off the column with pentane to yield (1,3-bis((trimethylsilyl)ethynyl)-2,4-bis(trimethylsilyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (**18**, 20 mg, 39 μmol, 0.81% yield). Sublimation (90–95 °C (2×10^{-3} torr)) gave yellow-orange crystals: mp 96.5–98.5 °C; *m/e* (relative intensity) 512 (M^+, 75.04), 318 (100), 73 (85.93); NMR (CCl_4) δ 4.78 (s, 5 H), 0.27 (s, 18 H), 0.15 (s, 18 H); IR ($CHCl_3$) 2135 (C≡C), 1247 ($SiMe_3$) cm^{-1}.

A second yellow band was then eluted off the column with pentane to provide (1,2-bis((trimethylsilyl)ethynyl)-3,4-bis(trimethylsilyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (**13**, 12 mg, 23.4 μmol, 0.49% yield). Recrystallization from methanol/water and sublimation (90–95 °C (1×10^{-3} torr)) gave yellow-orange crystals: mp 96.5–97.5 °C; *m/e* (relative intensity) 512 (M^+, 74.91), 318 (100), 73 (66.17); NMR (CCl_4) δ 4.78 (s, 5 H), 0.20 (s, 18 H), 0.17 (s, 18 H); IR ($CHCl_3$) 2141 (C≡C), 1246 ($SiMe_3$) cm^{-1}.

As the concentration of diethyl ether in the eluent was gradually increased, several reddish brown bands eluted off the column. A prominent dark red band was then collected with 65% diethyl ether/35% pentane eluent to afford (2,4-bis((trimethylsilyl)ethynyl)-3,5-bis(trimethylsilyl)-η^4-cyclopentadienone)(η^5-cyclopentadienyl)cobalt (**14**, 616 mg, 1.14 mmol, 23.7% yield). Recrystallization from hexane gave red needles: mp 167–169 °C (dec); *m/e* (relative intensity) 540 (M^+, 21.95), 525 ($M - CH_3$, 100), 467 ($M - SiMe_3$, 81.24); NMR (CCl_4) δ 4.86 (s, 5 H), 0.48 (s, 9 H), 0.36 (s, 9 H), 0.24 (s, 9 H), 0.20 (s, 9 H); IR ($CHCl_3$), 2155 (C≡C), 1587 (C=O), 1248 ($SiMe_3$) cm^{-1}.

A second red band was then eluted off the column with methanol to yield (4(2)-((trimethylsilyl)ethynyl)-2(4)-ethynyl-3,5-bis(trimethylsilyl)-η^4-cyclopentadienone)(η^5-cyclopentadienyl)cobalt (**15**, 603 mg, 1.29 mmol, 26.8% yield). Recrystallization from diethyl ether/hexane gave red crystals: mp 172–174 °C (dec); *m/e* (relative intensity) 468 (M^+, 14.45), 73 (100); NMR ($CDCl_3$) δ 4.94 (s, 5 H), 3.22 (s, 1 H), 0.49 (s, 9 H), 0.395 (s, 9 H), 0.20 (s, 9 H); IR ($CHCl_3$) 3306 (C≡CH), 2156 (C≡C), 2107 (C≡C), 1587 (C=O), 1248 ($SiMe_3$) cm^{-1}.

(1,2-Diethynyl-3,4-bis(trimethylsilyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (19). (1,2-Diethynyl-η^4-cyclobutadiene)CpCo complex **13** (302 mg, 0.589 mmol) was dissolved in 30 mL of absolute ethanol containing 1% KOH. The resulting dark yellow solution was magnetically stirred at room temperature under air for 30 min before submitting it to aqueous workup (with added pentane). The resulting yellow solution was dried ($MgSO_4$) and evaporated (<25 °C), and the resulting yellow-orange crystalline residue was chromatographed on alumina with 5% diethyl ether, 95% pentane eluent to provide **19** (204 mg, 0.554 mmol, 94% yield) as the only major yellow band. Recrystallization from methanol/water and sublimation (65 °C (2×10^{-3} torr)) gave yellow-orange crystals: mp 84–85 °C; *m/e* (relative intensity) 368 (M^+, 100), 294 (27.93), 246 (62.07), 73 (93.08); NMR (CCl_4) δ 4.83 (s, 5 H), 2.98 (s, 2 H), 0.17 (s, 18 H); IR ($CHCl_3$) 3300 (C≡CH), 2094 (C≡C), 1247 ($SiMe_3$) cm^{-1}.

(1,3-Diethynyl-2,4-bis(trimethylsilyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (20). (1,3-Diethynyl-η^4-cyclobutadiene)CpCo complex **18** (38 mg, 75 μmol) was protodesilylated as described for the synthesis of **19** to afford solid **20** (27 mg, 73 μmol, 97% yield). Sublimation (35–50 °C (3×10^{-3} torr)) gave yellow-orange crystals: mp 49–51 °C; *m/e* (relative intensity) 368 (M^+, 39.02), 246 (31.57), 73 (100); NMR (CCl_4) δ 4.86 (s, 5 H), 2.83 (s, 2 H), 0.26 (s, 18 H); IR ($CHCl_3$) 3303 (C≡CH), 2091 (C≡C), 1246 ($SiMe_3$) cm^{-1}.

(1,3-Diethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (21). A. From **20**. A solution of complex **20** (652 mg, 1.77 mmol) in Me_2SO (4 mL) was added to a stirred suspension of finely divided tetramethylammonium fluoride (370 mg, 3.97 mmol) in Me_2SO (20 mL) containing water (70 μL). The resulting mixture, which consisted of a dark yellow-brown solution and a white solid, was magnetically stirred at room temperature under nitrogen for 1 h before being partitioned between pentane and water. After separation from the pentane phase, the aqueous phase was extracted with three more portions of pentane. The yellow-brown pentane phases were combined, washed with ten portions of water, dried over $MgSO_4$, filtered, and evaporated (<25 °C) to a yellow-brown crystalline residue that was virtually pure **21** (373 mg, 1.664 mmol, 94% yield) according to NMR analysis. The crude **21** was recrystallized from CCl_4 (2 mL)/pentane (13 mL) with dry ice coolant and then sublimed (65–70 °C (1×10^{-4} torr)) to yield brownish yellow crystals: mp 95–96 °C (dec); *m/e* (relative intensity) 224 (M^+, 59.24), 198 (M − HC≡CH, 7.38), 174 (M − HC≡C-C≡CH, 5.39), 165 (M − Co, 100); NMR (CCl_4) δ 4.94 (s, 5 H), 4.45 (s, 2 H), 2.77 (s, 2 H); IR ($CHCl_3$) 3003 (C≡CH), 2110 (C≡C) cm^{-1}.

