

of up to 72° could explain the NMR spectrum of IV. The crystal structure of III, however, reveals that the compound with three pentamethylene bridges is eclipsed. The measured twist angle is 0.7 (1)°. Thus, the length of the bridge is not the major determinant for staggering or eclipsing the cyclopentadienyl rings.

The feature that appears to be the driving force is the arrangement of the protons of the bridges. It is apparent from models that an eclipsed conformation of the rings for a molecule containing a tetramethylene bridge forces the proton on the bridge to be eclipsed with resulting short hydrogen-hydrogen distances. This is relieved by twisting the rings by the 12-14° observed in I and II. On the other hand, twisting of the rings in a compound containing a pentamethylene bridge forces the protons on the bridge to have a much higher probability of interaction than when the rings are eclipsed. With eclipsed rings, there are several possible conformations for a pentamethylene bridge. From models it can be seen that the conformation that gives the least eclipsing of the bridge protons is the one used by all of the bridges in III. The repulsion of the γ -proton by the iron is more easily alleviated by enlarging the bond angles.

While extrapolating from crystal structures to phenomena in solution is dangerous, an intramolecular interaction

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would be common to both. Conformations that avoid eclipsing of protons are expected to occur in solutions as well as in crystals. Thus, there is a high likelihood that the predominant pentamethylene conformation in solution is the same as observed in the crystal structure of III. In the case of V, however, the ease of conversion of this conformation to others is indicated by the rapid flipping observed in the NMR spectrum of V.

It is possible that the staggered conformation of the rings that is observed in tetramethylene-bridged ferrocenes is a source of the anomalous arrangement of the ring-proton peaks in the NMR spectra of bridged ferrocenes. Additional evidence is required.

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Supplementary Material Available: Tables of anisotropic thermal parameters and structure factors for $\text{FeC}_{18}\text{H}_{22}$, $\text{FeC}_{22}\text{H}_{28}$, and $\text{FeC}_{25}\text{H}_{34}$ and isotropic thermal parameters for $\text{FeC}_{25}\text{H}_{34}$ (51 pages). Ordering information is given on any current masthead page.

Thermally Induced Diastereoisomerization of (Cyclobutadiene)cobalt Complexes as a Probe for the Reversibility of Their Formation from Complexed Alkynes

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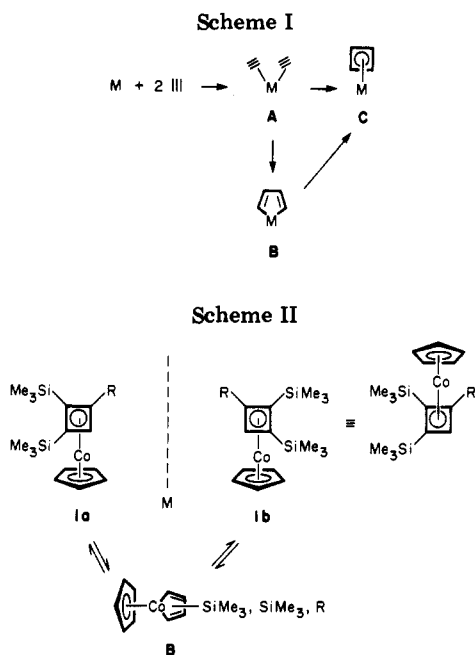
The synthesis and separation of a series of racemic diastereomers 2-5 of formula $\text{Co}[\eta^4\text{-C}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)\text{CHCCHMeR}](\eta\text{-C}_5\text{H}_5)$ by cocyclization of $\text{Co}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$, $\text{Me}_3\text{SiC}_2\text{SiMe}_3$ (btmse), and HC_2CHMeR are described. Gas- and solution-phase pyrolyses for both diastereomers of $\text{Co}[\eta^4\text{-C}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)\text{CHCCHMePh}](\eta\text{-C}_5\text{H}_5)$ (5) reveal extensive mutual interconversion. A crossover experiment demonstrates the unimolecular character of this reaction and studies on enantiomerically enriched $\text{Co}[\eta^4\text{-C}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)\text{CHCCHMeOH}](\eta\text{-C}_5\text{H}_5)$ (2) show that the cobalt unit is the site of diastereoisomerization rather than the alternative carbon chiral center. During gas-phase pyrolysis of 5 small amounts of the geometrical isomer $\text{Co}[\eta^4\text{-C}(\text{SiMe}_3)\text{CHC}(\text{SiMe}_3)\text{CCHMePh}](\eta\text{-C}_5\text{H}_5)$ (12) are formed. Similarly, gas-phase pyrolysis of 12 results in a small extent of positional isomerization to both diastereomers of 5. Heating one diastereomer of 26, i.e., $\text{Co}[\eta^4\text{-C}(\text{SiMe}_3)\text{C}(\text{SiEt}_3)\text{CHCCHMePh}](\eta\text{-C}_5\text{H}_5)$ (26a), results in one diastereomer of 27, $\text{Co}[\eta^4\text{-C}(\text{SiEt}_3)\text{C}(\text{SiMe}_3)\text{CHCCHMePh}](\eta\text{-C}_5\text{H}_5)$ (27b), but none of 26b. An experiment utilizing the 1,2-¹³C-labeled cyclobutadiene 26a results only in 1,3-¹³C-labeled 27b. The results are best interpreted by assuming that the cyclobutadiene rings open directly to bis(alkyne)cobalt species without the intermediacy of cobaltcyclopentadiene intermediates. Alternative rationales are discussed.

Introduction

By what mechanisms are metal cyclobutadiene complexes formed from alkynes? To what extent are such transformations reversible? This paper addresses these questions for cyclopentadienylcobalt chemistry.²

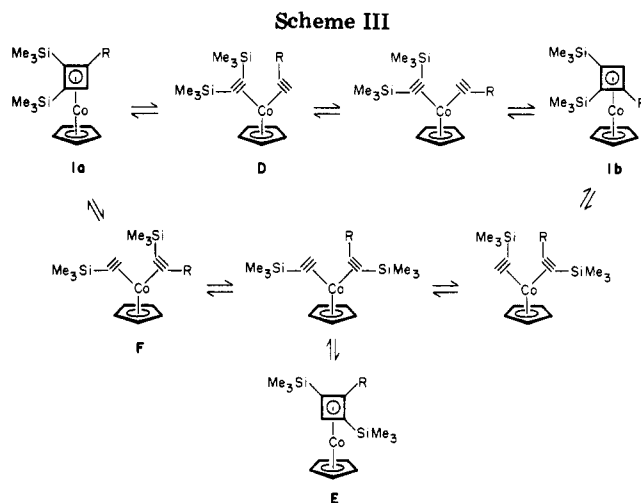
Interactions of transition-metal compounds with alkynes lead to many types of complexes. Among them those

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bearing cyclobutadiene ligands are common,³ although their formation is unpredictable.⁴ An unambiguous mechanism for their mode of formation under these conditions has never been established (indeed, there is no requirement for a common mechanism). Two frequently invoked pathways are illustrated in Scheme I. The first ($A \rightarrow C$) may be regarded as a concerted $(2 + 2)\pi$ cycloaddition reaction taking place within the coordination sphere of the metal. The process is postulated as being unfavorable on theoretical grounds when occurring within the vicinity of a single metal center although this restriction is lifted in the presence of two metals.^{5,6} Perhaps the more accepted mechanism is the process ($A \rightarrow B \rightarrow C$) comprising oxidative coupling of the two complexed alkynes followed by valence tautomerization of the resulting metallacyclopentadiene to the observed metal cyclobutadiene complex.^{3-5,7}

The species in Scheme I are relevant to other transformations. Thus, metallacyclopentadienes of type B are significant since they are regarded as intermediates in cyclotrimerization pathways of alkynes to arenes.⁸ Cyclobutadiene complexes have been suggested on occasion to be transients in cyclooctatetraene formation from alkynes,^{3,9} are held responsible for the catalyst death in some



catalytic cyclotrimerization reactions¹⁰ and thought possible as intermediates in alkyne metathesis.¹¹

Precedent exists for the conversion of metallacyclopentadienes B to give C,¹² even though the reaction appears to be forbidden on symmetry grounds.¹³ The direct transition of a bis(alkyne) complex of type A to cyclobutadiene C has also been observed.¹⁴ Finally, both the $A \rightarrow C^{11a}$ and $B \rightarrow C^{15}$ interconversions appear to be reversible, although mechanistic information is virtually nonexistent. Does the former pass through the intermediacy of B or the latter through A?

This work examines the potential equilibration of the structural types A, B, and C for $(\eta^5\text{-cyclopentadienyl})\text{cobalt}(\text{CpCo})$ systems.

Basic Strategic Considerations. We start with the realization (Scheme II) that cyclobutadiene complexes of type 1 exist as enantiomers related by the mirror plane M. Oxidative insertion of the CpCo fragment into the four-membered ring would lead to a cobaltacyclopentadiene B. Reformation of the cyclobutadiene complex may then proceed to either enantiomer, according to which side of the four-carbon fragment the CpCo unit migrates. Such a route therefore provides a path for racemization at the metal center.

Alternative racemization pathways also exist for the direct retrocyclization pathway ($C \rightarrow A$) through alkyne rotations (Scheme III) which also provides for the possibility of formation of an alternative isomer E.

If the substituent R is chosen to be chiral, the relationship between the pair 1a, 1b is diastereomeric. Each

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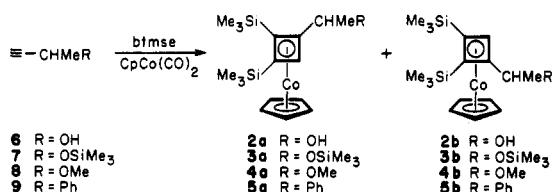
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diastereomer should be separable from the other by conventional techniques and distinguishable by virtue of its differing spectroscopic properties. Provided that R is configurationally stable, inversion at the chiral cobalt center results in diastereoisomerization of the molecule if any of the processes depicted in Schemes II and III operate.

