

Unexpected Cis,Cis to Trans,Trans Isomerization of a Disilanyl Analogue of 1,5-Cyclooctadiene

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Received June 24, 1998

We report the synthesis and unanticipated cis,cis to trans,trans isomerization of a unique disilanyl analogue of 1,5-cyclooctadiene. Scheme 1 shows the synthesis of *cis,cis*-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**1**) and its Ru-catalyzed isomerization to *trans,trans*-1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilacycloocta-3,7-diene (**2**).^{1,2} 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(I) hydrocarbonyl (HCo(CO)₄) and tris(triphenylphosphine)rhodium(I) chloride (RhCl(PPh₃)₃) also failed to effect the isomerization.^{6–8}

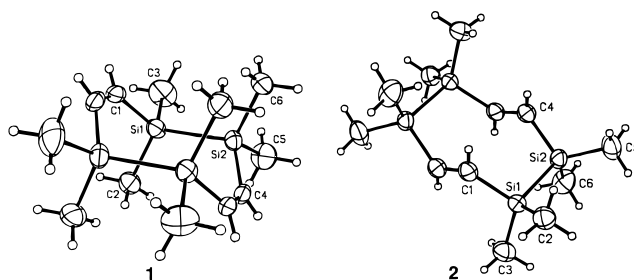
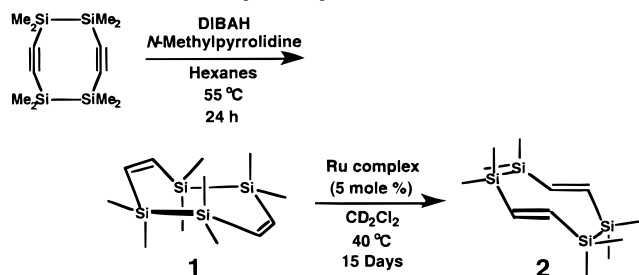


Figure 1. ORTEP drawings (40% probability level) for **1** (left) and **2** (right).

Scheme 1. Synthesis of **1** and Its Isomerization to **2** Catalyzed by Ruthenium



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) ([Ph₃P]₃Ru(Cl)H) and dihydridotetrakis(triphenylphosphine)ruthenium(II) ([Ph₃P]₄RuH₂). Indeed, exposure of **1** to these ruthenium(II) hydrides in CD₂Cl₂ at 40 °C leads to isomer **2**. We also found that bis(cyclopentadienyl)zirconium(II) chloride hydride (Cp₂Zr(Cl)H) 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

(9) See, for example: McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224.

(10) Molecular mechanics calculations (MM2) were performed using PC Model (version 5.13). Semiempirical calculations were performed with Spartan 5.0 using the PM3 and AM1 parametrizations.^{11,12} In all cases, optimal geometries were determined without the use of additional symmetrization of the Hamiltonian (NOSYMMTRY option). The absence of imaginary normal-mode frequencies confirmed that the structures correspond to local energy minima.

(11) Spartan version 5.0, Wavefunction, Inc., Irvine, CA 1997.

(12) For a review of semiempirical methods, see: Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1986.

(13) We note that minimization with the PM3 Hamiltonian appears to provide the closest qualitative resemblance to the X-ray structures of **1** and **2** in terms of bond lengths and angles.

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(4) In kinetics studies of the isomerization of **1** to **2** using ferrocene as an internal standard for integration by ¹H NMR spectroscopy, we have found that **2** is more labile than **1** under the isomerization conditions. Furthermore, at the latter stages of the isomerization, the rate of loss of **2** becomes competitive with the rate of isomerization of **1** to **2**. Consequently, we feel that the inability to detect trace amounts of **1** in the attempted isomerization of **2** to **1** provides strong (albeit negative) evidence that **2** is thermodynamically more stable than **1** within the limits described in the text.

