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The Cis−Trans Isomerization of 1,2,5,6-Tetrasilacycloocta-3,7-dienes: Analysis by Mechanistic Probes and Density Functional Theory

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A series of alkyl- and aryl-substituted derivatives of *cis,cis*-1,2,5,6-tetrasilacycloocta-3,7-diene were prepared. Isomerization of these compounds to the corresponding *trans,trans*-1,2,5,6-tetrasilacycloocta-3,7-dienes by exposure to Ru and Zr hydride complexes was explored. Experimental probes of the isomerization were consistent with a stepwise mechanism involving metal hydride addition/elimination rather than one involving radical intermediates. Analysis of the low energy conformers of the various cis and trans isomers of 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene using density functional theory suggested the following trend in stability: trans,trans > cis,trans > cis,cis. The calculated trend in stability was consistent with the experimentally observed unidirectional isomerization of the carbon−carbon double bonds from all cis to all trans and supports a cis,trans isomer as a tenable intermediate.

Introduction

The interconversion of cis and trans alkenes has long been of interest to the organic chemist.[1,2] Since the cis and trans double bonds of organic compounds are usually quite stable, relatively drastic conditions are often required for isomerization. In the case of some highly conjugated compounds, however, cis−trans isomerization occurs so readily that precautions must be taken to avoid unwanted interconversion.[1,2] Typical strategies for inducing cis−trans isomerization can be classified as photochemical,[3,4] thermal,[5,6] and catalytic.[7−9] Photochemical isomerization can be induced by irradiation with ultraviolet or visible light and tends to produce less stable isomers.[3] Thermal isomerization proceeds via rotation about the double bond without any change in the multiplicity of the electronic state of the molecules, or via rotation during which the molecule goes through a triplet state, or via a combination of both.[1,5,6] In any event, the product of a thermal isomerization is typically the more stable isomer. The isomerization of alkenes by

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(1) Wyman, G. M. *Chem. Rev.* **1955**, *55*, 625.

(2) Crombie, L. *Quart. Rev. (London)* **1952**, *6*, 106.

(3) Whitesides, G. M.; Goe, G. L.; Cope, A. C. *J. Am. Chem. Soc.* **1969**, *91*, 2608.

(4) Chow, Y. L.; Core, G. E.; Shen, Y. *Organometallics* **1985**, *3*, 702.

(5) Calvin, M.; Alter, H. W. *J. Chem. Phys.* **1951**, *19*, 768.

(6) Kalra, B. L.; Afriyie, Y.; Brandt, B.; Lewis, D. K.; Baldwin, J. E. *J. Phys. Chem.* **1995**, *99*, 8142.

(7) McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224.

(8) Cramer, R.; Lindsey, R. V., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 3535.

(9) Alibrandi, G.; Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1994**, 951.

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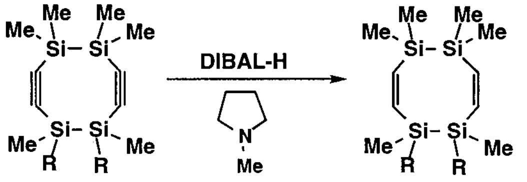
transition metal catalysts has been an important and extensively studied aspect of organometallic chemistry.[7−10] There are now two commonly accepted transition metal catalyzed mechanisms. One involves an intramolecular 1,3-hydrogen shift, and the other an intermolecular hydrogen addition−elimination.[7,10] Typically, transition metal catalyzed isomerizations yield the more stable isomer.

Of all transition metal-catalyzed isomerizations of aliphatic and alicyclic olefins, the isomerization of 1,5-cyclooctadiene (**COD**) has received considerable attention theoretically[11,12] and experimentally[3,13−17] due to the variety of conformations available to the cycloalkene before, during, and after the isomerization process. For example, optimized geometries at energy minima by ab initio calculations show that **COD** has six low energy conformers: cis,cis-twistboat (*c*,*c*-twistboat), cis,cis-chair (*c*,*c*-chair), cis,cis-halfchair (*c*,*c*-halfchair), cis,trans-crown (*c*,*t*-crown), trans,trans-twist (*t*,*t*-twist), and trans,trans-chair (*t*,*t*-chair).[12] Moreover, of all six conformers, the *c*,*c*-twistboat is the most stable, and the *t*,*t*-chair is the least stable, with an energy difference spanning 28.2 kcal/mol.[12] In general, the cis,cis isomers of **COD** are more stable than all others. Nevertheless, both the irradiation of *c*,*c*-**COD** by UV light in the presence of cuprous(I) chloride and the Hofmann elimination of 1,5-bis(*N*,*N*-dimethylamino)cyclooctane dimethiodide have been shown to produce *c*,*t*- and *t*,*t*-**COD** among mixtures of isomers.[3,13−17] The two highly strained conformers of *t*,*t*-**COD**, twist and chair, cannot readily interconvert.[11,12,18] Energy calculations favor the twist form over the chair form by 5.35 (MM1)[11] and 8.1 (ab initio)[12] kcal/mol. Furthermore, due to its remarkably high ring strain,[3,11,12] the experimental isolation of the chair conformer of *t*,*t*-**COD** has yet to be reported.

In this paper, we explore the mechanism of the unexpected cis,cis to trans,trans isomerization of some unique disilanyl analogues of **COD**, the alkyl-substituted 1,2,5,6-tetrasilacycloocta-3,7-dienes. An example of this reaction has been communicated by us in preliminary form.[19] By using a variety of experimental and theoretical methods, we find that, in contrast to **COD**, the most stable isomer of 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene possesses the *t*,*t*-chair conformation. Moreover, we find that the isomerization from cis,cis to trans,trans proceeds via a metal-hydride addition/elimination mechanism and involves the participation of a relatively stable cis,trans diolefin intermediate.

Results and Discussion

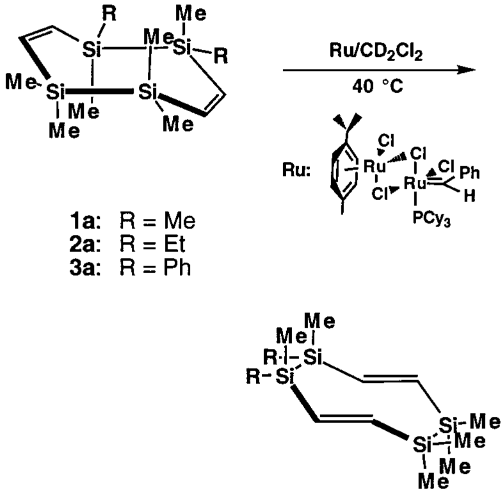
Synthesis and Isomerization of the 1,2,5,6-Tetrasilacycloocta-3,7-dienes. Methods for the synthesis of strained 1,2,5,6-tetrasilacycloocta-3,7-diynes have been known since 1983.[20−22] Until our recent report,[19] however, a general method for the reduction of the alkyne bonds in these compounds to alkene bonds was unknown. Starting from diyne precursors,[20−23] eq 1 illustrates the



(1)

R = Me (**1a**), Et (**2a**), and Ph (**3a**)

syntheses of *cis*,*cis*-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**1a**), *cis*,*cis*-1,2,5,5,6,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**2a**), and *cis*,*cis*-1,2,5,5,6,6-hexamethyl-1,2-diphenyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**3a**). Equation 2 illustrates the Ru-catalyzed isomerizations of **1a** and **2a** to *trans*,*trans*-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**1b**) and *trans*,*trans*-1,2,5,5,6,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**2b**), respectively. The isomerizations were observed to proceed slowly in methylene chloride upon exposure of **1a** and **2a** to a catalytic portion of the recently described dimeric ruthenium(II) alkylidene complex $(Cy_3P)RuCl_2(=CHPh)Ru(p\text{-cymene})Cl_2$ (**Ru**).[24] Because an induction period for the formation of the active form of the catalyst was observed upon dissolution of **Ru** in the solvent,[25] the reactions were carried out in the presence of **Ru** that had been preincubated under ambient light at 40 °C in CD_2Cl_2 for 5 days prior to the addition of diene. Under these reaction



1a: R = Me
2a: R = Et
3a: R = Ph

(2)

1b: R = Me
2b: R = Et

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(10) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248.

