$C_6H_6^{+}\cdot + NO$,[11] where only a π complex is formed with no evidence for a σ complex.

We believe this to be the first clear example of a reaction of an aromatic radical cation with NO_2 to produce a nitroaromatic species. We have also observed similar reactions for other aromatic radical cations. While solvation effects may change, in some cases, the relative stabilities of the radical cation and NO_2^+, these results show that further consideration is warranted of the aromatic radical cation as an intermediate in nitration reactions.

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[11] Unpublished results.

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§

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

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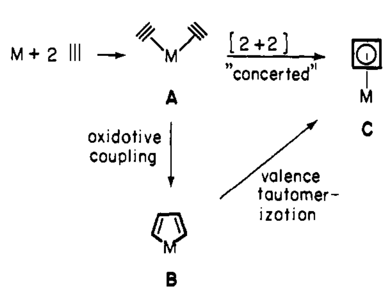
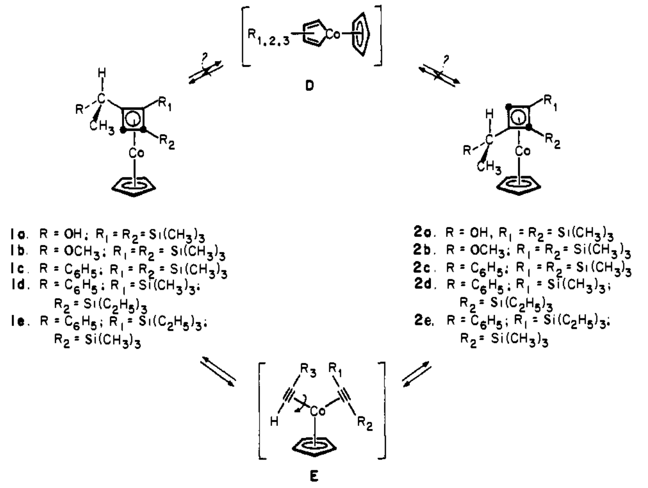
The interaction of transition-metal complexes with alkynes frequently results in the formation of η^4-cyclobutadiene-metal complexes.[1] However, the mechanism of their formation has never been elucidated. Two obvious pathways are illustrated in Scheme I. The first involves a concerted one-step [2 + 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" 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 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

Scheme I



Scheme II



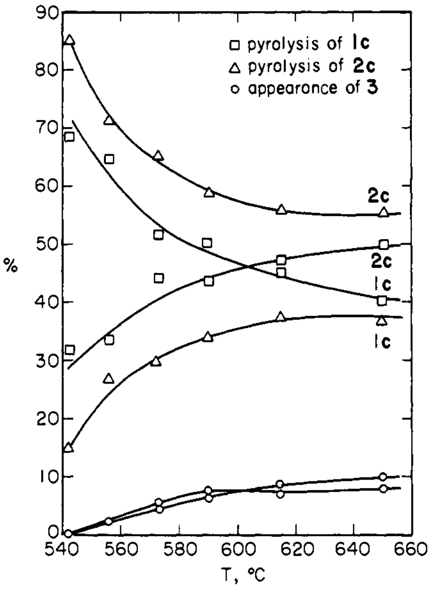


Figure 1. Flash vacuum pyrolysis results of diastereomers **1c** (squares) and **2c** (triangles). Percentages of the cyclobutadiene isomers are normalized to sum to 100%.

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† NATO Postdoctoral Fellow, 1980–1981.

‡ Camille and Henry Dreyfus Teacher–Scholar, 1978–1983.

§ SRC–NATO Postdoctoral Fellow, 1978–1980.

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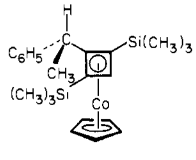
compelling evidence for the reversible formation of A from C in the pyrolysis of η^5-cyclopentadienyl-η^4-cyclobutadiene–cobalt complexes. While we cannot rule out B as an intermediate in this process, if it is present, our data demand that it be relatively configurationally stable when M = η^5-CpCo.

