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ON THE REVERSIBILITY OF η^4-CYCLOBUTADIENE METAL FORMATION FROM COMPLEXED ALKYNES: UNIMOLECULAR ISOMERIZATION OF LABELED RACEMIC AND ENANTIOMERICALLY ENRICHED η^5-CYCLOPENTADIENYL-η^4-CYCLOBUTADIENE COBALT COMPLEXES

G. Ville, K. Peter C. Vollhardt, and Mark J. Winter

June 1981

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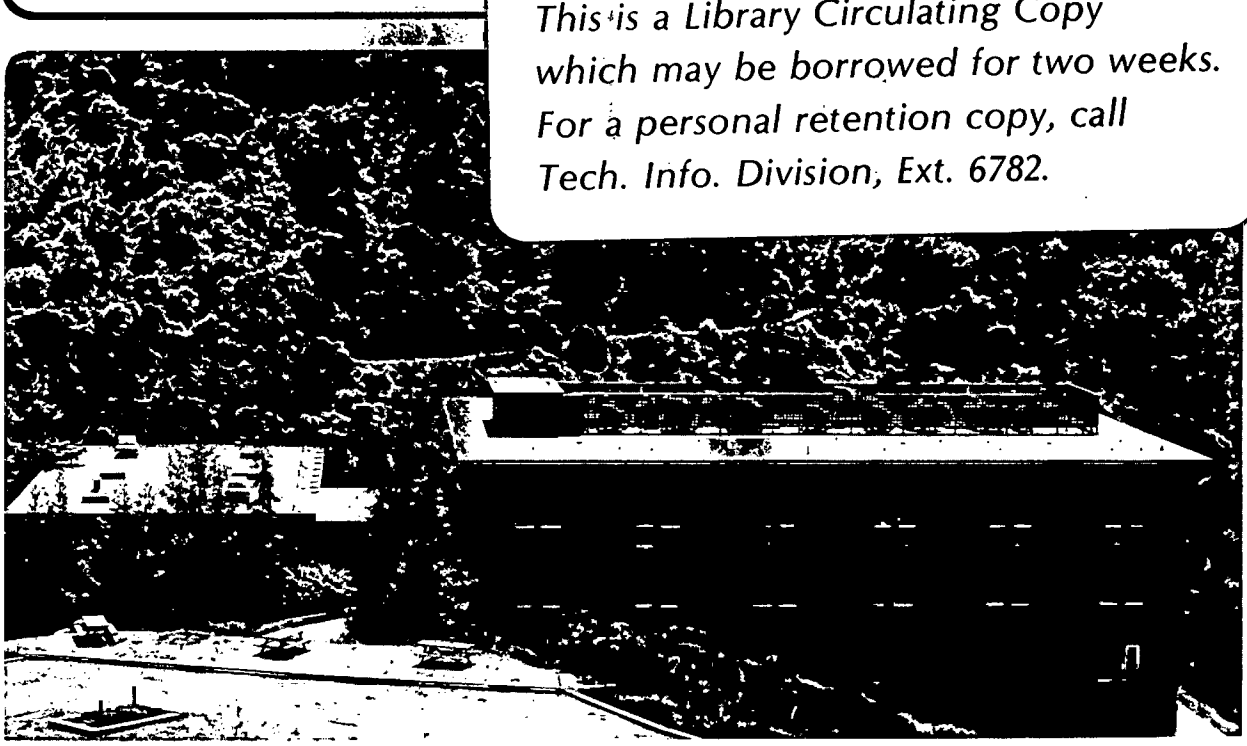

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On the Reversibility of η^4-Cyclobutadiene Metal Formation From Complexed Alkynes: Unimolecular Isomerization of Labeled Racemic and Enantiomerically Enriched η^5-Cyclopentadienyl-η^4-cyclobutadiene Cobalt Complexes

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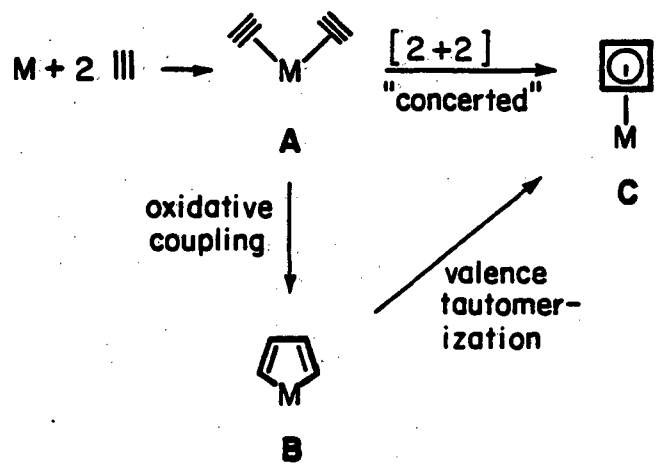
Abstract