B. From **18**. A solution of **18**, (4.143 g, 8.08 mmol) in absolute diethyl ether (30 mL) was added to a stirred suspension of finely divided tetramethylammonium fluoride trihydrate (7.0 g, 47.56 mmol) in Me_2SO (250 mL). The resulting mixture was magnetically stirred at room temperature under air for 45 min and then worked up as above to provide crystalline **21** (1.844 g, 8.23 mmol, 100% yield).

(1,3-Bis((trimethylsilyl)ethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (22). *n*-Butyllithium (1.86) in hexane (3.82 mL, 7.11 mmol) was added by syringe in four portions over 10 min to a solution of **21** (765 mg, 3.41 mmol) in dry THF (10 mL) magnetically stirred at −78 °C (dry ice/acetone bath) under

(59) G. Emanuel, *Int. J. Chem. Kinet.*, 4, 591 (1972).

nitrogen. A yellowish brown solid precipitated. After the reaction mixture had been allowed to warm to room temperature and while it continued to be stirred under nitrogen, chlorotrimethylsilane (0.95 mL, 7.485 mmol) was added by syringe in five portions over 10 min. Within a minute after the chlorotrimethylsilane addition had been completed, the yellowish brown solid dissolved and a white granular solid precipitated. The dark yellow-orange reaction mixture was then stirred magnetically at room temperature under nitrogen for 3.5 h. Aqueous workup as in the preparation of **21** gave a yellow-brown solid residue which was virtually pure **22** (1.217 g, 3.303 mmol, 97%) according to NMR analysis. The crude **22** was recrystallized from hexane and then sublimed (130 °C (1 × 10^{-3} torr)) to give yellow-orange crystals: mp 156–158 °C; *m/e* (relative intensity) 368 (M^+, 100), 246 (10.30); NMR (CCl_4) δ 5.03 (s, 5 H), 4.56 (s, 2 H), 0.16 (s, 18 H); IR ($CHCl_3$) 2134 (C≡C), 1248 ($SiMe_3$) cm^{-1}.

The Reaction of $CpCo(CO)_2$ with Bis(trimethylsilyl)butadiyne Followed by Basic Workup. A degassed solution of $CpCo(CO)_2$ (4.50 g, 25.0 mmol) and bis(trimethylsilyl)butadiyne (9.82 g, 50.5 mmol) in *n*-decane (75 mL) was added by syringe pump over 11 h to a degassed, magnetically stirred, nitrogen-flushed (15 mL·s^{-1}), refluxing solution of bis(trimethylsilyl)butadiyne (1.23 g, 6.32 mmol) in *n*-decane (1200 mL). After the syringe pump addition had been completed and while magnetic stirring and the nitrogen flush were continued, the dark yellowish brown reaction mixture was refluxed for an additional 20 min before being cooled to room temperature. The solvent was then vacuum distilled off (60–70 °C water bath (0.05 torr)) on a rotary evaporator. The viscous, dark brown oily residue was suspended in 150 mL of absolute ethanol containing 1% KOH, and the resulting mixture was magnetically stirred at room temperature under air for 2 h before being added to diethyl ether (200 mL) and water (400 mL) in a separatory funnel. After the mixture had been shaken vigorously, a copious dark brown greasy emulsion prevented separation of the aqueous and ether phases. Therefore, the entire mixture was suction filtered through a fritted glass filter funnel containing "Celite" filter aid. After the filtered emulsion had been washed with several portions of diethyl ether, the filtrate was poured back into a clean separatory funnel, where the aqueous and ether phases were readily separated. The aqueous phase was then extracted with four more portions of diethyl ether. The ether extracts were combined, washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated to a dark reddish brown oily residue that was subsequently chromatographed on alumina.

The first colorless band was eluted off the column with pentane to provide 1,3,5-triethynyl-2,4,6-tris(trimethylsilyl)benzene[36] (**24**, 766 mg, 2.09 mmol, 11.0% yield). Recrystallization from methanol and then from hexane and sublimation (70 °C (3 × 10^{-3} torr)) gave colorless crystals: mp 166.5–169 °C, (lit.[36] mp 170–172 °C); *m/e* (relative intensity) 366 (M^+, 32.78), 351 (M − CH_3, 100); NMR (CCl_4) δ 3.32 (s, 3 H), 0.48 (s, 27 H); IR ($CHCl_3$) 3300 (C≡CH), 2100 (C≡C), 1246 ($SiMe_3$) cm^{-1}.

A first yellow band was then eluted off the column with 2% diethyl ether/98% pentane to afford a yellow-orange crystalline solid that was identified on the basis of its NMR and mass spectra as **20** (4.68 g, 12.7 mmol, 51% yield).

A second colorless band was then eluted off the column with 4% diethyl ether/96% pentane to yield 1,2,4-triethynyl-3,5,6-tris(trimethylsilyl)benzene[36] (**25**, 148 mg, 0.404 mmol, 2.13% yield). Recrystallization from methanol/water and sublimation (85 °C (1 × 10^{-3} torr)) gave colorless crystals: mp 102.5–104 °C dec (lit.[36] mp 108 °C dec); *m/e* (relative intensity) 366 (M^+, 24.33), 73 (100); NMR (CCl_4) δ 3.45 (s, 1 H), 3.41 (s, 1 H), 3.31 (s, 1 H), 0.47 (s, 9 H), 0.42 (s, 9 H), 0.40 (s, 9 H); IR ($CHCl_3$) 3303 (HC≡C), 2101 (C≡C), 1248 ($SiMe_3$) cm^{-1}.

A second yellow band was then eluted off the column with 7% diethyl ether/93% pentane to provide an orange crystalline solid that was identified on the basis of its NMR and mass spectra as **19** (190 mg, 0.517 mmol, 2.07% yield).