Results and Discussion

Preparation and Separation of Complexes. Reasonable yields of the diastereomers 2–5 were obtained by addition of a mixture of bis(trimethylsilyl)ethyne (btmse) and equimolar quantities of the appropriate alkyne 6–9



and CpCo(CO)₂ to boiling btmse at approximate rates of 0.02 mmol h⁻¹. Although it was not necessary to take strenuous precautions concerning the dryness of glassware, admission of any air caused losses in yield while prerinising the glassware with hexamethyldisilazane resulted in increased yields and cleaner product mixtures. Interestingly, use of the alcohol 6 gave mixtures of 2a and 2b together with quantities of the silyl ethers 3a and 3b when using nonsilylated glassware. Conversely, some hydrolysis occurred when employing the silyl ether 7 which again furnished a mixture of 2a, 2b, 3a, and 3b. In the cases of 6–8 the products were separable by conventional chromatography on alumina. However, to separate 5, high performance liquid chromatography (HPLC) was required. No attempts were made to assign relative stereochemistries. The a series of complexes corresponds to the higher R_f and series b to the lower R_f isomers on chromatography on alumina (2, 3, and 4) and HPLC (5). In all cases the diastereomers are readily distinguishable by their diagnostic ¹H NMR spectra (for the ¹H NMR spectra of these and other complexes see Table I). They are all yellow oils or relatively low melting solids, mildly air sensitive in solution.

Interconversion of the Diastereomers. Two sets of reaction conditions were employed. The first involved flash vacuum pyrolyses,¹⁶ the second solution thermolyses. The former employed very short contact times (ca. 5 ms at 10⁻⁵ torr) within the temperature range 540–650 °C. The solution experiments simply involved monitoring a hot dilute solution in a high boiling solvent such as pristane or triglyme. In all cases most consistent results were obtained by using silylated glassware.

Flash vacuum pyrolysis of 2b at 520 °C led largely to recovery of starting material in addition to a new compound. Two signals in the ¹H NMR spectrum with an intensity ratio of 15:85 were assignable to the respective cyclopentadienyl groups of 2a and 2b, respectively. No decomposition was apparent.

The ¹H NMR spectrum of the reaction mixture after a similar pyrolysis at 582 °C was more complex. Of the four signals assignable to cyclopentadienyl groups those for 2a and 2b were the most intense (2a/2b, 46:54). However, two other compounds were present in the mixture. Chromatography on alumina resulted in the separation of

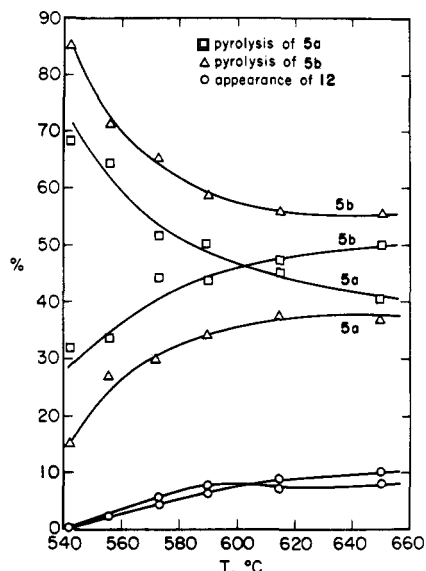
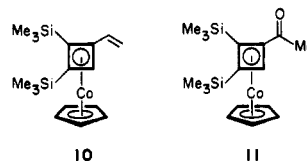


Figure 1. Results of the flash vacuum pyrolyses of diastereomers 5a (□) and 5b (Δ). Percentages of the isomers are derived from Table III and IV.

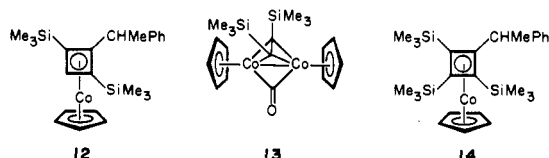
four cyclobutadiene complexes characterized respectively as 10, 11, 2a, and 2b. Complexes 10 and 11 could be formed by dehydration and dehydrogenation, respectively, of 2b.

Pyrolysis of the other diastereomer 2a at 560 °C gave a similar mixture (2a/2b, 66:34). Because the formation of 10 and 11 in these experiments complicated the analysis



of the results, alternative systems 3 and 4 were investigated, in which the hydroxy group had been protected. Both sets of compounds also underwent extensive equilibration in the temperature range 543–581 °C, as exemplified by the results in Table II for 4a,b. In all runs a certain amount of decomposition was observed, indicated by the formation of a cobalt mirror within the pyrolysis tube and the isolation of free alkynes derived by retrocyclization of the four-membered ring.^{11a} Small amounts of a new uncharacterized organometallic complex were also formed, very likely the 1,3-bis(silyl) isomer of 4 (vide infra).

Work with these systems was terminated because they were also unsuitable for solution studies (vide infra), and our attention turned to 5 in which the apparently troublesome oxygen function was not present. Again extensive diastereoisomerization was the result when either 5a or 5b was subjected to flash vacuum pyrolysis in the temperature range of 542–650 °C (Tables III and IV; Figure 1). At higher temperatures small quantities were found of a third organometallic species which, based on spectroscopic data, was assigned the structure of a geometrical isomer of 5, the 1,3-bis(trimethylsilyl) complex 12. A chemical



structure proof was obtained by an independent synthesis, as follows. Cyclization of 1-(trimethylsilyl)-3-phenylbut-

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Table I. ¹H NMR Data (90 MHz) for the New Complexes (δ from Me₄Si, J in Hz)

complex	solvent	C ₃ H ₄ R'	SiMe ₃	cyclobutadiene	CHMeR	CHMeR	CHMeR (and other)
2a	C ₆ D ₆	4.86 (s, 5 H)	0.22 (s, 9 H) 0.16 (s, 9 H)	4.26 (s, 1 H)	4.03 (m, 1 H)	1.26 (d, 3 H, $J = 7$)	1.61 (d, 1 H, $J = 5$)
2b	C ₆ D ₆	4.75 (s, 5 H)	0.45 (s, 9 H) 0.23 (s, 9 H)	4.26 (s, 1 H)	4.16 (q, 1 H, $J = 6$)	1.25 (d, 3 H, $J = 6$)	1.12 (d, 1 H, $J = 6$)
3a	C ₆ D ₆	4.93 (s, 5 H)	0.29 (s, 18 H)	4.33 (s, 1 H)	4.23 (q, 1 H, $J = 7$)	1.37 (d, 3 H, $J = 7$)	0.36 (s, 9 H) ^a
3b	C ₆ D ₆	4.79 (s, 5 H)	0.30 (s, 9 H) 0.27 (s, 9 H)	4.30 (s, 1 H)	4.45 (q, 1 H, $J = 7$)	1.37 (d, 3 H, $J = 7$)	0.41 (s, 9 H) ^a
4a	C ₆ D ₆	4.95 (s, 5 H)	0.33 (s, 9 H) 0.25 (s, 9 H)	4.26 (s, 1 H)	3.53 (q, 1 H, $J = 7$)	1.22 (d, 3 H, $J = 7$)	3.17 (s, 3 H)
4b	C ₆ D ₆	4.80 (s, 5 H)	0.36 (s, 9 H) 0.24 (s, 9 H)	4.33 (s, 1 H)	3.95 (q, 1 H, $J = 7$)	1.25 (d, 3 H, $J = 7$)	3.22 (s, 3 H)
5a	CD ₂ Cl ₂	4.94 (s, 5 H)	0.20 (s, 9 H) -0.05 (s, 9 H)	4.49 (s, 1 H)	3.42 (q, 1 H, $J = 7$)	1.35 (d, 3 H, $J = 7$)	7.19 (m, 5 H)
5a	C ₆ D ₆	4.87 (s, 5 H)	0.27 (s, 9 H) 0.08 (s, 9 H)	4.44 (s, 1 H)	3.40 (q, 1 H, $J = 1$)	1.32 (d, 3 H, $J = 7$)	
5b	CD ₂ Cl ₂	4.58 (s, 5 H)	0.29 (s, 9 H) 0.17 (s, 9 H)	4.06 (s, 1 H)	3.28 (q, 1 H, $J = 7$)	1.64 (d, 3 H, $J = 7$)	7.26 (m, 5 H)
5b	C ₆ D ₆	4.63 (s, 5 H)	0.38 (s, 9 H) 0.25 (s, 9 H)	4.18 (s, 1 H)	3.31 (q, 1 H, $J = 7$)	1.47 (d, 3 H, $J = 7$)	
10	C ₆ D ₆	4.81 (s, 5 H)	0.32 (s, 9 H) 0.24 (s, 9 H)	4.60 (s, 1 H)			6.20 (dd, 1 H, $J = 17, 11$) ^b 5.25 (dd, 1 H, $J = 17, 2$) ^b 5.07 (dd, 1 H, $J = 11, 2$) ^b 1.85 (s, 3 H) ^c
11	C ₆ D ₆	4.71 (s, 5 H)	0.48 (s, 9 H) 0.19 (s, 9 H)	4.44 (s, 1 H)			7.19 (m, 5 H)
12	CD ₂ Cl ₂	4.87 (s, 5 H)	0.20 (s, 9 H) -0.14 (s, 9 H)	4.02 (s, 1 H)	3.39 (q, 1 H, $J = 7$)	1.37 (d, 3 H, $J = 7$)	
12	C ₆ D ₆	4.87 (s, 5 H)	0.33 (s, 9 H) 0.24 (s, 9 H)	4.12 (s, 1 H)	3.46 (q, 1 H, $J = 7$)	1.46 (d, 3 H, $J = 7$)	
14	CD ₂ Cl ₂	4.92 (s, 5 H)	0.22 (s, 9 H) 0.19 (s, 9 H)		3.44 (q, 1 H, $J = 7$)	1.43 (d, 3 H, $J = 7$)	7.14 (m, 5 H)
14	C ₆ D ₆	4.94 (s, 5 H)	-0.02 (s, 9 H) 0.40 (s, 9 H)		3.52 (q, 1 H, $J = 7$)	1.50 (d, 3 H, $J = 7$)	
17a	CD ₂ Cl ₂	4.88 (s, 5 H)	0.20 (s, 9 H) 0.13 (s, 9 H) -0.13 (s, 9 H)	4.42 (s, 1 H)	3.05 (dd, 1 H, $J = 10, 3$)		7.12 (m, 5 H) 1.95 (m, 2 H) ^d 0.79 (t, 3 H, $J = 8$) ^d 2.03 (m, 2 H) ^d 0.97 (m, 3 H) ^d 7.25 (m, 5 H) 1.80 (quin, 2 H, $J = 8$) ^d 0.80 (t, 3 H, $J = 7$) ^d 1.90 (m, 2 H) ^d 0.93 (m, 3 H) ^d 7.14 (m, 5 H)
17a	C ₆ D ₆	4.91 (s, 5 H)	0.32 (s, 9 H) 0.12 (s, 9 H)	4.47 (s, 1 H)	3.16 (dd, 1 H, $J = 10, 4$)		
17b	CD ₂ Cl ₂	4.48 (s, 5 H)	0.26 (s, 9 H) 0.14 (s, 9 H)	4.07 (s, 1 H)	2.93 (q, 1 H, $J = 8$)		
17b	C ₆ D ₆	4.59 (s, 5 H)	0.44 (s, 9 H) 0.31 (s, 9 H)	4.20 (s, 1 H)	3.02 (dd, 1 H, $J = 9, 6$)		
18a	CD ₂ Cl ₂	4.77 (m, 4 H) 2.11 (s, 3 H)	0.13 (s, 9 H) -0.13 (s, 9 H)	4.24 (s, 1 H)	3.29 (q, 1 H, $J = 7$)	1.29 (d, 3 H, $J = 7$)	
18a	C ₆ D ₆	4.76 (m, 4 H) 2.12 (s, 3 H)	0.34 (s, 9 H) 0.13 (s, 9 H)	4.30 (s, 1 H)	3.38 (q, 1 H, $J = 7$)	1.37 (d, 3 H, $J = 7$)	
18b	CD ₂ Cl ₂	4.50 (m, 3 H) 4.16 (m, 1 H) 1.66 (s, 3 H)	0.23 (s, 9 H) 0.13 (s, 9 H)	3.79 (s, 1 H)	3.23 (q, 1 H, $J = 7$)	1.40 (d, 3 H, $J = 7$)	7.22 (m, 5 H)