(11) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.

(12) Shimitzu, T.; Iwata, K.; Kamigata, N.; Ikuta, S. *J. Chem. Res., Synop.* **1994**, 436.

(13) Srinivasan, R. *J. Am. Chem. Soc.* **1964**, *86*, 3318.

(14) Cope, A. C.; Howell, C. F.; Bowers, J.; Lord, R. C.; Whitesides, G. M. *J. Am. Chem. Soc.* **1967**, *89*, 4024.

(15) Whitesides, G. M.; Goe, G. L.; Cope, A. C. *J. Am. Chem. Soc.* **1967**, *89*, 7136.

(16) Anet, F. A. L.; Kozerski, L. *J. Am. Chem. Soc.* **1973**, *95*, 3407.

(17) Boeckh, D.; Huisgen, R.; Nöth, A. *J. Am. Chem. Soc.* **1987**, *109*, 1248.

(18) Eckehard, V. D.; Stiehm, T. *Tetrahedron Lett.* **1990**, *31*, 1841.

(19) Zhang, L.; Jung, D.-Y.; Bittner, E. R.; Sommer, M. S.; Dias, E. L.; Lee, T. R. *J. Org. Chem.* **1998**, *63*, 8624.

(20) Sakurai, H.; Nakadaira, A.; Hosomi, A.; Eriyama, Y.; Kabuta, C. *J. Am. Chem. Soc.* **1983**, *105*, 3359.

(21) Iwahara, T.; West, R. *J. Chem. Soc., Chem. Commun.* **1988**, 954.

(22) Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Funai, A.; Miyai, A.; Ishita, T.; Tsukihara, T.; Yamanaka, T.; Koike, T.; Shioya, J. *Organometallics* **1992**, *11*, 1604.

(23) West, R.; Hayase, S.; Iwahara, T. *J. Inorg. Organomet. Polym.* **1991**, *1*, 545.

(24) Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758.

(25) Zhang, L.; Borysenko, C. W.; Lee, T. R. *J. Org. Chem.* **2001**, **66**, 5284.

conditions, the isomerizations were monitored by examining the relative ratios of the olefinic resonances at δ 6.89 (for **1a** and **2a**) and δ 6.32 (for **1b** and **2b**) in the ^{1}H NMR spectra. Approximately 15 days were required for the ratio of **1b**:**1a** to reach 3:1, and approximately 42 days were required for the ratio of **2b**:**2a** to reach 3:2 as judged by ^{1}H NMR integration against an internal standard. Under the same conditions, compound **3a** failed to isomerize.

Characterization of the 1,2,5,6-Tetrasilacycloocta-3,7-dienes. We confirm the syntheses and structures of the molecules shown in eqs 1 and 2 through physical characterization by ^{1}H NMR, ^{13}C NMR, IR, and UV−vis spectroscopies (vide infra). In addition, while the X-ray crystal structures of **1a** and **1b** were reported in our previous communication,[19] we report here the X-ray crystal structure of compound **3a**.

The ^{1}H NMR spectrum of **1a** suggests a high degree of symmetry for this molecule in solution. Only two resonances are observed: one at δ 0.19 (s, 24 H) due to the methylsilyl hydrogens and one at δ 6.89 (s, 4 H) due to the olefinic hydrogens. The ^{13}C NMR spectrum of **1a** further confirms the high symmetry with resonances at δ −1.4 due to the methylsilyl carbons and at δ 152.1 due to the olefinic carbons. In contrast, the ^{1}H NMR spectrum of **1b** shows three resonances: singlets at δ 0.18 (s, 12 H) and 0.21 (s, 12 H) due to axial and equatorial methylsilyl hydrogens, respectively, and an unusually broad peak at δ 6.32 (br, 4 H) due to the olefinic hydrogens. The peak assignments for **1b** formed via the reaction of **1a** with preincubated **Ru** are based on the observed resonances of authentic, crystalline **1b**.[19] The broadness of the olefinic resonance arises from the interconversion of conformers (vide infra). The ^{13}C NMR spectrum of **1b** shows resonances at δ −6.1 and −3.7 due to axial and equatorial methylsilyl carbons, respectively, and at δ 153.4 due to the olefinic carbons. The ^{1}H NMR spectrum of **2a** shows resonances at δ 0.21 (s, 18 H) arising from the methylsilyl hydrogens, at δ 0.73 (q, 4 H) and 0.99 (t, 6 H) arising from the ethylsilyl hydrogens, and at δ 6.89 (d, 4 H) arising from the olefinic hydrogens. The ^{13}C NMR spectrum of **2a** shows resonances at δ −3.8 and −0.7 due to the methylsilyl carbons, at δ 8.1 and 8.6 due to the ethylsilyl carbons, and at δ 151.7 and 152.9 due to the olefinic carbons. In contrast, the ^{1}H NMR spectrum of **2b** shows resonances at δ 0.20 (s, 18 H) arising from the methylsilyl hydrogens, at δ 0.74 (q, 4 H) and 1.01 (t, 6 H) arising from the ethylsilyl hydrogens, and at δ 6.32 (broad, 4 H) arising from the olefinic hydrogens. The ^{13}C NMR spectrum of **2b** shows resonances at δ −3.5 and −0.7 due to the methylsilyl carbons, at δ 8.7 and 9.0 due to the ethylsilyl carbons, and at δ 152.0 and 153.2 due to the olefinic carbons. The ^{1}H NMR spectrum of **3a** exhibits resonances at δ 0.01−0.48 (m, 18 H) arising from the methylsilyl hydrogens, at δ 7.08 (s, 4 H) arising from the olefinic hydrogens, and at δ 7.21−7.40 (m, 10 H) arising from the phenyl hydrogens. The ^{13}C NMR spectrum of **3a** exhibits a multiplet at δ −0.9 due to the methylsilyl carbons, resonances at δ 128.2 and 129.1 due to the olefinic carbons, and resonances at δ 135.2, 149.4, and 154.7 due to the phenyl carbons.

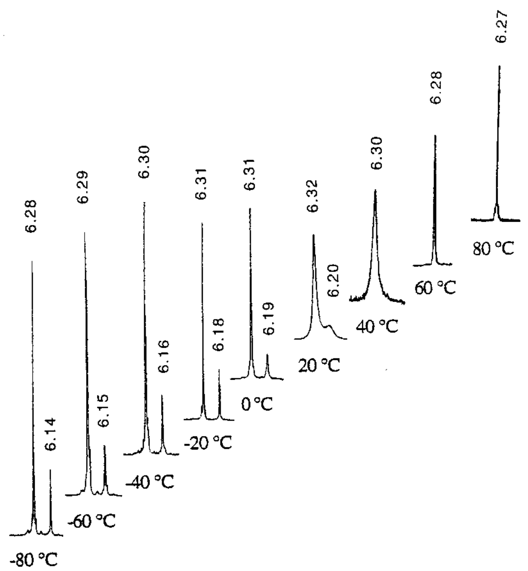

Figure 1. Variable-temperature 300 MHz ^{1}H NMR spectrum of **1b** in CD_2Cl_2 (−80 to 20 °C) and in C_6D_6 (40−80 °C). For the latter experiments, the value of δ was calibrated to CD_2Cl_2.