After several minor yellow-orange bands and a reddish brown band had been eluted off the column with diethyl ether, ethyl acetate gave a red band of (2,4-diethynyl-3,5-bis(trimethylsilyl)-η^4-cyclopentadienone)(η^5-cyclopentadienyl)cobalt (**23**, 706 mg, 1.78 mmol, 7.12% yield). Sublimation (150 °C (1 × 10^{-3} torr)) and recrystallization from diethyl ether/hexane yielded dark red crystals: mp 165–167 °C dec; *m/e* (relative intensity) 396 (M^+, 47.17), 395 (24.39), 73 (100); NMR ($CDCl_3$) δ 4.97 (s, 5 H), 3.21 (s, 1 H), 3.09 (s, 1 H), 0.50 (s, 9 H), 0.41 (s, 9 H); IR ($CHCl_3$) 3303 (C≡CH), 2113 (C≡C), 1592 (C=O), 1247 ($SiMe_3$) cm^{-1}.

Further elution gave a second red band containing (2,4-diethynyl-5-(trimethylsilyl)-η^4-cyclopentadienone)(η^5-cyclopentadienyl)cobalt (**26**) (312 mg, 0.96 mmol, 3.85% yield). Recrystallization from diethyl ether/hexane gave dark red crystals: mp 138.5–140 °C; *m/e* (relative intensity) 324 (M^+, 100), 323 (53.76); NMR ($CDCl_3$) δ 5.66 (s, 1 H), 5.00 (s, 5 H), 3.17 (s, 1 H), 3.07 (s, 1 H), 0.40 (s, 9 H); IR ($CHCl_3$) 3304 (C≡CH), 2111 (C≡C), 1590 (C=O), 1247 ($SiMe_3$) cm^{-1}.

In a preparation employing $CpCo(CO)_2$ (3.90 g, 21.7 mmol) and bis(trimethylsilyl)butadiyne (19.00 g, 97.7 mmol), a pale brownish orange band was eluted on column chromatography with 3% diethyl ether/97% pentane to provide pale orange crystalline 1,2,4,5-tetrakis((trimethylsilyl)ethynyl)-3,6-bis(trimethylsilyl)benzene (**27**) (3.44 g, 5.66 mmol). This compound was recrystallized from pentane and also from diethyl ether/methanol to yield colorless crystals: mp 275.5–276 °C; *m/e* (relative intensity) 606 (M^+, 100); NMR (CCl_4) δ 0.48 (s, 18 H), 0.25 (s, 36 H); IR ($CHCl_3$) 2141 (C≡C), 1247 ($SiMe_3$) cm^{-1}.

1,2,4,5-Tetraethynyl-3,6-bis(trimethylsilyl)benzene (28). Tetraethynylbenzene **27** (1.0 g) was protodesilylated as described in the preparation of **19**. The crude **28** was recrystallized from pentane (with dry ice coolant) and then sublimed (60 °C (5 × 10^{-3} torr)) to afford colorless crystals: mp 120.5–121.5 °C dec; *m/e* (relative intensity) 318 (M^+, 100); ^1H NMR (CCl_4) δ 3.40 (s, 4 H), 0.49 (s, 18 H); ^{13}C NMR ($CDCl_3$, $Cr(acac)_3/CDCl_3$) δ (relative peak height) 145.89 (1.00), 131.47 (1.94), 88.12 (3.86), 83.55 (2.09), 2.04 (4.95); IR ($CHCl_3$) 3306 (C≡CH), 2107 (C≡C), 1248 ($SiMe_3$) cm^{-1}.

1,4-Bis(trimethylsilyl)-2,3,5,6-tetraethylbenzene (29). Tetraethynylbenzene **28**, (30 mg, 94.2 μmol), benzene (8 mL), absolute ethanol (7 mL), and a magnetic stirring bar were placed inside a Pyrex bomb. The resulting solution was degassed by several freeze–evacuation–thaw cycles before tris(triphenylphosphine)rhodium chloride (87 mg, 94 μmol) was added under a stream of H_2. The bomb was subsequently purged thoroughly with H_2. After the initially brown suspension had been stirred at room temperature under 82 psi of H_2 for 33 h, the resulting brownish green suspension was filtered and the reddish brown filtrate was evaporated under aspirator vacuum on a rotary evaporator. The solid evaporation residue was then extracted with diethyl ether. The ether extracts were evaporated to a pale yellow crystalline residue that contained **29** and no incompletely hydrogenated ethynyl groups according to NMR and TLC analyses. The crude **29** was purified by preparative thin-layer chromatography (silica gel, pentane eluent) and then sublimation (60–70 °C (1 × 10^{-3} torr)) to yield colorless crystals: mp 109–111 °C; *m/e* (relative intensity) 334 (M^+, 19.69), 73 (100.0); NMR (CCl_4) δ 2.77 (q, J = 7.33 Hz, 8 H), 1.08 (t, J = 7.3 Hz, 12 H), 0.41 (s, 18 H); IR ($CHCl_3$) 1248 ($SiMe_3$) cm^{-1}.

Protodesilylation of 1,4-Bis(trimethylsilyl)-2,3,5,6-tetraethylbenzene (29). Trifluoroacetic acid (6.0 μL, 77.9 μmol) was added to a solution of **29** (11 mg, 32.9 μmol) in CCl_4 (0.5 mL) inside an NMR tube to give 1,2,4,5-tetraethylbenzene: NMR (CCl_4) δ 6.75 (s, 2 H), 2.545 (q, J = 7.4 Hz, 8 H), 1.18 (t, J = 7.5 Hz, 12 H). Preparative gas chromatography (20% SE-30 on 60-80 mesh Chromosorb W-AW inside a $^3/_8$ in. × 10 ft glass column at 211 °C; helium flow rate = 50 mL·min^{-1}) of the reaction mixture provided pure 1,2,4,5-tetraethylbenzene (retention time = 13.4 min) as a colorless oil identified (*m/e*, IR, NMR, GC coinjection) by comparison with authentic material.[44]

Bis(trimethylsilyl)hexatriyne. A THF solution of hexatriyne was prepared as follows:[45] 1,6-dichlorohexa-2,4-diyne[55] (2.99 g, 20.3 mmol) was syringed into a degassed suspension of NaOH (31.7 g, thoroughly pulverized and then dried at 110 °C (1 × 10^{-3} torr) for about 10 h) in dry THF (50 mL) magnetically stirred at room temperature under vacuum. After the resulting dark brown reaction mixture had been stirred for 30 s, a clean receiving flask connected to the reaction flask through a bump guard was cooled with liquid nitrogen. The stirred reaction mixture was warmed with a water bath at room temperature while the volatile hexatriyne product and THF solvent vacuum transferred into the liquid-nitrogen-cooled receiving flask. Although the vacuum transfer appeared to be complete after 20 min, the reaction flask

was maintained at room temperature, the receiving flask was cooled with liquid nitrogen, and the entire apparatus was kept under static vacuum for an additional 15 min before the vacuum-transferred volatiles were allowed to warm to 0 °C under nitrogen.