18b	C ₆ D ₆	4.68 (m, 3 H) 4.34 (m, 1 H) 1.78 (s, 3 H) 4.95 (s, 5 H)	0.44 (s, 9 H) 0.34 (s, 9 H) 0.51 (s, 9 H) 0.23 (s, 9 H) 0.16 (s, 9 H)	3.98 (s, 1 H) 4.95 (s, 1 H) 4.62 (s, 2 H)	3.32 (q, 1 H, J = 7)	1.52 (d, 3 H, J = 7)	2.23 (m, 2 H) ^e 1.51 (m, 3 H) ^e 0.98 (m, 14 H) ^e 2.21 (m, 2 H) ^e 1.50 (m, 3 H) ^e 1.00 (m, 14 H) ^e 10.6 (bs, 1 H) ^f 3.47 (s, 3 H) ^g
21	C ₆ D ₆	4.68 (m, 3 H) 4.34 (m, 1 H) 1.78 (s, 3 H) 4.95 (s, 5 H)	0.44 (s, 9 H) 0.34 (s, 9 H) 0.51 (s, 9 H) 0.23 (s, 9 H) 0.16 (s, 9 H)	3.98 (s, 1 H) 4.95 (s, 1 H) 4.62 (s, 2 H)	3.32 (q, 1 H, J = 7)	1.52 (d, 3 H, J = 7)	2.23 (m, 2 H) ^e 1.51 (m, 3 H) ^e 0.98 (m, 14 H) ^e 2.21 (m, 2 H) ^e 1.50 (m, 3 H) ^e 1.00 (m, 14 H) ^e 10.6 (bs, 1 H) ^f 3.47 (s, 3 H) ^g
22	C ₆ D ₆	4.68 (m, 3 H) 4.34 (m, 1 H) 1.78 (s, 3 H) 4.95 (s, 5 H)	0.44 (s, 9 H) 0.34 (s, 9 H) 0.51 (s, 9 H) 0.23 (s, 9 H) 0.16 (s, 9 H)	3.98 (s, 1 H) 4.95 (s, 1 H) 4.62 (s, 2 H)	3.32 (q, 1 H, J = 7)	1.52 (d, 3 H, J = 7)	2.23 (m, 2 H) ^e 1.51 (m, 3 H) ^e 0.98 (m, 14 H) ^e 2.21 (m, 2 H) ^e 1.50 (m, 3 H) ^e 1.00 (m, 14 H) ^e 10.6 (bs, 1 H) ^f 3.47 (s, 3 H) ^g
23	CS ₂	4.87 (s, 5 H)	0.24 (s, 9 H) 0.15 (s, 9 H)	4.73 (s, 1 H)	3.30 (q, 1 H, J = 7)	1.49 (d, 3 H, J = 7)	1.15 (t, 9 H, J = 7) ^h 0.75 (q, 6 H, J = 7) ^h
24	C ₆ D ₆	4.84 (s, 5 H)	0.44 (s, 9 H) 0.17 (s, 9 H)	4.84 (s, 1 H)	3.41 (q, 1 H, J = 7)	1.33 (d, 3 H, J = 7)	1.17 (t, 9 H, J = 7) ^h 0.76 (q, 6 H, J = 7) ^h
26a	C ₆ D ₆	4.63 (s, 5 H)	0.49 (s, 9 H)	4.20 (s, 1 H)	3.26 (q, 1 H, J = 7)	1.52 (d, 3 H, J = 7)	1.23 (t, 9 H, J = 7) ^h 0.85 (q, 6 H, J = 7) ^h
26b	C ₆ D ₆	4.93 (s, 5 H)	0.49 (s, 9 H)	4.48 (s, 1 H)	3.37 (q, 1 H, J = 7)	1.33 (d, 3 H, J = 7)	1.11 (t, 9 H, J = 7) ^h 0.69 (q, 6 H, J = 7) ^h
27a	C ₆ D ₆	4.60 (s, 5 H)	0.25 (s, 9 H)	4.23 (s, 1 H)			
27b	C ₆ D ₆	4.92 (s, 5 H)	0.39 (s, 9 H)	4.49 (s, 1 H)			

^a Tentative assignment. ^b Vinyl substituent. ^c Acetyl substituent. ^d Ethyl substituent. ^e Methyl substituent. ^f Acid proton. ^g Ester methyl. ^h Triethylsilyl substituent.

Table II. Results of the Gas-Phase Pyrolyses of Diastereomers 4a and 4b

compd pyrolyzed	temp, °C	4a/4b	4a/4b/unknown	% retrocyclizatn
4a	543	77:23	77:22:1	9
4a	563	64:36	62:35:3	26
4a	582	56:44	52:41:7	39
4b	563	22:78	21:77:2	17
4b	581	36:64	34:60:6	44

Table III. Relative Yields of the Organometallic Products Formed in the Pyrolyses of 5a, 5b, and 12

temp, °C	products ^a			ratio 5a/5b	% retrocyclizatn
	5a	5b	12		
Pyrolysis of 5b					
542	31.6	68.4	0	31.6:68.4	22.8
556	33.5	64.6	2.0	34.1:65.9	21.6
573	44.0	51.5	4.5	46.1:53.9	34.6
589	43.7	50.0	6.3	46.6:53.4	48.6
615	46.2	45.1	8.7	50.6:49.4	56.4
650	50.0	40.0	10.0	55.6:44.4	80.3
Pyrolysis of 5a					
542	85.3	14.7	0	85.3:14.7	7.6
556	71.2	26.7	2.1	72.7:27.3	27.0
572	65.2	29.5	5.4	68.9:31.2	32.0
589	58.7	33.8	7.5	63.5:36.5	57.5
615	55.9	37.1	7.0	60.1:39.9	54.1
650	55.5	36.5	8.0	60.3:39.7	80.5
Pyrolysis of 12					
589	4.5	3.0	92.5		

^a Values were obtained from the relative heights of the respective cyclopentadienyl signals in the ¹H NMR spectrum, summed to 100%.

1-yne with btmse and CpCo(CO)₂ furnished a complex mixture. The major component was the known alkyne-bridged complex 13.¹⁷ One of the minor components (5.5%) was the tris(trimethylsilyl) complex 14 (Table I). Interestingly (and fortunately), protodesilylation of 14 proceeded *selectively* to give complex 12 in good yield (Table I).

In addition to 12, the four alkynes derived from retrocyclization formed in increasing amounts at higher temperatures. The yields of (trimethylsilyl)ethyne were somewhat erratic, due to its oligomerization in the NMR tube upon standing. Analysis by GC-MS revealed the presence of two isomers of the phenylalkynes (*m/e* 130 and 202) believed to be the corresponding allenes. Only 20% of the cobalt was recovered in the form of its cyclobutadiene complexes after pyrolysis at 650 °C. The cyclopentadienyl ligand from decomposed material emerged as cyclopentadiene and dihydrofulvalene, although the latter rapidly polymerized on standing in the product solutions.^{11a} Inspection of the data allows the extrapolation of the apparent equilibrium concentrations of 5a and 5b (58:42), although this number (which was used later in kinetic runs) may be slightly inaccurate if 5a and 5b decompose at somewhat different rates.

Pyrolysis of a sample of 12 at 589 °C rules out the possibility that the rather low observed quantities of the isomer 12 were of thermodynamic (electronic?) origin. This experiment gave small quantities of 5a and 5b [12/(5a + 5b) = 92.5:7.5], the extent of isomerization to the diastereomeric pairs 5a and 5b being rather similar to that of 12 upon pyrolysis of either 5a or 5b under the same

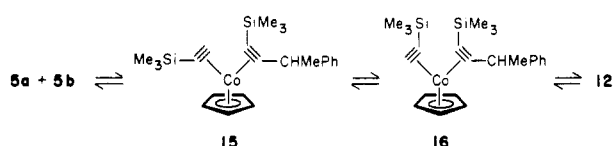
(17) Sakurai, H.; Hayashi, J. *J. Organomet. Chem.* 1972, 39, 365; 1974, 70, 85.