As noted above, the olefinic resonances at δ 6.32 in the ^{1}H NMR spectra of **1b** and **2b** appear unusually broad, whereas the olefinic resonances of the *c*,*c* isomers **1a**, **2a**, and **3a** appear as sharp singlets. To probe the origin of the broadness of the former resonances, we explored the temperature dependence of this resonance for **1b** (see Figure 1). Upon increasing the temperature from 20 °C to 80 °C, the broad peak narrows to a sharp peak centered at δ 6.27. Upon decreasing the temperature from 20 °C to −80 °C, the broad peak splits into two sharp peaks having a constant ratio of integrated areas (100:23). These results are consistent with the rapid interconversion of two separate trans,trans conformers of **1b** at temperatures ≥ 20 °C.

The IR spectra of **1a**, **1b**, **2a**, **2b**, and **3a** exhibit strong Si−CH_3 stretching bands at 1245−1248 cm^{-1} and strong Si−CH_3 bending modes at 830−836 cm^{-1}. And while the IR spectra of **1a**, **1b**, **2a**, **2b**, and **3a** exhibit strong antisymmetric methyl C−H stretching bands at ~2950 cm^{-1}, only compounds **2a** and **2b** exhibit strong symmetric methyl C−H stretching bands at 2874 cm^{-1}. Moreover, only compound **3a** shows strong aromatic or olefinic C−H stretching bands at 3045 and 3067 cm^{-1}. In contrast to **1a**, **2a**, and **3a**, the IR spectra of **1b** and **2b** exhibit strong olefinic C−H out-of-plane bends at 1002−1003 cm^{-1}, consistent with the presence of trans double bonds.

The UV−vis spectra of **1a**, **1b**, **2a**, **2b**, and **3a** were collected over the range of 220−750 nm in THF with absorption maxima observed at 242, 242, 252, 250, and 258 nm, respectively. The strong absorptions between 242 and 258 nm are bathochromically shifted relative to those of 1,2,5,6-tetrasilacycloocta-3,7-diynes (216−220 nm)[20−22] and are consistent with enhanced σ−π electron delocalization through the 1,2,5,6-tetrasilacycloocta-3,7-dienes.

Compounds **1a**, **1b**, and **3a** were obtained as clear crystals that were characterized by single-crystal X-ray diffraction. Similar attempts to grow crystals of **2a** and **2b** were unsuccessful. The X-ray thermal ellipsoid plot for **3a** is presented as Supporting Information; those for **1a** and **1b** have been reported in our preliminary communication.[19] The thermal ellipsoid plot for **3a** confirms the cis configuration of the olefinic groups. In contrast, however, to the solid-state chair conformations observed for both **1a** and **1b**, compound **3a** exists as a twisted boat

Table 1. Selected Bond Lengths and Angles for Compound 3a

bond lengths (Å)		bond angles (deg)	
Si(1)−C(5)	1.873(4)	C(5)−Si(1)-C(4)	104.73(17)
Si(1)−C(4)	1.876(4)	C(5)−Si(1)-C(6)	106.03(16)
Si(1)−C(6)	1.882(3)	C(4)−Si(1)-C(6)	109.27(15)
Si(1)−Si(2)	2.3699(13)	C(5)−Si(1)-Si(2)	107.36(13)
Si(3)−Si(4)	2.3573(14)	C(4)−Si(1)-Si(2)	118.22(12)
Si(2)−C(1)	1.866(3)	C(1)−Si(2)-Si(1)	111.06(12)
Si(2)−C(12)	1.865(3)	C(6)−Si(1)-Si(2)	110.39(11)
Si(2)−C(13)	1.883(4)	C(13)−Si(2)-Si(1)	104.77(11)
Si(3)−C(19)	1.879(4)	C(2)−Si(3)-C(19)	110.59(18)
Si(3)−C(20)	1.880(4)	C(2)−Si(3)-C(20)	103.75(18)
Si(4)−C(21)	1.883(4)	C(2)−Si(3)-Si(4)	119.65(12)
Si(4)−C(22)	1.871(4)	C(3)−Si(4)-Si(3)	109.85(12)
C(1)−C(2)	1.336(5)	C(2)−C(1)-Si(2)	127.9(3)
C(3)−C(4)	1.335(5)	C(3)−C(4)-Si(1)	133.2(3)
Si(3)−C(2)	1.870(4)	C(1)−C(2)-Si(3)	134.8(3)
Si(4)−C(3)	1.870(4)	C(4)−C(3)-Si(4)	129.9(3)

in the solid state. The selected bond lengths and angles for **3a** given in Table 1 provide further evidence of the twist (i.e., distortion) of the boat conformation. In particular, the $Si-Si-C_{olefin}$ bond angles of **3a** vary from ~110 to 120°, while the analogous bond angles in **1a** vary over a substantially smaller range (114−115°).[19] The distortion of the ring in **3a** probably arises from steric interactions along the Si(1)−Si(2) bond (i.e., between the phenyl groups and the neighboring substituents on adjacent silicon atoms).

Experimental Probes of the Mechanism of the Isomerization of 1a to 1b. The experiments described above demonstrate (1) that the methodology used to reduce the cyclic diynes successfully affords the corresponding cis,cis dienes and (2) that two of the cis,cis dienes unexpectedly convert to the corresponding trans,-trans dienes upon exposure to **Ru**. In this section, we explore the mechanism of the unexpected cis,cis to trans,-trans conversion using a variety of experimental probes.

The general features of the mechanism of the isomerization of **1a** to **1b** were systematically probed through the following experiments. First, treatment of **1a** in CD_2Cl_2 in the absence of **Ru** produced no trace of **1b**, even upon heating at 40 °C for 20 days. Second, the rate of isomerization increased in direct proportion to the concentration of **Ru**.[25] Third, exposure of **1b** to **Ru** in CD_2Cl_2 produced no trace of **1a**, even upon heating at 40 °C for 20 days. These results suggest that the isomerization is catalyzed by **Ru**, and that the *t,t*-isomer **1b** is more stable than the *c,c*-isomer **1a** by at least 1.8 kcal/mol (assuming a ratio of products >95:5 based on a conservative estimate of our ability to detect trace amounts of **1b** by ^1H NMR spectroscopy). Furthermore, the first-order dependence on **Ru** is consistent with the presence of an intermediate in which each of the two olefinic sites undergoes isomerization independently; otherwise, the reaction would be expected to exhibit at least second-order dependence on **Ru**.

