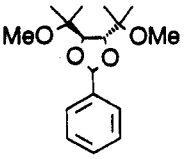
preferential abstraction of the *pro-R* proton.



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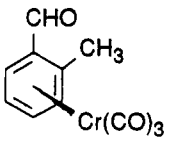

(-)-8

An understanding of the mechanistic reasoning for the observed selectivities is complicated by several facts. First, 2 equiv of base are required for complete arene deprotonation. Also, there is evidently both a kinetic and a thermodynamic diastereoselectivity of deprotonation, and they are in some cases quite dissimilar. Furthermore, the results vary greatly with the choice of base. Finally, it is well established that alkyl- and aryllithiums are rarely monomeric in solution.[12] Nevertheless, it is clear, in the most successful case, that the high diastereoselectivity observed is thermodynamic in origin. We envision that there is a competition between diastereomeric aryllithium species A and B (Figure 2), with the former having a cis-fused 5,5-ring system versus the trans-fused 5,5-system of the latter. Since a 6.0 kcal relative stabilization of the cis over the trans 5,5-fused ring system is known for the all-carbon framework,[13] A would be the preferred aryllithium. This corresponds to abstraction of the *pro-R* hydrogen, which is in agreement with experiment. We have included a second molecule of alkyllithium base, complexed to the remaining oxygen atoms of the auxiliary, in the aryllithium species. The reason for the necessity of this second equivalent is unknown at this time.

Acknowledgment. We are grateful for the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support.

Supplementary Material Available: Complete spectral details for compounds **2–8** (including experimental details) and crystallographic data for compound **3a** (including atomic coordinates, thermal parameters, bond distances, and bond angles) (12 pages). Ordering information is given on any current masthead page.

(12) For a list of references on alkyllithium aggregation, see: (a) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 6190. For aryllithium aggregation studies, see: (b) Harder, S.; Boersma, J.; Brandsma, L.; van Heterten, A.; Kanters, J. A.; Bauer, W.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1988**, *110*, 7802. (c) Setzer, W. N.; Schleyer, P.v.R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(13) Barrett, J. W.; Linstead, R. P. *J. Chem. Soc.* **1936**, 611.

Articles

Preparation and Isomerization of 1-Phenylseleno 1,3-Dienes

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The preparation of a series of 1-phenylseleno 1,3-dienes is described starting from enyne derivatives via a hydrozirconation/transfer sequence. Hydrozirconation of a series of conjugated enynes having the general formula HC≡CCR^1=CR^{2}R^3 (**3a**: R^1 = R^2 = R^3 = H; **3b**: R^1 = R^3 = H, R^2 = OMe; **3c**: R^1 = R^2 = H, R^3 = OMe; **3d**: R^1 = R^2 = -(CH$_2$)$_4$-, R^3 = H) leads to the formation of zirconium dienyls of the formula (η^5-C$_5$H$_5$)$_2$Zr(Cl)—CH=CHCR^1=CR^{2}R^3, **4a–d**, respectively; this reaction is both completely stereoselective and chemoselective. Use of the deuterium-substituted reagent (η^5-C$_5$H$_5$)$_2$Zr(D)Cl generates the corresponding isotopomers (η^5-C$_5$H$_5$)$_2$Zr(Cl)—CH=CDCR^1=CR^{2}R^3, **4a–d-d_1**. Addition of PhSeX (X = SePh, Cl, or *N*-phthalimido) to the zirconium dienyl derivatives **4a–d** at low temperature (-20 °C) and in the dark results in the formation of the 1-phenylseleno 1,3-dienes (PhSeCH=CHCR^1=CR^{2}R^3 (**5a**: R^1 = R^2 = R^3 = H; **5b**: R^1 = R^3 = H, R^2 = OMe; **5c**: R^1 = R^2 = H, R^3 = OMe; **5d**: R^1 = R^2 = -(CH$_2$)$_4$-, R^3 = H). This transfer of the dienyl unit from zirconium to selenium proceeds with complete stereoselectivity and with retention of configuration at the 1-position as long as light is excluded and the reaction is carried out at low temperatures. In the presence of room light (fluorescent), mixtures of stereoisomers are obtained for the seleno dienes **5a–c**; no apparent isomerization is observed for **5d**; similar results are obtained upon thermolysis (80 °C for 24–48 h). The mechanism of this isomerization process was determined to be intermolecular on the basis of crossover experiments; in addition, the use of radical traps established that the process was a radical chain mechanism, probably via addition of PhSe$^\bullet$ to the seleno diene followed by single-bond rotation.

Introduction

The synthesis of dienes for use in the Diels–Alder reaction[1,2] is still an important challenge in organic synthetic chemistry.[3,4] One particularly attractive approach has been the incorporation of heteroatom substituents[5] that can both activate the diene, thereby extending the range of workable dienophiles, and also provide a focal point for

† E. W. R. Steacie Fellow, 1990–92.

(1) Wolliveber, H. *Diels–Alder Reaction*; Georg Thieme Verlag: Stuttgart, 1972.
(2) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876–889.
(3) March, J. *Advanced Organic Chemistry*; 2nd ed.; McGraw-Hill: Toronto, 1977.

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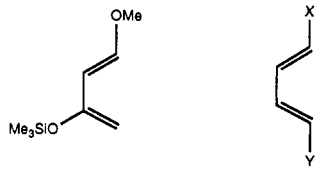
later synthetic elaboration. A good case in point is the Danishefsky diene,[6] **1**, in which is embodied both enhanced reactivity and latent functionality.



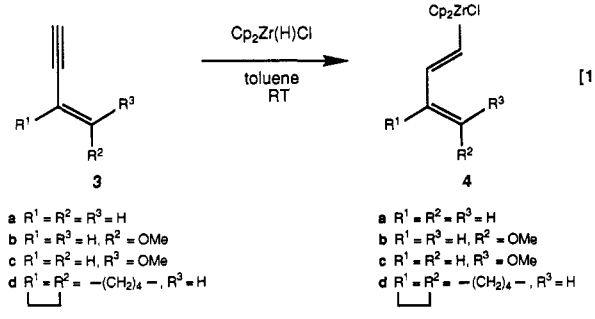
1 **2**

To take advantage of the endo stereoselectivity, the ortho- and para-directing regioselectivity, and the cis stereochemistry of the Diels–Alder cycloaddition, it is implicit that the diene be both stereochemically defined and configurationally stable under the reaction conditions. Thus, a general 1,4-disubstituted acyclic diene of the type **2**, having the *E,E* stereochemistry and an s-cis planar conformation, is most able to overlap in the preferred endo transition state; other stereoisomers of **2**, such as the *E,Z*, the *Z,E*, and the *Z,Z* would encounter steric repulsion either in attaining the necessary s-cis conformation or in the formation of the endo transition state. More importantly, a mixture of these diene stereoisomers could generate a mixture of products by virtue of the stereospecifiity inherent in the Diels–Alder process.