The cold pale yellow-brown THF solution of hexatriyne was then immediately syringed under air-free conditions into an ice-cooled THF suspension of ethylmagnesium bromide (50 mmol) stirred under nitrogen. During the addition of hexatriyne, a large amount of white fluffy solid precipitated and a gas, presumably ethane, boiled off the reaction mixture. The reaction mixture was then heated to 35–45 °C for 1 h. After the mixture was cooled to 3 °C, chlorotrimethylsilane (5.99 g, 7.0 mL, 55.2 mmol) was added by syringe over 5 min. The resulting mixture was then stirred at 50 °C under nitrogen for 2 h. During this period, the white fluffy solid completely dissolved to give a clear, light brown solution. A granular white solid, presumably a mixture of magnesium halide salts, precipitated as the reaction mixture was subsequently cooled to room temperature.

The reaction mixture was then partitioned between pentane (50 mL) and a mixture of ice (50 g) and saturated aqueous ammonium chloride (50 mL). After separation from the pentane phase, the aqueous phase was extracted with three more portions of pentane. The light brown pentane phases were combined, dried over $MgSO_4$, filtered, and evaporated to a brown oily residue that solidified on standing. The resulting crude, brown solid product was sublimed (50–55 °C (2×10^{-3} torr)) to provide colorless crystals of bis(trimethylsilyl)hexatriyne[33] (1.666 g, 7.63 mmol, 37.5% yield).

The Reaction of Bis(trimethylsilyl)hexatriyne and $CpCo(CO)_2$ in Refluxing BTMSA. Unambiguous Synthesis of (1,2-Diethynyl-η^4-cyclobutadiene)CpCo Complex 13. A degassed solution of bis(trimethylsilyl)hexatriyne (1.09 g, 5.01 mmol) and $CpCo(CO)_2$ (0.906 g, 5.03 mmol) in BTMSA (3 mL) was added by syringe pump over 53 h to degassed, magnetically stirred, nitrogen-flushed (2 mL·s^{-1}), refluxing BTMSA (100 mL). After the syringe pump addition had been completed and while magnetic stirring and the nitrogen flush were continued, the dark yellowish brown reaction mixture was refluxed for an additional 3.4 h before being cooled to room temperature. Unreacted BTMSA was then vacuum transferred off the reaction mixture (20–45 °C water bath (1×10^{-3} torr)), and the remaining oily brown residue was chromatographed on alumina.

A yellowish pink band was eluted off the column with pentane. Evaporation of the eluent from this band provided a pale yellow crystalline solid that was identified as tetrakis(trimethylsilyl)butatriene[24d] (30 mg, 88 μmol) on the basis of silica gel TLC, NMR, IR, and mass spectral analyses.

A prominent yellow band was then eluted off the column with pentane. Evaporation of the eluent from this band afforded a yellow-orange crystalline solid identified at **13** (1.648 g, 3.213 mmol, 64.2% yield).

A second yellow band was then eluted off the column with 2% diethyl ether/98% pentane. The eluent from this band was evaporated to an orange oil: *m/e* (relative intensity) 854 (M^+, 65.04), 684 (M − $Me_3SiC{\equiv}CSiMe_3$, 35.56), 660 (M − $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, 10.25), 560 (M − CpCo − $Me_3SiC{\equiv}CSiMe_3$, 21.96), 294 (100.00); NMR (CCl_4) δ 4.945 (s, 10 H), 0.30 (s, 9 H), 0.25 (b s, 27 H), 0.125 (s, 9 H), 0.075 (3 s, 9 H); IR ($CHCl_3$, selected peaks) 2134 (C≡C), 1246 ($SiMe_3$) cm^{-1}. On the basis of these data, this appears to be a mixture of isomers of bis(cyclobutadiene) complexes derived from **13** by further cocylization with another molecule of triyne (378 mg, 0.442 mmol, 17.6% yield based on triyne).

A third yellow band was then eluted off the column with 20% diethyl ether/80% pentane. Evaporation of the eluent from this band yielded an orange oil identified as (1,2,3-tris(trimethylsilyl)-4-((1-hydroxy-1-methyl)ethyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (50 mg, 0.111 mmol, 1.1% yield based on cobalt). This material was recrystallized from methanol/water and then sublimed (75 °C (1×10^{-3} torr)) to give yellow crystals: mp 220–221.5 °C; *m/e* (relative intensity) 450 (M^+, 7.40), 432 (M − H_2O, 22.08), 294 (100.00), 262 (M − Me_3Si − C≡C-$SiMe_3$ − H_2O, 37.08); NMR (CCl_4) δ 4.87 (s, 5 H), 1.32 (s, 6 H), 1.12 (s, 1 H), 0.20 (s, 27 H); ^{13}C NMR (benzene-d_6, Cr(acac)$_3$/benzene-d_6) δ (relative peak height) 108.79 (1.00), 79.76 (12.47), 71.85 (2.06), 71.35 (1.01), 69.61 (1.89), 32.23 (6.32), 3.434 (8.25), 3.288 (12.76); IR ($CHCl_3$) 3552 (OH), 1244 ($SiMe_3$) cm^{-1}.

A fourth yellow band was then eluted off the column with 20% diethyl ether/80% pentane to provide (1-(trimethylsilyl)-2,3-bis((trimethylsilyl)ethynyl)-4-((1-hydroxy-1-methyl)ethyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (118 mg, 0.237 mmol, 4.7% yield based on cobalt). The compound was sublimed (70–95 °C (1×10^{-3} torr)) to give yellow-orange crystals: mp 83–88 °C; *m/e* (relative intensity) 498 (M^+, 34.78), 480 (M − H_2O, 22.12), 286 (M − $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ − H_2O, 9.12), 262 (M − $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ − H_2O, 59.02), 73 (100.00); NMR (CCl_4) δ 4.84 (s, 5 H), 1.40 (b s, 3 H), 1.30 (b s, 3 H), 1.17 (b s, 1 H), 0.22 (s, 27 H); IR ($CHCl_3$) 3559 (OH, m), 2139 (C≡C), 1248 ($SiMe_3$) cm^{-1}.

