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. 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. Typical strategies for inducing cis–trans isomerization can be classified as photochemical, thermal, and catalytic. Photochemical isomerization can be induced by irradiation with ultraviolet or visible light and tends to produce less stable isomers. 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. In any event, the product of a thermal isomerization is typically the more stable isomer. The isomerization of alkenes by...
transition metal catalysts has been an important and extensively studied aspect of organometallic chemistry.\textsuperscript{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.\textsuperscript{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\textsuperscript{11,12} and experimentally\textsuperscript{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-twist (c,c-twist), cis,cis-chair (c,c-chair), cis,cis-halfchair (c,c-halfchair), trans-crown (c,t-crown), trans-twist (t,t-twist), and trans-chair (t,t-chair).\textsuperscript{12} Moreover, of all six conformers, the c,c-chair is the most stable, and the t,t-chair is the least stable, with an energy difference spanning 28.2 kcal/mol.\textsuperscript{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-dimethylaminocyclooctane dimethiodide have been shown to produce c,t- and t,t-COD among mixtures of isomers.\textsuperscript{13–17} The two highly strained conformers of t,t-COD, twist and chair, cannot readily interconvert.\textsuperscript{11,12,18} Energy calculations favor the twist form over the chair form by 5.35 (MM1)\textsuperscript{14} and 8.1 (ab initio)\textsuperscript{12} kcal/mol. Furthermore, due to its remarkably high ring strain,\textsuperscript{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.\textsuperscript{18} 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-hexamethyl-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 diene 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-dienes have been known since 1983.\textsuperscript{20–22} Until our recent report,\textsuperscript{23} however, a general method for the reduction of the alkene bonds in these compounds to alkene bonds was unknown. Starting from diyne precursors,\textsuperscript{20–23} eq 1 illustrates the syntheses of cis,cis-1,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (1a), cis,cis-1,2,5,5,6,6-hexamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (2a), and cis,cis-1,2,5,5,6,6-hexamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (3a).

\[
\text{RuCl}_{2}\xrightarrow{40^\circ \text{C}} \xrightarrow{\text{C,H}} \text{COD} \quad (2)
\]

\[
1a: R = \text{Me} \\
2a: R = \text{Et} \\
3a: R = \text{Ph}
\]

In methylene chloride upon exposure of 1a and 2a to a catalytic portion of the recently described dimeric ruthenium(II) alkylidene complex (Cy3p)RuCl2(=CHP)(p-cymene)Cl2 (Ru).\textsuperscript{24} Because an induction period for the formation of the active form of the catalyst was observed upon dissolution of Ru in the solvent,\textsuperscript{25} the reactions were carried out in the presence of Ru that had been preincubated under ambient light at 40 °C in CD2Cl2 for 5 days prior to the addition of diene. Under these reaction

\[
\text{Me} \quad \text{Si} \quad \text{Si} \quad \text{Me} \quad \text{Si} \quad \text{Si} \quad \text{Me} \quad \text{Si} \quad \text{Me} \\
\text{Si} \quad \text{Me} \quad \text{Si} \quad \text{Me} \quad \text{Si} \quad \text{Me} \quad \text{Si} \quad \text{Me}
\]

\[
\begin{align*}
\text{Me} & \quad \text{Si} \quad \text{Si} \quad \text{Me} \\
\text{Si} & \quad \text{Me} \quad \text{Si} \quad \text{Me}
\end{align*}
\]
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 1H 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 1H 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 1H NMR, 13C NMR, IR, and UV–vis spectroscopies (vide infra). In addition, while the X-ray crystal structures of 1a and 2b were reported in our previous communication,19 we report here the X-ray crystal structure of compound 3a.

The 1H 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 13C 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 1H 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 pristine Ru are based on the observed resonances of authentic, crystalline 1b.18 The broadness of the olefinic resonance arises from the interconversion of conformers (vide infra). The 13C 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 1H 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 13C 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 1H 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 13C 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 1H 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 13C 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.

