Experimental and Theoretical Investigation of *Z*−*E* Alkene Isomerization in $[(Cy_3P)_2Cl_2Ru]_2(\mu$-CHCH=CHCH) and Related Vinylalkylidenes

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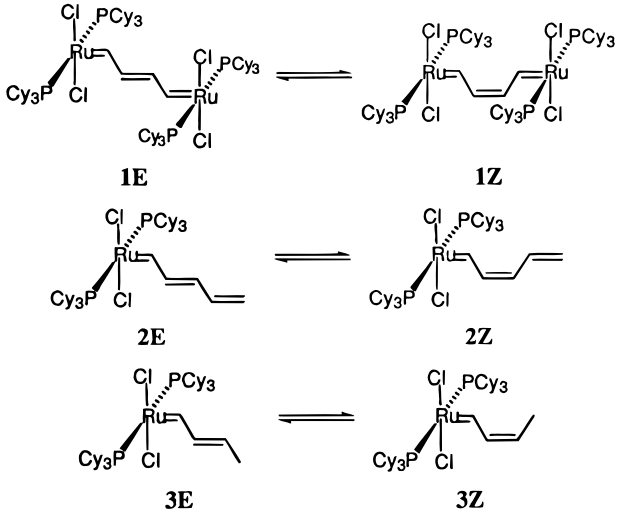
The conjugated diruthenium bisalkylidene complex $[(Cy_3P)_2Cl_2Ru]_2(\mu$-CHCH=CHCH) (**1**, an inseparable 10:1 mixture of *E* and *Z* alkene isomers **1E** and **1Z**) and the separate *E* and *Z* isomers of the monoruthenium alkylidene complexes $(Cy_3P)_2Cl_2Ru$=CHCH=CHCH=CH_2 (**2E** and **2Z**) and $(Cy_3P)_2Cl_2Ru$=CHCH=$CHCH_3$ (**3E** and **3Z**) have each been synthesized through the stoichiometric reaction of olefin metathesis catalysts. Each pair of isomers undergo *Z*−*E* isomerization, though the isomerization rates and their dependencies on excess alkene and PCy_3 are very different. Isomerization in **1** is the fastest, with $\Delta H^{\ddagger} = 100 \pm 5$ kJ/mol and $\Delta S^{\ddagger} = 67 \pm 3$ J/(mol K) (**1Z** to **1E**) or 49 ± 3 J/(mol K) (**1E** to **1Z**) as determined by dynamic NMR, giving $t_{1/2} = 11$ s for the approach to equilibrium at 25 °C. The rate of this isomerization shows no phosphine dependence. Isomerizations of **2Z** and **3Z** are slower ($t_{1/2} = 5-20$ h), but the former is promoted by PCy_3, while the latter is inhibited. In the presence of (*Z*)-1,3,5-hexatriene, the isomerization of **2Z** is much slower, while the isomerization of **3Z** is accelerated by (*Z*)-1,3-pentadiene. Density functional calculations were performed to help interpret these results and elucidate which of several possible isomerization mechanisms operates in each case.

Introduction

In recent years, interest has been growing in complexes with metal centers linked by π-conjugated organic bridges.[1] Following the study in our laboratory of several butadienediyl-bridged diiron complexes ($[CpFeL_2]_2(\mu$-CH=CHCH=CH)),[2] we now report the synthesis of the bisalkylidene diruthenium complex $[(Cy_3P)_2Cl_2Ru]_2(\mu$-CHCH=CHCH) (**1**), also with a $(CH)_4$ bridge. The *Z* (**1Z**) and *E* (**1E**) forms of this complex have been found to be inseparable, due to a relatively rapid equilibration at room temperature (Scheme 1). Similar

Scheme 1



but slower isomerization processes have been observed for the separable isomers of the mononuclear complexes $(Cy_3P)_2Cl_2Ru$=CHCH=CHCH=CH_2 (**2Z** and **2E**) and $(Cy_3P)_2Cl_2Ru$=CHCH=$CHCH_3$ (**3Z** and **3E**).

The use of ruthenium alkylidene complexes as alkene metathesis catalysts has become widespread in the past few years.[3] These complexes, especially Grubbs's cata-

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(1) Ward, M. D. *Chem. Soc. Rev* **1995**, 121−134. Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129−7138. Weyland, T.; Lapinte, C.; Frapper, G.; Calhorda, M. J.; Halet, J.-F.; Toupet, L. *Organometallics* **1997**, *16*, 2024−2031. Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775−788. Peters, T. B.; Bohling, J. C.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1999**, *18*, 3261−3263. Xia, H. P.; Yeung, R. C. Y.; Jia, G. *Organometallics* **1997**, *16*, 3557−3560. Jia, G.; Wu, W. F.; Yeung, R. C. Y.; Xia, H. P. *J. Organomet. Chem.* **1997**, *539*, 53−59. Lang, H. *Angew. Chem., Intl. Ed. Engl.* **1994**, *33*, 547−550. Beck. W.; Niemer. M.; Wieser, M. *Angew. Chem., Intl Ed. Eng.* **1993**, *32*, 923−949. Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993−1019. Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707−1716. Beljonne, D.; Colbert, M. C. B.; Raithby, P. R.; Friend, R. H.; Brédas, J. L. *Synth. Met.* **1996**, *81*, 179−183.

(2) Etzenhouser, B. A.; Cavanaugh, M. D.; Spurgeon, H. N.; Sponsler, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 2221−2222. Etzenhouser, B. A.; Chen, Q.; Sponsler, M. B. *Organometallics* **1994**, *13*, 4176−4178. Sponsler, M. B. *Organometallics* **1995**, *14*, 1920−1927.

(3) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2036−2056. Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413−4450.

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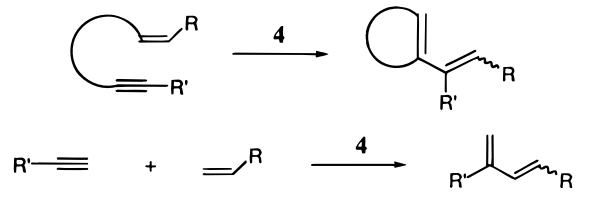
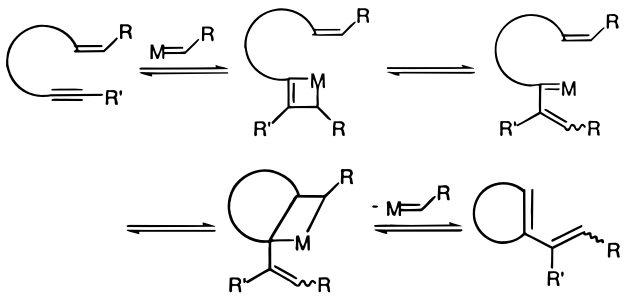
Scheme 2



Scheme 3

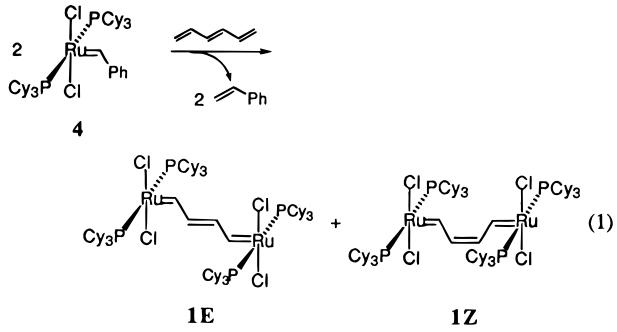


lyst(**4**),[4] have also proven useful for the production of 1,3-dienes by alkene−alkyne metathesis, both intramolecular[5] and intermolecular[6] (Scheme 2). 1,3-Dienes have also been produced in the catalytic and stoichiometric reactions of Fischer carbenes.[7] Some of the reported diene products have *Z* and *E* isomers, and the reported stereoselectivities are quite variable. A proposed intermediate in the alkene−alkyne metathesis mechanism (Scheme 3) is a vinylalkylidene complex. The results reported herein suggest that *Z*−*E* isomerization of these complexes with respect to the β,γ bond can occur through several possible mechanisms, and this isomerization could impact the stereoselectivity of 1,3-diene syntheses.[8]

Our goal in the preparation of these complexes was not the synthesis of organic products, but rather the study of the electronic structures of the ruthenium complexes. Though the *Z*−*E* isomerizations have complicated this effort, the isomerization processes have themselves proven very interesting. A number of potential mechanisms have been identified, and our experimental and theoretical results suggest that at least three of them are important.

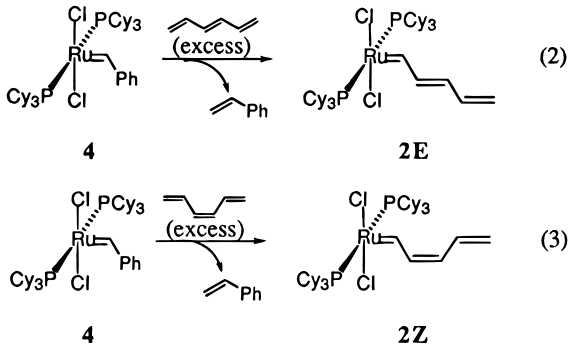
Results and Discussion

Synthesis of the Vinylalkylidene Complexes. The ruthenium complexes were synthesized by the stoichiometric reaction of olefin metathesis catalysts.[9] Reaction of 2 equiv of **4** with 1 equiv of (*E*)-1,3,5-hexatriene in dichloromethane produced complex **1** as a 10:1 mixture of **1E** and **1Z** in 50% yield after purification (eq 1).[10]



The isolated yield was lower than the NMR yield (80%), due to the pentane washes that were required to remove small amounts of the more soluble **2E** and **4**. The ethylidene $(Cy_3P)_2Cl_2Ru{=}CHCH_3$ (**5**)[4] was sometimes used in the place of **4**. The assignment of *E* and *Z* structures was done by simulation of the observed AA′XX′ patterns for the bridge protons in the ^{1}H NMR spectrum, giving $J_{\beta\beta'} = 15.0$ Hz for **1E** and 11.2 Hz for **1Z** (Figure 1). The coupling patterns and all of the coupling constants (see Experimental Section) are fully consistent with those reported for (*E*)- and (*Z*)-hexatriene and derivatives.[11]

By using excess (*E*)-hexatriene (2 equiv per equivalent of **4** or **5**), complex **2E** was obtained in quantitative yield (eq 2). Complex **2Z** was likewise prepared by reaction with (*Z*)-hexatriene (eq 3), but we were unable to isolate this complex in clean form. Upon removal of the excess



(*Z*)-hexatriene, significant isomerization to **2E** was observed. Both **2E** and **2Z** were significantly less stable in solution than **1**, **3E**, **3Z**, **4**, **5**, or $(Cy_3P)_2Cl_2Ru{=}CH_2$, showing significant decomposition after 2−6 h. Decomposition was faster in more concentrated samples. No

(4) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.