A previous communication[7] from our laboratory outlined the synthesis of 1-phenylseleno 1,3-dienes via transmetalation from zirconium and their stereochemical lability under photochemical and thermal duress. In this paper, we give full details of the preparation of these new selenium-substituted dienes and include our studies on the mechanism of the isomerization process. A future paper will detail the Diels–Alder reactivity of these dienes.[8]

Results and Discussion

Synthesis. Preparation of Dienyl Zirconium Reagents. As previously communicated,[9] the synthesis of the zirconium dienyl complexes **4a–d** proceeds via the chemoselective and regioselective hydrozirconation of a variety of readily available conjugated enyne substrate molecules **3a–d** as shown in eq 1. These particular sub-



3

a $R^1 = R^2 = R^3 = H$
b $R^1 = R^3 = H$, $R^2 = OMe$
c $R^1 = R^2 = H$, $R^3 = OMe$
d $R^1 = R^2 = -(CH_2)_4-$, $R^3 = H$

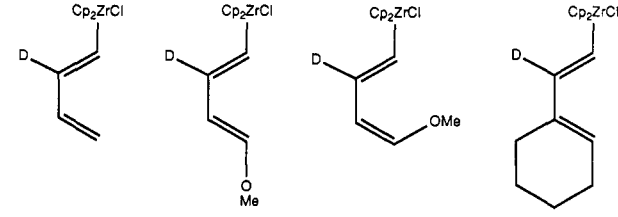
4

a $R^1 = R^2 = R^3 = H$
b $R^1 = R^3 = H$, $R^2 = OMe$
c $R^1 = R^2 = H$, $R^3 = OMe$
d $R^1 = R^2 = -(CH_2)_4-$, $R^3 = H$

[1]

strates were chosen both for ease of preparation and also for the functionality and substitution patterns that would be obtained in the resulting dienyl products **4**. Thus, the parent zirconium dienyl **4a** is available via hydrozirconation of commercially available vinylacetylene (**3a**), and the 4-methoxy-substituted zirconium dienyls **4b** and **4c** are obtained from the corresponding (*E*)- and (*Z*)-methoxy enynes **3b** and **3c**, respectively. It should be noted that the enyne **3b** was in fact prepared (see Experimental Section) as an inseparable 4:1 mixture of the *E* and *Z* stereoisomeric forms; however, it was observed empirically that the *E* isomer reacted more rapidly (as a mixture) with $(\eta^5\text{-}C_5H_5)_2Zr(H)Cl$ than the pure *Z* isomer (obtained commercially). Thus, by running the reaction with a 20% excess of the 4:1 mixture of **3b** and **3c**, virtually pure **4b** could be obtained from the crude isolated product. Small amounts (3–5%) of the zirconium dienyl **4c** produced could be easily removed by recrystallization. The zirconium dienyl **4d**, having a cyclohexenyl unit, is generated upon reaction of $(\eta^5\text{-}C_5H_5)_2Zr(H)Cl$ with the cyclohexenyl alkyne **3d**. Throughout this paper the dienes are all drawn in the s-cis conformation for the sake of convenience.

In all cases, the zirconium hydride addition is cis across the alkyne and no isomerization of the adjacent double bond is observed.[10] This was confirmed by reaction of $(\eta^5\text{-}C_5H_5)_2Zr(D)Cl$ with all of the above enynes to give **4a–d-d_1** with deuterium incorporation exclusively at the 2-position. This is consistent with a kinetic preference



d_1-**4a** d_1-**4b** d_1-**4c** d_1-**4d**

for the hydride (deuteride) addition across the alkyne unit rather than the alkene. Thus, the observed chemoselectivity in the hydrozirconation of enynes is a result of a kinetic preference for alkyne migratory insertion into the zirconium hydride bond rather than just a thermodynamic preference for the formation of an sp^2 Zr–C bond.[11,12] If alkene insertion was kinetically viable and reversible, one would observe some deuterium label incorporation[13] at the 3-position of the zirconium dienyls **4** and incomplete deuterium incorporation at the 2-position. Although other examples of chemoselective hydrometalation of 1-ene-3-ynes are known,[14,15] hydrozirconation of the unsubstituted 1-buten-3-yne (vinylacetylene, **3a**) is to our knowledge the most selective and highest yielding.

Dienyl Transfer from Zirconium to Selenium. The reaction of the (*E*)-1-bis(η^5-cyclopentadienyl)chlorozirconium 1,3-dienes **4** with any of a variety of electrophilic PhSeX reagents, where X = SePh, Cl or *N*-phthalimido, is almost instantaneous even at −20 °C and results in the formation of nearly quantitative yields of the 1-phenylseleno 1,3-dienes **5** as shown in eq 2.

The use of *N*-(phenylselenyl)phthalimide[16] (*N*-PSP) is preferred since the organozirconium byproduct, (η^5-

(4) Desimoni, G.; Tacconi, G.; Bario, A.; Pollini, G. P. *Natural Product Syntheses Through Pericyclic Reactions*; ACS Monograph No. 180; American Chemical Society: Washington, D.C., 1984; Chapter 5.
(5) Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753–786.
(6) Danishefsky, S.; Kitahara, T.; Yan, C.-F.; Morris, J. *J. Am. Chem. Soc.* **1979**, *101*, 6996–7000.
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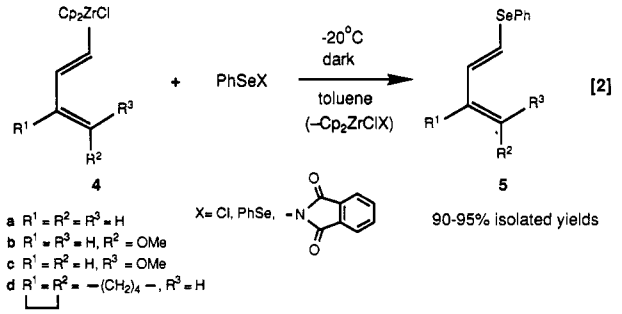
(8) Fryzuk, M. D.; Bates, G. S.; Stone, C. Manuscript in preparation.
(9) Fryzuk, M. D.; Bates, G. S.; Stone, C. *Tetrahedron Lett.* **1986**, *27*, 1537–1540.
(10) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340.
(11) Kozikowski, A. P.; Kitigawa, Y. *Tetrahedron. Lett.* **1982**, *23*, 2087.
(12) Zweifel, G.; Clark, G. M.; Polston, N. L. *J. Am. Chem. Soc.* **1970**, *93*, 3395.
(13) This analysis assumes that β-elimination is slower than C–C bond rotation.
(14) Juenge, E. C.; Hawkes, S. J.; Snider, T. E. *J. Organomet. Chem.* **1973**, *51*, 189–195.
(15) Connolly, J. W. *J. Organomet. Chem.* **1974**, *64*, 343–349.
(16) Nicolaou, K. C.; Claremon, D. A.; Barnett, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704.



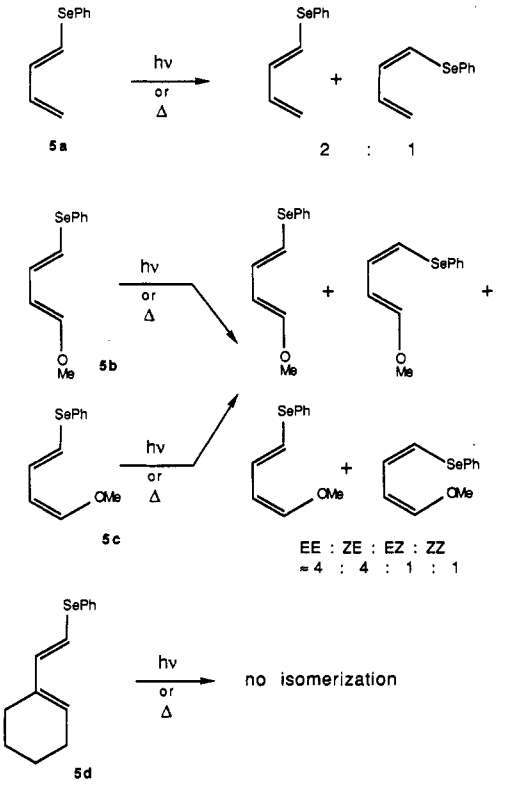
$C_5H_5)_2Zr(Npth)Cl$, is sparingly soluble in toluene and facilitates isolation of the product. Typically, workup involves filtering the resultant toluene suspension through a pad of basic alumina and removing the solvent to give the analytically pure phenylseleno dienes **5**. These dienes are oils and can be stored under argon for months in the dark at −20 °C.