To further examine the conversion of **1a** to **1b**, we explored several alternative methods known to catalyze the cis to trans isomerization of olefins. Iodine, which isomerizes *c,t*-**COD** to *c,c*-**COD** in 65% yield,[14] failed to isomerize **1a** to **1b** or **1b** to **1a**, even upon heating at 40 °C for 10 days. Transition metal-based isomerization catalysts such as hydridotetracarbonylcobalt(I) ($HCo(CO)_4$) and tris(triphenylphosphine)rhodium(I) chloride ($RhCl(PPh_3)_3$) also failed to effect the isomerization of **1a** to **1b**.[26−28]

Ruthenium(II) hydrides have been implicated as catalysts in the isomerization of olefins, even when the source of the hydride remains obscure.[7] These considerations prompted us to examine the reactivity of **1a** with the commercially available ruthenium(II) hydride complexes chlorohydridotris(triphenylphosphine)ruthenium(II) ($(Ph_3P)_3Ru(Cl)H$) and dihydridotetrakis(triphenylphosphine)ruthenium(II) ($(Ph_3P)_4RuH_2$). In these experiments, we found that exposure of **1a** to the ruthenium(II) hydrides in CD_2Cl_2 at 40 °C afforded isomer **1b**. We also found that bis(cyclopentadienyl)zirconium(II) chloride hydride ($Cp_2Zr(Cl)H$) effected the isomerization, although this catalyst was less efficient than the ruthenium(II) hydrides. These results, in conjunction with the aforementioned induction period for the formation of active form of **Ru**,[25,29] suggest that a ruthenium(II) hydride is the active catalyst in the isomerizations promoted by $(Cy_3P)RuCl_2(=CHPh)Ru(p\text{-cymene})Cl_2$.

To distinguish whether the isomerization of **1a** to **1b** proceeds via metal hydride addition/elimination or an alternative pathway involving radical reactions, we explored separate isomerization reactions in the presence of free radical initiators and free radical scavengers (i.e., we conducted a series of experiments to distinguish between hydride and radical isomerization mechanisms by employing conditions that were designed to either produce or eliminate free radicals). First, **Ru** was incubated in CD_2Cl_2 at 40 °C in the absence of light. An aliquot of **1a** was then added. No isomerization was observed after 20 days, indicating that light is required to activate the isomerization catalyst. Second, 1 equiv of the radical scavenger tributyltin hydride and 1 equiv of the radical scavenger 9,10-dihydroanthracene were included separately in reactions of **1a** with preincubated **Ru**. The isomerization proceeded uninhibited in the presence of tributyltin hydride, but not in the presence of dihydroanthracene. Given that isomerizations catalyzed by metal hydrides can tenably be inhibited by coordination of the catalyst to aromatic systems, we added 1 equiv of *o*-xylene and 1 equiv of benzene to separate reactions of **1a** with **Ru** and observed no isomerization after 5 days in both systems. We therefore conclude that, rather than radical scavenging, the failure to isomerize **1a** to **1b** in the presence of dihydroanthracene is due to deactivation of **Ru** via coordination of the aromatic rings of dihydroanthracene to the metal center. Third, we added 5 mol % of the radical initiator AIBN to **1a** in a series of reactions (1) with **Ru** (5 mol % relative to **1a**, no preincubation), (2) without **Ru**, and (3) without **Ru** but with chloranil (5 mol % relative to **1a**), followed by UV photolysis to initiate radical formation. For all of the experiments, we observed no trace of isomerization after fifteen hours of photolysis. We therefore propose that the **Ru**-catalyzed isomerizations of **1a** to **1b** proceed via metal hydride addition/elimination rather than via radical reactions (even though light is required to generate the active catalyst).

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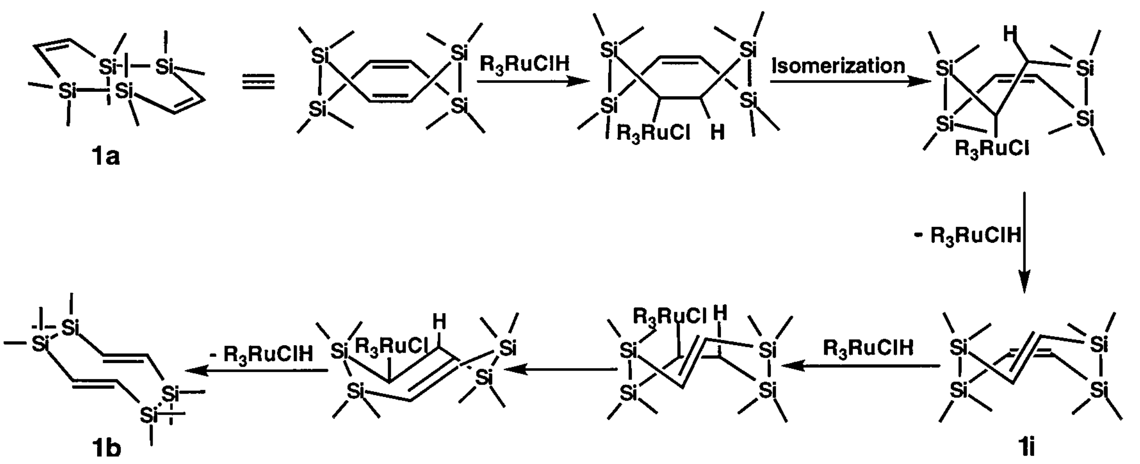
(26) Roos, L.; Orchin, M. *J. Am. Chem. Soc.* **1965**, *87*, 5502.

(27) Hendrix, W. T.; Rosenberg, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 4850.

(28) Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1973**, *38*, 3224.

(29) Comparable induction periods for the activation of metal hydride isomerization catalysts have been reported. See, for example: Patil, S. R.; Sen, D. N.; Chaudhari, R. V. *J. Mol. Catal.* **1984**, *23*, 51.

Scheme 1



Collectively, the data above are consistent with an isomerization mechanism involving metal hydride addition/elimination. A probable intermediate in this pathway would be the cis,trans isomer. Although we have been unable to unambiguously identify or isolate this intermediate, there are several results that are consistent with the presence of an intermediate of this type. First, the fact that the isomerization is first order in **Ru** necessitates the formation of an intermediate, given that the diolefin **1a** possesses two reactive sites. If the sites were isomerized simultaneously, the reaction would be second order in **Ru** (presuming that for geometric reasons, **Ru** cannot bridge both olefinic coordination sites). Second, the results of a detailed kinetic study of the isomerization of **1a** to **1b** are also consistent with the existence of a relatively long-lived intermediate.[25] As monitored by ^{1}H NMR spectroscopy, the loss of **1a** is accompanied by a lag in the formation of **1b** and the concomitant formation of another species, designated **1i**, indicating that **1a** is initially converted into **1i**, which is subsequently converted into **1b.**

The ruthenium hydride addition−elimination mechanism of the isomerization of **1a** is proposed in Scheme 1, explicitly including the cis,trans isomer as intermediate **1i**. In this mechanism, **1a** coordinates to a kinetically long-lived ruthenium hydride catalyst and subsequently inserts into the ruthenium-hydride bond to yield a ruthenium alkyl. The ruthenium alkyl twists from a pro-cis configuration to a pro-trans configuration. Subsequent β-elimination yields **1i** and regenerates the ruthenium hydride. Repetition of this process on the remaining cis double bond of **1a** yields **1b** and regenerates the ruthenium hydride.

Reaction via the proposed ruthenium hydride addition/elimination pathway can perhaps rationalize the relative rates described above for the isomerization of the various *cis,cis*-tetrasilacyclooctadienes (i.e., **1a** $>$ **2a** $\gg$ **3a**). Specifically, the relative rates of isomerization vary directly with the degree of steric bulk in the vicinity of the olefinic moieties. Steric interactions can plausibly hinder the approach of the catalyst to the substrate and thus inhibit Ru−H addition across the double bonds.[30] While this effect might appear most evident for compound **3a**, in which the degree of steric bulk is substantially larger than that of the other two substrates, we note that the isomerization of **3a** can also be inhibited by coordination of the pendant aromatic groups of **3a** to the **Ru** metal center (vide supra).