Diastereomeric 1,2-bis(trimethylsilyl)-3-alkylcyclobutadiene cyclopentadienyl cobalt complexes in which the alkyl group contains a chiral center may be synthesized, separated, and equilibrated in the gas phase at 540-650° by flash vacuum pyrolysis or in solution in refluxing pristane (301°C). The process is unimolecular as shown by crossover experiments and kinetic analysis. Isomerization occurs by inversion at the four-ring, demonstrated by the pyrolysis of complexes enantiomerically enriched at the chiral carbon center and analysis of the products by optically active NMR shift reagents. No other processes but diastereoisomerization are observed in solution. In the gas phase increasing temperatures lead to increasing decomposition of starting complexes to cobalt metal and alkynes derived by retrocyclization of the cyclobutadiene ligand, in addition to positionally isomerized complexes. Such positional isomerization is also the mechanism of diastereoisomerization as shown by the pyrolysis of 1-triethylsilyl-2-trimethylsilyl substituted and ^{13}C-labeled complexes. The data strongly imply that the cyclization

of alkynes to cyclobutadienes in the coordination sphere of cobalt is reversible.

The interaction of transition metal complexes with alkynes frequently results in the formation of η^4-cyclobutadiene metal complexes.[1] However, the mechanism of their formation has never been elucidated. Two obvious pathways are illustrated in Scheme 1. The first involves a concerted one step [2+2] cycloaddition in the coordination sphere of the metal (A→C). This reaction, when occurring in the neighborhood of only one metal, is postulated to be unfavorable on theoretical grounds,[2,3] although its symmetry dictated "forbiddenness"