(5) Kinoshita, A.; Sakakibara, N.; Mori, M. *Tetrahedron* **1999**, *55*, 8155−8167. Zuercher, W. J.; Scholl, M.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 4291−4298. Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801−10802.

(6) Stragies, R.; Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2518−2520.

(7) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737−738. Waters, M. L.; Bos, M. E.; Wulff, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 6403−6413. Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271−288.

(8) The mechanism of ref 6 suggests that the ruthenacyclobutene ring opening is not the stereochemistry-determining step in the intermolecular reactions. However, an alternative mechanism that is more consistent with the ones proposed for the intramolecular reactions (ref 5) does have the stereochemistry determined in this step. The mechanism of these processes will be addressed in a later publication: Masingale, M. P.; Niu, X.; Sponsler, M. B. Manuscript in preparation.

(9) Stoichiometric use of metathesis catalysts to prepare new alkylidene complexes has been previously reported. See ref 4, and for several dimolybdenum examples, see: Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759−768. In these complexes, *Z*−*E* isomerization was apparently not observed. A related conjugated diruthenium complex, $[(Cy_3P)_2Cl_2Ru]_2(\mu\text{-}CHC_6H_4CH)$, was prepared by a nonmetathesis route: Weck, M.; Schwab, P.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1789−1793.

(10) In some contexts, as here, "**1**" will be used to denote the inseparable mixture of isomers. Elsewhere, the designations "**1**", "**2**", and "**3**" will be used to denote the isomers of these compounds collectively.

(11) Barber, M. S.; Hardisson, A.; Jackman, L. M.; Weedon, B. C. L. *J. Chem. Soc.* **1961**, 1625−1630. Bothner-By; A. A.; Harris, R. K. *J. Am. Chem. Soc.* **1965**, *87*, 3451−3455. Albriktsen, P.; Harris, R. K. *Acta Chem. Scand.* **1973**, *27*, 1875−1882.

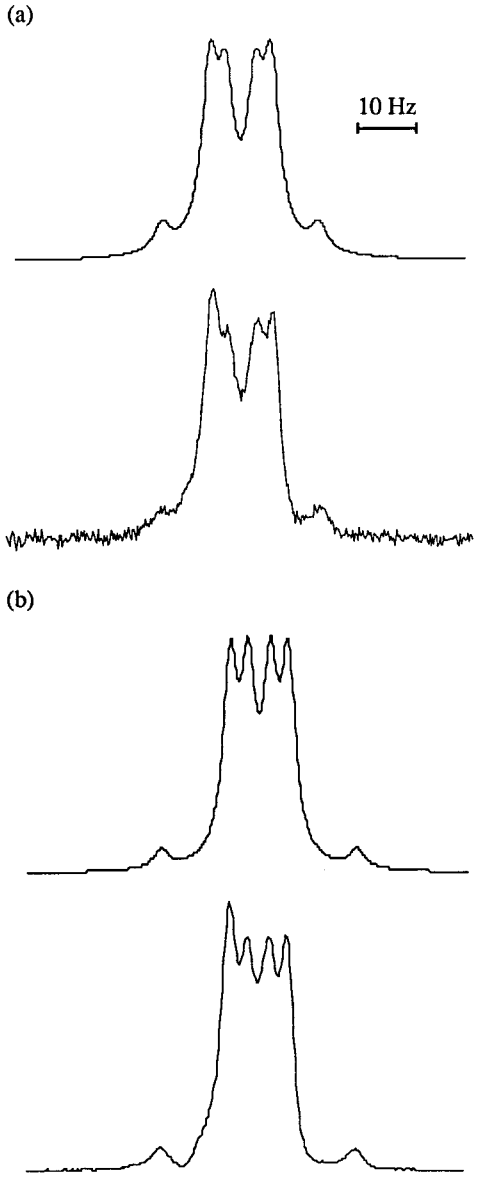


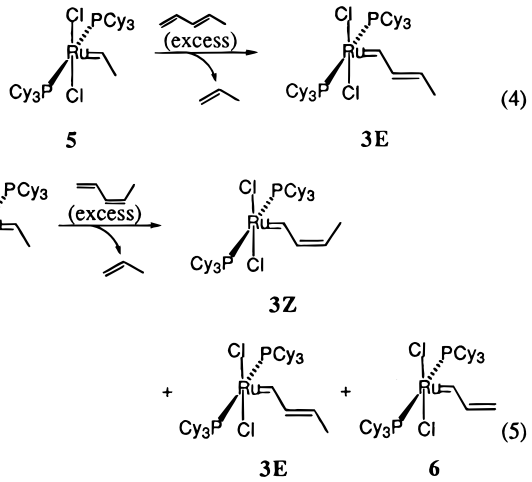
Figure 1. Simulated (top) and experimental (bottom) ^{1}H NMR signals for H_α in (a) **1Z**, appearing at 21.35 ppm, and (b) **1E**, appearing at 19.86 ppm. Each signal represents half of an AA'XX' pattern at 300 MHz.

products were identified by ^{1}H NMR, since no new peaks were observed in the region near 20 ppm and the alkenyl peaks faded into a slightly wavy baseline, leaving the PCy_3 peaks relatively unchanged.[12] We observed similar instability in $(Cy_3P)_2Cl_2Ru{=}CHCH{=}CH_2$ (**6**),[4] suggesting that decomposition of these complexes involves reaction at the conjugated, terminal alkene.

The metathesis steps in the formation of **1** were found to be reversible. Thus, addition of (*E*)-hexatriene to **1** cleanly produced **2E**. Complex **1** could also be prepared from **2E** by addition of **4** or **5**. We attempted to make the C_2H_2 version of **1**, $[(Cy_3P)_2Cl_2Ru]_2(\mu$-CHCH), through the analogous reaction of **6** and **4** or **5**, but no reaction was observed.[13]

Attempts to prepare **1Z** through the reaction of **4** or **5** with (*Z*)-hexatriene were unsuccessful. The metathesis reactions of both (*Z*)-hexatriene and **2Z** were considerably slower than those of (*E*)-hexatriene and **2E**. More importantly, however, was that **1E** and **1Z** were already in their 10:1 equilibrium ratio at the earliest time the ratio could be determined by ^{1}H NMR (about 3 min). Attempts to prepare nonequilibrium mixtures of **1E** and **1Z** by recrystallization or by visible or UV irradiation at low temperature also failed.

Complexes **3E** and **3Z**[14] were prepared by reaction of **5** with (*E*)- and (*Z*)-1,3-pentadiene, respectively (eqs 4 and 5). Complex **3E** was obtained quantitatively, but **3Z** was contaminated by **3E** (17%) and **6** (12%). Complex **6** is presumably formed from metathesis at the internal double bond. Its formation is noteworthy, especially since **6** is not formed in the preparation of **3E** or either isomer of **2**.



As shown by the reversibility of the transformation from **2E** to **1**, even the diruthenium complex retains some metathesis activity. The reactivity of vinylalkylidenes in metathesis, however, is known to be lower than that of **4** and **5**,[4] and our observations are consistent with this. Nonetheless, metathesis still does play a role in the isomerization of some of the complexes (see below).

***Z*−*E* Isomerization Results.** The half-lives for isomerization of the vinylalkylidene complexes is summarized in Table 1, and included are the effects of added PCy_3 and excess alkene. While the results for **1** should be reliable, the values given for **2** and **3** should be viewed as approximate and are presented only to demonstrate qualitative trends.

Though interconversion of **1E** and **1Z** is slow on the NMR time scale (separate signals are observed), it is apparently fast relative to the minutes time scale. Through spin-saturation transfer ^{1}H NMR experiments, we determined that the interconversion is slower than the 0.1 s time scale (saturation transfer was not observed). Chemical exchange between the ^{1}H NMR signals of **1E** and **1Z** was observed between 55 and 135

(12) We interpret this to mean either that paramagnetic products are formed, though no EPR signal was observed, or that a number of alkene products are formed such that none of the products are major.

(13) A molecular mechanics calculation suggested that the $(CH)_2$-bridged species might exist with only moderate strain. In this structure, the ruthenium coordination spheres were rotated relative to each other to allow each PCy_3 ligand to nestle between the two on the other ruthenium.

(14) Complex **3** has been previously reported, though with no stereochemical information or characterization data: Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867−3869.

Table 1. Isomerization Half-Lives at 25 °C[a]

	1Z ⇌ 1E[b]	**2Z ⇌ 2E**[c]	**3Z ⇌ 3E**[d]
no additives	11 s	7.6 h	5−20 h[e]
PCy_3[f]	11 s	1.2 h	80 h
0.02 M alkene[g]		>30 h	1.5 h

[a] Half-lives for approach to equilibrium. Determined by dynamic NMR for **1** and by NMR monitoring of the *Z* to *E* reactions for **2Z** and **3Z**. Values for **2** and **3** are approximate, due to signficant decomposition on the time scale of isomerization. The processes were analyzed as first-order, and reasonable fits were obtained. [b] In toluene-d_8. [c] In benzene-d_6. The half-life in CD_2Cl_2 with no additives was 4.6 h. [d] In CD_2Cl_2. [e] This half-life is dependent on the amount of **6** present in the mixture. See text. [f] Concentration 0−0.8 M for **1**, 0.02 M for **2Z**, and 0.01 M for **3Z**. [g] (*Z*)-1,3,5-Hexatriene for **2Z**, (*Z*)-1,3-pentadiene for **3Z**. Hexatriene could not be added to **1** without conversion to **2**.