When the reaction is carried out in the dark and at low temperature (−20 °C), the transfer of the dienyl unit from zirconium to selenium is completely stereoselective. Particularly diagnostic for this is the coupling constant between the geminal proton H_A to selenium and the vicinal proton H_B; typical values of $^3J_{H_AH_B}$ are in the range 16–18 Hz which is consistent[17] with an *E* configuration for the double bond containing the PhSe unit. The absence of light is critical for the isolation of stereochemically pure material. If the reaction is performed in ordinary room fluorescent light, complex mixtures are obtained for **5a–c**; the seleno diene **5d** is obtained apparently stereochemically pure regardless of the presence of light or if the reaction is performed at room temperature (however, vide infra). Analysis of these mixtures of stereoisomers by ^1H NMR spectroscopy was somewhat complicated due to the near overlap of resonances; however, homonuclear decoupling and NOEDIFF experiments indicated that the mixtures obtained are all the possible geometric isomers of the seleno dienes. This was confirmed by ^{77}Se NMR spectroscopy which indicated that similar but different selenium species were present. As shown in Scheme I, **5a** is obtained as a 2:1 mixture of *E* and *Z* stereoisomers, respectively. With the methoxy dienes **5b** and **5c**, the *identical* mixture of all four possible diene stereoisomers is observed; in this case, the ratio of geometric isomers is ≈4:1:4:1 for *E,E/E,Z/Z,E/Z,Z*, respectively. The ^{77}Se NMR spectrum of this mixture is shown in Figure 1. It should be noted that these isomeric mixtures are still >95% pure after exposure to room light as determined by ^1H NMR spectroscopy with the only impurity observed being trace (<5%) amounts of diphenyl diselenide, PhSeSePh.

That the isomerization occurs after transmetalation is readily established since the stereochemically pure seleno dienes can be isolated and separated from the organozirconium byproduct by carrying out the reaction at low temperature and in the dark as described above. ^1H NMR spectral analysis at −20 °C shows a single stereoisomer in each case. Raising the probe temperature by 10 °C increments to ambient and finally to 90 °C in the dark (in the probe of a superconducting magnet) causes no noticeable isomerization even after 1 h at 90 °C (vide infra).

(17) Silverstein, R. W.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*; 4th ed.; Wiley: New York, 1981.
(18) Toshimitsu, A.; Uemura, S.; Okana, M. *J. Chem. Soc., Chem. Commun.* **1982**, 965.
(19) Danishefsky, S.; Yan, C.-F.; Singh, R. K.; Gammill, R. B.; McCurry, P. M., Jr.; Fritsch, N.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 7001–7008.

Scheme I



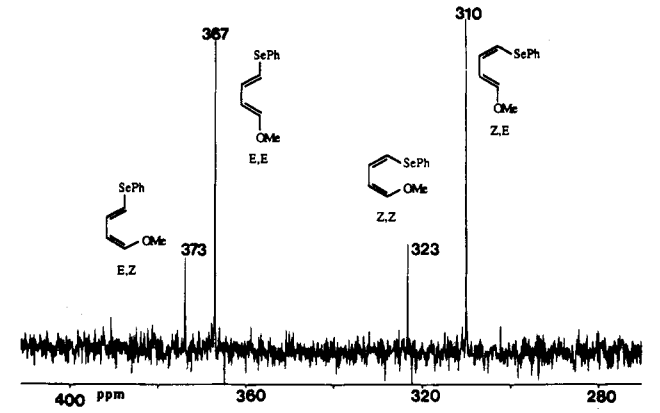


Figure 1. 76.3-MHz ^{77}Se NMR spectrum of the four stereoisomers of **5b** in $CDCl_3$.

However, if the sample is removed and exposed to room light (fluorescent), complete isomerization results after 1.5 h. In order to be consistent, a simple set-up was utilized: the NMR sample tube was placed approximately 3–4 cm away from a fluorescent light tube (Sylvania Cool White). The temperature of the sample remained relatively constant and did not rise above 29 °C under these conditions.

These observed isomeric mixtures are in fact equilibrium mixtures. This was established by enriching the initial isomerized mixture and further exposing the new mixture to room light. Thus, addition of pure (*E*)-1-(phenylseleno)-1,3-butadiene, (*E*)-**5a**, to the 2:1 isomeric mixture of (*E*)- and (*Z*)-**5a**, and subsequent exposure to room light reestablished the equilibrium 2:1 ratio. Similarly, the mixture of all four possible isomers of **5b** or **5c** could be disturbed by addition of either pure (*E,E*)-**5b** or (*E,Z*)-**5c**; within 1 h after exposure to room light, the original equilibrium mixture could be observed on the basis of ^1H NMR spectroscopy.

The isomerization could also be promoted thermally in the dark. However, this process is less efficient since

similar equilibrium ratios to that observed in the light-induced isomerization were only obtained after extended and somewhat irreproducible periods, i.e., 48 h at 80 °C. As previously mentioned, the isomerically pure cyclohexenyl diene **5d** was stereochemically stable to these thermal conditions.

There are only two other reports in the literature of selenium-containing dienes.[18,19] In both cases no mention was made of the stereochemical lability of these materials.

The facility of these isomerization reactions coupled with the fact that they are relatively clean provided the incentive to examine the origins of the isomerization, the reason for the apparent stereochemical stability of the cyclohexenyl diene **5d**, and the different efficiencies of the light-promoted vs. thermally induced reactions. These efforts are described in the sections that follow.

Mechanistic Studies

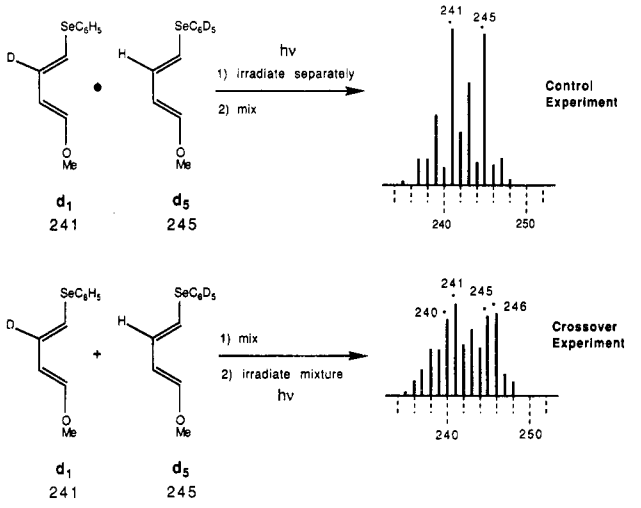
General Considerations. Because of the efficiency and reproducibility of the fluorescent light promoted isomerization, this process was studied in considerable detail. The less reproducible thermal process was also examined to provide a comparison for the light-induced reaction. Although the cyclohexenyl diene **5d** did not show any apparent isomerization under the conditions employed, it was still included in the mechanistic study for completeness.

There are two general classes of mechanism to be considered for this isomerization process: (i) intramolecular and (ii) intermolecular. As examples of each, one can speculate that intramolecular processes such as cyclobutene ring closures and subsequent nonspecific ring openings[20-22] or electron-pair delocalization followed by bond rotation are reasonable and would involve different types of experiments to distinguish these possibilities from intermolecular processes such as radical-chain-type mechanisms or heterolytic cleavage of the carbon–selenium bond. Therefore, to first differentiate between these two general mechanistic regimes, a crossover experiment was devised.

