We report the synthesis and unexpected cis-to-trans trans-isomerization of a disilanyl analogue of 1,5-cyclooctadiene. Scheme 1 shows the synthesis of cis,cis-1,2,5,6,6-octamethyl-1,2,5,6-tetrasilacyclopenta-3,7-diene (1) and its Ru-catalyzed isomerization to trans,trans-1,2,5,6,6-octamethyl-1,2,5,6-tetrasilacyclopenta-3,7-diene (2). The isomerization proceeds slowly in methylene chloride upon exposure of 1 to a catalytic portion of the recently described dimeric ruthenium(II) alkylidene complex (Cy3P)RuCl2(=CHPh)Ru(p-cymene)Cl2.3 Compounds 1 and 2 were characterized by single-crystal X-ray diffraction (Figure 1). Both compounds exist as chair conformers in the solid state. Table 1 shows selected bond lengths and angles of the chair conformers.

We probed the mechanism of the isomerization with a variety of experiments. First, dissolution of 1 in CD2Cl2 in the absence of the Ru(II) complex produced no trace of 2, even upon heating at 40 °C for 20 days. Second, the rate of isomerization increased when we increased the concentration of the Ru(II) complex from 2.5 mol % to 5.0 mol % to 10 mol %. Third, exposure of 2 to the Ru(II) complex in CD2Cl2 produced no trace of 1, even upon heating at 40 °C for 20 days. These results suggest that the isomerization is catalyzed by Ru and that the trans,trans conformer 2 is more stable than the cis,cis conformer 1 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 1 by 1H NMR spectroscopy).4

We explored several alternative methods known to catalyze the cis-to-trans isomerization of olefins. Iodine, which isomerizes cis,trans-1,5-cyclooctadiene to cis,cis-1,5-cyclooctadiene in 65% yield,5 failed to isomerize 1 to 2, even upon heating at 40 °C for 10 days. Transition-metal-based isomerization catalysts such as cobalt(II) hydrocarbonyl (HCo(CO)4) and tris(triphenylphosphine)rhodium(I) chloride (RhCl-(PPh3)3) also failed to effect the isomerization.6,8

Ruthenium(II) hydrides have been implicated as catalysts in the isomerization of olefins, even when the source of the hydride remains obscure.9 These considerations prompted us to examine the reactivity of 1 with the commercially available ruthenium(II) hydride complexes chlorohydridotris(triphenylphosphine)ruthenium(II) [PPh3]2Ru(ClH)] and dihydridotetrakis(triphenylphosphine)ruthenium(II) [PPh3]2RuH2. Indeed, exposure of 1 to these ruthenium(II) hydrides in CD2Cl2 at 40 °C led to isomer 2. We also found that bis(cyclopentadienyl)zirconium(II) chloride hydride (CP2-ZrClH) effects the isomerization, although this catalyst appears to be less efficient than the ruthenium(II) hydrides. Taken together, these results suggest that a ruthenium(II) hydride is the active catalyst in the isomerization promoted by (Cy3P)RuCl2(=CHPh)Ru(p-cymene)Cl2.

In considering possible reaction pathways, it is likely that the isomerization proceeds via a hydride addition/elimination mechanism.9 A probable intermediate in this pathway would be the cis,trans isomer. Although we have been unable to identify or isolate this intermediate, we undertook a series of calculations to evaluate the energy of this isomer relative to isomers 1 and 2.10–12 In our calculations, we employed the MM2 force field and two semiempirical methods (based on the PM3 and AM1 parametrizations, respectively).13 Table 2 shows the results of the calculations. The methods suggest a similar trend in stabilities: cis,cis > trans,trans > cis,trans. We note, however, that the
We also examined the thermodynamics of the isomerization in the context of the known chemistry of 1,5-cyclooctadiene.\(^{15-18}\) Optimized geometries of 1,5-cyclooctadiene at minima show that the cis,cis isomer has three low energy conformers, the twistboat, the half-chair, and the chair; the trans,trans isomer has two low energy conformers, the twist and the chair; and the cis,trans isomer has one low energy conformer: the twist.\(^{18}\) Of all six conformers, the cis,cis twistboat is the most stable and the trans,trans chair is the least stable; the difference in energy between these two conformers is 28.2 kcal/mol.\(^{18}\) The trans,trans chair conformer might be destabilized by electron repulsions between the \(\pi\) electrons of the double bonds: the \(\pi\) orbitals lie on the same axes with the transannular \(sp^2\) carbons only 2.59 Å apart.\(^{18}\) Perhaps due to this destabilization, no trans,trans chair conformer has been observed experimentally; only the labile trans,trans twist conformer has been isolated.\(^{15,17}\)

In contrast to 1,5-cyclooctadiene, the most stable solid-state conformer of 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilaadamantane-3,7-diene appears to be the trans,trans chair conformer.\(^{17}\) While the bond length of the C(sp\(^3\))–C(sp\(^3\)) bond in the trans,trans chair conformer of 1,5-cyclooctadiene was calculated to be 1.60 Å,\(^{18}\) the corresponding Si–Si bond length of the trans,trans chair conformer is 2.38 Å. The longer Si–Si bond probably leads to reduced \(\pi\)–\(\pi\) repulsion between the parallel double bonds,\(^{18}\) which affords the trans,trans chair conformation greater stability in the case of the disilanyll analogue.

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**Supporting Information Available:** Syntheses and analytical data for 1 and 2; X-ray analyses for 1 and 2 including a summary of crystallographic parameters, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, space-filling views, and packing diagrams (17 pages).

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