Table 2. Rate Data for Chemical Exchange between 1E and 1Z

T, °C	*k*,[a] s^{-1}	k_{ct},[b] s^{-1}
55	2 ± 1	1.8
60	5 ± 1	4.5
70	14 ± 2	12.6
80	60 ± 5	53.8
90	140 ± 10	126
95	230 ± 30	206
100	300 ± 50	269
120	1300 ± 200	1166
135	2400 ± 400	2150

[a] *k* is the exchange rate constant obtained from line-shape analysis. [b] $k_{ct} = kp_{trans}$, where k_{ct} is the rate constant for **1Z** → **1E** and $p_{trans} = 0.90$ is the fractional population of **1E**.[42]

°C in toluene-d_8, with a coalescence temperature of about 100 °C. Through line-shape analysis, rate constants were obtained at each temperature (Table 2). The Eyring plot (Figure 2) was linear, and $\Delta H^{\ddagger}$ was found to be 100 ± 5 kJ/mol for the isomerization in either direction. $\Delta S^{\ddagger}$ was found to be 67 ± 3 J/(mol K) for the **1Z** to **1E** direction and 49 ± 3 J/(mol K) for the opposite direction. These activation parameters give a half-life of 11 s for the approach to equilibrium at 25 °C, which is consistent with our ambient-temperature results.

The isomerization in **1** was observed by dynamic NMR in both the presence and absence of added PCy_3. The complex was found to be considerably more stable at the elevated temperatures in the presence of added PCy_3. However, the rate of isomerization and equilibrium ratio were both independent of phosphine concentration up to 150 equiv of PCy_3 (0.8 M).

The observation that the activation parameters for **1E** and **1Z** differ in $\Delta S^{\ddagger}$ and not in $\Delta H^{\ddagger}$ deserves comment, though there is uncertainty in this result since the temperature independence of the equilibrium constant could only be observed for the lower part of the temperature range. Complex **1E**, having C_{2h} symmetry (or nearly so), would be expected to have no (or a very small) dipole moment. The moment should be larger for **1Z**, having approximate C_{2v} symmetry. Thus, **1Z** should cause more ordering of the solvent through electrostatic interactions, and this isomer would therefore have a lower entropy in solution.[15] If the transition states are entropically similar for the two isomers, this would explain the higher $\Delta S^{\ddagger}$ for **1Z**. This effect would also explain the higher **1E**/**1Z** equilibrium ratio in the more polar CD_2Cl_2 relative to toluene-d_8 (10 vs 8.7). Dipole moments calculated with ZINDO for the PH_3 analogues of **1E** and **1Z** (**1E′** and **1Z′**) were 0.06 and 1.1 D, respectively, reasonably consistent with the relatively small observed effects.

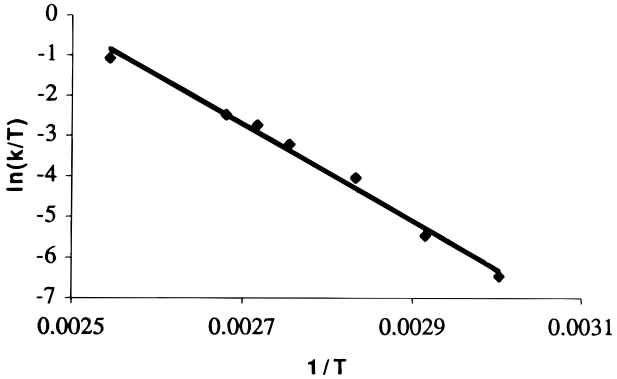
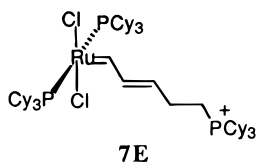


Figure 2. Eyring plot obtained for the isomerization of **1Z** to **1E** from ^1H NMR chemical exchange data in the temperature range from 60 to 120 °C. Correlation coeff = 0.995.

The isomerization of **2** was more difficult to study, due to the lower stability of both isomers. The isomerization and decomposition rates were found to be quite sensitive to the purity of the solvent used for synthesis of **2Z**. Commercial CD_2Cl_2 apparently contains an impurity that catalyzes both isomerization and decomposition of **2Z**. Isomerization half-lives of about 10 min were observed for samples prepared in unpurified solvent. The use of purified solvent provided samples of **2Z** that were more stable, and the rates in Table 1 are for these samples. The isomerization catalyst in CD_2Cl_2 is not strong acid, since addition of triflic acid to clean samples of **2Z** had little effect on the isomerization rate, even though decomposition was accelerated. In the presence of excess (*Z*)-hexatriene, the isomerization of **2Z** was much slower and too slow to be explained by a dilution effect.[16] The isomerization from **2E** to **2Z** was also observed, though the rate was less certain due to the equilibrium preference for **2E** ($K \approx 15$).

The addition of PCy_3 to **2Z** (in the presence of (*Z*)-hexatriene) led to both faster isomerization and conversion to two products (ca. 1:1 ratio). One of the products has been identified as the phosphonium cation **7E**.[17] From the evolution of the product mixture from **2Z**, it appears that isomerization to **2E** occurs somewhat faster than the formation of the other products. Addition of PCy_3 to **2E** gave the same two products in a similar ratio over about 2 h.[18]



7E

Compexes **3E** and **3Z** each produced the same 16:1 equilibrium mixture of **3E** and **3Z** after 1−4 days at

(15) Birge, R. R.; Sullivan, M. J.; Kohler, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 358−367.

(16) The metathesis reaction between **2E** and (*Z*)-hexatriene regenerates **2Z** along with (*E*)-hexatriene. While this "dilution" of the isomerized double bond will lead to a slower isomerization of **2Z**, this alone cannot explain the inhibition effect of hexatriene. At the concentrations employed, only 0.5 equiv of hexatriene was present.

room temperature, with less concentrated samples showing faster rates. The isomerization of **3Z** was considerably faster in the presence of (*Z*)-1,3-pentadiene. Addition of 2 equiv of PCy_3 to **3Z** caused a marked reduction in the rate of isomerization in both the presence and absence of (*Z*)-1,3-pentadiene. In the absence of additives, the isomerization rate for **3Z** was somewhat variable between samples and was significantly reduced when all of the **6** (present as an impurity, eq 5) had decomposed.

The isomerization rates for **1**, **2**, and **3**, as well as their dependencies on alkene and PCy_3 (Table 1), are all markedly different despite the close structural similarities between the complexes. Without additives, the isomerization of **1** is more than 1000 times faster than that of **2** or **3**. The presence of alkene inhibits isomerization in **2Z** and promotes it in **3Z**. Added PCy_3 has no effect on **1**, promotes isomerization in **2Z**, and inhibits isomerization in **3Z**. These differences suggest that different mechanisms are operating in the three cases.

Mechanistic Analysis. Eight isomerization mechanisms that we considered are presented in Chart 1. The possible role of each mechanism is evaluated below.

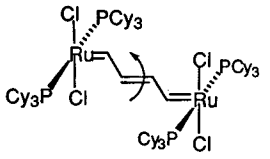
Thermally activated rotation at the double bond (mechanism 1) seems unlikely in all cases, given that the reported barrier to rotation in (*E*)-1,3,5-hexatriene is 185 kJ/mol.[19] However, the ruthenium centers could possibly stabilize the biradical-like transition state enough to significantly lower the barrier.[20] This mechanism can be eliminated for **3**, at least as the primary mechanism, based upon the observed phosphine inhibition. The related simple rotation after loss of phosphine (mechanism 2) could apply to **3**, but not likely to **1** or **2**, based upon their observed phosphine effects. Postulating that simple rotation should be most favored in **1** since it has two ruthenium centers, we can safely eliminate mechanism 2 for all three cases based upon the phosphine independence of **1**. Nonetheless, mechanisms 1 and 2 were both addressed computationally (see below).

Photochemically induced isomerization (mechanism 3) was eliminated for all cases, since the isomerizations of **1** and **2Z** were observed in the darkness of the NMR probe, and identical samples of **3Z** were observed to isomerize at the same rate when only one was shielded from ambient light.