Table IV. Complete Results of the Pyrolyses of 5a and 5b^a

starting material	temp, °C	products			Me ₃ SiCCH	Me ₃ SiCCSiMe ₃	PhCHMeCCH	m/e 130	PhCHMeCCSiMe ₃	m/e 202
		5b	5a	12						
5b	542	62.0	28.6	0.0	5.4	2.6	2.1	0.6	6.5	0.2
5b	556	54.1	28.0	1.7	9.0	4.5	3.5	0.6	11.4	0.4
5b	573	38.8	33.1	3.3	20.0	7.9	7.1	1.8	14.4	1.4
5b	589	25.7	22.5	3.2	9.2	9.1	10.9	4.2	32.0	2.5
5b	615	18.0	18.3	3.5	17.6	18.4	13.2	5.6	37.0	4.8
5b	650	8.2	10.1	2.1	21.3	24.7	16.2	7.8	47.6	7.3
5a	542	13.9	80.3	0.0	3.4	1.4	1.2	~0	4.4	~0
5a	556	22.9	61.0	1.8	10.9	4.2	3.0	0.6	9.6	0.6
5a	572	19.1	42.2	3.5	9.6	8.4	7.3	2.7	23.1	2.2
5a	589	12.5	21.7	2.8	7.8	13.6	12.2	5.7	39.8	5.3
5a	615	17.7	27.0	3.3	22.5	16.1	10.7	4.6	31.0	4.7
5a	650	7.2	9.1	1.6	27.6	24.5	15.1	6.2	48.8	6.9

^a Yields were normalized to 100% for purposes of comparison. The experimental yields of the organic products were obtained by comparison to integrated GC signals for known quantities of dioxane as internal standard and those for the respective organic compounds. The yields of organometallic compounds were measured by comparison of the dioxane reference in the ¹H NMR spectrum with the respective cyclopentadienyl signals. In all cases the mass balances were excellent (quantitative within estimated error margins).

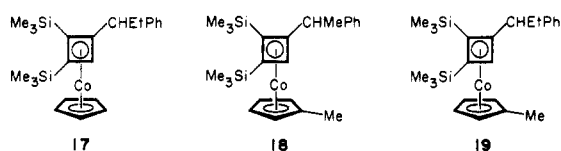
Scheme IV



conditions [(5a + 5b)/12 = 93.7:6.3 and 92.5:7.5 for 5b and 5a, respectively]. Assuming for the moment the intermediacy of bis(alkyne) complexes 15 and 16 (Scheme IV) in this isomerization, these results may indicate a high alkyne rotational barrier for interconversion of 15 and 16, a relatively facile decomplexation from 15 and 16 to provide free alkynes, or the kinetic inaccessibility of 15 and 16 from 5a,b and 12, respectively, at 589 °C under the flash vacuum pyrolysis conditions.

Molecularity of Diastereoisomerization. So far in our discussion we have formulated only intramolecular pathways. Confidence in the exclusive occurrence of the latter rested on the likelihood that bimolecular reactions were unlikely under the vacuum conditions employed.¹⁶ A crossover experiment involving the joint pyrolysis of 17 and 18 indicated that this expectation was justified. These compounds were chosen to maximize molecular similarity and ensure near equal volatility.

Complexes 17 and 18 were prepared by cyclization of the appropriate alkynes with CpCo(CO)₂ and (η⁵-C₅H₄Me)Co(CO)₂, respectively, and the diastereomers



separated by HPLC in a manner similar to that employed in the separation of 5a from 5b. Both 17b and 18a when pyrolyzed independently at 589 °C underwent diastereoisomerization (Table V). Copyrolysis of 17b and 18a under the same conditions gave a mixture of the complexes 17a,b and 18a,b (Table V), but none of the crossover products 5 and 19 as determined by NMR and, more accurately, GC-MS. Thus, the isomerization clearly proceeds in an intramolecular fashion under these conditions.

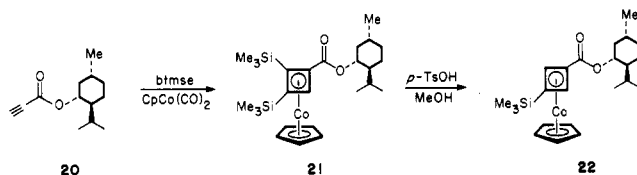
Which Chiral Center Is Inverting? We have until now tacitly assumed that inversion of the chiral cobalt center is responsible for the isomerization of the diastereomeric cyclobutadiene complexes. It is also possible that this transformation occurs through inversion at the ap-

Table V. Results of the Pyrolysis of Complexes 17b and 18a at 589 °C

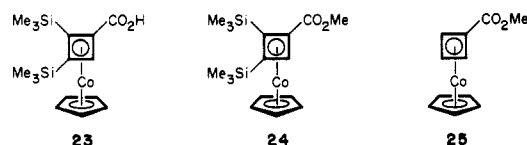
compd pyrolyzed	ratio a/b after reactn	% retro-cyclizatr
18a	60:40	36
17b	34:66	28
18a + 17b	18 59:41	31
	17 29:71	

ended chiral substituent. Such inversion could proceed through the intermediacy of a "cyclobutadienyl" radical or some other mechanism involving the metal. The identity of the reacting center was established by the results of the pyrolysis of an enantiomerically enriched complex.

Initial experiments aimed to synthesize an optically active CpCo cyclobutadiene lacking the additional chiral substituent in order to study its simple racemization under the above conditions. However, *l*-menthyl propynoate 20¹⁸ when cocyclized to 21, formed an inseparable mixture of



diastereomers in the ratio of 58:42. Attempted transesterification of the mixture with methanol in the presence of catalytic *p*-toluenesulfonic acid (*p*-TsOH) led to surprisingly regioselective protodesilylation furnishing 22, which exists as only one compound. Treatment of 21 with hydroxide ion in aqueous methanol gave only recovered starting material. Hydrolysis was finally accomplished in basic boiling ethylene glycol to form the cyclobutadiene-carboxylic acid 23. The latter was smoothly converted



to the methyl ester 24 on treatment with diazomethane in ether at 0 °C. Chemical structural proof for 24 was provided both by its independent synthesis from methyl

(18) Pfaendler, H. R.; Gosteli, J.; Woodward, R. B. *J. Am. Chem. Soc.* 1979, 101, 6306.

propynoate and btmse in the presence of $\text{CpCo}(\text{CO})_2$ and by protodesilylation with fluoride to give the known¹⁹ **25**. Unfortunately, **24** was obtained in racemic form, as rigorously shown by a proton NMR spectrum recorded with added tris[3-(trifluoromethyl)hydroxymethylene]-*d*-camphoratoeuropium, $\text{Eu}(\text{tfc})_3$. Because of this problem, the difficulties in separating the diastereomers of **21**, and our failure to resolve the acid **23** (brucine, strychnine, ephedrine, quinidine) our attention turned to the partial resolution²⁰ of 1-butyne-3-ol **6**. The enriched *R*-(+)-enantiomer was cyclized to give optically active diastereomers **2a** and **2b**. The enantiomeric excess obtained, measured by ¹H NMR with $\text{Eu}(\text{tfc})_3$ which causes unequal downfield shifts for the cyclopentadienyl resonances of each enantiomer, was 81:19 for **2a** and 80:20 for **2b**.

Pyrolysis of the enantiomerically enriched **2a** at 571 °C under flash vacuum conditions lead to a mixture of **2a/2b** = 65.6:34.4. Small quantities of complexes **10** and **11** also resulted from this reaction, the latter was generated with 20% ee.

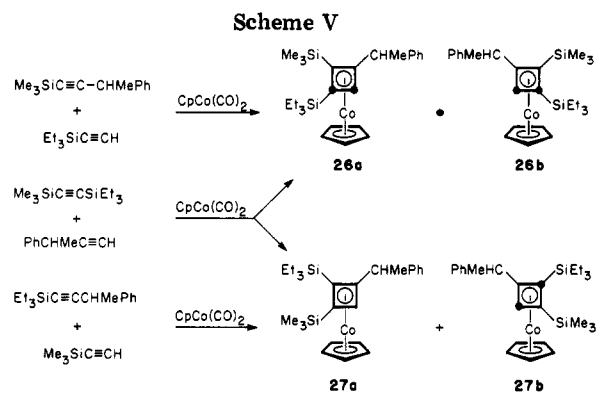
The enantiomer ratios in which the diastereomers of **2** were produced in this pyrolysis were 78:22 for **2a** and 79:21 for **2b**. The employment of only partially enriched **2a** in this experiment was usefully diagnostic. The europium shifted NMR peaks of **2a** show the Cp singlet of the major enantiomer (arbitrarily designated *RS*) shielded somewhat more than that of the minor one (*SR*). After pyrolysis the pattern observed for **2b** (*RR/SS* = 4:1) was identical with that recorded in the NMR spectrum of synthetic **2b** obtained from enriched **6** by cyclization. This clearly indicates that inversion in the diastereoisomerization of **2** occurs at the cobalt center. Were it to take place at the chiral carbon, an inverse NMR pattern should have been observed for pyrolytic **2b** (*RR/SS* = 1:4).

Solution-Phase Studies. It was felt that further mechanistic information would be forthcoming from condensed phase experiments, in which perhaps side reactions could be minimized and kinetic parameters determined. Initial experiments were carried out with **4**.

Two compounds formed when a dilute solution of **4a** was heated to reflux in toluene: the vinyl complex **10** (66%) and the ketone **11** (7%), corresponding to the formal loss of methanol and methane, respectively. Disappointingly, none of the second diastereomer **4b** was apparent by HPLC analysis.