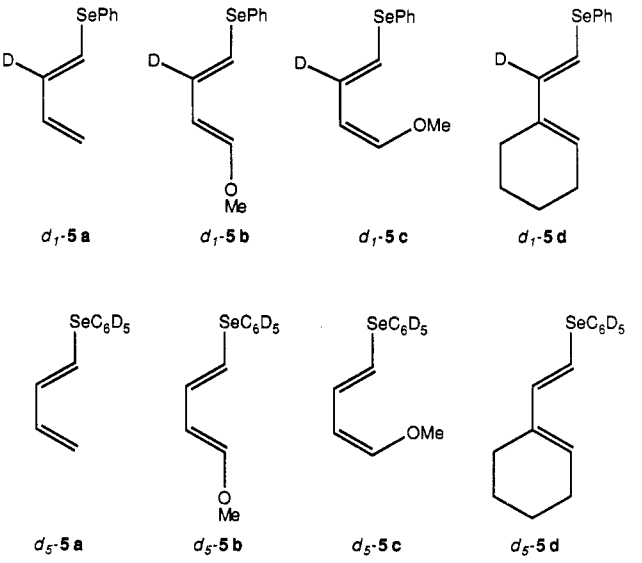
Crossover Experiments. Reasoning that if any intermolecular process was operative, it would most probably involve cleavage of the carbon–selenium bond of the diene, both the arylselenyl group and the diene unit were separately labeled. The diene portion was labeled by reaction of the enyne substrate with the deuterated zirconium reagent $(\eta^5\text{-}C_5H_5)_2Zr(D)Cl$ to generate the dienylzirconium-d_1 complexes, **4a–d-d_1**, as described above. The arylselenyl unit was labeled in two ways: C_6D_5SeCl was prepared using standard procedures and converted to the analogous phthalimide, *N*-PSP-d_5; also prepared was *N*-[(*p*-chlorophenyl)seleno]phthalimide, *N*-ClPSP. The former reagent, being different only by virtue of the presence of deuterium, does not change the electronic character of the resulting seleno diene; however, the latter reagent, possessing the electron-withdrawing *p*-chloro substituent, can potentially introduce changes in the product dienes. Fortunately, this was not observed. As is discussed below, the two labels provide for complementary techniques to detect and/or follow crossover.

Performing the dienyl transfer at −20 °C in the dark using defined permutations of the labeled and unlabeled zirconium dienyl complexes with the arylselenium reagents

Scheme II



provides for the preparation of the stereochemically pure materials having the isotopic structures as shown below.



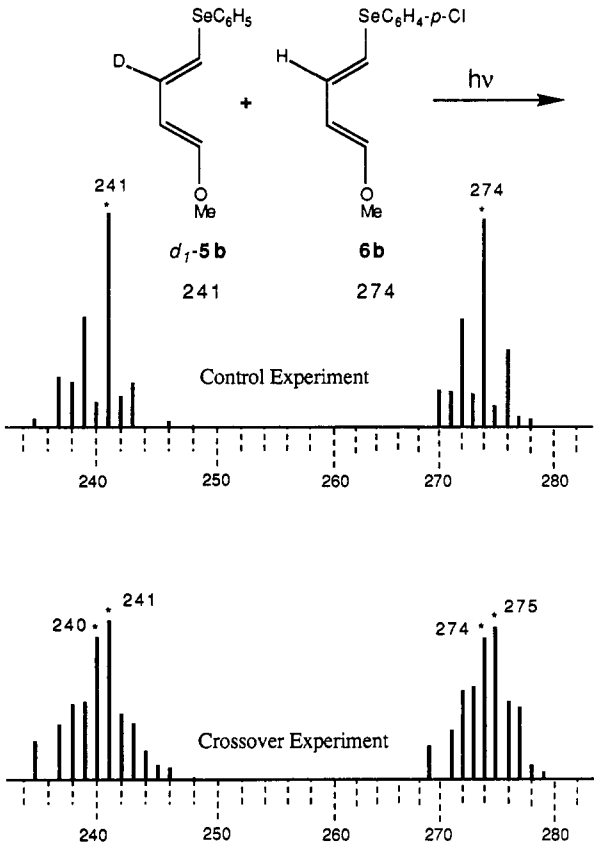
Thus, the procedure generates **5a–d-d_1** and **5a–d-d_5**, all having >98% theoretical deuterium incorporation as measured by mass spectroscopy and ^1H NMR spectroscopy.

The following experiments were performed for each of the seleno dienes. First, a control experiment was devised whereby **5a–d-d_1** and **5a–d-d_5** were *individually* isomerized by room light then immediately combined and examined by mass spectroscopy. This resulted in a molecular ion fragmentation pattern which was consistent with no crossover, thus establishing that the measurement itself is not inducing crossover. The second experiment involved premixing the stereochemically pure seleno dienes **5a–d-d_1** and **5a–d-d_5**, followed by exposure to room light and finally measurement of the mass spectrum. The results of these experiments are shown in Scheme II for the isomerization of the (*E,E*)-methoxy diene **5b**.

The control experiment exhibits a pattern with two major peaks at *m/e* 241 and 245 corresponding to **5b-d_1** and **-d_5**, respectively. The complexity of this pattern is due to the presence of the following selenium isotopes: ^{74}Se (0.9%), ^{76}Se (9.0%), ^{77}Se (7.6%), ^{78}Se (23.5%), ^{80}Se (49.8%), and ^{82}Se (9.2%). Upon photolysis of the mixture of **5b-d_1** and **-d_5**, a pattern is produced which has major peaks at *m/e* 240, 241, 245, and 246 corresponding to the

(20) Trost, B. M.; Godleski, S. A.; Ippen, J. *J. Org. Chem.* **1978**, *43*, 4559.
(21) Aben, R. W.; Scheeren, H. W. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3132.
(22) Leigh, W. J.; Zheng, K. *J. Am. Chem. Soc.* **1991**, *113*, 4019.

Scheme III

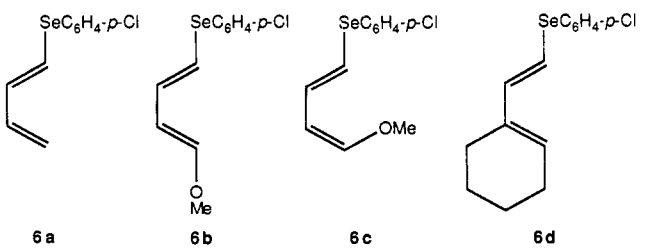


presence of all possible isotopomers **5b**-d_0, -d_1-, -d_5-, and -d_6.

Surprisingly, the cyclohexenyl diene **5d** also showed crossover despite the fact that by NMR spectroscopy no apparent isomerization was observed. Thus, after photolysis of a mixture of **5d**-d_1 and -d_5, the observed mass spectrum was significantly different from the control experiment consistent with the presence of **5d**-d_0, -d_1, -d_5, and -d_6.

Up to this point, the crossover experiments using the deuterated phenylseleno unit have only established that crossover occurs, but not that it is directly connected to the isomerization process. Because the mass spectral analysis was performed after photolysis, the possibility exists that isomerization and crossover occur, but are independent processes. It remained to be established therefore that as the isomerization proceeded, so did crossover, and that all the stereoisomers experience crossover to the same extent.

Performing the dienyl transfer from Zr to Se using the *N*-[(*p*-chlorophenyl)seleno]phthalimide reagent, *N*-ClPSP, using the identical conditions outlined in eq 2 generates the corresponding stereochemically pure (*p*-chlorophenyl)seleno dienes **6a–d** below. The introduction of the



(*p*-chlorophenyl)selenyl substituent causes shifts in the geminal proton H_A of the dienes **6a–d** as compared to the phenylseleno dienes **5a–d**. Therefore, crossover experiments were performed with the (*p*-chlorophenyl)seleno dienes **6a–d** and the monodeuterated phenylseleno dienes **5a–d**-d_1. One such experiment is shown in Scheme III below. The difference between mass spectral patterns of the control and the crossover experiments again indicates that crossover occurs under these conditions. In addition to mass spectrometry, proton NMR spectroscopy could also be used both to observe the occurrence of crossover and to follow the isomerization as a function of time. It was observed that there was a direct correlation between the amount of isomerization and crossover, and within the accuracy of the NMR experiment, all stereoisomers were observed to undergo complete crossover as well. It is therefore concluded that the process by which these arylselenyl 1,3-dienes isomerize is *intermolecular*.