Metathesis at internal double bonds (mechanism 4) is a long-known mechanism for *Z*−*E* isomerization.[21] For reactions that were run in the presence of alkene, isomerization of the complexes could occur through isomerization of the alkene followed by incorporation of the isomerized alkene through metathesis at the

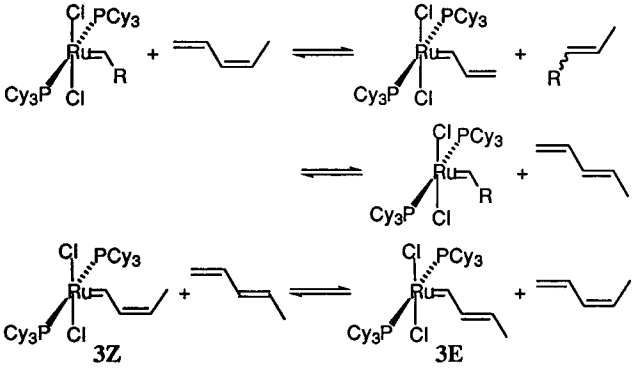
Chart 1. Possible Isomerization Mechanisms

1. Thermally activated rotation



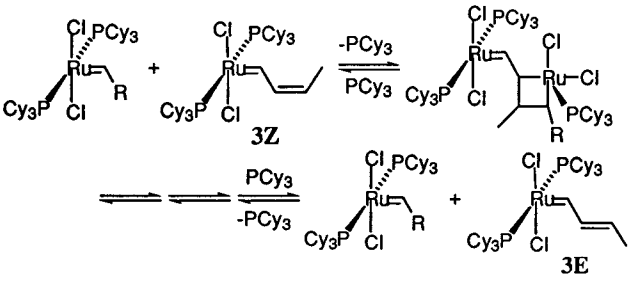
1E

2. Thermally activated rotation after loss of phosphine
3. Photochemically induced isomerization
4. Metathesis at an alkene internal double bond



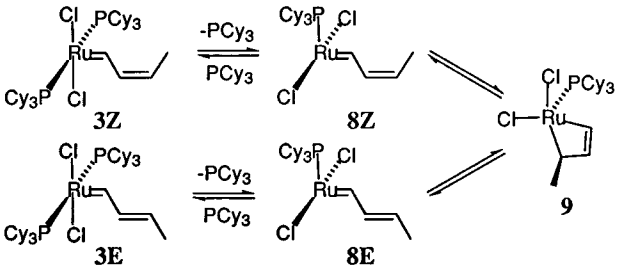
3Z **3E**

5. Metathesis at the vinylalkylidene β,γ internal double bond



3Z **3E**

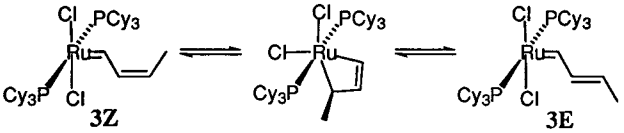
6. Through ruthenacyclobutene after loss of phosphine



3Z **8Z** **9**

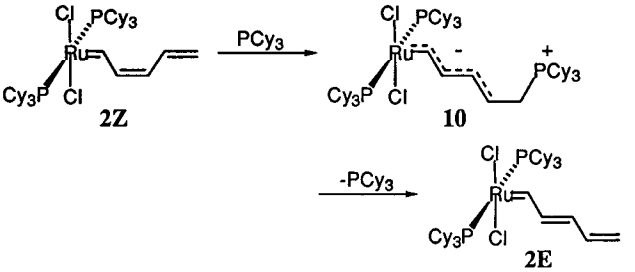
3E **8E**

7. Through ruthenacyclobutene without loss of phosphine



3Z **3E**

8. Nucleophilic attack of PCy_3



2Z **10** **2E**

(17) This product is partially deuterated when formed in CD_2Cl_2, though the fully protiated form has been made for characterization. This reaction will be reported more completely: Niu, X.; Masingale, M. P.; Sponsler, M. B. Submitted for publication.

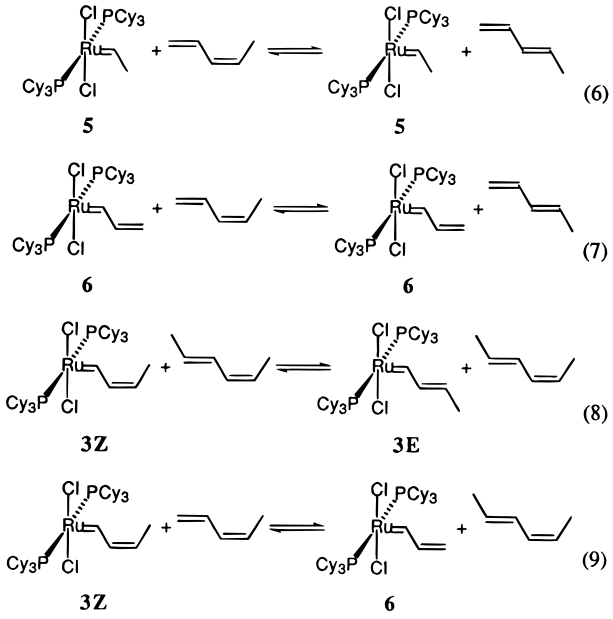
(18) We were unable to determine whether any isomerization to **2Z** occurred due to the production of the other products.

(19) Doering, W. v. E.; Roth, W. R.; Bauer, F.; Boenke, M.; Breuckmann, R.; Ruhkamp, J.; Wortmann, O. *Chem. Ber.* **1991**, *124*, 1461−1470.

(20) For an analysis of radical-stabilizing substituent effects on *Z*−*E* isomerization of alkenes, see: Leigh, W. J.; Arnold, D. R. *Can. J. Chem.* **1981**, *59*, 609−620.

(21) Bilhou, J. L.; Basset, J. M.; Mutin, R.; Graydon, W. F. *J. Chem. Soc., Chem. Commun.* **1976**, 970−971.

terminal double bond. This mechanism is possible and quite reasonable for **3Z** in the presence of (*Z*)-1,3-pentadiene, since a product from metathesis at the internal double bond (**6**) was observed and the isomerization was accelerated by added alkene. Several even more direct metathesis reactions could also contribute to isomerization, as shown in eqs 6−8. Careful inspection of the alkene region of the ^{1}H NMR spectrum reveals the likely presence of a small amount of (*Z*,*E*)-2,4-hexadiene,[22] the alkene reactant in eq 8. This alkene might be formed by the reaction in eq 9. The observed rate suppression of **3Z** to **3E** by phosphine is consistent with a metathesis mechanism, since metathesis is known to be inhibited by phosphine.[23] Mechanism 4 apparently does not operate for **2Z**, since **6** is not observed in the presence of (*Z*)-hexatriene.



This metathesis pathway might even explain the isomerization of **3Z** in the absence of added alkene. The observation that the rate was faster in the presence of **6** might be explained by eq 7, as long as a small amount of alkene is also present. Though the products of the decomposition of **6** and **3** are unknown, related alkylidenes are known to give alkene products primarily from dimerization of the alkylidene ligand.[24] Such dimers, or indeed any monosubstituted alkene or polyene product, would be expected to react with **3Z** to produce (*Z*)-1,3-pentadiene, the other reactant of eq 7. Isomerization could continue more slowly even after complex **6** is gone, through eqs 8 and 9, for example.

Mechanism 5 is a related metathesis mechanism involving the β,γ bond of a vinylalkylidene complex and would not require the presence of alkene. It presumably would be less favorable than mechanism 4 due to steric hindrance, so it would seem to be viable only for **3**, the only candidate for mechanism 4. However, this mechanism can be eliminated even in this case, because the observed concentration effect is the opposite of the expected effect. The rate was observed to decrease with increasing concentration of **3Z**. Also, the isomerization of **3Z** is not accelerated by the presence of **5**, a much more active metathesis catalyst.

The mechanism for alkene−alkyne metathesis (Scheme 3) provides another possible mechanism for *Z*−*E* isomerization. Ruthenacyclobutenes, postulated intermediates from the cycloaddition of ruthenium alkylidenes with alkynes, are said to undergo electrocyclic ring opening to vinylalkylidenes. The latter step, if reversible, provides a reasonable pathway for isomerization at the β,γ π bond of a vinylalkylidene (mechanism 6). The ruthenacyclobutene **9**, for example, could open to either **8E** or **8Z**, effecting the interconversion of **3Z** and **3E**. A rate suppression by phosphine should be expected for this mechanism by analogy with the metathesis mechanism,[23] both of which begin with loss of phosphine. This mechanism could still operate for **1**, however, if the loss of phosphine is the rate-limiting step. In this case, the ruthenacyclobutene would be formed essentially every time phosphine is lost from **1Z** or **1E**, removing any rate dependence on free phosphine. Even **2Z**, whose isomerization is promoted by PCy_3, could isomerize by this mechanism in the absence of phosphine, with a change of mechanism being induced by the addition of phosphine. Mechanism 6 was investigated through computation (see below).

The observed concentration effect for **3Z**, that isomerization is faster for more dilute samples, is consistent with mechanism 6 and any of the mechanisms that begin with dissociation of phosphine. Dissociation equilibria are shifted toward products at lower concentrations.

The possibility that a ruthenacyclobutene might be formed without the loss of phosphine is presented as mechanism 7. This possibility deserves consideration, since Grubbs and co-workers determined that ruthenium-catalyzed metathesis reactions proceed both with and without initial loss of PCy_3, with somewhat less than 10% of the reaction attributable to the nondissociative pathway.[23] Therefore, the phosphine independence of the isomerization of **1** might be explained by proposing that the nondissociative pathway is dominant in this system. On the basis of our computational results, this does not appear to be a likely possibility.

The final pathway, mechanism 8, is the only one that is consistent with promotion of isomerization by added phosphine, as we observed for **2Z**. Nucleophilic attack of phosphine on the end CH_2 would serve to weaken the β,γ π bond in the zwitterionic intermediate **10**, which could undergo rapid rotation.[25] Loss of phosphine would then produce **2E**. The observation of **7E**, presumably arising from protonation of **10**, offers strong support for this mechanism. Apparently, the methyl group of **3Z** offers sufficient steric protection to prevent the nucleophilic attack of PCy_3. We observed that **6**, lacking a methyl group for steric protection, also reacted with PCy_3 at a rate similar to that of **2E**. In this case, however, identifiable products were not observed.

No **7E** or other alkylidene products were observed from **2Z** or **2E** in the absence of added PCy_3. Therefore,

(22) Comparison was made to the spectrum in: *The Aldrich Library of C and ^{1}H FT NMR Spectra*; Aldrich Chemical Co.: Milwaukee, 1993.