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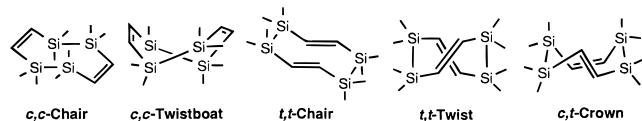
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Table 1. Selected Bond Lengths and Angles for Compounds 1 (Cis,Cis) and 2 (Trans,Trans)

	bond lengths (Å)		bond angles (deg)	
	cis,cis	trans,trans	cis,cis	trans,trans
Si(1)–Si(2)	2.342(1)	2.383(1)	Si(2)–Si(1)–C(1)	114.9(1)
Si(1)–C(2)	1.876(3)	1.873(2)	C(1)–Si(1)–C(2)	112.4(2)
Si(2)–C(4)	1.872(3)	1.874(2)	C(1)–Si(1)–C(3)	104.9(2)
Si(2)–C(6)	1.873(3)	1.876(2)	Si(1)–Si(2)–C(4)	114.4(1)
Si(1)–C(1)	1.872(3)	1.871(2)	Si(2)–Si(1)–C(2)	110.1(1)
Si(1)–C(3)	1.895(4)	1.877(2)	Si(2)–Si(1)–C(3)	105.9(1)
Si(2)–C(5)	1.890(3)	1.878(2)	C(2)–Si(1)–C(3)	108.1(2)
C(1)–C(1')	1.338(7)		C(5)–Si(2)–C(6)	107.9(2)
C(4)–C(4')	1.333(6)		Si(1)–C(1)–C(1')	133.2(1)
C(1)–C(4')		1.321(3)	Si(1)–C(1)–C(4')	127.0(2)

Table 2. Calculated Heats of Formation (kcal/mol) for the Lowest Energy Conformations of 1 and 2

method	conformers				
	c,c-chair	c,c-twistboat	t,t-chair	t,t-twist	c,t-crown
MM2	-22.6	-22.0	-18.0	-21.9	-18.6
PM3	-98.7	-100.4	-97.2	-97.2	-95.0
AM1	-71.6	-72.0	-68.1	-68.3	-67.6

Table 3. Relative Values of ΔG (kcal/mol) at 40 °C for the Lowest Energy Conformations of 1 and 2

method	conformers				
	c,c-chair	c,c-twistboat	t,t-chair	t,t-twist	c,t-crown
PM3	0.0	0.0	-0.4	-1.8	2.1
AM1	0.0	-1.0	-0.7	-0.9	2.3

calculations provide values of enthalpy; entropic contributions are thus neglected. In contrast, the experimental results, which are dictated by free energies, suggest that the trans,trans conformer **2** is the most stable of all (vide supra).

From the X-ray structures, the transannular methyl groups in **1** appear to experience greater steric crowding than those in **2**. Consequently, the conversion of **1** to **2** might be accompanied (or rather driven) by a gain in rotational entropy of the methyl groups. Using theoretical methods, we examined potential entropic contributions to the isomerization by calculating relative entropies from the rotational and vibrational data. Utilizing the relationship $\Delta G = \Delta H - T\Delta S$, we calculated relative values of ΔG for the conformers where the data permitted (see Table 3). While the PM3 calculations suggest that the conformers of **2** have lower free energies than those of **1** (consistent with our experimental observations), the AM1 calculations are inconclusive.¹³

In the absence of reliable thermodynamic data, it is tempting to suggest that **2** might represent a kinetic rather than a thermodynamic product.¹⁴ The present system, however, does not conceptually afford this opportunity (particularly since we typically use only 0.05 molar equiv of catalyst to effect the isomerization; thus, trapping of **2** by complexation to Ru is untenable). It is interesting to further note that neither semiempirical method accurately predicts the solid-state conformer observed for either **1** or **2**. As a consequence of this result and the discrepancies observed when comparing the output from the two semiempirical methods, we regard the calculated energies shown in Tables 2 and 3 with some degree of reservation. We feel, however, that the calculations are useful in establishing the viability of the proposed cis,trans intermediate.

We also examined the thermodynamics of the isomerization in the context of the known chemistry of 1,5-cyclooctadiene.^{5,15–18} 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 π electrons of the double bonds: the π 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.^{5,15–17}

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-tetracycloocta-3,7-diene appears to be the trans,trans chair conformer **2**. 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 **2** 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 disilanyl analogue.

Acknowledgment. The National Science Foundation (CAREER Award to T.R.L.; CHE-9625003), the Camille and Henry Dreyfus Foundation (New Faculty Award to T.R.L.; NF-93-040), the Texas Advanced Research Program (Grant No. 003652-162), the Robert A. Welch Foundation (Grant No. E-1337), and the Texas Center for Superconductivity at the University of Houston provided generous support for this research. We thank Dr. James Korp for technical assistance with the X-ray crystallographic analyses and Margaret Shaffer for some of the initial synthetic work. We also thank Bob Grubbs, Jonathan Friedman, Monte Pettit, and especially Tom Albright for helpful advice and assistance.

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).

JO981213Y

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