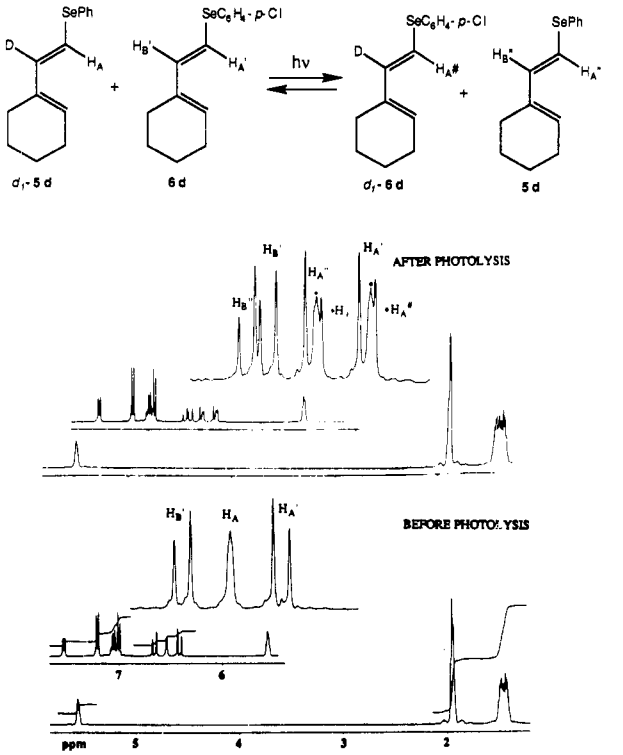
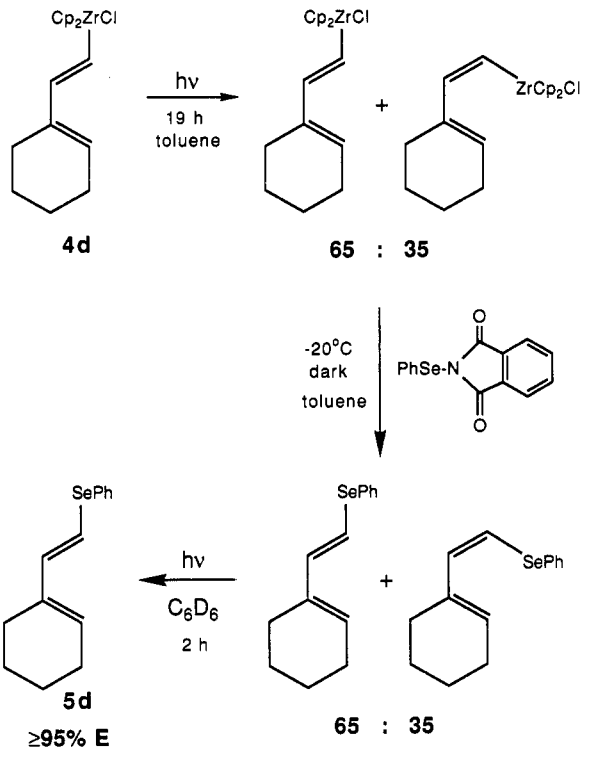


Figure 2. Crossover experiment between **5d**-d_1 and **6d** for the photolytic isomerization as monitored by ^{1}H NMR spectroscopy (400 MHz, C_6D_6). Before photolysis (bottom spectrum, inset) only the resonances due to **5d**-d_1 and **6d** are observed; however, after photolysis (top spectrum, inset) the crossover products **6d**-d_1 and **5d** as well as the starting derivatives are evident.

The same crossover experiments were repeated for the thermal isomerization process. Although less reproducible as already mentioned, the results suggest that isomerization is predominantly an intermolecular process as well since crossover was observed by both mass spectroscopy using the deuterium-labeled materials and by ^{1}H NMR spectroscopy using the (*p*-chlorophenyl)seleno group. It is noteworthy that the isomerization process could be virtually suppressed by performing the thermolysis in the dark under N_2 in flame-sealed NMR tubes; when samples were heated in capped NMR tubes under N_2, isomerization was observed. Other experiments to identify the mechanism of this isomerization are discussed later in this paper and outlined in the Experimental Section.

The (arylseleno)cyclohexenyl dienes **5d** and **6d** showed curious behavior. On the one hand, they apparently do not isomerize under either photochemical or thermal duress, yet, the evidence is clear that under these conditions there is crossover. Shown in Figure 2 is the ^{1}H NMR spectrum resulting from the light-promoted isomerization

Scheme IV



of the (*p*-chlorophenyl)seleno derivative **6d** in the presence of the monodeuterated phenylseleno diene **5d**-d_1 wherein crossover is not accompanied by isomerization; this is evident from the NMR spectrum "after photolysis" which shows resonances attributable to an equilibrium mixture of the starting dienes and the crossover products with each material having only the *E* stereochemistry.

To probe this anomalous result further, the starting zirconium cyclohexenyl diene complex **4d** was isomerized[23] by extended exposure to fluorescent light. In this way, a mixture of the zirconium dienyls (*E*)- and (*Z*)-**4d** was obtained in the ratio 65:35 as determined by ^{1}H NMR spectroscopy. Subsequent transfer to selenium employing *N*-PSP at −20 °C in the dark generated *stereospecifically* (*E*)- and (*Z*)-**5d** in the identical ratio of 65:35. When this mixture was then exposed to fluorescent light, the ratio changed to generate predominantly (*E*)-**5d** in ≥95% isomeric purity (Scheme IV). Indeed, upon examining previous spectra of **5d** after exposure to light or after heating do show the presence of the *Z* isomer in quantities which can be estimated as ≤5%.

It would appear therefore, that there is nothing anomalous with this particular arylselenyl 1,3-diene. Under thermal or photochemical conditions, an equilibrium ratio of the two isomers of **5d** (and **6d**) is obtained, but in this case, the *E* isomer is much more stable than the *Z* isomer, presumably because of steric repulsion between the arylselenyl substituent and the cyclohexenyl group.

This last experiment represents the first clear proof that the transfer of alkenyl groups from zirconium to other metals and metalloids is completely stereospecific. Previous work[24] could only conclude that the reaction was stereoselective because the alkenylzirconium reagents were obtained as one pure stereoisomer from the hydrozirconation of alkynes.

Isomerization Mechanism. Having established that crossover was occuring during isomerization, we examined a number of trapping experiments to distinguish between free-radical (homolytic Se–C cleavage) and ionic (heterolytic Se–C cleavage) pathways. The empirical observation that both the rate of isomerization and degree of crossover were unaffected by changing the solvent from C_6D_6 or C_7D_8 to CD_2Cl_2 or even $CDCl_3$ tends to rule against an ionic process. To probe the mechanism further, the effects of 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 1,4-cyclohexadiene on the isomerization process were examined. Both of these reagents can intercept free radicals or in some way affect mechanisms that involve free radicals. The reagent (4-oxo-2,2,6,6-tetramethylpiperidinyl)oxy radical (TEMPONE) was also examined, but because it is a free radical, greater than 5 mol % concentrations of this reagent caused significant loss of spectral resolution and thus analysis by ^{1}H NMR spectroscopy was inconclusive. The presence of up to 2 equiv of BHT was required to significantly affect the isomerization rate. With 1,4-cyclohexadiene, the results were more straightforward. Exposure of a 0.20–0.25 M solution of **5a** in neat 1,4-cyclohexadiene to fluorescent light for 2 h resulted in a 9:1 *E*/*Z* mixture of isomerized seleno dienes; this represents a significant retardation of the isomerization process since in the absence of 1,4-cyclohexadiene, a 2:1 *E*/*Z* mixture is formed. Similar results were obtained for **5b** and **5c**, although isomerization was retarded to a lesser extent than for **5a**. When the crossover experiment for the mixture of **5d**-d_1 and **5d**-d_5 was performed in neat 1,4-cyclohexadiene, there was no evidence of any crossover products as determined by mass spectroscopy.