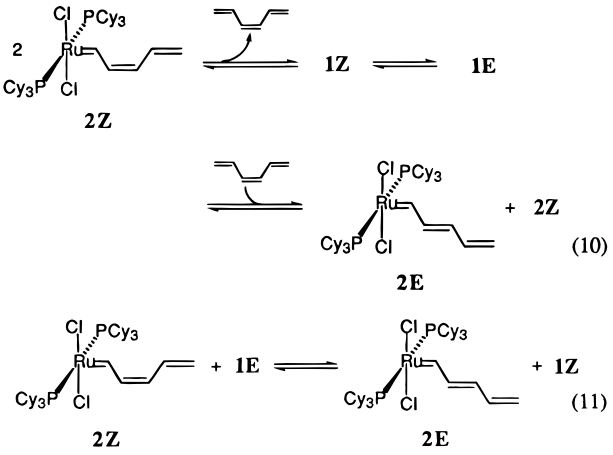
(23) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887−3897.

(24) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202−7207.

(25) For related nucleophilic reactions with tungsten vinylcarbenes, see: Macomber, D. W.; Hung, M.-H.; Verma, A. G.; Rogers, R. D. *Organometallics* **1988**, *7*, 2072−2074.

the isomerization of **2Z** under these conditions apparently goes by a different mechanism. Of the mechanisms in Chart 1, only mechanism 6 seems reasonable given that the isomerization is inhibited by (*Z*)-hexatriene. This mechanism would presumably be inhibited by any ligand, such as (*Z*)-hexatriene or PCy_3. Both ligands are reactive, but the metathesis reaction of (*Z*)-hexatriene is an identity reaction (since no metathesis occurs at the central bond) and PCy_3 leads to isomerization through mechanism 8.

Another reasonable explanation exists for the isomerization of **2Z** in the absence of PCy_3. Through the methathesis equilibrium in eq 10, **2Z** and **2E** might be interconverted via **1** as an intermediate. In fact, samples of **2Z** and **2E** generally contained small amounts (2−8%) of **1**, which presumably formed through eq 10 as the hexatriene was removed. In samples that contain **1**, a direct metathesis between **1E** and **2Z** (eq 11) could also lead to isomerization. In the presence of (*Z*)-

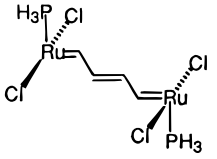


hexatriene, the first equilibrium in eq 10 is shifted away from **1** (**1** is not observable by NMR), resulting in slower isomerization of **2Z**, as was observed. Addition of **1** to samples of **2Z** did indeed lead to increases in the isomerization rate, but the increases indicated that the reaction was much less than first-order in **1**. This mechanism is probably operating, but it is apparently not the only mechanism for **2Z** in the absence of added PCy_3.

Other possible mechanisms could have been included in Chart 1. Some transition metal complexes are known to promote isomerization of alkenes, particularly those with electron-withdrawing groups, and an electron-transfer mechanism has been postulated.[26] While intramolecular electron transfer is possible, it does not seem likely in the cases reported herein. A variation on the direct rotation pathway (mechanism 1) is one in which the metal centers of **1** stabilize the transition state through coordination of the β-carbons. However, the positive $\Delta S^{\ddagger}$ seems inconsistent with this mechanism. An electrophilic attack of H^+ on **2Z** similar to the nucleophilic mechanism 8 was ruled out by the observed insensitivity of the isomerization rate to the addition of triflic acid.

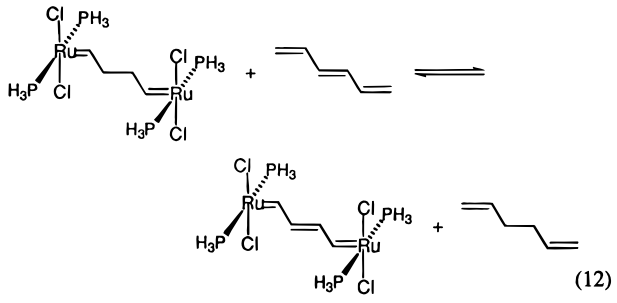
Density Functional Calculations. We have used density functional (DF) calculations[27] to investigate the viability of the isomerization mechanisms. PH_3 groups were substituted for PCy_3, and the PH_3 analogue of **1E** (**1E′**) was calculated in C_{2h} symmetry. A calculation of the PMe_3 analogue of **1E** (**1E″**) showed no qualitative difference in geometry, orbital structure, or orbital energy spacing, so all other DF calculations were done with PH_3 ligands.

Our first observation from the calculations was that the central double bond of **1E′** appears to be a normal alkene bond. The bond length, 1.369 Å, is slightly longer than the computed central bond of (*E*)-hexatriene, 1.352 Å,[28] and the computed bond order, 1.813, is slightly less than that for hexatriene, 1.847. The experimental isomerization barrier for **1E**, 100 kJ/mol, is very far below that for hexatriene, 185 kJ/mol.[19] From these measurements, the isomerization of **1** seems unlikely to arise from simple rotation at the π bond (mechanism 1). Similar observations were made for the complex in which one PH_3 ligand was removed from each Ru (**11E′**), optimized in C_i symmetry. In this complex, 90° rotations were observed at each Ru=C bond such that the bridge plane contained the remaining P atoms[29] (taking the symmetry back to nearly C_{2h}), but the π bonding through the bridge was affected only slightly (central C=C distance 1.376 Å).



11E′

The bond length and bond order results suggest that conjugation is somewhat stronger in **1E′** than in hexatriene.[30] Wishing to put this comparison in terms of energy, we considered the isodesmic reaction in eq 12. From the computed DF energies of each compound,



1E′

the heat of this reaction was found to be −21 kJ/mol.

(26) Helliwell, M.; Vessey, J. D.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1994**, 1193−1204.

(27) Restricted Hartree−Fock calculations of ruthenium alkylidenes have been reported (Benson, M. T.; Cundari, T. R. *Int. J. Quantum Chem.* **1997**, *65*, 987−996), and a DF study of alkene metathesis by a titanium catalyst has recently appeared (Axe, F. U.; Andzelm, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 5396−5402).

(28) An experimental bond length for (*E*)-hexatriene is 1.348 Å: Benet-Buchholz, J.; Boese, R.; Haumann, T.; Traetteberg, M. In *The Chemistry of Dienes and Polyenes*; Rappoport, Z., Ed.; Wiley: New York, 1997; Vol. 1, pp 25−65.

(29) This rotation has been previously inferred from experimental data (ref 23) and has also been found by calculation: Aagaard, O. M.; Meier, R. J.; Buda, F. *J. Am. Chem. Soc.* **1998**, *120*, 7174−7182.

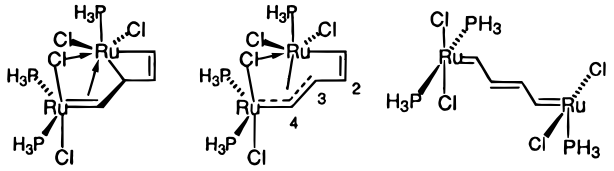
(30) Comparisons of the single bonds also support this conclusion. The single bonds in **1E′** were found to be 1.447 Å with bond orders of 1.119, while the corresponding bonds in hexatriene were 1.451 Å with bond orders of 1.068.

This result is reinforced by the qualitative experimental observation that such equilibria between alkyl- and vinyl-substituted alkylidenes, for example eq 4, strongly favor the vinylalkylidene. The result also supports the idea that conjugation is stronger in **1E′** than in hexatriene, though the question remains as to whether breaking the conjugation by rotation about the central bond will require significantly less energy.

To more directly address the possibility of mechanism 1, calculations were performed on rotated analogues of **1**. Single-point DF calculations on **1′** and hexatriene, both with constrained central C−C−C−C dihedral angles of 110°,[31] showed no signs of special delocalization for **1′**, as both structures were found to lie 260 kJ/mol above their trans (180°) rotamers.[32] Reasoning that the bulky PCy_3 ligands might play a significant role in either hindering or promoting mechanism 1, molecular mechanics geometry optimizations were done on rotamers of **1**, as well as **1′** and hexatriene. These calculations revealed no major effects of the PCy_3 ligands, as the 110° structures for **1**, **1′**, and hexatriene were found to have similar energies (71−79 kJ/mol higher) relative to the corresponding 180° structures. Similar calculations using PM3(tm) gave a similar result, with the 110° structures lying 92−98 kJ/mol higher in each of the three cases.[33]

The stronger conjugation of **1E′** in comparison to (*E*)-hexatriene seems to be a minor effect relative to the very large difference in experimental isomerization barriers. Though our calculations do not support mechanism 1, we cannot rule it out. The mechanism is an attractive possibility for **1**, given the observation of a phosphine-independent rate, but the lack of computational support, as well as the large, positive value for $\Delta S^{\ddagger}$, leads us to view this mechanism as improbable.

Relating to mechanism 6, calculations were done on **8E′** and on the ruthenacyclobutenes **9′** and **12′**. Complex **9′** was found to lie 116 kJ/mol above **8E′**. In contrast, complex **12′**[34] was only 9 kJ/mol above the open form (**13E′**). This striking difference between the two cases is accounted for by the fact that the diruthenium intermediate is able to form a chelated structure. The chelation includes a chloride bridge and close interactions of the ruthenacyclobutene ruthenium with the other ruthenium (2.89 Å) and the alkylidene carbon (2.20 Å). A contribution from resonance structure **12a′** is suggested by the relatively short C_3-C_4 bond (1.43 Å) and the fact that the hydrogen on C_3 lies nearly in the $C_2-C_3-C_4$ plane. In total, the chelation was calculated to be worth approximately 77 kJ/mol.[35] The calculated trend agrees qualitatively with the experimental observation that the isomerization of **1** is much faster than that of **3**. The agreement is also quantitatively reasonable, especially considering the substitution of PH_3 for PCy_3. A minimum barrier for **1E′** to **1Z′**, computed as the energy difference between **12′** + PH_3 and **1E′**, is 81 kJ/mol, which is consistent with the experimental barrier of 100 kJ/mol for **1E**.