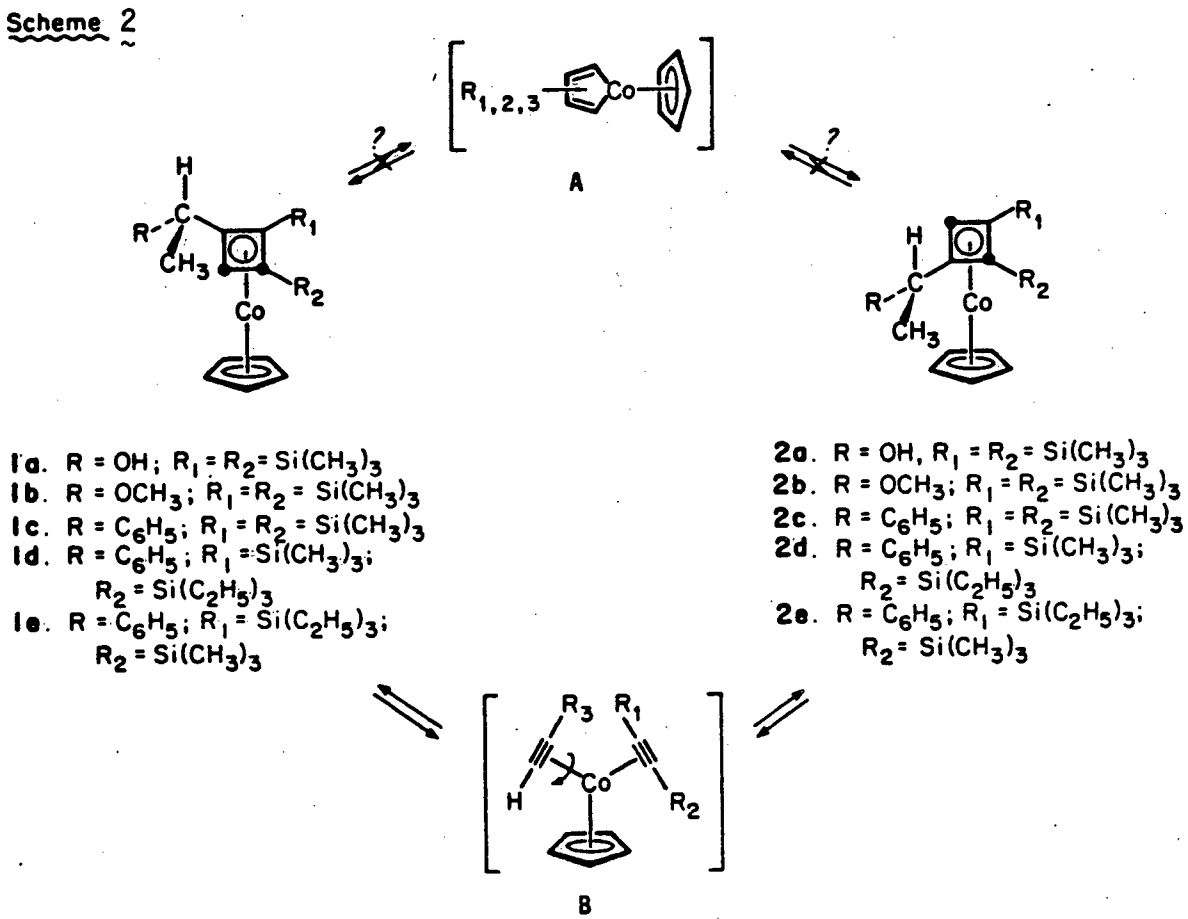
Scheme I



is removed for binuclear metal catalysis. The second, currently most accepted mechanistic possibility is a stepwise process comprising initial oxidative coupling of the two alkynes followed by valence tautomerization (A→B→C).[1,2,4] Metallacyclopentadienes of the type B have been invoked as crucial intermediates in the cyclotrimerization of alkynes to benzenes.[5a] Cyclobutadiene complexes C may be relay points in the synthesis of cyclooctatetraene from acetylene,[1,5b], and in alkyne

metathesis.[5c] Some isolable representatives of B thermally convert to cyclobutadiene metal complexes,[6a] supporting the notion that they might also be intermediates en route to C. However, it is not clear whether this reaction, which appears to be forbidden,[6b] proceeds through initial retrocyclization (e.g. B→A→C). There are indications that complexes of type C may react through representatives of B.[5d] We present for the first time compelling evidence for the reversible formation of A from C in the pyrolysis of η^5-cyclopentadienyl-η^4-cyclobutadiene cobalt complexes. While we cannot rule out B as an intermediate in this process, if it is present, our data demand that it be relatively configurationally stable when M = η^5-CpCo.

Scheme 2



Starting materials 1a-c and 2a-c were prepared in good yield by adding the appropriate alkyne to refluxing bis(trimethylsilyl)acetylene (BTMSA) in the presence of stoichiometric amounts of $CpCo(CO)_2$,[8] and the diastereomers separated by column chromatography on alumina and/or by reverse phase high pressure liquid chromatography (CH_3OH-H_2O eluant).[9] Their relative stereochemistry is arbitrarily assigned as 1 for the high R_f isomer, 2 for the other. When either diastereomer 1 or 2 (racemic) is exposed to flash vacuum pyrolysis conditions at very short contact times (ca. 0.005 s, ca. 10^{-5} torr)[10] between 540°C and 650°C extensive equilibration between the two is observed. This is illustrated for compounds 1c and 2c in Figure 1.

Several observations are significant. At higher temperatures increasing decomposition of the starting complexes is observed furnishing a cobalt mirror and the four alkynes derivable from retrocyclization of the four-ring.[11] At all temperatures the mass balance is excellent[12,13] and the ratio of trapped alkynes approximately constant.[14] Decomposition with concomitant isomerization to the 1,3-bis(trimethylsilyl) isomer 3[7] is observed, but only to a small extent (Figure 1). The identity of this compound was ascertained by independent synthesis.[15] When independently pyrolyzed, 3 is stable at temperatures (540-650°C) at which 1c and 2c show substantial interconversion, but furnishes small amounts (589°C, 2c+1c, 4%) of its isomers at higher temperatures