Fortunately, **5** was considerably better behaved than **4**. Exposure of either diastereomer **5a** or **5b** in silylated vessels to boiling pristane (301 °C) gave clean mutual interconversion. Under these conditions none of the positional isomer **12** was generated and, remarkably, decomposition was not evident. By using the equilibrium ratio of **5a/5b** = 58:42 a good fit for the rate of conversion following first-order kinetics was obtained [rate(**5a** → **5b**)_{301°C} = $2.226 \times 10^{-5} \text{ s}^{-1}$; $\Delta G^\ddagger = 51.7 \text{ kcal mol}^{-1}$]. The absence of crossover also in solution was established by an experiment identical with that executed in the gas phase (vide supra).

Interconversion of Silicon Labeled Complexes. Despite the considerable mechanistic information accumulated thus far there are still various widely divergent options by which the rearrangements described could proceed. The simplest involves the metal traversing through the plane of the cyclobutadiene ring via an intermediate metallacyclopentadiene **B** as previously out-



Bold dots indicate ¹³C label.

lined in Scheme II. On the other hand, the operation of Scheme III cannot be excluded, although isomerization to **E** would have to be (inexplicably) slow. Perhaps if retrocyclization preferentially forms only **D**, isomerization might proceed through a single rotation of $\text{RC}\equiv\text{CH}$ followed by closure. Finally, one must consider some type of (possibly wall-catalyzed) silyl migration mechanism,²¹ however unlikely, which could give rise to the observed results.

To gain some information about the likelihood of these possibilities the silicon group has to be labeled. Intermediate formation of **B** would leave the initial connectivity of the ring intact. However, the other options are likely to cause scrambling of the label. 1-(Triethylsilyl)-2-(trimethylsilyl)ethyne was cocyclized with 3-phenyl-1-butyne to give all four possible diastereomers (two pairs of positional isomers, each of course racemic) of the cyclobutadiene products: **26a**, **26b**, **27a** and **27b** (Scheme V), all separable by HPLC. We had hoped to utilize the normally diagnostic mass spectral fragmentation patterns for these complexes²² (intense peaks for $\text{CpCoR}^1\text{C}\equiv\text{CR}^{2+}$) to unambiguously assign the structure of the pairs of related positional isomers (e.g., **26a,b** vs. **27a,b**). This proved impossible because all possible permutations of $[\text{CpCoR}^1\text{C}\equiv\text{CR}^{2+}]^+$ fragments appeared in their mass spectra. This finding suggests that the technique is not reliable as the sole means by which to establish the substitution patterns of CpCo cyclobutadienes. Instead, the pairs **26** and **27** were independently synthesized from triethylsilylethyne and 1-(trimethylsilyl)-3-phenyl-1-butyne on the one hand and (trimethylsilyl)ethyne and 1-(triethylsilyl)-3-phenyl-1-butyne on the other. In each case four compounds formed, the respective pairs **26** and **27** and the two corresponding 1,3-bis(silyl)cyclobutadiene diastereomers (not isolated). Analytical HPLC confirmed the identity of **26** and **27**. As observed with the other systems the structures of the complexes belonging to the **a** series (high *R_f*) or **b** series (low *R_f*) appeared to be similar, based on the similarities of the ¹H NMR spectra (Table I).

What is to be expected on pyrolysis of any one of the silyl labeled systems? Should isomerization proceed through **B** then equilibration should occur only within each pair of compounds (e.g., **26a** ↔ **26b** and **27a** ↔ **27b**). Intermediacy of **D** would lead to complete equilibration of any isomer with all the others, assuming free rotation of both alkynes in the coordination sphere of the metal. Should there be (well-precedented²³) restricted rotation,

(19) Rosenblum, M.; North, B.; Wells, D.; Giering, W. P. *J. Am. Chem. Soc.* 1972, 94, 1239.

(20) Weidmann, R.; Schoofs, A.; Horeau, A. *Bull. Soc. Chim. Fr.* 1976, 645.

(21) Trimethylsilyl migrations occur on the benzene nucleus; see: Hillard, R. L., III; Vollhardt, K. P. C. *J. Am. Chem. Soc.* 1977, 99, 4058 and references therein.

(22) Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* 1982, 1, 590; *J. Am. Chem. Soc.* 1978, 100, 3643.

presumably of the bulkier bis(silyl)alkyne, then **26a** would equilibrate only with **27b** and **26b** with **27a**. The alternative mode of opening the four-membered ring to furnish initially **F** and involving restricted rotation of the benzyl(silyl)alkyne appeared not to be operating competitively as it would have given 1,3-bis(silyl) isomers, which are not observed during solution phase pyrolysis. Finally, a silyl migration process could give either result depending on its specificity.

To our great surprise, solution pyrolyses of the individual isomers of **26** and **27** under standard conditions when monitored by HPLC revealed clean interconversion between **26a** and **27b**, as well as between **26b** and **27a**. This clearly rules out a metallacyclopentadiene as being responsible for all of the isomerizations described in this paper.

An additional labeling experiment (vide infra) involving ^{13}C confirms the above mechanistic ramifications and dispenses with the bothersome (and deliberately unspecified) silyl migration "mechanism" for isomerization.

Pyrolysis of Hexalabeled Cyclobutadiene Complexes. The postulate of **D** in Scheme III as the crucial intermediate in the observed transformations requires unique carbon-carbon bond breaking. The occurrence of such a topological change if observed to be coupled with the above silyl positional shifts and concomitant isomerization would constitute powerful mechanistic evidence. For this purpose the "hexalabeled" (two chiral, two silyl, two ^{13}C labels) **26- $^{13}\text{C}_2$** was synthesized starting from $\text{Et}_3\text{Si}^{13}\text{C}\equiv^{13}\text{CH}$ (Scheme V). Pyrolysis of isomer **26a- $^{13}\text{C}_2$** in solution gave **27b- $^{13}\text{C}_2$** in which the label was clearly located at $\text{C}_{2,4}$ (**26a- $^{13}\text{C}_2$** : $J_{^{13}\text{C}-^{13}\text{C}} = 24.1$ Hz; $J_{^{13}\text{C}-^{13}\text{CH}} = 5.5$ Hz; $J_{^{13}\text{C}-\text{H}} = 177$ Hz. **27b- $^{13}\text{C}_2$** : $J_{^{13}\text{C}-^{13}\text{C}} = 2$ Hz; $J_{^{13}\text{C}-^{13}\text{CH}} = 9$ Hz; $J_{^{13}\text{C}-\text{H}} = 190$ Hz).^{24,25} Thus, C-C bond rupture accompanies the silyl shift in a specific way, ruling out silyl carbon bond cleavage during the diastereoisomerization process.

Conclusions and Further Questions

We have for the first time observed thermal intramolecular diastereomerizations of complexed cyclobutadienes involving inversion at the complexed four-membered ring. Surprisingly, the mechanism of this transformation does not conform to the currently accepted pathways associated with alkyne cyclizations (and their reverse). Thus, the most obvious intermediate, a metallacyclopentadiene, is not involved (at least directly) in the isomerization step. One is forced to seriously consider an alternative, suggested years ago by Mango,⁵ namely, a metal-mediated concerted (retro)cyclization in the (retro)-(2 + 2) cycloaddition sense. The regioselectivity of this reaction in the present case is interesting. There is a clear tendency to generate a [bis(silyl)alkyne]cyclopentadienylcobalt fragment, also observed as dominant molecular ions in the mass spectra of these compounds. In the gas phase the alternative mode of retrocyclization, cleaving the SiC-CSi bond, is barely competitive and gives rise to the 1,3-bis(trimethylsilyl) substitution pattern as in **12**. On the other hand, decomplexation of the complexed alkynes appears to be kinetically comparable regardless of substituents (Table IV).

(23) For recent work, see: Winston, P. B.; Nieter-Burgmayer, S. J.; Templeton, J. L. *Organometallics* 1983, 2, 167. Davidson, J. L.; Vasapollo, G. *Polyhedron* 1983, 2, 305. Herrick, R. S.; Templeton, J. L. *Organometallics* 1982, 1, 842.

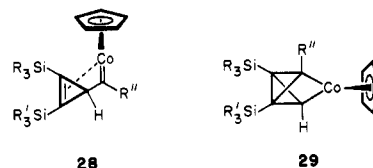
(24) Ville, G.; Vollhardt, K. P. C. *J. Magn. Reson.* 1981, 45, 525.

(25) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley: New York, 1980. Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: Philadelphia, 1978.

The extent to which our findings may be generalized to other systems involving additional ligands¹² and other metals³⁻⁵ is not clear. However, it is evident that direct cyclization pathways are not as unlikely as commonly thought and deserve serious consideration in other systems.

It should be pointed out that our results do not rigorously negate the presence of metallacyclopentadienes as equilibrium or intermediate species along the observed isomerization path. Thus, it is still possible that oxidative addition by the metal into the cyclobutadiene bond precedes retrocyclization. In that case our data demand that such a metallacycle be nonplanar and configurationally stable. While this is not implausible (a planar 16-electron Cp cobaltacyclopentadiene might be forced by symmetry to adopt an unfavorable open-shell configuration),^{13,26} calculations imply a negligible barrier to ring flip,^{12b} which makes it unlikely.

Finally, we note the (superficial?) similarity of our isomerizations to the substituent scrambling that occurs in five-ring heterocycles such as pyrrole, furan, and thiophene.²⁷ These studies lead to the consideration of novel metal-containing intermediates of the type **28**, **29**,



and others in the present system, possibly constructible through the intermediacy of a cobaltacyclopentadiene or directly from the cyclobutadiene fragment.²⁸ However, these structures are only feasible if the metal maintains configurational stability in order to explain the selectivity observed in the pyrolyses of **26** and **27**. Future work aimed at the isolation of some of the postulated reactive transients might shed additional light on these problems.