For the isomerization of **1**, we favor mechanism 6 with a rate-determining loss of PCy_3. The $\Delta S^{\ddagger}$ values of 67 and 49 J/(mol K) are most consistent with a dissociative mechanism. Also, the DF calculations are consistent with a markedly lower barrier for the formation of the ruthenacyclobutene in this case due to the stabilization afforded by chelation. This chelation would presumably require the dissociation of phosphine.[36]

The role of chelation was further explored by considering whether chelation is also possible in **13E′** and its *Z* analogue (**13Z′**). Ruthenium alkylidene complexes with M-Cl−Ru bonding are known,[37] as are examples with other chelating groups.[38] Molecular mechanics calculations suggested that chloride chelation is reasonable in both **14E′** and **14Z′**, so we performed a DF calculation on the *E* isomer **14E′**. Despite the *E* double bond in the seven-membered ring, the energy of **14E′** was found to be comparable (3 kJ higher) to that of **12′**. Therefore a more complete mechanism for the isomerization of **1** is proposed in Scheme 4. We expect that chelation might accelerate the electrocyclic step not only by stabilization of the intermediates but also by forcing the vinylalkylidene into a cisoid conformation that is favorable for the electrocyclic closure. In other words, chelation can have both enthalpic and entropic effects on the reaction.

Chelation could also help to explain the isomerization of **2Z**. Coordination of the terminal vinyl group is possible both before and after cyclization to the ruthenacyclobutene, and molecular mechanics calculations showed that both structures are reasonable. A rhodium

(31) This dihedral angle was chosen to avoid spurious computational results that might be obtained at 90°.

(32) The full delocalization effect would only be seen in geometry-optimized structures, but if ruthenium were able to provide special radical stabilization, it seems likely that some of that would emerge even without geometry optimization.

(33) The PM3(tm) results for **1** have significant uncertainty, due to difficulties in the geometry optimizations. Many local minima were found in the molecular mechanics calculations on **1**, caused by steric hindrances on Ru−P and P−C rotations. The molecular mechanics energies were obtained only after many optimizations with different starting geometries and very small convergence criteria. Such measures were less practical and employed in a very limited way with PM3(tm), so the reported energies correspond to structures that may not represent global minima. Nonetheless, both methods suggest that the cyclohexyl groups, while clearly leading to conformational constraints, do not very significantly affect the twisted double bond rotamer differently than the planar form.

(34) Two isomers of **12′** were geometry optimized. The structure shown, meridional with respect to the ring-containing ligands, was found by optimization from a monocyclic ruthenacyclobutene geometry. Another structure with a facial configuration and a chloride bridge as the only chelation was optimized from a molecular mechanics-optimized geometry. This structure was found to be higher in energy by 37 kJ/mol.

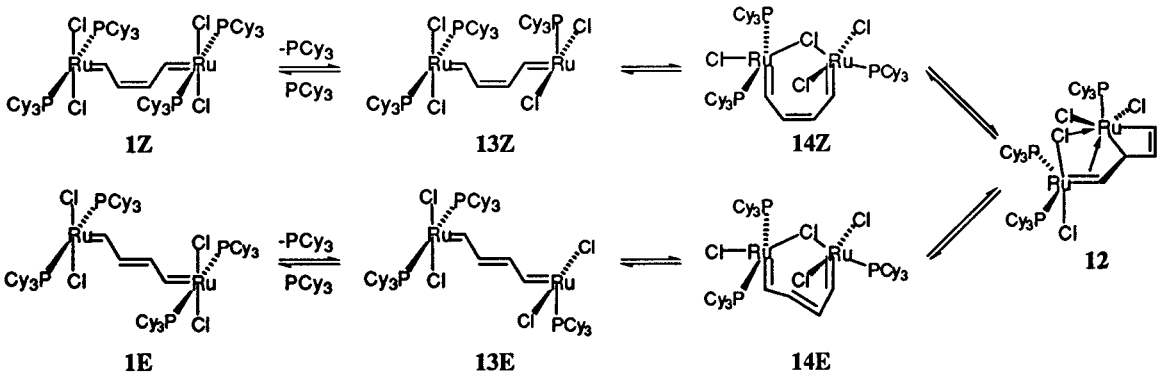
(35) This figure was obtained by comparison with a partially optimized structure of **12′** that did not possess any chelation.

(36) The complex with four PCy_3 ligands could avoid exceeding six-coordination by chelation of a chloride of the ruthenacyclobutene to the alkylidene ruthenium, but the PCy_3 ligands on the latter center would be forced into a very unfavorable cis arrangement. A molecular mechanics calculation of this structure showed it to be prohibitively high in energy. The energy gained from chelation of a single chloride would also be less than that gained by chelation in **12′**. (See ref 34.)

(37) Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758−2767.

(38) See, for example: Tallarico, J. A.; Bonitatebus, P. J., Jr.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157−7158. Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791−799.

Scheme 4



analogue of the cyclized intermediate has recently been structurally characterized.[39] As for **1**, chelation could accelerate the isomerization of **2Z** through both enthalpic and entropic effects.

Another factor might also be important in lowering the barriers for the electrocyclic closure steps in the isomerizations of **1** and **2Z**. Due to conjugation, the frontier π orbitals increase in energy and the π^* orbitals decrease in energy (i.e., come closer to the "frontier") on going from **3** to **2** to **1**. These significant differences in orbital energies could have strong effects on the rates of the electrocyclic processes.

Without the extra conjugation and the possibility of chelation, the electrocyclic closure for **3** is less favored. A minimum barrier for **3Z′** to **3E′**, calculated similarly as above for **1E′**,[40] is 188 kJ/mol, a value that seems inconsistent with the observed isomerization of **3Z** to **3E**. Assuming the same $\Delta S^{\ddagger}$ as for **1Z**, the experimental $\Delta H^{\ddagger}$ for **3Z** would be 122 kJ/mol, and a barrier of 130 kJ/mol would be high enough to make the isomerization imperceptible. The high calculated minimum barrier is suggestive that mechanism 6 is not viable in this case. However, we choose not to rule out the mechanism on this basis alone, since the calculation is uncertain. For example, 12 diastereomers of the ruthenacyclobutene **9′** are possible (presuming octahedral coordination), and one of these might have a lower energy than the one we calculated.

Mechanistic Conclusions. On the basis of both experimental observations and theoretical computations, we have arrived at a set of mechanisms, outlined in Table 3, that we believe are responsible for isomerization of the complexes. Of the eight possibilities in Chart 1, three have been proposed to be important under different circumstances. Mechanism 6 is believed to cause isomerization in at least two and possibly all three *Z*−*E* pairs. We have not ruled out the possibility that mechanism 1 might explain the isomerization of **1**, though we do not favor this pathway based upon our calculations. In the presence of alkene or PCy_3, both

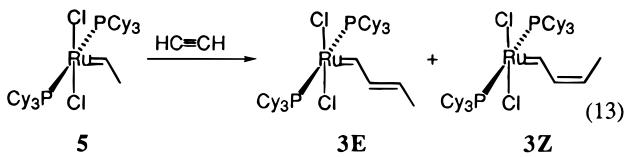
Table 3. Proposed Mechanisms for Isomerization[a]

	1Z ⇌ 1E	2Z ⇌ 2E	3Z ⇌ 3E
no additives	6	6[b]	4[c] or 6
with PCy_3	6	8	4[c] or 6
with alkene[d]		6	4

[a] Numbers refer to mechanisms in Chart 1. [b] Some isomerization also occurs through **1** (eqs 10 and 11) under these conditions. [c] The alkene necessary for mechanism 4 could come from decomposition of **6** or **3** (see text). [d] (*Z*)-1,3,5-Hexatriene for **2Z**, (*Z*)-1,3-pentadiene for **3Z**. Hextriene could not be added to **1** without conversion to **2E**.

ligands that should inhibit mechanism 6, two other pathways are accelerated. For **3Z**, the presence of (*Z*)-1,3-pentadiene promotes isomerization through metathesis (mechanism 4). In the absence of added alkene, the slow decomposition of **6** and **3** might provide low concentrations of alkene products that can similarly allow isomerization through metathesis. For **2Z**, the presence of PCy_3 allows isomerization and other reactions through nucleophilic attack at the carbon end of the conjugated chain (mechanism 8). Also apparently important for **2Z** in the absence of additives is the metathesis route through **1** (eqs 10 and 11).

Kinetic Stereoselectivity. To strengthen the link between this work and alkene−alkyne metathesis, we have prepared the kinetic mixture of **3E** and **3Z** through reaction of **5** and acetylene (eq 13). At 14% conversion (after 35 min with 1 equiv of acetylene), a 1.3:1 ratio of **3E** and **3Z** was observed, which is far from the equilibrium ratio of 16:1. Since the isomerization proceeds on the time scale of days under these conditions, the 1.3:1 ratio may be taken as the kinetic ratio for opening of ruthenacyclobutene **9**.



(13)

General Conclusions

Isomerization at the β,γ bond in three ruthenium vinylalkylidene complexes was observed, though the rates and mechanisms of the isomerizations were not uniform. We believe that mechanism 6, involving a reversible electrocyclic closure to a ruthenacyclobutene, is an important pathway for at least **1** and **2**. The loss of phosphine becomes rate-limiting in the case of **1** due to an especially favorable electrocyclic closure, aided by

(39) Hughes, R. P.; Trujillo, H. A.; Egan, J. W.; Rheingold, A. L. *Organometallics* **1999**, *18*, 2766−2772.

(40) This value is the energy difference of **9′** and **8E′** (116 kJ/mol) plus the PH_3 binding energy determined for **1E′** (the energy difference between **13E′** + PH_3 and **1E′** = 72 kJ/mol). Thus, the assumption is made that the PH_3 binding energies are the same for **1′** and **3′**. This calculation also assumes that the energies of **8E′** and **8Z′** are equal, i.e., that the equilibrium constant of 16 is due to differences in $\Delta S^{\ddagger}$, as determined for **1**. Alternatively, if we assume that the equilibrium constant is due to differences in $\Delta H^{\ddagger}$, the minimum barrier would be lower by only 7 kJ/mol.

chelation. In **2Z**, nucleophilic mechanism 8 becomes dominant in the presence of added PCy_3, and in **3Z**, metathesis mechanism 4 dominates in the presence of (*Z*)-1,3-pentadiene.