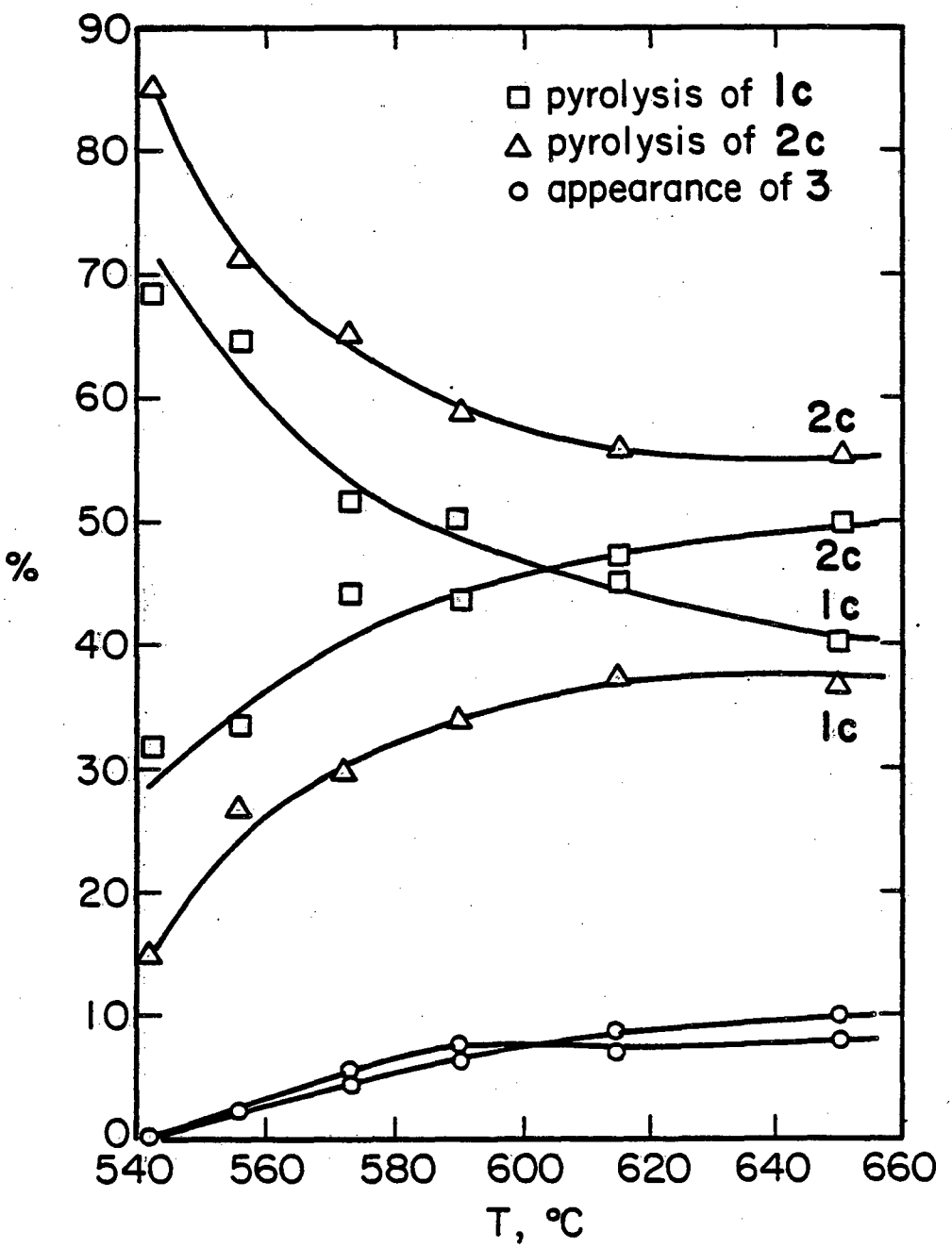
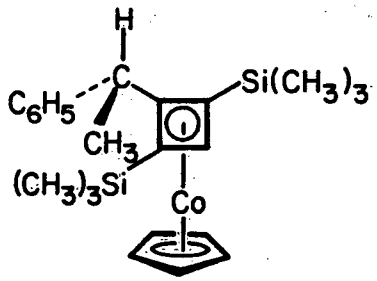


Figure 1: Flash vacuum pyrolysis results of diastereomers 1c (squares) and 2c (triangles). Percentages of the cyclobutadiene isomers are normalized to sum to 100%.



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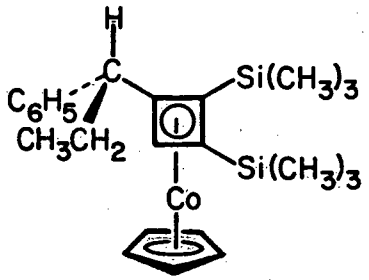

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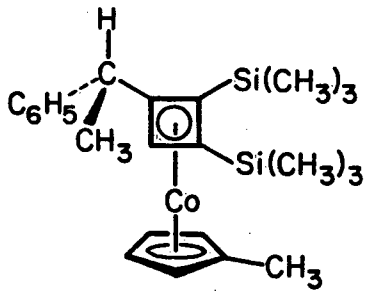

5

when alkyne formation is extensive. Copyrolysis of one diastereomer each of 4 and 5[7] (racemic) at 589°C gives the respective other diastereomer, but no crossover product.