As noted above, the olefinic resonances at δ 6.32 in the 1H 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–CH3 stretching bands at 1245–1248 cm⁻¹ and strong Si–CH3 bending modes at 830–836 cm⁻¹. 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-dienes (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
Cl2 produced no trace of trans dienes upon exposure to dienes unexpectedly convert to the corresponding trans, reduce the cyclic diynes successfully affords the corre-
above demonstrate (1) that the methodology used to Isomerization of 1a to 1b. The experiments described
adjacent silicon atoms). 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 CD2-
Cl2 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 CD2-
Cl2 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 'H 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 cis,COD to cis,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 hydridotetraacarbonyl(1)(HCO-
(CO)4) and tris(triphenylphosphine)ruthenium(II) chloride (RhCl(PPh3)3) also failed to effect the isomerization of 1a to 1b.26–28

<table>
<thead>
<tr>
<th>Table 1. Selected Bond Lengths and Angles for Compound 3a</th>
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<tr>
<td>bond lengths (Å)</td>
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<tr>
<td>Si(1)–C(5)</td>
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<td>Si(1)–C(6)</td>
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<tr>
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<td>1.335(5)</td>
</tr>
<tr>
<td>C(3)–Si(2)</td>
<td>1.870(4)</td>
</tr>
<tr>
<td>C(4)–Si(3)</td>
<td>1.870(4)</td>
</tr>
</tbody>
</table>

Ruthenium(II) hydrides have been implicated as catala-
ysts 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) ((Ph3P)_2Ru(C(1)H)) and dihydridodetrakis(triphenylphosphine)ruthenium(II) ((Ph3P)_3RuH2). In these experiments, we found that exposure of 1a to the ruthenium(II) hydrides in CD2Cl2 at 40 °C afforded isomer 1b. We also found that bis(cyclopentadienyl)zirconium(II) chloride hydride (Cp2Zr(1)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 (Cp2)RuH(2)-(CHPh)Ru(p-cymene)Cl2.

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 CD2Cl2 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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(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.
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 diolfin 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 1H 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-d configuration to a pro-trans configuration. Subsequent $\beta$-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-empirical level using the PM3 basis set, we performed a harmonic frequency analysis about each minimal energy conformation.32 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.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.34 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 C3, C4, C7, and C8 carbon atoms of the various COD conformers were replaced by silicon atoms to afford the 1,2,5,6-tetrasilacycloocta-3,7-diene (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 >
t,¿-twist > 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,¿-twist > t,¿-chair > c,¿-crown > c,¿-chair > c,¿-twistboat. While the c,¿ conformers of COD are calculated to be the most stable, the 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 1H 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,¿-twist conformer is more stable than the 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 noted 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 2. Comparison of DFT Energies 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) (kcal/mol)

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<th>SiMe</th>
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<td>abs</td>
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<td>abs</td>
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</tr>
<tr>
<td>c,¿-chair</td>
<td>312.13783</td>
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</table>

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

### 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)

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<th>COD</th>
<th>SiH</th>
<th>SiMe</th>
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<tr>
<td>C=C</td>
<td>C=C-Cod</td>
<td>Si1-Si2</td>
</tr>
<tr>
<td>t,¿-chair</td>
<td>1.63</td>
<td>3.79</td>
</tr>
<tr>
<td>t,¿-twist</td>
<td>1.60</td>
<td>3.78</td>
</tr>
<tr>
<td>c,¿-crown</td>
<td>1.57</td>
<td>3.72</td>
</tr>
<tr>
<td>c,¿-twistboat</td>
<td>1.55</td>
<td>3.28</td>
</tr>
<tr>
<td>c,¿-chair</td>
<td>1.57</td>
<td>3.11</td>
</tr>
</tbody>
</table>

*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).*

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 π–π repulsion between the parallel double bonds in COD is the major factor that prevents the formation of the unstable t,¿-chair conformer of COD.12 Table 3 shows that for the t,¿-chair conformer of SiH, both the calculated bond length of Si1–Si2 (2.40 Å) and the distance between the Si1 and Si4 atoms (4.56 Å) are much larger than those of COD, where the corresponding C=C bond length is 1.63 Å and the corresponding distance between C3 and C9 is 3.79 Å (see also Figure 2). Consequently, the π–π 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,¿-chair conformer of COD lies ~26 kcal/mol above the ground-state potential, while...
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., \(\Delta = E_{t,t}-E_{t,c}\)), the t,t-chair conformer of SiH is still less stable than both of its lowest energy ci,ci conformations. Consequently, the opposite trend observed for SiMe (i.e., that \(E_{t,c}\) is more stable than \(E_{t,t}\)) 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 \(\pm\) 0.01 Å). We further note that the solid-state structure of 1b includes four ediplsided methyl–methyl interactions across the relatively long Si1–Si2 and Si3–Si2 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 Si1 and Si2 and those attached to Si2 and Si3, 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-1,2-2,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene, 1l. The existence of 1l is supported both by kinetic probes and by calculations of various conformational 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 1l. The driving force for the isomerization of 1a to 1b appears to involve the relief of trans-annular steric interactions between axial methyl groups in 1a.