Though multiple mechanisms have been implicated in the *Z*−*E* isomerization at the β,γ bond of vinylalkylidene complexes, the impact of these isomerizations on the stereoselectivity of 1,3-diene syntheses by alkene−alkyne metathesis is expected to be minimal for most reactions. In the absence of chelating groups the isomerization was observed on the hours time scale, while the lifetime of the vinylalkylidene intermediates in the catalytic reaction is presumably much shorter. The stereoselectivity of such 1,3-diene syntheses is likely to be determined by kinetic control in the ring-opening reaction of the ruthenacyclobutene intermediates. Our results suggest that any isomerization that does occur would lead to an improvement in stereoselectivity for the *E* isomer and that this might be exploited in stoichiometric intermolecular alkene−alkyne couplings in which the vinylalkylidene is given sufficient time for isomerization before introduction of the alkene reactant.

We are continuing to study these complexes, particularly with respect to the nature of the conjugation and the interaction between the ruthenium centers in **1**. Due to the isomerizations reported herein, we are also studying ring-constrained complexes that are unable to isomerize.

Experimental Section

General Considerations. All reactions were performed under nitrogen using standard Schlenk techniques or with a nitrogen-filled drybox (MBraun MB 150M). Pentane and CH_2Cl_2 were distilled under nitrogen from calcium hydride. CD_2Cl_2 (Cambridge Isotopes) was vacuum transferred from calcium hydride after standing for 2 days. Some experiments were done with unpurified CD_2Cl_2, but later control experiments with purified solvent established that the isomerization rates of **1** and **3Z** were not affected by solvent purity, even though a strong effect was observed when **2Z** was prepared in unpurified CD_2Cl_2. All reagents were obtained from common commercial sources unless otherwise stated and were used as received. Commercial 1,3,5-hexatriene (Aldrich) was verified by ^{1}H NMR to be a mixture of *E* and *Z* isomers. From this mixture, the pure isomers were prepared according to literature procedures[41] and stored in the drybox freezer. The isomers of 1,3-pentadiene ((*E*)- and (*Z*)-piperylene) were used as received from Aldrich. Complex **4** was purchased from Strem Chemicals. Complex **5** was prepared from **4** by using the literature method.[4] (We found (*Z*)-2-butene as the olefin reactant much preferable to propene, which in our hands gave significant amounts of the methylidene complex $(Cy_3P)_2Cl_2Ru{=}CH_2$ as an impurity.) ^{1}H and ^{13}C NMR spectra were recorded in CD_2Cl_2 on a 300 MHz Bruker DPX-300 spectrometer, unless otherwise indicated. ^{31}P NMR spectra were recorded in CD_2Cl_2 on a Bruker DRX-500 spectrometer. All chemical shifts were referenced to TMS by using known shifts of residual proton (5.32 ppm) or carbon (54.0 ppm) signals in CD_2Cl_2 or to external 85% phosphoric acid (^{31}P NMR). NMR simulation of the AA′XX′ patterns for **1Z** and **1E** were done by using gNMR version 3.6.5 (Cherwell Scientific Publishing) and WinDNMR 1.5 (Journal of Chemical Education: Software). Mass spectra were obtained from the MS facilities at University of Illinois, Urbana−Champaign. Elemental analyses were performed by E & R Microanalysis Co., Parsippany, NJ. Attempted photochemical isomerizations of **1** were done using either a 150 W spot lamp (visible) or a 450 W Hanovia Hg arc lamp (UV). Pyrex filters were used with both lamps.

$[(Cy_3P)_2Cl_2Ru]_2(\mu$-CHCH=CHCH) (1). To a solution of $(Cy_3P)_2Cl_2Ru{=}CHPh$ (**4**, 189 mg, 230 μmol) in CH_2Cl_2 (3 mL) was added 12.5 μL (115 μmol) of (*E*)-1,3,5-hexatriene. The mixture was stirred for 3 min at room temperature, and the solvent was removed under vacuum. The residue was repeatedly washed with pentane (1.5 mL portions) until the washings became light colored. The residue was then dried under vacuum for several hours. An inseparable 10:1 mixture of **1E** and **1Z** was obtained as a brown-orange microcrystalline solid. Yield: 86.3 mg (50%). Compound **1** is indefinitely stable in the solid state under nitrogen at room temperature. It is reasonably soluble in methylene chloride and chloroform and partially soluble in pentane. It is stable in CD_2Cl_2 for well over 24 h. **1E**: ^{1}H NMR: δ 19.86 (AA′XX′, $J_{\alpha\beta}$ = 10.7 Hz, $J_{\beta\beta'}$ = 15.0 Hz, $J_{\alpha\beta'}$ = −0.6 Hz, 2H, H_α), 7.96 (AA′XX′, identical to 19.86 pattern, 2H, H_β), 2.58, 1.86, 1.82, 1.72, 1.50, 1.25 (all m, Cy, 132H). ^{13}C{^{1}H} NMR: δ 291.6 (m, C_α), 136.9 (s, C_β), 32.4 (pseudo-t, J_{app} = 9.1 Hz, C_1 of Cy), 30.0 (s, C_3 of Cy), 28.4 (pseudo-t, J_{app} = 4.8 Hz, C_2 of Cy), 27.1 (s, C_4 of Cy). ^{31}P{^{1}H} NMR: δ 35.5. **1Z**: 21.35 (AA′XX′, $J_{\alpha\beta}$ = 11.3 Hz, $J_{\beta\beta'}$ = 11.2 Hz, $J_{\alpha\beta'}$ = −0.6 Hz, 2H, H_α), 7.87 (AA′XX′, identical to 21.35 pattern, slightly obscured, 2H, H_β), Cy signals not distinguishable from those of **1E**. ^{13}C NMR (obtained by HMQC and HMBC experiments on a Bruker 600 MHz spectrometer): δ 288.2 (C_α), 127.0 (C_β), Cy signals not distinguishable from those of **1E**. ^{31}P{^{1}H} NMR: δ 37.2. **1E** and **1Z**: MS(FAB): 1238 ($M^+ - PCy_3$), 1203 ($M^+ - PCy_3 - Cl$), 923 ($M^+ - 2PCy_3 - Cl$), 784 ($M^+ - RuCl_2(PCy_3)_2$) (correct isotope patterns observed for each fragment). Anal. Calcd for $C_{76}H_{136}Cl_4P_4Ru_2$: C, 60.14; H, 9.03. Found: C, 60.08; H, 9.01.

(*E*)-$(Cy_3P)_2Cl_2Ru{=}CHCH{=}CHCH{=}CH_2$ (2E). To a solution of **4** (57.6 mg, 70.0 μmol) in CH_2Cl_2 (2 mL) was added 15 μL (139 μmol) of (*E*)-1,3,5-hexatriene. The mixture was stirred for 2 min at room temperature, and the solvent and excess triene were removed under vacuum. The residue was left under vacuum for several hours. Compound **2E** was obtained quantitatively as a brown microcrystalline solid, though solution samples were contaminated with a few percent of **1**. Compound **2E** is stable indefinitely in the solid state under nitrogen. It shows significant decomposition in CD_2Cl_2 over several hours. ^{1}H NMR: δ 19.08 (d, $J_{\alpha\beta}$ = 10.8, 1H, H_α), 7.84 (dd, $J_{\alpha\beta}$ = 10.8 Hz, $J_{\beta\gamma}$ = 15.0 Hz, 1H, H_β), 7.05 (dd, $J_{\beta\gamma}$ = 15.0 Hz, $J_{\gamma\delta}$ = 10.5 Hz, 1H, H_γ), 6.34 (dt, $J_{\delta\epsilon}$ = 16.8 Hz, $J_{\gamma\delta} \approx J_{\delta\epsilon'} \approx$ 10.5 Hz, 1H, H_δ), 6.10 (d, $J_{\delta\epsilon}$ = 16.8 Hz, 1H, H_ϵ), 5.98 (d, $J_{\delta\epsilon'}$ = 10.5 Hz, 1H, $H_{\epsilon'}$), 2.57, 1.86, 1.81, 1.70, 1.49, 1.24 (all m, 66 H, Cy). ^{13}C{^{1}H} NMR: δ 290.3 (m, C_α), 149.8 (s, C_β), 139.8 (s), 131.6 (s), 122.6 (s), 32.5 (pseudo-t, J_{app} = 9.2 Hz, C_1 of Cy), 30.0 (s, C_3 of Cy), 28.4 (pseudo-t, J_{app} = 5.1 Hz, C_2 of Cy), 27.1 (s, C_4 of Cy). (The weak C_α signal was measured by using an HMQC experiment on a Bruker 600 MHz spectrometer.) ^{31}P-{^{1}H} NMR: δ 37.5. Anal. Calcd for $C_{41}H_{72}Cl_2P_2Ru$: C, 61.64; H, 9.08. Found: C, 61.70; H, 9.10.