Calculations of the Lowest Energy Conformations of 1a,b,i. The pathway proposed in Scheme 1 includes the cis,trans intermediate **1i** in the isomerization of **1a** to **1b**. Since we were unable to isolate this intermediate, we chose to investigate its stability and thus plausible intermediacy through a series of density functional theory calculations (DFT) as implemented in the Spartan 5.0 (SGI) package.[31] After optimizing the geometry of each conformation at the semi-emperical level using the PM3 basis set, we performed a harmonic frequency analysis about each minimal energy conformation.[19] For each case, we obtained only real frequencies, which verifies the location of local minima rather than saddle points on the total energy surface. These geometries were then utilized as starting points for the DFT geometry optimizations using the Becke−Perdew exchange functional,[32,33] which self-consistently introduces nonlocal correlations, and the DN** double numerical basis, which includes polarization functions on each atom. This level of theory is comparable to the MP2 theory using a 6/31G** basis.[31] All of the computational results reported here were derived using this approach.

Specifically, we located and evaluated the two lowest energy conformers of **1a** and **1b** as well as the single lowest energy conformer of **1i** (see Scheme 2) and compared the energies and bond lengths of these conformers to the analogous conformers of 1,5-cyclooctadiene (**COD**) and 1,2,5,6-tetrasilacycloocta-3,7-diene (**SiH**). The calculations were designed to examine the conformational changes and energy differences when the C_3, C_4, C_7, and C_8 carbon atoms of the various **COD** conformers were replaced by silicon atoms to afford the 1,2,5,6-tetrasilacycloocta-3,7-dienes (**SiH**) and, subsequently, when the hydrogens on the silicon atoms in **SiH** were replaced by methyl groups to afford the 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-dienes (**SiMe**).

A comparison of the DFT energies of **COD** and **SiH** (Table 2) suggests the following general trend in stability of the isomers: *c,c*-twistboat $>$ *c,c*-chair $>$ *c,t*-crown $>$

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[30] Two observations provide indirect support for a steric rather than an electronic effect: (1) although the substituent effects for methyl and ethyl are similar, the rate of isomerization of **1a** is markedly faster than that of **2a**; and (2) despite the substitution of an ethyl group for a methyl group on one of the neighboring silicon atoms, the olefinic resonances observed in the ^{1}H NMR spectra of **1a** and **2a** are indistinguishable (as well as those for **1b** and **2b**).

[31] Spartan version 5.0, Wavefunction, Inc., Irvine, CA 1997.

[32] Perdew, P. P. *Phys. Rev. B* **1986**, *33*, 8822.

[33] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

Scheme 2

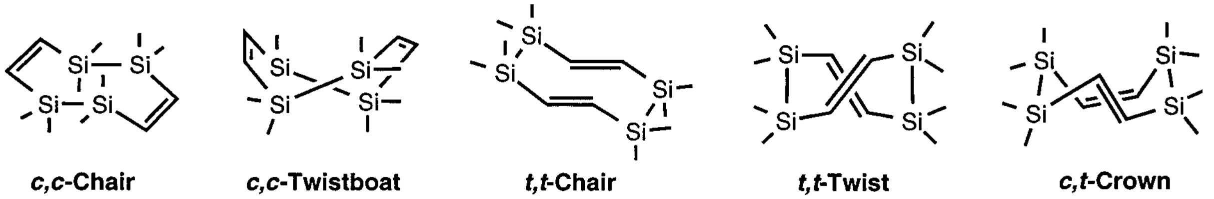

Table 2. Comparison of DFT Energies[a] for Various Low Energy Conformers of 1,5-Cyclooctadiene (COD), 1,2,5,6-Tetrasilacycloocta-3,7-diene (SiH), and 1,1,2,2,5,5,6,6-Octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (SiMe)

	conformers					
	COD		**SiH**		**SiMe**	
	abs	rel	abs	rel	abs	rel
t,t-chair	−312.09569	26.44	−1317.80209	5.10	−1632.53634	−1.97
t,t-twist	−312.10626	19.81	−1317.80655	2.30	−1632.53721	−2.52
c,t-crown	−312.11895	11.85	−1317.80550	2.96	−1632.53354	−0.21
c,c-twistboat	−312.13949	−1.04	−1317.81207	−1.16	−1632.53277	0.27
c,c-chair	−312.13783	0.00	−1317.81022	0.00	−1632.53320	0.00

[a] Absolute energies (abs) are given in hartrees, and relative energies (rel) are given in kcal/mol relative to the *c,c*-chair conformer in each case.

t,t-twist > *t,t*-chair. This trend is consistent with the results calculated for **COD** by force field and ab initio methods.[11,12] The relative trend in stability of the isomers of **SiMe** is, however, markedly different: *t,t*-twist > *t,t*-chair > *c,t*-crown > *c,c*-chair > *c,c*-twistboat. While the *c,c* conformers of **COD** are calculated to be the most stable, the *t,t* conformers of **SiMe** are calculated to be the most stable (by ~2.0−2.5 kcal/mol). The latter results are consistent with the experimental finding (vide supra) that heating a mixture of **1b** and **Ru** in methylene chloride fails to generate any detectable **1a** (and consequently that **1b** is more stable than **1a** by at least 1.8 kcal/mol). The agreement between experiment and theory demonstrates the accuracy of the calculational method in evaluating the relative energy of these types of molecules,[34] and thus lends confidence in the calculation of the relative energy of the experimentally inaccessible intermediate **1i**.

Furthermore, as described above, the unusually broad olefinic resonance at δ 6.32 in the ^{1}H NMR spectrum of **1b** was examined by variable-temperature NMR spectroscopy. At low temperature (<20 °C), **1b** appears to exist as an equilibrium mixture of two conformers with integrated areas of 100:23, suggesting a free energy difference between these conformers of ~0.85 kcal/mol at 20 °C. Correspondingly, the DFT energies in Table 2 indicate that the *t,t*-twist conformer is more stable than the *t,t*-chair conformer by ~0.55 kcal/mol (20 °C), which is further consistent with the interpretation that the NMR resonances observed at low temperature correspond to a mixture of these conformers. Again, the close agreement between experiment and theory further demonstrates the reliability of the calculational method.

Given these considerations, we note that the calculated lowest energy conformer of **1i** is comparable in energy to those of **1a** and **1b** (see Table 2). Given the similar energies, we thus conclude that the DFT calculations provide strong support for the plausible existence of the cis,trans intermediate **1i** in the **Ru**-catalyzed isomerization of **1a** to **1b.**

Table 3. Comparison of DFT Bond Lengths (Å) and Through-Space Equivalent Atom Distances (Å) of 1,5-Cyclooctadiene (COD), 1,2,5,6-Tetrasilacycloocta-3,7-diene (SiH), and 1,1,2,2,5,5,6,6-Octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (SiMe)

	conformers					
	COD[a]		**SiH**[a]		**SiMe**[a]	
	C_3-C_4	C_3-C_8	Si_1-Si_2	Si_1-Si_4	Si_1-Si_2	Si_1-Si_4
t,t-chair	1.63	3.79	2.40	4.56	2.43	4.61
t,t-twist	1.60	3.78	2.39	4.55	2.42	4.63
c,t-crown	1.57	3.72	2.37	3.79	2.39	4.56
c,c-twistboat	1.55	3.28	2.37	3.63	2.40	3.91
c,c-chair	1.57	3.11	2.37	3.67	2.39	3.97

[a] For each molecule, the left column represents bond lengths and the right column represents through-space equivalent atom distances (see Figure 2). The variation in the C−C double bond lengths was negligible for all conformers of all species (1.350 ± 0.005 Å).

Figure 2. Illustration of the numbering scheme used for **COD** (left) and for **SiH** and **SiMe** (right).