The orange oil obtained from the second yellow band and tentatively identified as a mixture of bis(cyclobutadiene) isomers (378 mg, 0.442 mmol) was protodesilylated as described in the preparation of **19**.

Four yellow bands were eluted off alumina with 2–6% diethyl ether/98–94% pentane. The eluent from each of these bands was collected and the solvent evaporated. On the basis of NMR analyses, the resulting reddish orange oils appeared to be mixtures of isomers of protodesilylated bis(cyclobutadiene) complexes.

The fifth and most prominent yellow band was then eluted off the column with 10% diethyl ether/90% pentane. Evaporation of the eluent from this band gave an orange oil tentatively identified as a single diastereomer of (2-butadiynyl-2′-ethynyl-3,3′,4,4′-tetrakis(trimethylsilyl)-1:1′-bi(η^4-cyclobutadienyl))bis-((η^5-cyclopentadienyl)cobalt) (128 mg, 0.18 mmol, 7.16% yield based on $CpCo(CO)_2$). The compound was crystallized from methanol/water to yield yellow-orange crystals: mp 126–128 °C dec; *m/e* (relative intensity) 710 (M^+, 100.00), 588 (M − $Me_3SiC{\equiv}CC{\equiv}CH$, 1.83), 540 (M − $Me_3SiC{\equiv}CSiMe_3$, 24.85), 516 (M − $Me_3SiC{\equiv}CC{\equiv}C$-$SiMe_3$, 6.01); NMR ($CCl_4$) δ 4.96 (s, 5 H), 4.89 (s, 5 H), 3.18 (s, 1 H), 1.99 (s, 1 H), 0.21 (s, 9 H), 0.195 (s, 9 H), 0.11 (s, 9 H), 0.035 (s, 9 H); ^{13}C NMR (benzene-d_6, Cr(acac)$_3$/benzene-d_6 δ (relative peak height) 105.94 (1.00), 97.33 (1.32), 85.88 (1.14), 83.20 (14.73), 82.62 (1.12), 81.80 (17.13), 81.42 (3.49), 81.12 (3.26), 80.83 (2.14), 72.04 (1.19), 71.26 (1.16), 70.34 (1.14), 65.38 (1.41), 62.63 (1.08), 61.74 (1.13), 1.054 (8.70), 0.914 (7.78), 0.328 (7.96), 0.148 (6.48); IR ($CHCl_3$) 3293 (C≡CH), 2128 (C≡C), 2096 (C≡C), 1247 ($SiMe_3$) cm^{-1}.

The Reaction of (1,2-Diethynyl-η^4-cyclobutadiene)CpCo Complex 19 and $CpCo(CO)_2$ in Refluxing BTMSA. A degassed solution of **19** (109 mg, 0.296 mmol) and $CpCo(CO)_2$ (53.3 mg, 37 μL, 0.296 mmol) in BTMSA (5 mL) was reacted as in the synthesis of **13** (using BTMSA). The resulting yellowish brown oily residue was chromatographed on alumina.

A faint yellow band was eluted off the column with pentane. Evaporation of the eluent from this band provided a yellow oil identified as (1,2,3-tris(trimethylsilyl)-4-((trimethylsilyl)-ethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt[24d] (0.69 mg, 1.41 μmol, 0.48% yield based on cobalt) on the basis of its mass spectrum.

A second yellow band was then eluted off the column with 1% diethyl ether/99% pentane to afford the minor diastereomer of (3-ethynyl-2,3,2′,3′-tetrakis(trimethylsilyl)-1:1′-bi(η^4-cyclobutadienyl))bis((η^5-cyclopentadienyl)cobalt) (**53**) [9 mg, 14 μmol, 4.6% yield based on $CpCo(CO)_2$]. This compound was sublimed (120 °C (1×10^{-3} torr)) to give yellow-orange crystals: mp 110–116 °C; *m/e* (relative intensity) 662 (M^+, 46.34), 564 (M − $Me_3SiC{\equiv}CH$, 3.91), 540 (M − $Me_3SiC{\equiv}C$-C≡CH, 2.27), 492 (M − $Me_3SiC{\equiv}CSiMe_3$, 17.42), 294 (100.00); NMR (benzene-d_6/benzene-d_5 δ 4.884 (s, 5 H), 4.703 (s, 5 H), 4.536 (s, 1 H), 2.78 (s, 1 H), 0.433 (s, 9 H), 0.248 (s, 9 H), 0.212 (s, 9 H), 0.115 (s, 9 H); ^1H NMR (CCl_4) δ 4.73 (s, 10 H), 4.23 (s, 1 H), 3.03 (s, 1 H), 0.31 (s, 9 H), 0.23 (s, 18 H), 0.107 (s, 9 H); IR ($CHCl_3$) 3300 (C≡CH), 2088 (C≡C), 1243 ($SiMe_3$) cm^{-1}.

A third yellow band was then eluted off the column with 1% diethyl ether/99% pentane. Evaporation of the eluent from this band yielded a yellow oil identified as the major meso diastereomer of (2,3,3′,4′,2″,3″-hexakis(trimethylsilyl)-1:1,2′:1″-ter(η^4-cyclobutadienyl))tris((η^5-cyclopentadienyl)cobalt) (**54**) (7 mg, 7.3 μmol, 4.94% yield based on $CpCo(CO)_2$): *m/e* (relative intensity) 956 (M^+, 9.30), 786 (M − $Me_3SiC{\equiv}CSiMe_3$, 9.56), 616 (M − 2 $Me_3SiC{\equiv}CSiMe_3$, 7.93), 540 (M − CpCo − $Me_3SiC{\equiv}CC{\equiv}CH$ − $Me_3SiC{\equiv}CSiMe_3$, 100.00); NMR (CCl_4) δ 4.74 (s, 15 H), 4.33 (b

s, 2 H), 0.26 (s, 18 H), 0.20 (s, 18 H), 0.17 (s, 18 H); NMR (benzene-d_6/benzene-d_5) δ 4.89 (s, 15 H), 4.43 (b s, 2 H), 0.304 (s, 18 H), 0.255 (s, 18 H), 0.21 (s, 18 H); IR ($CHCl_3$) 1246 ($SiMe_3$) cm^{-1}.