(*Z*)-$(Cy_3P)_2Cl_2Ru{=}CHCH{=}CHCH{=}CH_2$ (2Z). To a solution of **4** (42 mg, 51 μmol) in CH_2Cl_2 (0.6 mL) was added 16 μL of *cis*-hexatriene (150 μmol) at room temperature. The mixture was stirred for 5 min at room temperature, and the solvent and excess triene were removed under vacuum. The residue was left under vacuum for several hours. Compound **2Z** was obtained as a mixture with **2E** (35%). Samples of **2Z** prepared in unpurified CD_2Cl_2 were significantly less stable both with respect to isomerization and decomposition. **2Z:** ^{1}H NMR: δ 20.00 (d, $J_{\alpha\beta}$ = 12.0 Hz, 1H, H_α), 7.64 (dd, $J_{\alpha\beta}$ = 12.0 Hz, $J_{\beta\gamma}$ =11.5 Hz, 1H, H_β), 7.23 (dt, $J_{\delta\epsilon}$ = 17.0 Hz, $J_{\gamma\delta} \approx J_{\delta\epsilon'} \approx$ 11.5 Hz, 1H, H_δ), 6.68 (t, $J_{\beta\gamma} \approx J_{\gamma\delta} \approx$ 11.5 Hz, 1H, H_γ), 5.87 (d, $J_{\delta\epsilon}$ = 17.0 Hz, 1H, H_ϵ), 5.82 (d, $J_{\delta\epsilon'}$ = 11.5 Hz, 1H, $H_{\epsilon'}$) 2.56, 1.85, 1.83, 1.70, 1.50, 1.24 (all m, 66 H, Cy). ^{13}C{^{1}H} NMR (C_6D_6, ref to 128.4): δ 285.8 (m, C_α, low S/N), 145.7 (s, C_β),

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135.7 (s), 120.4 (s), 119.7 (s), 32.7 (br s, C_1 of Cy), 30.2 (br s, C_3 of Cy), 28.3 (br s, C_2 of Cy), 27.1 (br s, C_4 of Cy). (The Cy peaks were not resolved from those of **2E**, which was formed during the acquisition.) $^{31}P\{^1H\}$ NMR: δ 37.9.

(*E*)-$(Cy_3P)_2Cl_2Ru$=CHCH=$CHCH_3$ (3E). To a solution of **5** (45 mg, 59 μmol) in CH_2Cl_2 (2.5 mL) was added 25 μL of (*E*)-1,3-pentadiene (253 μmol) at room temperature. The mixture was stirred for 7 min, and the solvent and excess alkene were removed under vacuum. The residue was left under vacuum for several hours. Compound **3E** was obtained as a brown microcrystalline solid in quantitative yield. ^1H NMR: δ 18.73 (d, $J_{\alpha\beta}$ = 10.8 Hz, 1H, H_α), 8.00 (ddq, $J_{\beta\gamma}$ = 15.0 Hz, $J_{\alpha\beta}$=10.8 Hz, $J_{\beta\delta}$ =1.5 Hz, 1H, H_β), 6.64 (dq, $J_{\beta\gamma}$ = 15.0 Hz, $J_{\gamma\delta}$ = 7.0 Hz, 1H, H_γ), 2.58, 1.86, 1.81, 1.70, 1.49, 1.24 (all m, 69 H, H_δ and Cy). $^{13}C\{^1H\}$ NMR: δ 294.5 (pseudo-t, J_{app}= 6.9 Hz C_α), 152.3 (s, C_β), 133.1 (s, C_γ), 32.5 (pseudo-t, J_{app} = 9.3 Hz, C_1 of Cy), 30.0 (s, C_3 of Cy), 28.4 (pseudo-t, J_{app} = 5.2 Hz, C_2 of Cy), 27.1 (s, C_4 of Cy), 19.1 (s, C_δ). $^{31}P\{^1H\}$ NMR: δ 37.1. Anal. Calcd for $C_{40}H_{72}Cl_2P_2Ru$: C, 61.05; H, 9.22. Found: C, 60.85; H, 9.02.

(*Z*)-$(Cy_3P)_2Cl_2Ru$=CHCH=$CHCH_3$ (3Z). To a solution of **5** (32 mg, 42 μmol) in CH_2Cl_2 (1.5 mL) was added 80 μL (809 μmol) of (*Z*)-1,3-pentadiene. The mixture was stirred for 5 min, and the solvent and excess alkene were removed under vacuum. The residue was left under vacuum for several hours. The resulting **3Z** obtained was contaminated with 17% **3E** and 12% $(Cy_3P)_2Cl_2Ru$=CHCH=CH_2. ^1H NMR: δ 19.70 (d, $J_{\alpha\beta}$ = 11.4 Hz, 1H, H_α), 7.83 (ddq, $J_{\alpha\beta} = J_{\beta\gamma}$ = 11.4 Hz, $J_{\beta\delta}$ = 1.8 Hz, 1H, H_β), 6.29 (dq, $J_{\beta\gamma}$ = 11.4 Hz, $J_{\gamma\delta}$ = 7.5 Hz, 1H, H_γ), 2.56, 1.86, 1.78, 1.70, 1.49, 1.26 (all m, 69 H, H_δ and Cy). $^{13}C\{^1H\}$ NMR: δ 289.2 (pseudo-t, J_{app} = 6.6 Hz C_α), 148.6 (s, C_β), 121.6 (s, C_γ), 32.4 (pseudo-t, J_{app} = 9.2 Hz, C_1 of Cy), 30.1 (s, C_3 of Cy), 28.4 (pseudo-t, J_{app} = 5.2 Hz, C_2 of Cy), 27.2 (s, C_4 of Cy), 15.6 (s, C_δ). $^{31}P\{^1H\}$ NMR: δ 37.6.

Dynamic NMR Studies on 1. ^1H NMR spectra of **1** in toluene-d_8 were recorded from 55 to 135 °C, and full line-shape analyses were executed on the C_4H_4 portions of the resulting spectra. The compound was found to decompose in this temperature region, but samples that contained added PCy_3 exhibited significantly greater stability. Therefore, spectra at the highest temperatures could only be obtained on PCy_3-containing samples. Samples without added PCy_3 were studied up to 90 °C, and suitable spectra were obtained up to 105 °C with 1 equiv of PCy_3 (0.005 M), up to 120 °C with 10 equiv of PCy_3 (0.05 M), and up to 135 °C with 150 equiv of PCy_3 (0.8 M). A number of spectra were obtained at common temperatures for the different PCy_3 concentrations, and in all cases the C_4H_4 line shapes were found to be identical. Signals for H_β were overlapped at all temperatures in toluene-d_8, and no changes were observed for this signal, appearing at 8.30 ppm. The H_α signals, appearing at 20.45 ppm for **1E** and 21.99 ppm for **1Z**, showed coalescence at about 100 °C, sharpening to a single peak at about 20.55 ppm above this temperature.

For purposes of determining the temperature dependence of the equilibrium constant, spectra at 25, 55, and 60 °C were usable. No significant change was detected in this range, with $K = 8.7 \pm 0.3$ (favoring **1E**). At 70 °C, K was found to be 9.4, a marginally different value with increased uncertainty due to exchange broadening of the **1Z** signal. Line shapes were not fit as well, especially near coalescence, when K was extrapolated as a temperature-dependent variable. Therefore, K was treated as temperature-independent, with the value of 8.7. Also from the lower temperature spectra, we determined that the chemical shifts were all temperature-independent. Coupling constants were found to be identical to those obtained from CD_2Cl_2 samples. Line shapes were therefore fit at all temperatures with the same chemical shifts and coupling constants. The line width used in the fitting for each temperature was determined by the width of the solvent peak at 7.09 ppm. Excellent fits to all line shapes were obtained with the simulated exchange spectra, providing rate constants for the exchange at each temperature (Table 1). Error bars represent the range of rate constants that provided reasonable line-shape fits. The Eyring plot for **1Z** to **1E** with all of the data points revealed that the outer two points lie furthest from the least-squares line (correlation coeff 0.990), and since the outer points are known to be the least accurate in dynamic NMR studies,[42] they were not used. The abridged Eyring plot, shown in Figure 2, gives a correlation coeff of 0.995 and activation parameters of $\Delta H^\ddagger = 100 \pm 5$ kJ/mol and $\Delta S^\ddagger = 67 \pm 3$ J/(mol K) (showing standard error from the least-squares analysis). A similar plot for the **1E** to **1Z** transformation gives an identical correlation and $\Delta H^\ddagger$ (a consequence of temperature-independent K), with $\Delta S^\ddagger = 49 \pm 3$ J/(mol K).

Spectra were also obtained in CD_2Cl_2 up to 70 °C. In these spectra exchange broadening was observed for both the H_α and H_β signals, and rate constants were obtained through line-shape analysis. The rate constants were essentially identical to those from the toluene-d_8 spectra. The equilibrium constant was found to be temperature-insensitive in the range between −70 and 40 °C ($K = 11 \pm 1$), though again a marginally significant though reproducible change was observed at 70 °C ($K = 14.5 \pm 1$).

Computational Methods. Geometries for **1E′**, **1E″**, and **11E′** were optimized using Gaussian 98.[43] The energy for **13E′** was from a single-point calculation on a structure built from the optimized **1E′** and **11E′** molecules. These calculations were carried out using the B3LYP hybrid functional[44] as implemented in the Gaussian program. The 6-31G* basis set was used for C, H, P, and Cl atoms, and the Stuttgart relativistic small-core effective core potential (RSC-ECP, 28 core electrons)[45] with its associated basis set[46] was used for Ru. Geometries for **8E′**, **9′**, **12′**, and **14E′** were optimized using Jaguar[47] using the 6-31G* basis set for C, H, P, and Cl atoms, and the LANL2DZ ECP for Ru. Single-point calculations were then carried out on the optimized **12′** and **14E′** structures using Gaussian 98 and the Stuttgart ECP. The use of two different ECPs was not expected to be significant because only energy differences are of interest, and these were only calculated using values that were determined using the same ECP. Natural bond orbital analysis was done by the method of

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Weinhold and co-workers,[48] and the natural bond orders of **1E′** and hexatriene were computed by the method of Reed and Schleyer.[49]

Molecular mechanics calculations were performed by using the MM2 parameters in CAChe, version 4.0.2 or 4.11, Oxford Molecular Ltd. ZINDO calculations were performed with CAChe, version 4.11. PM3(tm) calculations were performed by using Spartan, version 5.1.1, Wavefunction, Inc.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, angles, dihedral angles, and total energies for the DF-optimized geometries of **1E′**, **1E″**, **8E′**, **9′**, **11E′**, **12′**, and **14E′**; ^{1}H NMR spectrum of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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