Experimental Section

General Consideration. Melting points are uncorrected and were measured on a Thomas Hoover Unimelt apparatus. Infrared spectra were recorded on Perkin-Elmer 337 and 681 spectrometers and calibrated to the 1601.4 and 906.7 cm^{-1} absorptions of a polystyrene film. Only the most characteristic or prominent peaks are quoted. ^1H NMR spectra were recorded on Varian Associates T-60 and EM-390 instruments and the UCB-250 system. Spectra are reported at 90 MHz in CCl_4 unless mentioned otherwise. ^{13}C NMR spectra were obtained by using a Nicolet TT-23 instrument. Low- and high-resolution mass spectra were recorded on AEI-MS 12 and Du Pont CEC-21-110B instruments, respectively, on a service basis at the University of California, Berkeley. Linked mass spectra were measured on a Finnigan-4023 machine using a 28-m SP-2100 capillary column. Only the most diagnostic or prominent peaks are quoted. Elemental analyses were performed by the Microanalytical Department of the University of California, Berkeley.

Chromatographic separations were effected with alumina [Ventron; activated, neutral, Camag; deactivated with water (5% w/w) unless otherwise noted] and silica gel 60 (E. Merck). An Altex HPLC system equipped with an ultraviolet detector (254 and 280 nm) using reversed phase columns (Ultrasphere—ODS, 250 \times 10 i.d. or 250 \times 4 i.d. mm), generally operating isocratically, was used for some separations.²⁹ A Hewlett-Packard 5710A gas chromatograph equipped with flame ionization detectors and columns packed with 20% UCW 98 on 60–80 mesh Chromosorb

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W-DMCS-AW in 10 ft × 0.25 in. o.d. stainless steel tubes using N₂ as the carrier gas was used for analytical GC work.

All reactions were performed under oxygen-free dinitrogen atmospheres using magnetic stirring in deoxygenated solvents. Glassware for reactions involving cobalt species was silylated by treatment with hexamethyldisilazane for a few seconds followed by a pentane rinse. Vacuum line operations were carried out by using a standard Schlenk double manifold for routine work or a line equipped with a simple mercury diffusion pump for flash vacuum pyrolyses. Solvents (Mallinckrodt, AR grade) were used as supplied, except for tetrahydrofuran which was distilled from sodium-benzophenone. Pentane was distilled away from higher boiling residues.

The following alkynes were used as supplied: 1-phenylprop-1-yne (Farchan), 3-butyn-2-ol (Farchan), and bis(trimethylsilyl)ethyne (PCR). CpCo(CO)₂ was used as supplied. The alkynes 3-phenylbut-1-yne,³⁰ 3-phenylpent-1-yne,³⁰ and 3-methoxy-1-butyne,³¹ were prepared according to literature methods.

3-[(Trimethylsilyloxy)-1-butyne (7). A cooled (-78 °C) magnetically stirred solution of 3-butyn-2-ol (9.93 g, 142 mmol) in ether (150 mL) was treated with *n*-butyllithium (65 mL, 2.18 M in hexane, 142 mmol) for 30 min and stirred for a further 15 min. Addition of chlorotrimethylsilane (15.5 g, 142 mmol) to the resulting straw-colored solution and warming to ambient temperature resulted in a white suspension. After 2 h the reaction mixture was worked up with water. Distillation of the resulting oil provided pure trimethylsilyl ether 7 (4.1 g, 20.3%) together with several grams of slightly impure material: colorless oil; bp 110–110 °C (720 mm) [lit.³² bp 111 °C (727 mm)]; MS, *m/e* (relative intensity) 141 (M⁺ - H, 5%), 127 (94), 83 (100), 73 (76); ¹H NMR δ 0.09 (s, 9 H), 1.32 (d, *J* = 6.5 Hz, 3 H), 2.17 (d, *J* = 2 Hz, 1 H), 4.37 (dq, *J* = 6.5, 2 Hz, 1 H).

1-(Trimethylsilyl)-3-phenylbut-1-yne. A cooled (-78 °C) magnetically stirred solution of 3-phenylbut-1-yne (9, 5.71 g, 43.9 mmol) in ether (150 mL) was treated with *n*-butyllithium (33 mL, 1.33 M solution in hexane, 43.9 mmol) and allowed to stir for 15 min. Addition of chlorotrimethylsilane (5 g, 46.1 mmol) at -78 °C and warming to ambient temperature resulted in a white precipitate. Aqueous workup gave crude 1-(trimethylsilyl)-3-phenylbut-1-yne (7.74 g, 87%) purified immediately prior to use by preparative GLC: colorless oil; MS, *m/e* (relative intensity) 202 (32%), 201 (100), 187 (29), 97 (97), 73 (83); ¹H NMR δ 0.28 (s, 9 H), 1.60 (d, *J* = 7 Hz, 3 H), 3.82 (9, *J* = 7 Hz, 1 H), 7.37 (m, 5 H); IR (neat) 2960, 2165, 1493, 1250, 840, 760, 697 cm⁻¹.

Preparation of (Triethylsilyl)ethyne-¹³C₂. A sample of ethyne-¹³C₂ (250 mL, 11.25 mmol) was frozen by using a liquid-nitrogen trap and dissolved in THF (15 mL) at -78 °C. Ethylmagnesium bromide (25 mL, 0.7 M in THF, 15.5 mmol) was added at -78 °C, the resulting solution stirred for 1 h, and the mixture allowed to warm to ambient temperature. After addition of chlorotriethylsilane (1.7 g, 11.25 mmol) and stirring for 2 h, the mixture was worked up with aqueous NH₄Cl. Analysis of the resulting liquid by GLC indicated a mixture of Et₃Si¹³C₂H and Et₃Si¹³C₂SiEt₃ (55:45). The former was purified by preparative GLC, while the bis(silyl)alkyne was selectively desilylated according to Holmes³³ to Et₃Si¹³C₂H (combined yield 1.2 g, 75%): colorless oil; MS, *m/e* 142; IR (neat) 3280, 2955, 2910, 2875, 1960, 1460, 1415, 1235, 1018, 725, 665 cm⁻¹.

[η⁴-1,2-Bis(trimethylsilyl)-3-(1-hydroxyethyl)cyclobutadiene](η⁵-cyclopentadienyl)cobalt (2). A mixture of CpCo(CO)₂ (0.8 g, 5 mmol), 3-butyn-2-ol (6, 0.35 g, 5 mmol), and btmse (4 mL) was added (0.092 mL h⁻¹) to boiling btmse (45 mL). After removal of excess btmse and filtration, the resulting brown oil was chromatographed on alumina (50 × 2.5 cm o.d.). Elution with ether-pentane (10:90) produced a yellow fraction containing a mixture of the diastereomers **3a,b** (0.82 g, 37%). Continued elution with ether afforded a mixture of the hydroxy diastereomers **2a,b** (0.625 g, 34%). Repeated chromatography on a similar column using ether-pentane (5:95) as eluant separated the mixture

of **3a** (0.402 g, 18.5%) and **3b** (0.315 g, 14.5%), the former as a yellow oil and the latter as a yellow crystalline solid (from pentane). Repeated chromatography of **2** on the same column with ether-pentane (20:80) gave **2a** (0.196 g, 11%): yellow oil; MS, *m/e* (relative intensity) 364 (100%), 346 (36), 294 (35), 266 (11), 222 (23); IR (neat) 3491, 3110, 3072, 2989, 2971, 2910, 1245, 831, 750 cm⁻¹. Anal. (C₁₇H₂₉CoOSi₂) C, H.

A second fraction furnished **2b** (0.353 g, 19.5%): yellow crystals; mp 65–67 °C; IR (neat) 364 (100%), 346 (41), 294 (89), 222 (34), 73 (100); IR (neat) 3362, 3100, 3062, 2971, 1239, 1075, 1037, 835, 749 cm⁻¹. Anal. (C₁₇H₂₉CoOSi₂) C, H.

[η⁴-1,2-Bis(trimethylsilyl)-3-[1-(trimethylsilyloxy)ethyl]-cyclobutadiene](η⁵-cyclopentadienyl)cobalt (3). The conditions employed in this preparation will be subsequently referred to as "standard". A mixture of CpCo(CO)₂ (0.18 g, 1 mmol), 3-(trimethylsilyloxy)but-1-yne (7) (0.142 g, 1 mmol), and btmse (5 mL) was added (0.13 mL h⁻¹) to boiling btmse (45 mL). After removal of excess btmse and filtration the resulting brown oil was chromatographed on alumina (40 × 2 cm o.d.). Elution with pentane produced minor quantities of yellow byproducts. Continued elution allowed the separation of the diastereomers furnishing first **3a** (0.170 g, 39%): yellow oil; MS, *m/e* (relative intensity) 436 (65%), 338 (20), 294 (58), 266 (5), 222 (13), 73 (100); HRMS calcd for C₂₀H₃₇CoOSi₃ 436.1483, found 436.1488; IR (neat) 3121, 3073, 2972, 2911, 1247, 844, 806, 749 cm⁻¹. Anal. Calcd for C₂₀H₃₇CoOSi₃: C, 55.04; H, 8.49. Found: C, 55.91; H, 8.21.

A second fraction gave **3b** (0.104 g, 24%): yellow crystals, mp 39–41 °C; MS, *m/e* (relative intensity) 436 (81%), 338 (25), 294 (75), 266 (6), 222 (17), 73 (100); IR (neat) 3090, 3053, 2954, 2894, 1245, 836, 805, 747 cm⁻¹. Anal. (C₂₀H₃₇CoOSi₃) C, H.

[η⁴-1,2-Bis(trimethylsilyl)-3-(1-methoxyethyl)cyclobutadiene](η⁵-cyclopentadienyl)cobalt (4). A mixture of CpCo(CO)₂ (0.9 g, 5 mmol), 3-methoxy-1-butyne (8, 0.42 g, 5 mmol), and btmse were subjected to cyclization conditions similar to those employed for the preparation of **3**. Chromatography on alumina using ether-pentane (5:95) gave two distinct yellow bands, the first resulting in **4a** (0.545 g, 29%): yellow oil; MS, *m/e* (relative intensity) 378 (67%), 346 (76), 294 (100), 280 (20), 248 (49), 222 (28); HRMS calcd for C₁₈H₃₁CoOSi₂ 378.1233, found 378.1241; IR (neat) 3107, 3050, 2955, 2891, 2818, 1242, 1101, 828, 750 cm⁻¹.