Finally, we are left to rationalize the origin of the difference in stability between **1a** and **1b** and to rationalize why the observed trend in stability for **SiMe** differs from that for **COD** and **SiH**. It has been suggested that $\pi-\pi$ repulsion between the parallel double bonds in **COD** is the major factor that prevents the formation of the unstable *t,t*-chair conformer of **COD**.[12] Table 3 shows that for the *t,t*-chair conformer of **SiH**, both the calculated bond length of Si_1-Si_2 (2.40 Å) and the distance between the Si_1 and Si_4 atoms (4.56 Å) are much larger than those of **COD**, where the corresponding C_3-C_4 bond length is 1.63 Å and the corresponding distance between C_3 and C_8 is 3.79 Å (see also Figure 2). Consequently, the $\pi-\pi$ repulsion between the parallel double bonds in **SiH** should be greatly reduced compared to that in **COD**. Indeed, this reduction is reflected in the energy calculations, where the energy of the *t,t*-chair conformer of **COD** lies ~26 kcal/mol above the ground-state potential, while

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(34) In the DFT analyses presented here, we use enthalpies rather than free energies because the latter calculations are highly demanding and unwieldy with our resources.

the energy of the *t,t*-chair conformer of **SiH** lies only ~5 kcal/mol above the ground-state potential. Despite the smaller difference in energy (i.e., $\Delta = E_{c,c\text{-chair}} - E_{t,t\text{-chair}}$), the *t,t*-chair conformer of **SiH** is still less stable than both of its lowest energy cis,cis conformations. Consequently, the opposite trend observed for **SiMe** (i.e., that $E_{t,t}$ is more stable than $E_{c,c}$) must arise, at least in part, from the presence of the methyl groups on the ring. Given this premise, we note that the electronic effect of the methyl substituents is probably negligible given that the C=C bond lengths of the various isomers are indistinguishably different (i.e., 1.34 ± 0.01 Å). We further note that the solid-state structure of **1b** includes four eclipsed methyl–methyl interactions across the relatively long Si_1-Si_2 and Si_3-Si_4 bonds, with a distance between these nonbonded methyl groups of 3.80 Å (equatorial) and 3.64 Å (axial).[19] In contrast, the solid-state structure of **1a** includes four gauche interactions with nonbonded distances of 3.68 and 4.06 Å and two nonbonded methyl–methyl interactions across the ring (i.e., between the axial methyl groups attached to Si_1 and Si_4 and those attached to Si_2 and Si_3, with nonbonded distances of 3.72 and 3.73 Å, respectively). We feel that these latter trans-annular interactions destabilize compound **1a** relative to **1b**, and thus provide the driving force for the isomerization of **1a** to **1b**.

Conclusions

A family of *cis,cis*-1,2,5,6-tetrasilacycloocta-3,7-dienes (**1a**, **2a**, and **3a**) was synthesized and characterized. Compounds **1a** and **2a** were observed to isomerize to the *trans,trans*-1,2,5,6-tetrasilacycloocta-3,7-dienes **1b** and **2b**, respectively, by treatment with metal hydride complexes. Sterically bulky compound **3a**, however, failed to undergo similar isomerization. Experimental probes suggest that the isomerizations proceed via metal-hydride addition/elimination pathways rather than ones involving radical intermediates. Furthermore, experimental and theoretical studies suggest that the isomerization of **1a** to **1b** proceeds via the intermediacy of *cis,trans*-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene, **1i**. The existence of **1i** is supported both by kinetics probes and by calculations of various conformer energies using density functional theory. The theoretical calculations suggest the following relative stability of the various isomers of 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene: trans,trans > cis,trans > cis,cis. These trends are consistent with the observed cis,cis to trans,trans isomerization of **1a** to **1b** via the cis,trans intermediate **1i**. The driving force for the isomerization of **1a** to **1b** appears to involve the relief of trans-annular steric interactions between axial methyl goups in **1a**.

Experimental Section

Materials and Methods. The compounds $HCo(CO)_4$,[26] $(PCy_3)RuCl_2(=CHPh)Ru(p\text{-cymene})Cl_2$,[24] 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne,[21] 1,2-diethyl-1,2-diethynyldimethyldisilane,[35] 1,2-diethynyl-1,2-dimethyldiphenyldisilane,[35] and 1,2-dichloro-1,1,2,2-tetramethyldisilane[36] were synthesized according to procedures provided in the indicated references. The chemicals $RhCl(PPh_3)_3$, $(Ph_3P)_3Ru(Cl)H$, $(Ph_3P)_4RuH_2$, $Cp_2Zr(Cl)H$, diisobutylaluminum hydride (1.0 M in hexanes), ethylmagnesium bromide (1.0 M in THF), ethynylmagnesium bromide (0.5 M in THF), phenylmagnesium bromide (1.0 M in THF), *N*-methylpyrrolidine (97%), aluminum chloride (99.99%), acetyl chloride (98%), 9,10-dihydroanthracene, tributyltin hydride, dimethyl sulfone, chloranil, and iodine were purchased from Aldrich Chemical Co. The solvents THF, hexanes, diethyl ether, as well as $MgSO_4$, and silica gel 62 (60–200 mesh ATM) were purchased from EM Sciences. Hexamethyldisilane was purchased from either Aldrich or United Chemical Technologies. Thin-layer chromatography (TLC) plates (2.5 × 7.5 cm, Baker-flex silica gel, IB-F, J. T. Baker, Inc. Germany), hydrogen chloride (Matheson, 99%), and 2,2′-azobisisobutyronitrile (AIBN) (98%, Alfa), were purchased from the indicated suppliers. The NMR solvents CD_2Cl_2 and C_6D_6 were purchased from Cambridge Isotope Laboratories. Elemental analyses were performed at the analytical facilities of National Chemical Consulting, Inc. All commercial reagents were used without purification unless otherwise specified.

All reactions were conducted under ambient light unless noted otherwise. Air- and moisture-sensitive reactions were conducted under argon or nitrogen using standard Schlenk line and drybox techniques unless otherwise specified. Solvents used in these reactions were dried by passage through activated alumna and degassed by passage through Q-5 reagent (Engelhard) and by freeze–pump–thaw techniques. Air- and moisture-sensitive compounds were stored in a nitrogen-filled drybox.

^1H and ^{13}C NMR spectra were recorded on either a General Electric QE-300 (300 MHz ^1H; 75.5 MHz ^{13}C) or a Bruker AMX-II 600 (600 MHz ^1H; 151 MHz ^{13}C) spectrometer. All spectra were referenced to internal solvent resonance (CD_2Cl_2: ^1H NMR δ 5.32 ppm; ^{13}C NMR δ 54.00 ppm; C_6D_6: ^1H NMR δ 7.15 ppm; ^{13}C NMR δ 128.39 ppm). IR spectra were recorded using a Nicolet MAGNA-IR 860 Fourier transform spectrometer over the spectral range 450–4400 cm^{-1} with a resolution of 4 cm^{-1}. UV–vis spectra were collected using a Hewlett-Packard 8452A diode array spectrometer over the spectral range of 220–800 cm^{-1} with a resolution of 2 cm^{-1}.