In rigorously purified pristane using silylated glassware (neat hexamethyldisilazane) and a glass encased magnetic stirrer 1c and 2c (racemic) equilibrate on heating following clean first order kinetics[13] (e.g. 2c→1c: $k_{301°C} = 2.226 \times 10^{-5}$ sec^{-1}; $\Delta G^{\neq} = 51.7$ kcal $mole^{-1}$). Under these conditions there is no decomposition and no isomerization to 3. A crossover experiment in solution using 4 and 5 confirmed the intramolecular character of the transformation.

The identity of the inverting center (cyclobutadiene ring versus chiral carbon) was ascertained using enantiomerically enriched 2a. For this purpose 1-butyne-3-ol was partially resolved[16] and the (+)(R) enantiomer reacted with BTMSA and $CpCo(CO)_2$ to furnish after h.p.l.c. (reverse phase, CH_3CN-H_2O, 93:7) 1a and 2a each as a 4:1 mixture of enantiomers determined by NMR using tris(3-trifluoromethylhydroxymethylene-d-camphorato) europium shift reagent. When enantiomerically enriched

2a was flash pyrolyzed at 571°C it equilibrated exclusively with enantiomerically enriched (4:1) 1a (2a:1a = 65.6:34.4), the major enantiomer being 1a, the minor its mirror image.[17] The enantiomeric purity of recovered starting material remains unchanged.

While the observed data are intuitively best accommodated by the intermediacy of D (Scheme 2), an alternative pathway could involve retrocyclization to a bisalkyne complex (such as E), followed by rotation and ring closure. To probe this possibility 1-triethylsilyl-2-trimethylsilylethyne was cocyclized with 3-phenyl-1-butyne to give four compounds 1d, e, 2d, e separated by h.p.l.c.[7,9] To unambiguously assign the structures of pairs of related positional isomers (e.g. 1d, 2e versus 1e, 2d) they were independently synthesized from triethylsilylethyne and 1-trimethylsilyl-3-phenyl-1-butyne[7] on the one hand and trimethylsilylethyne and 1-triethylsilyl-3- phenyl-1-butyne[7] on the other.[18] Should D be responsible for the equilibration of (1a-c)⇄(2a-c), 1d would reversibly give 2e, and 1e will lead to 2d. On the other hand the intermediacy of E should equilibrate all isomers 1d, e, 2d, e with each other, if both alkyne ligands are free to rotate, but should isomerize only 1d⇄2d or 1e⇄2e respectively, if one ligand (most likely the more hindered bissilylalkyne) were immobile.[19] <u>Surprisingly, equilibration occurs only</u> within the pairs 1d⇄2d and 1e⇄2e, strongly implicating the occurrence of the latter process. This is further corroborated by a ^{13}C-labelling experiment with 1,4-^{13}C-labeled cyclobutadiene complex 1d (indicated by dark dots in Scheme 2), prepared from $(C_2H_5)_3Si^{13}C_2H$. Isomerization

of this compound proceeds cleanly to the 1,3-^{13}C-labeled isomer.[20]

We conclude that 1 and 2 reversibly isomerize through the intermediacy of E by single alkyne rotation. Although we cannot rule out D as being kinetically accessible, if formed it cannot be planar and has to be configurationally stable, since planarization would interconvert 1d and 2e, and 1e and 2d.