The second gave **4b** (0.40 g, 21%): yellow oil; MS, *m/e* (relative intensity) 378 (100%), 294 (92), 280 (29), 248 (43), 222 (26); HRMS calcd for C₁₈H₃₁CoOSi₂ 378.1245, found 378.1233; IR (neat) 3092, 3055, 2965, 2896, 2815, 1247, 1095, 841, 752 cm⁻¹.

[η⁴-1,2-Bis(trimethylsilyl)-3-(1-phenylethyl)cyclobutadiene](η⁵-cyclopentadienyl)cobalt (5). CpCo(CO)₂ (0.90 g, 5 mmol), 3-phenyl-1-butyne (0.65 g, 5 mmol) and btmse were cocyclized according to the above standard conditions. Chromatography on alumina gave a yellow oil of **5a,b** (1.58 g, 74%). Samples of the mixture were separated by HPLC²⁹ using a reversed phase column operating isocratically with water-methanol (7:93) eluant. The pure complexes **5a** and **5b** were obtained by addition of pentane and water to each fraction, followed by separation of the layers, drying (MgSO₄) of the pentane layer, rotary evaporation, and finally pumping under high vacuum. Complex **5a**: yellow crystals; mp 65–66 °C; MS, *m/e* (relative intensity) 424 (100%), 326 (38), 294 (68), 253 (58), 222 (12); HRMS calcd for C₂₃H₃₃CoSi₂ 424.1452, found 424.1440; IR (neat) 3095, 3045, 3012, 2959, 2882, 1242, 822, 804, 750 cm⁻¹. Anal. (C₂₃H₃₃CoSi₂) C, H. Complex **5b**: yellow crystals, mp 62–63 °C; MS, *m/e* (relative intensity) 424 (100%), 326 (41), 294 (71), 253 (58), 222 (12); HRMS calcd for C₂₃H₃₃CoSi₂ 424.1452, found 424.1456; IR (neat) 3045, 3009, 2938, 2904, 2888, 2847, 1245, 886, 808, 701 cm⁻¹. Anal. (C₂₃H₃₃CoSi₂) C, H.

Gas-Phase Pyrolyses—General Method. Compounds were pyrolyzed through a 20 × 1.8 cm o.d. quartz glass tube whose surface was silylated (hexamethyldisilazane) prior to use. Heating was accomplished with a 13-in. Hoskins electric furnace equipped with an Omega Model 4001 KC thermostat. Temperatures quoted are uncorrected and obtained at the oven center. Routine pressures of less than 10⁻⁴ torr were maintained throughout by a simple mercury diffusion pump in series with a mechanical pump. Products and/or unreacted starting materials were collected on a liquid-nitrogen-coated surface and subsequently transferred into an NMR tube with deoxygenated C₆D₆, while

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maintaining a static vacuum. Reaction products were analyzed by ^1H NMR spectroscopy (internal dioxane standard, 2–8 μL), GLC (dioxane standard corrected by measured response factors), and GC–MS. Typical pyrolysis rates were maintained at 15–20 mg over 1–2 h, using an external heating element to volatilize materials where necessary.

Formation of Side Products 10 and 11 in the Pyrolyses of 2, 3, and 4. The products could be observed by NMR and GC–MS in the pyrolyses of 2–4. They were isolated from the gas-phase pyrolysis of 4 at 571 $^\circ\text{C}$ using column chromatography on alumina eluting before the mixture of diastereomers 4 (pentane). [η^4 -1,2-Bis(trimethylsilyl)-3-vinylcyclobutadiene](η^5 -cyclopentadienyl)cobalt (10) (major): yellow oil; MS, *m/e* (relative intensity) 346 (100%), 294 (73), 248 (57), 222 (32), 176 (5); HRMS calcd for $\text{C}_{17}\text{H}_{29}\text{CoSi}_2$ 346.0983, found 346.0990; IR (neat) 2936, 2900, 2884, 1247, 836, 808, 754 cm^{-1} . [η^4 -1,2-Bis(trimethylsilyl)-3-acetylcyclobutadiene](η^5 -cyclopentadienyl)cobalt (11) (minor): yellow oil; MS, *m/e* (relative intensity) 362 (100%), 294 (76), 264 (63), 222 (28).

[η^4 -1,2,3-Tris(trimethylsilyl)-4-(1-phenylethyl)cyclobutadiene](η^5 -cyclopentadienyl)cobalt (14). $\text{CpCo}(\text{CO})_2$ (0.90 g, 5 mmol), 1-(trimethylsilyl)-3-phenylbut-1-yne (1.01 g, 5 mmol), and *btmse* were cocyclized by using standard conditions. The resulting black oil was chromatographed on alumina. Elution with pentane provided a yellow fraction (1.3 g) containing several components followed by the black, slightly air-sensitive complex 13 (0.539 g, 48%), crystallized in two crops from pentane (-78°C). The yellow mixture was subjected to HPLC on a reversed phase column operating isocratically using water–methanol (7:93) eluant. Many uncharacterized minor components were separated, but a major fraction produced yellow cyclobutadiene complex 14 (0.135 g, 5.5%) crystallized from pentane: yellow crystals, mp 195–196 $^\circ\text{C}$; MS, *m/e* (relative intensity) 496 (4%), 324 (19), 294 (53). Anal. ($\text{C}_{26}\text{H}_{41}\text{CoSi}_3$) C, H.

[η^4 -1,3-Bis(trimethylsilyl)-2-(1-phenylethyl)cyclobutadiene](η^5 -cyclopentadienyl)cobalt (12). A mixture of tris(trimethylsilyl)cyclobutadiene complex 14 (0.07 g, 0.14 mmol), *p*-toluenesulfonic acid monohydrate (0.027 g, 0.14 mmol), and C_6D_6 (1 mL) contained in a 5-mm NMR tube was subjected to sonic vibration for 2 h at 30 $^\circ\text{C}$ and monitored by ^1H NMR spectroscopy. Extraction with pentane followed by HPLC using a reversed phase column and methanol eluant produced two minor and one major fraction. The major fraction contained complex 12 (0.045 g, 75%) recrystallized from pentane: yellow crystals; mp 103–104 $^\circ\text{C}$; MS, *m/e* (relative intensity) 424 (100%), 326 (58), 294 (30), 253 (65), 222 (17); HRMS calcd for $\text{C}_{23}\text{H}_{35}\text{CoSi}_2$ 424.1452, found 424.1456; IR (Nujol) 1241, 905, 839, 801, 752, 697 cm^{-1} . Anal. ($\text{C}_{23}\text{H}_{35}\text{CoSi}_2$) C, H.

[η^4 -1,2-Bis(trimethylsilyl)-3-(1-phenylpropyl)cyclobutadiene](η^5 -cyclopentadienyl)cobalt (17). $\text{CpCo}(\text{CO})_2$ (0.70 g, 3.89 mmol), 3-phenyl-1-pentyne (0.55 g, 3.89 mmol), and *btmse* were subjected to the standard cyclization conditions to give 17 (1.385 g, 84%). Separation by HPLC as for 5 gave first 17a: yellow oil; MS, *m/e* (relative intensity) 438 (100%), 340 (48), 294 (78), 267 (19), 239 (14), 222 (11); HRMS calcd for $\text{C}_{24}\text{H}_{35}\text{CoSi}_2$ 438.1609, found 438.1610; IR (neat) 3097, 3064, 3022, 2959, 2900, 2875, 1246, 841, 806, 749, 698 cm^{-1} . Anal. ($\text{C}_{24}\text{H}_{35}\text{CoSi}_2$) C, H.

Complex 17b eluted second: yellow oil; MS, *m/e* (relative intensity) 438 (100%), 340 (38), 294 (68), 267 (17), 239 (16), 222 (10); HRMS calcd for $\text{C}_{24}\text{H}_{35}\text{CoSi}_2$ 438.1609, found 438.1615; IR (neat) 3103, 3072, 3030, 2965, 2905, 1245, 843, 750, 698 cm^{-1} . Anal. ($\text{C}_{24}\text{H}_{35}\text{CoSi}_2$) C, H.

[η^4 -1,2-Bis(trimethylsilyl)-3-(1-phenylethyl)cyclobutadiene](η^5 -methylcyclopentadienyl)cobalt (18). (η^5 - $\text{C}_5\text{H}_4\text{Me}$) $\text{Co}(\text{CO})_2$ (1.1 g, 5.67 mmol), 3-phenyl-1-butyne (0.78 g, 6 mmol), and *btmse* were subjected to the standard cyclization conditions to give 18 (1.8 g, 72%). HPLC gave first 18a: yellow oil; MS, *m/e* (relative intensity) 438 (100), 340 (34), 308 (62), 267 (33), 236 (11); HRMS calcd for $\text{C}_{24}\text{H}_{35}\text{CoSi}_2$ 438.1609, found 438.1623; IR (neat) 3079, 3055, 3023, 2961, 2922, 2892, 1244, 838, 808, 753, 698 cm^{-1} . Anal. ($\text{C}_{24}\text{H}_{35}\text{CoSi}_2$) C, H.

Subsequently 18b eluted: yellow crystals; mp 46–47 $^\circ\text{C}$; MS, *m/e* (relative intensity) 438 (100%), 340 (35), 308 (66), 267 (36), 236 (13); HRMS calcd for $\text{C}_{24}\text{H}_{35}\text{CoSi}_2$ 438.1609, found 438.1615; IR (neat) 3095, 3066, 3038, 2966, 2923, 2906, 1244, 838, 808, 768, 754, 698 cm^{-1} . Anal. ($\text{C}_{24}\text{H}_{35}\text{CoSi}_2$) C, H.

[η^4 -1,2-Bis(trimethylsilyl)-3-[(1-menthyloxy)carbonyl]cyclobutadiene](η^5 -cyclopentadienyl)cobalt (21). $\text{CpCo}(\text{CO})_2$ (0.9 g, 5 mmol) and *l*-menthylpropionate (20)¹⁸ (1.04 g, 5 mmol) in THF (2 mL) were cocyclized with *btmse* using standard conditions to give 21 (1.94 g, 77%) as an inseparable mixture: yellow oil; MS, *m/e* (relative intensity) 502 (100%), 294 (63), 266 (37), 222 (27); IR (neat) 2924, 1704, 1435, 1251, 837 cm^{-1} . Anal. ($\text{C}_{26}\text{H}_{43}\text{CoO}_2\text{Si}_2$) C, H.