Synthetic Procedures. Synthesis of *cis,cis*-1,1,2,2,5,5,6,6-Octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (1a). Under argon, a flame-dried 250 mL Schlenk flask equipped with a magnetic stirring bar and a 100 mL dropping funnel was charged with 2.00 g (7.13 mmol) of 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne and 40 mL of diethyl ether. To this solution was added dropwise a degassed mixture of 15.7 mL (15.7 mmol) of diisobutylaluminum hydride, 1.34 g (15.7 mmol) of *N*-methylpyrrolidine, and 30 mL of hexanes.[37] The solution was stirred at 55 °C for 24 h under argon. After cooling, water was added, and the organic layer was separated and dried with $MgSO_4$. The solvent was removed by rotary evaporation, and the resulting pale yellow solid was chromatographed on silica gel using hexanes. The fraction containing the product ($R_f = 0.71$) was collected and evaporated to dryness to give 0.440 g of **1a** as white crystals (1.55 mmol, 22% isolated yield based on 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne). Recrystallization from ethanol gave white platelets of **1a**. ^1H NMR (CD_2Cl_2, 300 MHz): δ 6.89 (s, 4 H, olefinic), 0.19 (s, 24 H, Me). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 152.1 (olefinic), −1.4 (Me). IR (neat film deposited on Si wafer): 2950, 2910, 1245, 835, 805, 767, 727, 609. UV–vis (THF): $\lambda_{max} = 242$ nm. Mp: 88–89 °C. Anal. Calcd for *cis,cis*-$C_{12}H_{18}Si_4$: C, 50.62; H, 9.91. Found: C, 50.03; H, 10.00.

Synthesis of *trans,trans*-1,1,2,2,5,5,6,6-Octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (1b). In a glass vial, 0.006 g (0.007 mmol) of $(Cy_3P)RuCl_2(=CHPh)Ru(p\text{-cymene})Cl_2$ was dissolved in a minimum amount of CD_2Cl_2 and allowed to incubate under ambient light at 40 °C for 5 days under argon. A Kontes air-free NMR tube was charged with 0.200 g (0.703 mmol) of **1a**, and a minimum amount of CD_2Cl_2 sufficient to dissolve **1a** was added. Under argon, the solution containing the catalyst was transferred via cannula to the

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[35] Oshita, J.; Matsuguchi, A.; Furumori, K.; Hong, R.; Ishikawa, M.; Yamanaka, T.; Koike, T.; Shioya, J. *Macromolecules* **1992**, *25*, 2134.

[36] Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, *45*, 5493.

[37] Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520.

NMR tube, and the reaction was allowed to proceed at 40 °C. Progress of the reaction was monitored by examining the ratios of the olefinic resonances at δ 6.89 (cis,cis) and 6.32 (trans,trans) relative to an internal standard (ferrocene at δ 4.18). After 2 weeks, the reaction was ca. 75% complete as judged by ^{1}H NMR integration. After removal of the solvent, the mixture of **1a** and **1b** was separated by preparative TLC on silica gel using hexanes. The product ($R_f = 0.63$) was collected to give 0.080 g (0.28 mmol, 40% isolated yield based on **1a**) of **1b** as white crystals. Recrystallization from ethanol gave white platelets of **1b**. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 6.32 (s, broad, 4 H, olefinic), 0.21 (s, 12 H, Me_{eq}), 0.18 (s, 12 H, Me_{ax}). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 153.4 (olefinic), −3.7 (Me_{eq}), −6.1 (Me_{ax}). IR (neat film deposited on Si wafer): 2952, 2925, 1244, 1002, 836, 804, 760, 731, 691. UV−vis (THF): $\lambda_{max} = 242$ nm. Mp: 83−85 °C (sublimes readily under vacuum). Anal. Calcd for *trans,trans*-$C_{12}H_{18}Si_4$: C, 50.62; H, 9.91. Found: C, 50.23; H, 9.50.

Synthesis of *cis,cis*-1,2,5,5,6,6-Hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (2a). A procedure analogous to that used to synthesize **1a** was employed utilizing 1,2,5,5,6,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (prepared by the Wurtz-type reaction between 1,2-dichloro-1,1,2,2-tetramethyldisilane[35] and 1,2-diethyl-1,2-diethynyldimethyldisilane[35] pretreated with EtMgBr)[22] as the starting material. The use of 5.00 g (16.2 mmol) of the starting diyne afforded a yellow oil (4.44 g), which was chromatographed on silica gel using hexanes. The fraction containing the product ($R_f = 0.77$) was collected and evaporated to dryness to give 1.49 g of the clear oily product **2a** (4.76 mmol, 29% isolated yield based on 1,2,5,5,6,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 6.89 (d, 4 H), 0.99 (t, 6 H), 0.73 (q, 4 H), 0.21 (s, 18 H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 152.9, 151.7, 8.6, 8.2, −0.7, −3.8. IR (neat film deposited on Si wafer): 2952, 2909, 2874, 1247, 1007, 830, 801, 770, 720. UV−vis (THF): $\lambda_{max} = 252$ nm. A satisfactory analysis could not be obtained.

Synthesis of *trans,trans*-1,2,5,5,6,6-Hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (2b). A procedure analogous to that used to prepare **1b** was employed. A Kontes air-free NMR tube was charged with 0.200 g (0.640 mmol) of **2a**, 0.011 g (0.013 mmol) of $(PCy_3)RuCl_2(=CHPh)$-Ru(*p*-cymene)Cl_2, and CD_2Cl_2 (∼0.5 mL). After 6 weeks at 40 °C, the reaction was ∼60% complete as judged by ^{1}H NMR integration. After removal of the solvent, the mixture of **2a** and **2b** was separated by preparative TLC on silica gel using hexanes. The product ($R_f = 0.71$) was collected to give 0.041 g (0.13 mmol, 20% isolated yield) of **2b** as a clear oil that readily decomposes under ambient conditions. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 6.32 (broad, 4 H), 1.01 (t, 6 H), 0.74 (q, 4 H), 0.20 (s, 18 H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 153.2, 152.0, 9.0, 8.7, −6.6, −3.1. IR (neat film deposited on Si wafer): 2952, 2909, 2874, 1246, 1003, 833, 796, 732, 698. UV−vis (THF): $\lambda_{max} = 250$ nm. A satisfactory analysis could not be obtained.

Synthesis of *cis,cis*-1,2,5,5,6,6-Hexamethyl-1,2-diphenyl-1,2,5,6-tetrasilacycloocta-3,7-diene (3a). A procedure analogous to that used to synthesize **1a** was employed utilizing 1,2,5,5,6,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diyne (prepared by the Wurtz-type reaction between 1,2-dichloro-1,1,2,2-tetramethyldisilane[36] and 1,2-diethynyl-1,2-dimethyldiphenyldisilane[35] pretreated with EtMgBr)[22,23] as the starting material. The use of 5.00 g (12.4 mmol) of the starting diyne afforded a yellow oil (2.17 g) that was chromatographed on silica gel using hexanes. The fraction containing the product ($R_f = 0.34$) was collected and evaporated to dryness to afford 0.771 g of **3a** as a clear oil (1.89 mmol, 15% yield on the basis of 1,2,5,5,6,6-hexamethyl-1,2-diphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne). Recrystallization from ethanol gave white needles of the product. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.21−7.40 (m, 10 H), 7.08 (s, 4 H), −0.13−0.48 (m, 18 H). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 154.7, 149.4, 135.2, 129.1, 128.2, −0.9 (m). IR (neat film deposited on Si wafer): 3067, 3049, 2951, 2909, 1248, 831, 803, 779, 735, 699. UV−vis (THF): $\lambda_{max} = 258$ nm. Mp: 48−49 °C. A satisfactory analysis could not be obtained.