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 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 and **2** for the other. When either diastereomer **1** or diastereomer **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 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-membered 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 when alkyne formation is extensive. Copyrolysis of one distereomer each of **4** and **5**[7] (racemic) at 589 °C gives the respective other diastereomer but *no crossover product.*



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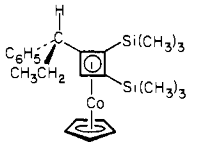

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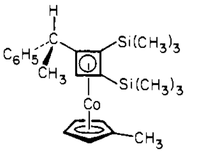

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In rigorously purified pristane, using silylated glassware (neat hexamethyldisilazane) and a glass-encased magnetic stirrer, **1c** and **2c** (racemic) equilibrate on heating following clean first-order kinetics[13] (e.g., **2c** → **1c**: $k_{301} = 2.226 \times 10^{-5}\ s^{-1}$; $\Delta G^{\ddagger} = 51.7$ kcal mol^{-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 vs. chiral carbon) was ascertained by using enantiomerically enriched **2a**. For this purpose 1-butyn-3-ol was partially resolved[16] and the (+)-(*R*) enantiomer reacted with BTMSA and $CpCo(CO)_2$ to furnish after HPLC (reverse phase, 93:7 CH_3CN–H_2O) **1a** and **2a** each as a 4:1 mixture of enantiomers determined by NMR spectroscopy using tris[3-[(trifluoromethyl)hydroxymethylene)]-*d*-camphorato]europium shift reagent. When enantiomerically enriched **2a** was flash pyrolyzed at 571 °C it equilibrated exclusively with enantiomerically enriched (4:1) **1a** (65.6:34.4 **2a–1a**), 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 II), an alternative pathway could involve retrocyclization to a bis-alkyne complex (such as E), followed by rotation and ring closure. To probe this possibility 1-(triethylsilyl)-2-(trimethylsilyl)ethyne was cocyclized with 3-phenyl-1-butyne to give four compounds **1d,e**, **2d,e** separated by HPLC.[7,9] To unambiguously assign the structures of pairs of related positional isomers (e.g., **1d**, **2e** vs. **1e**, **2d**) they were independently synthesized from (triethylsilyl)ethyne and 1-(trimethylsilyl)-3-phenyl-1-butyne[7] on the one hand and (trimethylsilyl)ethyne 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 bis(silylalkyne)] were immobile.[19] *Surprisingly, equilibration occurs only* within the pairs **1d** ⇄ **2d** and **1e** ⇄ **2e**, strongly implicating the occurrence of the latter process. This is further corroborated by a ^{13}C-labeling experiment with 1,4-^{13}C-labeled cyclobutadiene complex **1d** (indicated by dark dots in Scheme II), prepared from $(C_2H_5)_3Si^{13}C_2H$. Isomerization of this compound proceeds cleanly to the 1,3-^{13}C-labeled isomer.[20]

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(7) All new compounds isolated gave satisfactory analytical and/or spectral data. Representative are the following compounds. **1c** (high R_f isomer): yellow crystals; mp 62–63 °C; *m/e* (relative 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 (90 MHz) ($CD_2Cl_2$) δ 7.26 (m, 5 H), 4.58 (s, 5 H), 4.06 (s, 1 H), 3.28 (q, *J* = 7 Hz, 1 H), 1.64 (d, *J* = 7 Hz, 3 H), 0.29 (s, 9 H), 0.17 (s, 9 H). **2c** (low R_f isomer): yellow crystals; mp 65–66 °C; *m/e* (relative intensity) 424.1440 (calcd 424.1452, M^+, 100%), 326 ($CpCoMe_3SiC_2C_6H_5C_2H_4$, 38%), 294 ($CpCoMe_3SiC_2SiMe_3$, 68%), 222 ($CpCoMe_3SiC_2H$, 12%), 73 ($SiMe_3$, 54%); NMR (90 MHz) ($CD_2Cl_2$) δ 7.19 (m, 5 H), 4.94 (s, 5 H), 4.49 (s, 1 H), 3.42 (q, *J* = 7 Hz, 1 H), 1.35 (d, *J* = 7 Hz, 3 H), 0.20 (s, 9 H), –0.05 (s, 9 H). **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 (90 MHz) ($CD_2Cl_2$) δ 7.19 (m, 5 H), 4.87 (s, 5 H), 4.02 (s, 1 H), 3.39 (q, *J* = 7 Hz, 1 H), 1.37 (d, *J* = 7 Hz, 3 H), 0.20 (s, 9 H), –0.14 (s, 9 H). 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 $\mathit{CH_2}CH_3$). 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 $\mathit{CH_2}CH_3$).