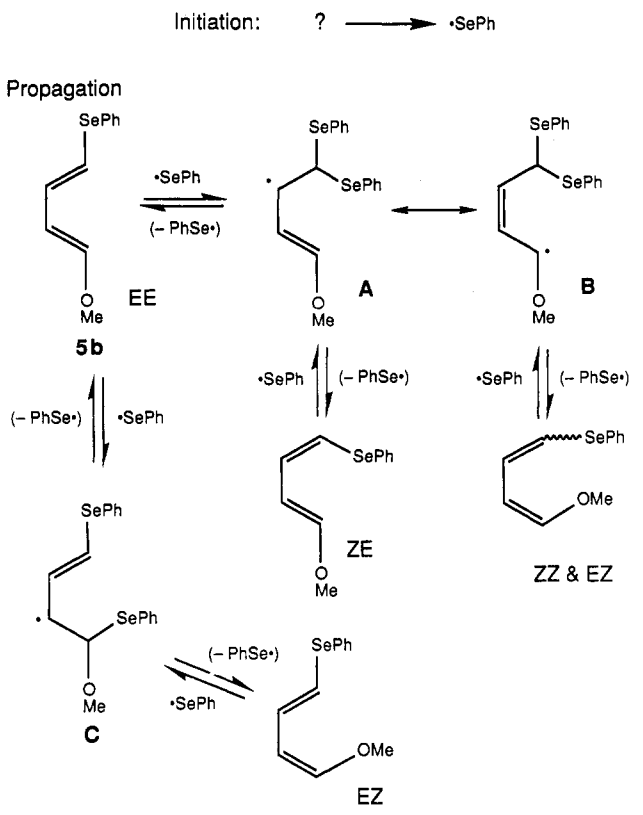
The thermal process was also examined in an effort to probe how this process is initiated. As mentioned above, little or no isomerization was observed upon heating in the dark in a sealed container whereas isomerization was observed if the materials were heated in capped NMR tubes for similar times. A separate experiment to probe the effect of oxygen was performed; isomerization of the dienes **5a** and **5b** in flame-sealed NMR tube containing dry O_2 gave identical results to that found for doing the thermolysis under N_2, that is little (for **5b**) or no (for **5a**) isomerization. In addition, acid-washed NMR tubes were found not to influence the amount of isomerization under these conditions. When the thermolysis was performed in the presence of azoisobutyronitrile (AIBN) isomerization rates were enhanced and equilibrium mixtures of stereoisomers of **5a** could be obtained after only 3 h of heating at 80 °C in the dark.

Both the photolytic and the thermal isomerization would appear to be free-radical processes; it should be reemphasized that after isomerization these dienes are still intact as judged by ^{1}H NMR spectroscopy. Assuming that both the thermal and the photochemical processes occur via a radical-chain-type mechanism, then clearly the fluorescent light produces some radical initiator extremely efficiently, more efficiently than the thermal process. An obvious question is how are these transformations initiated? As already mentioned, small amounts of PhSeSePh are observed after isomerization which is consistent with the presence of the phenylselenium radical, PhSe$^\bullet$. Indeed, one could suggest that slight amounts of decomposition would lead to production of PhSe$^\bullet$ which could then propagate isomerization; this is shown below in Scheme V for the isomerization of the *E*,*E* methoxy diene **5b**.

In Scheme V, the isomerization is propagated by addition of PhSe$^\bullet$ to either of the double bonds of the diene. For example, addition to the double bond containing the phenylseleno group generates the diselenoacetal radical A which can then lose PhSe$^\bullet$ to generate the *Z*,*E* isomer; in

(23) Fromberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 355.
(24) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521–3531.

Scheme V



addition, the radical A can also be represented by the resonance form B which allows isomerization at the distal double bond (distal to the phenylseleno moiety of the diene). Alternatively, the distal double bond can be isomerized by direct addition of PhSe• to generate C which, after bond rotation, can induce isomerization.

Although we have not explicitly indicated the source of the radical initiator PhSe•, that it could have arisen from trace amounts of PhSeSePh was tested by similar crossover experiments already mentioned by using $(C_6D_5)SeSe(C_6D_5)$. Thus, addition of $(C_6D_5)SeSe(C_6D_5)$ to a solution of seleno diene **5a** or **5b**, followed by photolysis or thermolysis (see Experimental Section), resulted in the formation of the crossover products $PhSeSe(C_6D_5)$ and **5a**-d_5 and **5b**-d_5, respectively, as determined by mass spectroscopy.

Photochemical isomerization of dienoic esters has been reported;[25] for example, UV irradiation of methyl (*E*,*E*)-2,4-hexadienoate at 254 nm, close to the λ_{max} of the ester, results in the formation of all four possible stereoisomers. However, in this case, charge delocalization and not bond cleavage is involved, presumably via an *intramolecular* one-bond, one-photon type isomerization mechanism. The phenylseleno dienes absorb strongly in the region 250–270 nm (ϵ 13 000–16 000); however, this is outside the range of 380–800 nm normally associated with a fluorescent light, although some stray UV emissions from these sources may occur.

Conclusions

Hydrozirconation of enynes leads to the chemoselective and regioselective formation of dienylzirconium complexes. Phenylseleno dienes can be prepared via dienyl transfer from zirconium using transmetalation-type procedures.[9,26] However, the conditions for the transfer reaction are quite stringent, requiring the absence of light and low temperatures to ensure that the products are formed stereoselectively as a single stereoisomer. In the presence of light (fluorescent room light), these phenylseleno dienes isomerize to generate an equilibrium mixture of stereoisomers; this also occurs thermally but long and variable reaction times are required even at 80 °C. The mechanism of the isomerization process has been shown to be a radical-chain-type process involving the formation of PhSe• radicals.

Experimental Section

General Procedures. All manipulations were performed under prepurified nitrogen in a glovebox, or in standard Schlenk-type glassware under argon (as supplied) or prepurified nitrogen. The term "reactor bomb" refers to a cylindrical, thick-walled vessel (50–75 mL in volume) equipped with a 5-mm Teflon needle valve and a ground-glass joint for attachment to a vacuum line. Larger reactor bombs (250–500 mL in volume) are equipped with 10-mm Teflon valves.

Infrared spectra (IR) were recorded as KBr pellets, on NaCl plates as Nujol mulls or liquid films, or as solutions in dichloromethane (CH_2Cl_2) and are reported in cm^{-1}. UV–vis spectra were obtained using spectroscopic-grade hexane and a 1-cm quartz cell; λ_{max} values are reported in nm. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained at 400 MHz as solutions in chloroform-d_1 ($CDCl_3$), dichloromethane-d_2 (CD_2Cl_2), benzene-d_6 (C_6D_6), or toluene-d_8 (C_7D_8). Signal positions are given on the δ scale in ppm with reference to $CHCl_3$ at 7.25 ppm, $CHDCl_2$ at 5.32 ppm, C_6D_5H at 7.15 ppm, or $C_6D_5CHD_2$ at 2.09 ppm.[17] $^{77}Se\{^1H\}$ NMR data were obtained at 76.3 MHz; signal positions are given relative to an external sample of diphenylselenide (Ph_2Se, 60% v/v in $CDCl_3$) at 416 ppm.[27] For compounds containing the η^5-cyclopentadienyl ligand (Cp), the integral for this resonance was consistently less than the expected value. This phenomenon has be previously observed and is believed to result from a long spin-lattice relaxation time for the Cp ligand.[28]

Microanalyses were performed by Mr. P. Borda of this department.