Single-Crystal X-ray Diffraction of 3a. A colorless flat crystalline needle of **3a** (*cis,cis*-$C_{22}H_{32}Si_4$, MW = 408.84) having the approximate dimensions 0.40 × 0.16 × 0.08 mm was measured with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30% in ω and an exposure time of 30 s per frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction on I was 1%. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A ψ scan absorption correction was applied on the basis of the entire data set. Redundant reflections were averaged. Final cell constants were refined using 8000 reflections having $I > 10/\sigma(I)$. The Laue symmetry was determined to be *mmm*, and from the systematic absences noted the space group was shown unambiguously to be *Pccn*.

Mechanistic Probes of the Isomerization of 1a to 1b. Attempted Reverse Isomerization of 1b to 1a. The procedure described above for the conversion of **1a** to **1b** using **Ru** was repeated with **1b** rather than **1a** as the starting material. Analysis by ^{1}H NMR spectroscopy over the course of 10 days revealed resonances consistent only with those of **1b**.

Attempted Isomerization Using Iodine.[14] A Kontes air-free NMR tube was charged with 0.050 g (0.18 mmol) of **1a**, 1 mg of iodine (0.0079 mmol), and 1 mL of CD_2Cl_2. The tube was wrapped with aluminum foil. The reaction was allowed to proceed in the dark at room temperature for 48 h and heated to 40 °C for 10 days. The reaction was monitored by examining the olefinic resonances at δ 6.89 (**1a**) and 6.32 (**1b**) in the ^{1}H NMR spectra. No resonances other than the characteristic resonances of **1a** were found. The same procedure was followed for the isomerization of **1b** to **1a**; similarly, no resonances attributable to **1a** were observed.

Attempted Isomerization Using Cobalt(I) Hydrocarbonyl ($HCo(CO)_4$).[26,27] A 50 mL Schlenk flask equipped with a magnetic stirring bar and a 50 mL dropping funnel was charged with 0.122 g (0.220 mmol) of $PPNCo(CO)_4$ and 15 mL of hexanes under CO. To this solution were added 2 mL of dry, degassed DMF. The solution was stirred at 0 °C in an ice bath for 10 min, and 5 mL of aqueous HCl solution (10 M) was added dropwise. The aqueous layer was removed by syringe, and the organic layer was washed with water (2 × 2 mL) and cooled to −70 °C. The organic layer was then transferred to a 50 mL round-bottomed flask equipped with a magnetic stirring bar. The flask was charged with 0.025 g of **1a** (0.088 mmol) and 5 mL of hexanes under CO. The solution was stirred and warmed to room temperature for 3 min. An aliquot (5 mL) of aqueous NaOH solution (0.1 N) was added, and the organic layer was separated, washed with water (3 × 5 mL), dried with $MgSO_4$, and filtered into a 50 mL round-bottomed flask. The solution was concentrated by rotary evaporation to give 0.021 g of product. Analysis by ^{1}H NMR spectroscopy revealed resonances consistent only with those of **1a**.

Attempted Isomerization Using Tris(triphenylphosphine)rhodium(I) Chloride [$RhCl(PPh_3)_3$].[28] A 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with 0.025 g (0.088 mmol) of **1a**, 0.0122 g (0.0132 mmol) of $RhCl(PPh_3)_3$, 15 mL of ethanol, and 1 mL of water under N_2. The solution was stirred at 50 °C for 5 h. An aliquot (1 mL) of aqueous HCl solution (0.1 N) was added, and the organic layer was separated, washed with water (3 × 5 mL), dried with $MgSO_4$, and filtered into a 50 mL round-bottomed flask. The solution was concentrated by rotary evaporation to give 0.019 g of product. Analysis by ^{1}H NMR spectroscopy revealed resonances consistent only with those of **1a**.

Isomerization Using Chlorohydridotris(triphenylphosphine)ruthenium(II) [$(Ph_3P)_3Ru(Cl)H$].[7] A Kontes air-free NMR tube was charged with 0.050 g (0.18 mmol) of **1a**, 0.00653 g (0.0351 mmol) of ferrocene (0.0050 g, 0.027 mmol as an internal standard), and a minimum amount of CD_2Cl_2 sufficient to dissolve the solids. In a separate vial, a solution of 0.0081 g (0.0088 mmol) of $[Ph_3P]_3Ru(Cl)H$ in a minimum amount of CD_2Cl_2 was prepared and transferred to the NMR tube. The reaction was allowed to proceed at 40 °C and was monitored by integrating the olefinic resonances at δ 6.89 (**1a**) and 6.32 (**1b**) relative to that of ferrocene (δ 4.18). After 17.5 days, the reaction was ~57% complete as judged by ^1H NMR integration.

Isomerization Using Dihydridotetrakis(triphenylphosphine)ruthenium(II) [$(Ph_3P)_4RuH_2$]. This reaction was conducted using the preceding procedure, but with 0.0101 g (0.00878 mmol) of $(Ph_3P)_4RuH_2$ as the hydride source. After 17.5 days, the reaction was ~18% complete as judged by ^1H NMR integration.

Isomerization Using Bis(cyclopentadienyl)zirconium(II) Chloride Hydride [$Cp_2Zr(Cl)H$]. This reaction was conducted using the preceding procedure, but with 0.0023 g (0.0089 mmol) of $Cp_2Zr(Cl)H$ as the hydride source. After 17.5 days, the reaction was ~10% complete as judged by ^1H NMR integration.

Isomerization Trials in the Darkness, with Radical Scavengers 9,10-Dihydroanthrocene and Tributyltin Hydride, and with *o*-Xylene and Benzene. A Kontes air-free NMR tube was charged with 0.0037 g (0.0044 mmol) of **Ru** and 0.5 mL of CD_2Cl_2. The solution was incubated at 40 °C for 5 days in the darkness prior to the addition of **1a**. An aliquot (0.0125 g; 0.044 mmol) of **1a** and ferrocene (0.0050 g; 0.027 mmol as an internal standard) was added to the NMR tube, which was kept in the darkness at 40 °C. The reaction was allowed to proceed for 20 days and was monitored by ^1H NMR spectroscopy as described above. No conversion of **1a** to **1b** was observed. The same procedure was repeated under ambient light in four separate Kontes air-free NMR tubes charged with **Ru**, **1a**, ferrocene, and CD_2Cl_2. An aliquot of one of the following was added to the separate NMR tubes: 0.0079 g (0.044 mmol) of 9,10-dihydroanthrocene, 0.0013 g (0.044 mmol) of tributyltin hydride, 0.0047 g (0.044 mmol) of *o*-xylene, and 0.0034 g (0.044 mmol) of benzene. The reactions were allowed to proceed at 40 °C for 20 days under ambient light. The conversion of **1a** to **1b** was observed only in the tube containing tributyltin hydride.

Isomerization Studies with the Radical Initiator AIBN. Three Kontes air-free NMR tubes were charged with 0.0125 g (0.044 mmol) of **1a**, 0.0004 g (0.002 mmol) of AIBN, 0.0004 g (0.004 mmol) of dimethyl sulfone (internal standard), and 0.5 mL of CD_2Cl_2. Two of the NMR tubes were further charged separately with 0.0037 g (0.0044 mmol) of **Ru** and with 0.0006 g (0.002 mmol) of chloranil. The reactions were allowed to proceed for 15 h at 40 °C under UV photolysis (medium-pressure Hg-arc lamp with a UV filter of nm >260). The reactions were monitored by ^1H NMR spectroscopy as described above. No isomerization of **1a** to **1b** was observed in any of the reactions.

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Supporting Information Available: Experimental methods used for the single-crystal X-ray diffraction analysis of **3a** and the corresponding thermal ellipsoid plot; complete computational results in the form of Cartesian coordinates with the computed total energies. These materials can be obtained free of charge via the Internet at http://pubs.acs.org.

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