The fourth and most prominent yellow band was then eluted off the column with 2% diethyl ether/98% pentane to provide the major diastereomer of **53** (111 mg, 0.167 mmol, 56.6% yield). This compound was sublimed (120 °C (1 × 10^{-3} torr)) to afford yellow-orange crystals: mp 138–141 °C; m/e (relative intensity) 662 (M^+, 70.61), 564 (M − $Me_3SiC{=}CH$, 2.99), 492 (M − $Me_3SiC{=}CSiMe_3$, 19.09), 294 (100.00); NMR (CCl_4) δ 4.965 (s, 5 H), 4.847 (s, 5 H), 4.053 (s, 1 H), 3.08 (s, 1 H), 0.171 (s, 9 H), 0.077 (s, 9 H), 0.040 (s, 9 H), 0.024 (s, 9 H); IR ($CHCl_3$) 3300 (C≡CH), 2088 (C≡C), 1244 ($SiMe_3$) cm^{-1}.

A faint fifth yellow band was then eluted off the column with 4% diethyl ether/96% pentane. Evaporation of the solvent yielded a yellow oil identified as the minor meso diastereomer of **54** (0.80 mg, 0.84 μmol, 0.56% yield based on $CpCo(CO)_2$): m/e (relative intensity) 956 (M^+, 19.19), 786 (M − $Me_3SiC{=}CSiMe_3$, 20.29); NMR (benzene-d_6/benzene-d_5) δ 4.927 (s, 5 H), 4.907 (s, 10 H), 4.39 (s, 2 H), 0.358 (s, 18 H), 0.228 (s, 18 H), 0.176 (s, 18 H).

A faint sixth yellow band was then eluted off the column with 4% diethyl ether/96% pentane to afford a yellow oil identified as the *d,l*-diastereomer of **54** (1.25 mg, 1.31 μmol, 0.88% yield based on $CpCo(CO)_2$): m/e (relative intensity) 956 (M^+, 69.31), 786 (M − $M_3SiC{=}CSiMe_3$, 31.29), 616 (M − $2Me_3SiC{=}CSiMe_3$, 2.60), 540 (100.00): NMR (benzene-d_6/benzene-d_5) δ 4.950 (s, 5 H), 4.933 (s, 10 H), 4.662 (s, 1 H), 4.559 (s, 1 H), 0.403 (s, 9 H), 0.257 (s, 9 H), 0.233 (s, 9 H), 0.182 (s, 9 H), 0.136 (s, 9 H), 0.053 (s, 9 H).

Five faint yellow bands were then eluted off the column with 50% pentane/50% diethyl ether. NMR and mass spectra of the resulting yellow-orange oils provided no evidence for the presence of any other materials derived from the cocyclization of **19** with BTMSA.

The Diethynylcyclobutadiene Rearrangement of 19 to (1,2-Bis((trimethylsilyl)ethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (30). With use of the general FVP procedure, freshly chromatographed **19** (38 mg, 103 μmol) was sublimed at 40–50 °C over 10.5 h through a hot (525 °C) quartz tube. The yellow-orange crystalline pyrolysate which collected inside the cold trap was then isolated as a CCl_4 (1% $SiMe_4$) solution inside an NMR tube sealed under vacuum. The NMR spectrum of this solution showed a single compound subsequently identified as **30**. After solvent had been evaporated, the resulting yellow-orange residue was chromatographed on alumina with 0.6% diethyl ether/99.4% pentane eluent to give a yellow-orange solid **30** [24 mg, 65.1 μmol, 63.1% yield based on total (sublimed and unsublimed) **19**]. Sublimation (50 °C (1 × 10^{-3} torr)) gave yellow-orange crystals: mp 62–63 °C; m/e (relative intensity) 368 (M^+, 61.59), 342 (M − HC≡CH, 1.15), 270 (M − $Me_3SiC{=}CH$, 4.87), 246 (M − $Me_3SiC{=}CC{=}CH$, 7.30), 73 (100.00); NMR (CCl_4) (180 MHz) δ 4.89 [s, 5 H; ^{13}C satellites, $J(^{13}C-H)$ = 176.6 Hz, m], 3.97 [s, 2 H; ^{13}C satellites, $J(^{13}C-H)$ = 190.7 Hz, s; $J(^{13}C-H)$ = 13.75 Hz, s; $J_{HH} \approx$ half-width of ^{13}C satellite peaks = 0.35 Hz], 0.20 (s, 18 H); ^{13}C NMR (benzene-d_6; $Cr(acac)_3$/benzene-d_6 (chemical shifts and relative peak heights taken from proton-decoupled spectrum; splitting patterns and coupling constants taken from proton-coupled spectrum)) δ 102.43 (s; 1.4), 97.69 (s; 1.3), 81.98 [d, $J(^{13}C-H)$ = 176 Hz; 4.3], 62.50 [d, $J(^{13}C-H)$ = 190 Hz; 2.0], 59.32 (s, 1.0)e, 0.336 [q, $J(^{13}C-H)$ = 123 Hz; 3.9]; IR ($CHCl_3$) 2137 (C≡C), 1248 ($SiMe_3$) cm^{-1}.

A similar FVP at 451 °C gave **30** (70.0%), unconverted **19** (30.0%), and no other compounds.

The quartz FVP tube remained clean during both pyrolyses. However, unsublimed brown oily starting material residues (30–40%) remained. ^1H NMR analysis found them to contain no **30**, very little **19**, and mostly decomposition products that were not identified.

(1,2-Diethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (9). Complex **30** (20 mg, 54.3 μmol) was protodesilylated as described in the synthesis of **19** to give a heat sensitive brownish yellow solid identified as **9**: m/e (relative intensity) 224 (M^+, 55.97), 198 (M − HC≡CH, 5.55), 174 (M − HC≡CC≡H, 5.0), 165 (100.0); NMR (CCl_4) δ 4.94 (s, 5 H), 3.98 (s, 2 H), 2.95 (s, 2 H); IR (neat) 3289 (C≡CH), 2099 (C≡C) cm^{-1}.