Experimental Section

Materials and Methods. The compounds HCo(CO)526 (PCy3)RuCl2, [(CH2PR)2Ru(p-cymene)Cl]2, 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene,21 1,2-diethyl-1,2-diethynylidimethylsilane,25 1,2-diethyl-1,2-dimethylidiphénylsilane,25 and 1,2-dichloro-1,2,2-tetramethyldisilane28 were synthesized according to procedures provided in the indicated references. The chemicals RhCl(PPh3)3, (Ph3P)Ru-

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 $\delta$ 6.89 (cis,cis) and 6.32 (trans,cis) -1,2,5,6-tetrasilacycloocta-3,7-diene (2a). A procedure analogous to that used to synthesize 1a was employed utilizing 1,2,5,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (2b). A procedure analogous to that used to synthesize 1b was employed using 1,2,5,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (prepared by the Wurtz-type reaction between 1,2-dichloro-1,2,2-tetramethyldisilane and 1,2-diethylidydimethyldisilane pretreated with EtMgBr) as the starting material. A procedure described above for the conversion of 1a to 1b was employed utilizing 1,2,5,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (prepared by the Wurtz-type reaction between 1,2-dichloro-1,2,2-tetramethyldisilane and 1,2-diethylidydimethyldisilane pretreated with EtMgBr) as the starting material. A procedure analogous to that used to synthesize 1a was employed utilizing 1,2,5,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (prepared by the Wurtz-type reaction between 1,2-dichloro-1,2,2-tetramethyldisilane and 1,2-diethylidydimethyldisilane). A procedure analogous to that used to synthesize 1a was employed utilizing 1,2,5,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (prepared by the Wurtz-type reaction between 1,2-dichloro-1,2,2-tetramethyldisilane and 1,2-diethylidydimethyldisilane). A procedure analogous to that used to synthesize 1a was employed utilizing 1,2,5,6-hexamethyl-1,2-diethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (prepared by the Wurtz-type reaction between 1,2-dichloro-1,2,2-tetramethyldisilane and 1,2-diethylidydimethyldisilane). A satisfactory analysis could not be obtained.
as an internal standard), and a minimum amount of CD$_2$Cl$_2$ sufficient to dissolve the solids. In a separate vial, a solution of 0.0081 g (0.0088 mmol) of [Ph$_3$P]$_3$Ru(Cl)H in a minimum amount of CD$_2$Cl$_2$ 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 $\delta$ 6.89 (1a) and 6.32 (1b) relative to that of ferrocene ($\delta$ 4.18). After 17.5 days, the reaction was ~57% complete as judged by $^1$H NMR integration.

Isomerization Using Dihydridotetrakis(triphenylphosphine)ruthenium(II) [(Ph$_3$P)$_4$RuH$_2$]. This reaction was conducted using the preceding procedure, but with 0.0101 g (0.00878 mmol) of (Ph$_3$P)$_4$RuH$_2$ as the hydride source. After 17.5 days, the reaction was ~18% complete as judged by $^1$H NMR integration.

Isomerization Using Bis(cyclopentadienyl)zirconium-chloride hydride [Cp$_2$Zr(Cl)H]. This reaction was conducted using the preceding procedure, but with 0.0023 g (0.0089 mmol) of Cp$_2$Zr(Cl)H as the hydride source. After 17.5 days, the reaction was ~10% complete as judged by $^1$H NMR integration.

Isomerization Trials in the Darkness, with Radical Scavengers 9,10-Dihydroanthracene 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$_2$Cl$_2$. 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 $^1$H 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$_2$Cl$_2$. An aliquot of one of the following was added to the separate NMR tubes: 0.0079 g (0.044 mmol) of 9,10-dihydroanthracene, 0.0013 g (0.044 mmol) of tributyltin hydride, 0.0034 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$_2$Cl$_2$. 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 $^1$H 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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