For reactions carried out at −20 °C, the reagents were cooled to this temperature in a refrigerator contained in the glovebox. Removal of bis(η^5-cyclopentadienyl)zirconium(IV) dichloride (Cp_2ZrCl_2), produced as a byproduct in most of the zirconium transfer reactions, was performed (unless stated otherwise) by filtration through basic alumina, Brockman Activity 1 (80–200 mesh). For reactions carried out in the dark, the appropriate vessel was simply covered with aluminum foil. All photolysis reactions were carried out in capped (or sealed) 5-mm 507PP NMR tubes under prepurified nitrogen (unless stated otherwise) using a Sylvania (GTE) 34 W Cool White fluorescent light. The irradiation source emitted white light covering the spectrum of wavelengths from 380 to 800 nm. Samples for photolysis were simply taped to the fluorescent light, the solution being ~3–4 cm from the source. Measurements indicated that the temperature of the sample did not exceed 29 °C.

Solvents and Reagents. NMR solvents $CDCl_3$, CD_2Cl_2, C_6D_6, and C_7D_8 were purchased from MSD Isotopes and were dried over 3-Å molecular sieves, with the exception of $CDCl_3$ which was distilled from calcium hydride (CaH_2). All solvents were dried under argon. Hexanes were dried over sodium–benzophenone ketyl. Toluene was predried over sodium wire and then distilled from sodium–benzophenone ketyl.

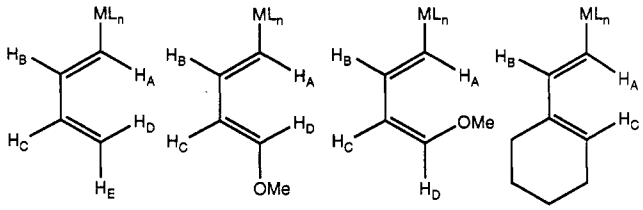
Bis(η^5-cyclopentadienyl)zirconium(IV) dichloride (Cp_2ZrCl_2), phenylselenenyl chloride (PhSeCl), diphenyl diselenide (PhSeSePh), 2,6-di-*tert*-butyl-4-methylphenol (BHT), 1,4-cyclohexadiene, azobisisobutyronitrile (AIBN), and (*Z*)-1-methoxy-1-buten-3-yne (**3c**) were all purchased from the Aldrich Chemical Co. All of the above reagents were purified by standard means prior to use. The reagent 1-buten-3-yne (**3a**) was purchased from Pfaltz and Bauer Chemicals, Inc., as a solution in xylene. The latter was dried over 4-Å molecular sieves and vacuum transferred

(25) Lewis, F. D.; Howard, D. K.; Barancyk, S. V.; Oxman, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 3016–3023.
(26) Fryzuk, M. D.; Bates, G. S.; Stone, C. *J. Org. Chem.* **1988**, *53*, 4425–4426.
(27) Gulliver, D. J.; Hope, E. G.; Levason, W.; Murray, S. G.; Potter, M.; Marshall, G. L. *J. Chem. Soc., Perkin Trans. 2* **1984**, 429.
(28) Adam, M. J.; Hall, L. D. *J. Organomet. Chem.* **1980**, *186*, 289.

several times to remove any xylene.

The following reagents were prepared by literature procedures: 1-methoxy-1-buten-3-yne (**3b**; ~4:1 *E*/*Z*),[29] 1-ethynylcyclohexene (**3d**),[29] chlorobis(η^5-cyclopentadienyl)hydridozirconium(IV), $Cp_2Zr(H)Cl$, and chlorobis(η^5-cyclopentadienyl)deuteriozirconium(IV), $Cp_2Zr(D)Cl$,[30] *N*-(phenylseleno)phthalimide (*N*-PSP),[16] and bis(*p*-chlorophenyl) diselenide.[31,32]

The following general structures are used for the NMR assignments.



4-6a **4-6b** **4-6c** **4-6d**

General Procedure 1: Preparation of $ZrCp_2Cl(CH{=}CH{-}CR{=}CR'R'')$. The hydride $Cp_2Zr(H)Cl$ was added in three portions, at room temperature in the dark, to a stirred solution in toluene of the appropriate 1-ene-3-yne **3a–d** (1 equiv). The resulting white slurry was stirred in the dark (reaction vessel was simply covered with aluminum foil) until a homogeneous solution was obtained. The solvent was evaporated to approximately one-third of its original volume, at which point hexanes was added to aid crystallization, and the solution was allowed to stand at −30 °C.

(*E*)-1,3-Butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV) (4a) and (*E*)-1,3-Butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV)-2-*d* (4a-d_1). The preparation of **4a** deviated slightly from general procedure 1 due to the low boiling point of 1-buten-3-yne **3a** (2 °C). To a stirred slurry of $Cp_2Zr(H)Cl$ (3.00 g, 11.63 mmol) in 60 mL of toluene, contained in a large reactor bomb, was vacuum transferred 1-buten-3-yne **3a** (1.82 g, 34.90 mmol). The mixture was stirred in the dark at room temperature until a red homogeneous solution resulted. Workup as described in general procedure 1 gave **4a** as yellow-orange crystals (2.92 g, 81%): IR (KBr) 3095, 2890, 1600, 1532, 1441, 1020, 1000, 908, 629 cm^{-1}; δ (C_6D_6, 400 MHz, ^{1}H NMR) 4.99 (1 H, ddd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz, J_{EB} = 0.75 Hz), 5.12 (1 H, ddd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz, J_{DB} = 0.75 Hz), 5.80 (10 H, s, Cp), 6.27 (1 H, dddd, H_C, J_{CD} = 17 Hz, J_{CB} = J_{CE} = 10 Hz, J_{CA} = 0.75 Hz), 6.59 (1 H, dddd, H_B, J_{BA} = 19 Hz, J_{BC} = 10 Hz, J_{BD} = J_{BE} = 0.75 Hz), 7.12 (1 H, dd, H_A, J_{AB} = 19 Hz, J_{AC} = 0.75 Hz). Anal. Calcd for $C_{14}H_{15}ClZr$: C, 54.24; H, 4.84; Cl, 11.46. Found: C, 53.85; H, 4.72; Cl, 11.65.

Reaction of $Cp_2Zr(D)Cl$ (1.00 g, 3.86 mmol) and 1-buten-3-yne **3a** (0.60 g, 11.59 mmol) afforded yellow crystals of **4a**-d_1 (0.99 g, 82%): δ (C_6D_6, 400 MHz, ^{1}H NMR) 5.02 (1 H, dd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz), 5.14 (1 H, dd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz), 5.78 (10 H, s, Cp), 6.28 (1 H, b dd, H_C, J_{CD} = 17 Hz, J_{CE} = 10 Hz), 7.11 (1 H, b t, H_A, J_{Ad} = 2.5 Hz).

(*E*,*E*)-Chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) (4b) and (*E*,*E*)-Chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV)-2-*d* (4b-d_1). To a stirred solution of 1-methoxy-1-buten-3-yne (**3b**; ~4:1 *E*/*Z*) (1.19 g, 13.96 mmol, 20% excess) in 60 mL of toluene was added $Cp_2Zr(H)Cl$ (3.00 g, 11.63 mmol) in three portions. Upon formation of an orange-red homogeneous solution, workup of the reaction mixture, as described in general procedure 1, was performed to yield yellow crystals of **4b** (3.36 g, 85%): IR (Nujol) 3104, 3048, 1617, 1543, 1294, 1214, 1144, 1018, 984, 913, 802 cm^{-1}; δ (C_6D_6, 400 MHz, ^{1}H NMR) 3.19 (3 H, s, O*Me*), 5.47 (1 H, ddd, H_C, J_{CD} = 13 Hz, J_{CB} = 10 Hz, J_{CA} = 0.75 Hz), 5.86 (10 H, s, Cp), 6.51 (1 H, ddd, H_B, J_{BA} = 18 Hz, J_{BC} = 10 Hz, J_{BD} = 0.75 Hz), 6.58 (1 H, dd, H_D, J_{DC} = 13 Hz, J_{DB} = 0.75 Hz), 7.17 (1 H, dd, H_A, J_{AB} = 18 Hz, J_{AC} = 0.75 Hz). Anal. Calcd for $C_{15}H_{17}ClOZr$: C, 52.98; H, 5.00; Cl, 10.45. Found: C, 52.81; H, 5.07; Cl, 10.66.