Acknowledgements

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(7) All new compounds isolated gave satisfactory analytical and/or spectral data. Representative are compounds 1c (high R_f isomer): yellow crystals; mp 62-63°C; m/e (rel intensity) 424.1456 (calcd 424.1452, M^+, 100%), 326 ($CpCoMe_3SiC_2C_6H_5C_2H_4$, 41%), 294 ($CpCoMe_3SiC_2SiMe_3$, 71%), 222 ($CpCoMe_3SiC_2H$, 12%), 73 ($-SiMe_3$, 75%); NMR (90MHz) ($CD_2Cl_2$) δ 7.26 (m,5H), 4.58(s, 5H), 4.06(s,1H), 3.28 (q, J = 7Hz, 1H), 1.64 (d, J = 7Hz, 3H), 0.29 (s, 9H), 0.17 (s,9H); 2c (low R_f isomer): yellow crystals; mp 65-66°C; m/e (rel. intensity) 424.1440 (calcd 424.1452, M^+, 100%), 326 ($CpCoMe_3SiC_2C_6H_5C_2H_4$, 38%), 294 ($CpCoMe_3Si$-$C_2SiMe_3$, 68%), 222 ($CpCoMe_3SiC_2H$, 12%), 73 ($-SiMe_3$, 54%); NMR (90MHz) ($CD_2Cl_2$) δ 7.19 (m,5H), 4.94 (s,5H), 4.49 (s,1H), 3.42 (q, J = 7Hz, 1H), 1.35 (d, J = 7Hz, 3H), 0.20 (s, 9H), -0.05 (s,9H); 3: yellow crystals; mp 103-104 C; m/e 424.1456 (calcd 424.1453, M^+, 100%), 326 ($CpCoMe_3SiC_2C_6H_5C_2H_4$, 58%), 253 ($M^+$-$Me_3Si$,-$Me_3SiC_2H$, 65%), 222 ($CpCoMe_3SiC_2H$, 17%), 73 ($-SiMe_3$, 61%); NMR (90MHz)($CD_2Cl_2$) δ 7.19 (m,5H), 4.87 (s,5H), 4.02(s,1H), 3.39 (q, J = 7Hz, 1H), 1.37 (d, J = 7Hz, 3H), 0.20 (s, 9H), -0.14 (s,9H). Compounds 1c-e and one isomer of 4

are assigned the same configuration with respect to cobalt based on very similar NMR chemical shifts: δ = 4.59-4.63 (Cp), 4.18-4.23 (cbd), 1.47-1.52 (CH_3 or CH_2CH_3). Compare with 2c-e and the other isomer of 4: δ = 4.87-4.91 (Cp), 4.44-4.49 (cbd), 1.32-1.37 (CH_3 or CH_2CH_3).

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(11) Fritch, J. R.; Vollhardt, K.P.C. Angew. Chem., 1979, 91, 439. Angew. Chem., Int. Ed. Engl., 1979, 18, 409. Traces of cyclopentadiene but no other Cp-derived products were identifiable. % Decomposition at various temperatures: 544°C: 7%; 576°C: 30%; 615°C: 55%; 650°C: 80%.

(12) The pyrolysis products were trapped at -196°C and subjected to g.c. mass spectral, g.c., NMR, and analytical h.p.l.c. analysis using, when appropriate, internal calibration standards.

(13) The equilibrium composition of 1c$\rightleftarrows$2c is extrapolated at 42:58, a value which furnishes good first order kinetics in the analysis of the solution rate studies.

(14) $(CH_3)_3Si\text{-}C{\equiv}C\text{-}Si(CH_3)_3$: $(CH_3)_3Si\text{-}C{\equiv}C\text{-}CH(CH_3)C_6H_5$= ~1:2.4

(15) Addition of $CpCo(CO)_2$ (1 equiv) and 1-trimethylsilyl-3-phenylbut-1-yne (1 equiv) to refluxing BTMSA followed by column chromatography on alumina and hplc (reverse phase, CH_3OH-H_2O eluant) to give 1,2,3-tris(trimethylsilyl)-4-(2-phenylethyl)cyclobutadiene cyclopentadienyl cobalt (5.5%).[7] This compound was selectively protodesilylated with p-toluenesulfonic acid in C_6D_6 to 3 (75%).

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(17) The europium shifted NMR absorptions of 2a show the Cp-singlet of the major enantiomer (herein designated RS) shifted somewhat less than that of the minor one (SR). After pyrolysis the same pattern was observed for 1a (RR : SS = 4 : 1), identical to that seen for synthetic 1a obtained from the reaction of enriched chiral alkyne with BTMSA. Had inversion at the chiral carbon taken place an inverse NMR absorption pattern should have been observed (RR : SS = 1 : 4).

(18) This gives four isomers in each case, the respective 1/2 pair and two new 1,3-bissilylcyclobutadiene isomers, all cleanly separated by h.p.l.c.[7]

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(20) This system is in fact "hexalabeled" (2 chiral, 2 silyl, 2 ^{13}C labels). 1d: $J_{^{13}C-^{13}C}$ = 24.1Hz; $J_{^{13}C-^{13}CH}$ = 5.5Hz; $J_{^{13}C-H}$ = 177Hz. 2d: $J_{^{13}C-^{13}C}$ = 2Hz; $J_{^{13}C-^{13}CH}$ = 9Hz; $J_{^{13}C-H}$ = 190Hz; as expected: Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy"; 2nd edn., Wiley: New York, NY, 1980. Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra", Heyden: Philadelphia, PA, 1978.

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