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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. Percent 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 GC, mass spectral, NMR, and analytical HPLC analysis using, when appropriate, internal calibration standards.

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

(14) $(CH_3)_3SiC{\equiv}CSi(CH_3)_3{:}(CH_3)_3Si{-}C{\equiv}C{-}CH(CH_3)C_6H_5 = \sim 1{:}2.4$.

(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)cyclopentadienylcobalt (5.5%).[7] This compounds 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 with 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-bis(silylcyclobutadiene) isomers, all cleanly separated by HPLC.[7]

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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**.

Acknowledgment. This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, and the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquefaction Division, of the U.S. Department of Energy under Contract No. W-7405-ENG-48 through the Pittsburgh Energy Technology Center, Pittsburgh, PA, and in part by NSF (CHE 79-03954). We are grateful for the astute comments of the referees.

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(20) This system is in fact "hexalabeled" (two chiral, two silyl, two ^{13}C labels). **1d**: $J_{^{13}C-^{13}C}$ = 24.1 Hz; $J_{^{13}C-^{13}CH}$ = 5.5 Hz; $J_{^{13}C-H}$ = 177 Hz. **2d**: $J_{^{13}C-^{13}C}$ = 2 Hz; $J_{^{13}C-^{13}CH}$ = 9 Hz; $J_{^{13}C-H}$ = 190 Hz; as expected. 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.

A New Geometrical Form of Silicon. Synthesis and Structure of Tetraethylammonium Bis(1,2-benzenediolato)fluorosilicate(IV)

John J. Harland, Roberta O. Day, Jean F. Vollano,
Arjun C. Sau, and Robert R. Holmes*

Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01003

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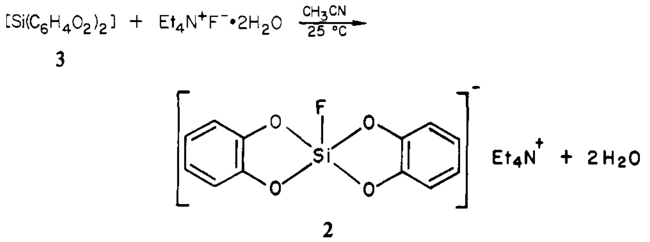
Anionic pentacoordinated silicon compounds,[1] isoelectronic with phosphoranes, are extremely rare. Of those synthesized, X-ray structural characterization of a spirocyclic derivative $[(C_6H_4O_2)_2SiPh]^-Me_4N^+$ (**1**) has been reported[2] and reveals a trigonal-bipyramidal form displaced about one-third the way toward a square pyramid.

We report here the preparation and X-ray crystal structure of the first pentacoordinated Si(IV) compound having a square-pyramidal conformation. The compound, tetraethylammonium bis(1,2-benzenediolato)fluorosilicate(IV) (**2**), mp 208–210 °C,


$[Si(C_6H_4O_2)_2] + Et_4N^+F^-\cdot 2H_2O \xrightarrow[25\ °C]{CH_3CN}$

3

2

was prepared by the reaction of bis(catecholato)silicon(IV) (**3**)[3] with $Et_4N^+F^-\cdot 2H_2O$ in methyl cyanide at room temperature. Crystals suitable for X-ray diffraction analysis were grown from a 1:2 mixture of methyl cyanide–diethyl ether at 0 °C. Anal. Calcd for $C_{20}H_{28}O_4NFSi$: C, 61.04; H, 7.17; N, 3.55. Found: C, 60.79; H, 7.15; N, 3.49.