[η^4 -1-(Trimethylsilyl)-3-[(1-menthyloxy)carbonyl]cyclobutadiene](η^5 -cyclopentadienyl)cobalt (22). A mixture of 21 (0.14 g, 0.28 mmol), *p*-toluenesulfonic acid monohydrate (a few crystals), and methanol (25 mL) was stirred for 24 h. After removal of solvent, the resulting oily yellow material was chromatographed on alumina. Ether–pentane (3:97) eluted a small quantity of starting material followed by 22 (0.045 g, 38%): yellow oil; MS, *m/e* (relative intensity) 430 (73%), 292 (100), 222 (25); IR (neat) 2958, 2924, 2874, 1704, 1439, 1245, 1180, 1005, 841, 811 cm^{-1} . Anal. ($\text{C}_{23}\text{H}_{35}\text{CoO}_2\text{Si}$) C, H.

[η^4 -2,3-Bis(trimethylsilyl)cyclobutadienecarboxylic acid](η^5 -cyclopentadienyl)cobalt (23). A mixture of 22 (0.75 g, 1.49 mmol), potassium hydroxide (3 g, 46 mmol), and ethylene glycol (60 mL) was heated to reflux for 90 min during which time the oily layer disappeared as the glycol became yellow. Addition of water (100 mL), careful neutralization with acid, and extraction into dichloromethane, followed by drying of the organic layer (MgSO_4) and evaporation gave 23 (0.46 g, 84%): yellow crystals; mp 207–209 $^\circ\text{C}$; MS, *m/e* (relative intensity) 364 (100%), 294 (64), 266 (21), 222 (38); IR (Nujol) 1665, 1244, 836 cm^{-1} . Anal. ($\text{C}_{16}\text{H}_{25}\text{CoO}_2\text{Si}_2$) C, H.

[η^4 -Methyl 2,3-bis(trimethylsilyl)cyclobutadienecarboxylate](η^5 -cyclopentadienyl)cobalt (24). A cold (0 $^\circ\text{C}$) solution of acid 23 (0.295 g, 0.81 mmol) in ether (70 mL) was treated dropwise with a solution of diazomethane in ether (ca. 0.3 M) until no further discoloration occurred. No evolution of gas was apparent, and the reaction was monitored by TLC on silica. Aqueous work up and filtration through alumina gave 24 (0.288 g, 94%) characterized by comparison with an authentic racemic sample (see below).

Synthesis of 24 by Cyclization. $\text{CpCo}(\text{CO})_2$ (0.90 g, 5 mmol), methyl propionate (0.42 g, 5 mmol), and *btmse* were cyclized as usual to give 24 (1.032 g, 55%): yellow crystals; mp 31–32 $^\circ\text{C}$; MS, *m/e* (relative intensity) 378 (100%), 294 (66), 280 (47), 222 (23); IR (neat) 2932, 2890, 1725, 1449, 1249, 1192, 842. Anal. ($\text{C}_{17}\text{H}_{27}\text{CoO}_2\text{Si}_2$) C, H.

(η^4 -Methyl cyclobutadienecarboxylate)(η^5 -cyclopentadienyl)cobalt (25). A mixture of 24 (0.075 g, 0.2 mmol), dry benzyltrimethylammonium fluoride (0.18 g, 1.16 mmol), and THF (20 mL) was heated to reflux for 18 h. Removal of solvent and chromatography on alumina (10 \times 2 cm o.d., activity II) using ether–pentane (5:95) as eluant produced a minor brown fraction followed by the complex 25 (0.033 mg, 71%): yellow crystals; mp 56–58 $^\circ\text{C}$ (lit.¹⁹ mp 55–57 $^\circ\text{C}$). Spectroscopic data are identical with those reported in the literature.¹⁹

Solution-Phase Pyrolyses—General Method. A solution of the sample to be pyrolyzed in pristane was injected directly into refluxing pristane contained in silylated glassware, stirring being maintained by a silylated glass covered magnetic stirrer. Samples for monitoring were obtained by syringe, and heating was maintained by sand contained in a heating mantle. Typical reaction scale: 30–50 mg.

Cocyclization of Triethylsilylethyne with 1-(Trimethylsilyl)-3-phenyl-1-butyne. A deoxygenated mixture of $\text{CpCo}(\text{CO})_2$ (0.81 g, 4.5 mmol), (triethylsilyl)ethyne (0.63 g, 4.5 mmol), and octane (15 mL) was added (0.26 mL h^{-1}) to a boiling mixture of 1-(trimethylsilyl)-3-phenyl-1-butyne (0.91 g, 4.5 mmol) and octane (30 mL) over a period of 59 h followed by a further 3 h of heating. After removal of solvent and filtration through alumina the dark oil was chromatographed on alumina (45 \times 2.5 cm o.d.). The first yellow band contained a mixture of the diastereomers 26 (1.36 g, 65%) subsequently separated by HPLC. These were identical with the diastereomers obtained from the cocyclization of 1-(triethylsilyl)-2-(trimethylsilyl)ethyne with 3-phenyl-1-butyne (vide infra). A second yellow band furnished minor amounts of the 1,3-bis(silyl) isomers (*m/e*), not fully characterized.

A similar reaction with $\text{Et}_3\text{Si}^{13}\text{C}_2\text{H}$ resulted in a mixture of 1,2- ^{13}C -labeled diastereomers 26.²⁴

Complex 26a: yellow oil; MS, m/e (relative intensity) 466 (83%), 365 (15), 336 (33), 326 (21), 253 (28), 222 (6), 57 (100); HRMS calcd for $C_{26}H_{39}CoSi_2$ 466.1922, found 466.1925. Anal. ($C_{26}H_{39}CoSi_2$) C, H. Complex 26b: yellow oil; MS, m/e (relative intensity) 466 (100%), 368 (18), 336 (37), 326 (28), 222 (7), 253 (41); HRMS calcd for $C_{26}H_{39}CoSi_2$ 466.1922, found 466.1920. Anal. ($C_{26}H_{39}CoSi_2$) C, H.

Cocyclization of (Trimethylsilyl)ethyne with 1-(Triethylsilyl)-3-phenyl-1-butyne. A mixture of $CpCo(CO)_2$ (0.90 g, 5 mmol), (trimethylsilyl)ethyne (0.49 g, 5 mmol), and octane (15 mL) was added (0.26 mL h^{-1}) to a boiling mixture of 1-(triethylsilyl)-3-phenyl-1-butyne in octane (30 mL). Workup as in the synthesis of 26 gave 27a,b (1.82 g, 78%) separable by HPLC to give first 27a: yellow oil; MS, m/e (relative intensity) 466 (100%), 368 (19), 336 (61), 326 (29), 253 (32), 222 (12); HRMS calcd for $C_{26}H_{39}CoSi_2$ 466.1922, found 466.1916. Anal. ($C_{26}H_{39}CoSi_2$) C, H. Subsequently 27b: yellow oil; MS, m/e (relative intensity) 466 (100%), 368 (17), 336 (33), 326 (27), 253 (29), 222 (4); HRMS calcd for $C_{26}H_{39}CoSi_2$ 444.1922, found 466.1920.

Cocyclization of 1-(Triethylsilyl)-2-(trimethylsilyl)ethyne and 3-Phenyl-1-butyne. $CpCo(CO)_2$ (0.90 g, 5 mmol), the bis-(silyl)ethyne³⁴ (30 mL), and 3-phenyl-1-butyne (0.65 g, 5 mmol) were cocyclized as in the above preparation of 26 and 27. A similar workup and HPLC separation gave 26a,b and 27a,b the identity of which was ascertained by coinjection on HPLC with authentic samples, isolation, and spectroscopic comparison.

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A Novel Type of Cyclopentadienyl Bridge—Structure of $(\mu-C_5H_5)(\mu-N(SiMe_3)_2)(ZnC_5H_5)_2$

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The compound $Cp_3Zn_2N(SiMe_3)_2$ was prepared from Cp_2Zn and $Zn[N(SiMe_3)_2]_2$ and characterized by X-ray diffraction analysis. It crystallizes in the monoclinic system of space group $P2_1/c$ with four molecules in a cell of dimensions $a = 15.447$ (3) Å, $b = 11.049$ (1) Å, $c = 14.503$ (3) Å, and $\beta = 108.35$ (2)°. The structure refinement, with anisotropic thermal parameters for the non-hydrogen atoms, converged at $R_F = 0.045$ ($R_{wF} = 0.049$) for 336 parameters and 3424 observed reflections with $I > 2.5\sigma(I)$. The molecule consists of two zinc atoms connected by a bridging cyclopentadienyl group and a bridging amide group; in addition, each zinc atom carries a terminal Cp group. This is the first example of a compound containing a Cp group that bridges between nonbonded metal atoms located on the same side of the ring plane. The Cp-Zn arrangements suggest that both σ - and π -type interactions contribute to the Cp-Zn bonds. In solution, intramolecular exchange of Cp groups occurs at elevated temperature, presumably via opening of the Cp bridge.

Introduction

Electron-deficient cyclopentadienyl compounds of the main-group metals are usually associated via bridging cyclopentadienyl groups. In these compounds, two metal atoms are located on different sides of the ring plane. The bridging mode can be symmetrical, as in $CpNa\cdot TMEDA^1$ or Cp_2Pb^2 (Figure 1a), or asymmetrical, as in $CpGaMe_2^3$ or $CpZnMe^4$ (Figure 1b). Cyclopentadienyl groups coordinating simultaneously to two⁵ or even three⁶ transition-metal atoms located on the same side of the ring plane

are known; in these cases, the metal atoms are invariably linked by direct metal-metal bonds as well. In this paper, we wish to report on the structure of a zinc compound

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