(1,2-Bis(deuterioethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (49). Complex **30** (40 mg, 108.5 μmol) was dissolved under nitrogen in 7 mL of a degassed 0.174 M solution of CH_3OK in CH_3OD. The resulting yellow solution was then stirred magnetically at room temperature under nitrogen for 70 min before being partitioned between D_2O (15 mL) and dry pentane (15 mL). After separation from the pentane phase, the D_2O phase was extracted with three more portions of *dry* pentane. The yellow pentane phases were combined, dried over $MgSO_4$, filtered, and evaporated (≤25 °C). The resulting **49** was found to contain the analogous d_1 compound as its only impurity: m/e (relative intensity) 226 (M^+, 65.36), 225 (M^+ for d_1 impurity, 5.33), 200 (M − HC≡CH, 4.07), 199 (M − DC≡CH, 3.81), 175 (M − DC≡CC≡CH, 4.96), 124 (100.00); NMR (CCl_4) δ 4.94 (s, 5 H), 3.99 (s, 2 H); IR ($CHCl_3$) 2581 (C≡CD), 1974 (C≡C) cm^{-1}.

FVP of (1,2-Bis(deuterioethynyl)-η^4-cyclobutadiene)CpCo (49). Complex **49** (24 mg, 106 μmol) freshly prepared from the previously described experiment was pyrolyzed at 520 °C as described in the synthesis of **30**. The brownish yellow oily solid was found to consist of an equimolar mixture of **49** and **50**: m/e (relative intensity) 226 (M^+, 67.69), 225 (M^+ for d_1 impurity, 11.30),200 (M − HC≡CH, 6.09), 199 (M − DC≡CH, 4.81), 175 (M − DC≡CC≡CH, 6.95), 59 (100.00); NMR (CCl_4) δ 4.94 (s, 5 H), 3.97 (s, 1.00 H), 2.94 (s, 1.00 H); IR ($CHCl_3$) 3300 (C≡CH), 2584 (C≡CD), 2101 (C≡CH), 1974 (C≡CD) cm^{-1}.

The pyrolysate of **49** was dissolved under nitrogen in a degassed, 0.211 M solution of KOH in absolute methanol (7 mL). The resulting yellow solution was magnetically stirred at room temperature under nitrogen for 20 min before being exposed to aqueous workup. An equimolar mixture of **50** and **9** was obtained: m/e (relative intensity) 226 (M^+ for **50**, 28.99), 225 (d_1 impurity in **50** and M + 1 peak of **9**, 6.94), 224 (M^+ for **9**, 30.21), 200 (**50** − HC≡CH, 1.91), 199 (**50** − DC≡CH, 1.91), 198 (**50** − DC≡CD, **9** − HC≡CH, 3.95), 175 (**50** − DC≡CC≡CH, 3.23), 174 (**9** − HC≡CC≡CH, 3.29), 124 (100.00); NMR (benzene-d_6/benzene-d_5) δ 4.70 (s, 5 H), 3.68 (s, 1.00 H), 2.80 (s, 2.00 H); IR ($CHCl_3$) 3300 (C≡CH, s), 2101 (C≡C) cm^{-1}.

Exact mass calcd for **50** ($C_{13}H_7D_2Co$): 226.0162. Found: 226.0159.

Exact mass calcd for **9** ($C_{13}H_9Co$): 224.0036. Found: 224.0032.

Exact mass calcd for $C_{13}H_8DCo$: 225.0099. Exact mass calcd for $^{12}C_{12}{}^{13}CH_9Co$: 225.0069. Found: 225.0086.

Diethynylcyclobutadiene Rearrangement of 19 to 30 in Refluxing Pristane. A degassed solution of freshly chromatographed **19** (94 mg, 225 μmol) in 2,6,10,14-tetramethylpentadecane (pristane, 5 mL) was added by syringe over 60 s to degassed, mechanically stirred, nitrogen-flushed (2 mL·s^{-1}), refluxing pristane (60 mL, bp 300 °C). During the addition of **19**, the reaction mixture initially turned yellow but then very suddenly turned dark yellowish brown. After the addition of **19** had been completed and while mechanical stirring and the nitrogen flush were continued, the reaction mixture was refluxed for an additional 60 s. The reaction flask was then allowed to cool in air for 75 s before the mechanically stirred reaction mixture was cooled to room temperature under nitrogen with a water bath.

The crude, unconcentrated mixture was then chromatographed on alumina. After the pristane reaction solvent had been eluted off the column with pentane, a faint yellow band was collected as elution with pentane continued. Evaporation of solvent gave a pale yellow oil (2 mg) whose NMR spectrum showed four cyclopentadienyl proton resonances (δ 4.9–4.5), aliphatic proton resonances (δ 1.7–0.8) similar to those of pristane, and a trimethylsilyl proton region (δ 0.5–0.1) consisting of four major peaks and many minor peaks. According to this spectrum, the pale yellow oil contained none of the known (η^4-1,2-bis(trimethylsilyl)benzocyclobutadiene)(η^5-cyclopentadienylcobalt).[24c] However, a mass spectrum of the crude product showed a parent ion at m/e 636 (13.54% relative intensity), which corresponds to an adduct between **19** and pristane. This might be indicative of some radical intermediates but is inconclusive.

A second yellow band was then eluted off the column with 1% diethyl ether/99% pentane. Evaporation of the eluent from this band yielded a yellow-orange crystalline residue identified as **30** (11 mg, 29.8 μmol, 11.7% yield) on the basis of its NMR and IR spectra.

A third yellow band was eluted off the column with 3% diethyl ether/97% pentane to afford an orange oily solid identified as (1-((trimethylsilyl)ethynyl)-2-ethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt (8 mg, 27 μmol, 10.6% yield): m/e (relative intensity) 296 (M^+, 47.76), 85 (100.00); NMR (CCl_4) δ 4.88 (s, 5 H), 3.96 (s, 2 H), 2.95 (s, 1 H), 0.19 (s, 9 H).

Acknowledgment. We are grateful for financial support by NIH (Grant CA-20713) and NSF (Grant CHE-79-03954) and stimulating discussions with Dr. D. M. Golden and Professors R. G. Bergman and R. J. Saykally.