Crystal Data for $C_{20}H_{28}O_4NFSi$ (**2**); Space group $C2/c$ (C_{2h}^6, No. 15),[4] with a = 28.091 (4), b = 11.213 (1), c = 33.582 (8) Å; β = 128.76 (1)°; Z = 16. Independent reflections (4711) were measured on an Enraf–Nonius CAD4 automated diffractometer, using graphite monochromated Mo K$\bar{\alpha}$ radiation and the θ–2θ scan mode, to a maximum $2\theta_{MoK\bar{\alpha}}$ of 43°. The structure was solved by using direct methods (MULTAN). Full-matrix least-squares refinement[5] (54 independent nonhydrogen atoms, anisotropic, varied; 32 independent hydrogen atoms, excluding methyl hydrogen atoms, isotropic, fixed) led to a conventional unweighted residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.064 for the 2705 independent reflections having $I \geq 2\sigma(I)$.

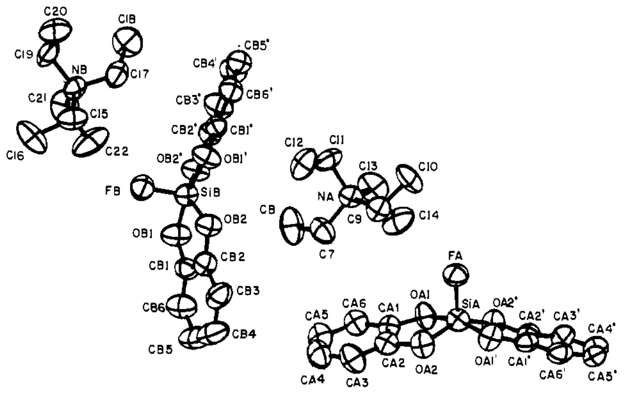


Figure 1. ORTEP plot of $[(C_6H_4O_2)_2SiF]^-Et_4N^+$ (**2**), with thermal ellipsoids shown at the 50% probability level. Bond parameters for anion A (those for anion B are in parentheses), lengths (Å): Si–F = 1.607 (4) (1.599 (4)), Si–O1 = 1.742 (5) (1.741 (5)), Si–O1′ = 1.736 (5) (1.738 (5)), Si–O2 = 1.704 (5) (1.699 (5)), Si–O2′ = 1.706 (5) (1.701 (5)). Angles (deg): O1–Si–O1′ = 164.0 (2) (168.4 (3)), O2–Si–O2′ = 145.5 (3) (140.7 (3)).

Two discrete molecules of **2** are present in the unit cell shown in the ORTEP plot of Figure 1. The bond angle data given in the legend indicate that the structure of the molecule labeled A is more square pyramidal than the B molecule. On the basis of the dihedral angle data, as applied to cyclic phosphoranes,[6,7] the geometry about the silicon atom for molecule A is displaced by 70.5% (68.7% using unit vectors) from the trigonal bipyramid toward the square-pyramidal configuration. The structure of the B molecule is displaced 54.6% (52.8%) toward the square pyramid. Both molecules follow the local C_{2v} constraint of the coordinate connecting the trigonal bipyramid to the rectangular pyramid. Each molecule has approximate 2-fold symmetry with the 2-fold axis coincident with the Si–F bond. Following the trend observed for cyclic phosphoranes,[6-8] the "axial" Si–O bonds are longer than the "equatorial" Si–O bonds, averaging 0.03 Å longer for each independent molecule.

Although crystal packing effects exert some influence on the structural form obtained for **2**, the recent discovery of the rectangular pyramidal geometry for related pentacoordinated Ge(IV)[9] and Sn(IV)[10] species suggests the operation of substituent effects as the principal structural determinant.

For each of these pentacoordinated derivatives, the structures obtained follow the factors deemed important in forming the rectangular pyramidal geometry for phosphoranes.[7,8]

The placement of the structures for **1** and **2** on the ligand exchange coordinate connecting the trigonal bipyramid and square pyramid suggests that fluxional behavior, common for phospho-

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