Registry No. 9, 67378-04-5; **13**, 80471-04-1; **14**, 80471-05-2; **15**, 80471-06-03; **16**, 18823-04-6; **17**, 18765-46-3; **18**, 80471-03-0; **19**, 67378-02-3; **20**, 67378-01-2; **21**, 77347-34-3; **22**, 69991-02-2; **23**, 80471-02-9; **24**, 80471-16-5; **25**, 80471-17-6; **26**, 80471-01-8; **27**, 80471-18-7; **28**, 80471-19-8; **29**, 80471-20-1; **30**, 67378-03-4; **49**, 80470-99-1; **50**, 80471-00-7; **53** isomer 1, 80470-98-0; **53** isomer 2, 80513-56-0; **54** isomer 1, 80470-97-9; **54** isomer 2, 80513-54-8; **54** isomer 3, 80513-55-9; bis(trimethylsilyl)butadiyne, 4526-07-2; 1,2,4,5-tetraethylbenzene, 635-81-4; 1,6-dichlorohexa-2,4-diyne, 16260-59-6; bis(trimethylsilyl)hexatriyne, 21751-86-3; (1,2,3-tris(trimethylsilyl)-4-((1-hydroxy-1-methyl)ethyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt, 80485-79-6; (1-(trimethylsilyl)-2,3-bis(trimethylsilyl)etnynyl)-4-((1-hydroxy-1-methyl)ethyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt, 80471-55-2; (2-butadiynyl-2′-ethynyl-3,3′,4,4′-tetrakis(trimethylsilyl)-1:1′-bi(η^4-cyclobutadienyl))bis((η^5-cyclopentadienyl)cobalt), 80471-56-3; (1,2,3-tris(trimethylsilyl)-4-((trimethylsilyl)ethynyl)-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt, 70657-45-3; (1-((trimethylsilyl)ethynyl)-2-ethynyl-η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt, 80470-96-8; $CpCo(CO)_2$, 12078-25-0.

Supplementary Material Available: Listing of complete low- and high-resolution mass and infrared spectral data as well as elemental analysis values for 22 compounds (16 pages). Ordering information is given on any current masthead page.

Photochemistry of Alkyldicarbonyl(η^5-cyclopentadienyl)iron and -ruthenium. Ligand Substitution and Alkene Elimination via Photogenerated 16-Valence-Electron Intermediates

Romas J. Kazlauskas and Mark S. Wrighton*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received October 9, 1981

Photoreaction of (η^5-C_5H_5)M(CO)$_2$R (M = Fe, Ru; R = CH_3, C_2H_5, n-C_5H_{11}) and (η^5-C_5Me_5)Fe(CO)$_2C_2H_5$ involves dissociative loss of CO as the primary photoprocess following near-UV excitation. The quantum yield for photosubstitution of (η^5-C_5H_5)M(CO)$_2CH_3$ is independent of the incoming ligand or its concentration (above 10^{-3} M); the quantum yield is 0.4 ± 0.05 for M = Ru and 0.7 ± 0.03 for M = Fe. All of the complexes for R having β-hydrogens yield the analogous (η^5-$C_5R'_5$)M(CO)$_2$H (R′ = H, Me) complexes upon near-UV irradiation at 298 K in fluid, alkane solution. For the (η^5-C_5H_5)Fe(CO)$_2C_2H_5$ complex the photochemical formation of the hydride occurs even at 77 K in alkane matrices, and there are no infrared detectable intermediates at an extent conversion of <5%. Irradiation of (η^5-C_5H_5)Ru(CO)$_2C_2H_5$ yields photoreaction at 77 K, initially giving infrared spectral changes consistent with the formation of (η^5-C_5H_5)Ru(CO)(C_2H_4)(H) followed by spectral changes consistent with the formation of the (η^5-C_5H_5)Ru(CO)$_2$H. Likewise in rigid (paraffin) media at 298 K, initial spectral changes accompanying near-UV irradiation of (η^5-C_5H_5)Ru(CO)$_2C_2H_5$ are consistent with the formation of the ethylene–hydride complex. At 298 K, high concentrations of PPh_3 suppress the formation of iron–hydride products from irradiation of (η^5-C_5H_5)Fe(CO)$_2C_2H_5$ in a manner consistent with the intermediacy of (η^5-C_5H_5)Fe(CO)C_2H_5 from the dissociative loss of CO from the starting dicarbonyl. For the (η^5-C_5H_5)Ru(CO)$_2CH_3$, irradiation at 77 K in an alkane matrix yields infrared spectral changes consistent with the formation of (η^5-C_5H_5)Ru(CO)CH_3, providing direct evidence for the photogeneration of a 16-valence-electron intermediate. The rate of β-hydrogen transfer for the Fe species created by light is estimated to be >3 × 10^2 s^{-1} at 298 K, and 77 K data suggest that the activation energy for β-hydrogen transfer from photogenerated intermediates is less than ~6 kcal/mol for both the Fe and Ru complexes.

The lowest excited state of many mononuclear transition element complexes undergoes decay by a ligand dissociation process.[1] In some cases the excited-state ligand dissociation has a very low thermal activation energy that allows the generation of coordinatively unsaturated species at low temperature.[2] We have recently exploited photochemistry of this sort to generate the 16-valence-electron alkyl complex (η^5-C_5H_5)W(CO)$_2$(n-pentyl) by extrusion of CO from the 18-valence-electron (η^5-C_5H_5)W(CO)$_3$(n-pentyl).[3] The low-temperature generation of the 16-electron species allowed us to spectroscopically monitor its thermal reaction (eq 1). The principle is that photolysis

$$(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl}) \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})(H) \quad (1)$$

may allow the generation and characterization of species that would be thermally unstable at temperatures where it would ordinarily be thermally accessible. For example, thermal routes to (η^5-C_5H_5)W(CO)$_2$(n-pentyl) would likely involve more activation energy than does the β-hydrogen-transfer process represented by eq 1. Generally, using light to change the rate-limiting step in a reaction sequence may have consequence with respect to possible reaction products and can provide insight into reaction mechanisms.

Our follow-up studies of the (η^5-C_5H_5)W(CO)$_3$(n-pentyl) and related complexes have confirmed that the alkene hydride product is the trans isomer,[3,4] and this may ac-

(1) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.
(2) Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakoff, M. *Pure Appl. Chem.* **1977**, *49*, 271.
(3) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1727.

0276-7333/82/2301-0602$01.25/0 © 1982 American Chemical Society