Reaction of $Cp_2Zr(D)Cl$ (1.00 g, 3.86 mmol) and 1-methoxy-1-buten-3-yne (**3b**; ~4:1 *E*/*Z*) (0.40 g, 4.83 mmol) afforded yellow crystals of **4b**-d_1 (1.14 g, 87%): δ (C_6D_6, 400 MHz, ^{1}H NMR) 3.19 (3 H, s, O*Me*), 5.47 (1 H, b d, H_C, J_{CD} = 12.5 Hz), 5.86 (10 H, s, Cp), 6.58 (1 H, d, H_D, J_{DC} = 12.5 Hz), 7.15 (1 H, b s, H_A).

(*E*,*Z*)-Chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) (4c) and (*E*,*Z*)-Chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV)-2-*d* (4c-d_1). To a stirred solution of (*Z*)-1-methoxy-1-buten-3-yne (**3c**; 0.95 g, 11.63 mmol) in 60 mL of toluene was added $Cp_2Zr(H)Cl$ (3.00 g, 11.63 mmol) in three portions. The resulting orange-red homogeneous solution was worked up as described in general procedure 1 to yield yellow crystals of **4c** (3.28 g, 83%): IR (Nujol) 3097, 1617, 1517, 1260, 1113, 1070, 990, 805 cm^{-1}; δ (C_6D_6, 400 MHz, ^{1}H NMR) 3.15 (3 H, s, O*Me*), 5.04 (1 H, ddd, H_C, J_{CB} = 8.5 Hz, J_{CD} = 6 Hz, J_{CA} = 0.75 Hz), 5.60 (1 H, ddd, H_D, J_{DC} = 6 Hz, J_{DA} = J_{DB} = 0.75 Hz), 5.83 (10 H, s, Cp), 7.20 (1 H, ddd, H_B, J_{BA} = 18 Hz, J_{BC} = 8.5 Hz, J_{BD} = 0.75 Hz), 7.27 (1 H, ddd, H_A, J_{AB} = 18 Hz, J_{AC} = J_{AD} = 0.75 Hz). Anal. Calcd for $C_{15}H_{17}ClOZr$: C, 52.98; H, 5.00; Cl, 10.45. Found: C, 52.69; H, 4.83; Cl, 10.52.

Reaction of $Cp_2Zr(D)Cl$ (1.00 g, 3.86 mmol) and (*Z*)-1-methoxy-1-buten-3-yne (**3c**; 0.32 g, 3.86 mmol) afforded yellow crystals of **4c**-d_1 (1.08 g, 82%): δ (C_6D_6, 400 MHz, ^{1}H NMR) 3.15 (3 H, s, O*Me*), 5.07 (1 H, b d, H_C, J_{CD} = 6 Hz), 5.60 (1 H, dd, H_D, J_{DC} = 6 Hz, J_{DA} = 0.5 Hz), 5.83 (10 H, s, Cp), 7.25 (1 H, b t, H_A, J_{Ad} = 2.75 Hz).

(*E*)-Chloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) (4d) and (*E*)-Chloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV)-2-*d* (4d-d_1). To a stirred solution of 1-ethynylcyclohexene **3d** (1.23 g, 11.63 mmol) in 60 mL of toluene was added $Cp_2Zr(H)Cl$ (3.00 g, 11.63 mmol) in three portions. Workup of the resulting red solution, as described in general procedure 1, afforded pale yellow crystals of **4d** (3.81 g, 90%): IR (KBr) 3102, 2926, 2853, 1621, 1522, 1439, 1316, 1018, 988, 804 cm^{-1}; δ (C_6D_6, 400 MHz, ^{1}H NMR) 1.54 (2 H, m), 1.61 (2 H, m), 2.08 (2 H, m), 2.15 (2 H, m), 5.74 (1 H, m, H_C), 5.87 (10 H, s, Cp), 6.66 (1 H, d, H_B, J_{BA} = 18.5 Hz), 7.14 (1 H, dd, H_A, J_{AB} = 18.5 Hz, J_{AC} = 0.75 Hz). Anal. Calcd for $C_{20}H_{21}ClZr$: C, 59.37; H, 5.77; Cl, 9.76. Found: C, 59.17; H, 5.67; Cl, 10.00.

Reaction of $Cp_2Zr(D)Cl$ (1.00 g, 3.86 mmol) and 1-ethynylcyclohexene **3d** (0.39 g, 3.86 mmol) afforded pale yellow crystals of **4d**-d_1 (1.25 g, 89%); δ (C_6D_6, 400 MHz, ^{1}H NMR) 1.54 (2 H, m), 1.61 (2 H, m), 2.08 (2 H, m), 2.15 (2 H, m), 5.74 (1 H, m, H_C), 5.87 (10 H, s, Cp), 7.13 (1 H, b t, H_A, J_{Ad} = 2.5 Hz).

General Procedure 2: Preparation of 1-Arylseleno 1,3-Dienes. To a stirred solution of the appropriate (*E*)-1-chlorobis(η^5-cyclopentadienyl)zirconium(IV) 1,3-diene **4a–d** in 1 mL of toluene, in the dark at −20 °C, was added 1 equiv of ArSeX: ArSeX = *N*-(phenylseleno)phthalimide (*N*-PSP, added as a solid), *N*-(phenylseleno)phthalimide-d_5 (*N*-PSP-d_5), or *N*-[(4-chlorophenyl)seleno]phthalimide (*N*-ClPSP). All reactions were complete within 5 min at −20 °C. The initial yellow (or orange in the case of **4a**) color of the zirconium 1,3-diene changed to colorless or pale yellow on addition of ArSeX. Workup of the reaction involved dilution with hexanes, resulting in precipitation of the zirconium byproduct, and filtration through basic alumina. Solvent evaporation yielded the desired products as colorless to pale yellow oils.

(*E*)-1-(Phenylseleno)-1,3-butadiene (5a). As outlined in general procedure 2, **4a** (75 mg, 0.24 mmol) was mixed with *N*-PSP (73 mg, 0.24 mmol) to yield a pale yellow oil **5a** (45 mg, 90%): IR (film) 3074, 3059, 3022, 2997, 1619, 1579, 1476, 1215, 996, 735, 690 cm^{-1}; λ_{max} (hexane) 278 nm (ϵ 16900); δ (C_6D_6, 400 MHz, ^{1}H NMR) 4.83 (1 H, dd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz), 4.87 (1 H, dd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz), 6.10 (1 H, ddd, H_C, J_{CD} = 17 Hz, J_{CB} = J_{CE} = 10 Hz), 6.39 (1 H, dd, H_B, J_{BA} = 15.5 Hz, J_{BC} = 10 Hz), 6.48 (1 H, d, H_A, J_{AB} = 15.5 Hz, J_{ASe} = 15.5 Hz), 6.95 (3 H, m), 7.38 (2 H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR) 379 (s). Anal. Calcd for $C_{10}H_{10}Se$: C, 57.43; H, 4.82. Found: C, 57.10; H, 4.86.

(*E*,*E*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene (5b). As outlined in general procedure 2, **4b** (75 mg, 0.22 mmol) was mixed with *N*-PSP (67 mg, 0.22 mmol) to yield a pale yellow oil **5b** (49

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mg, 92%): IR (film) 3054, 3020, 2935, 2837, 1633, 1578, 1474, 1438, 1220, 1144, 966, 735, 689, 626 cm^{-1}; λ_{max} (hexane) 250 (ϵ 14 000), 264 (ϵ 13 800), 268 nm (ϵ 13 900); δ (CD_2Cl_2, 400 MHz, ^1H NMR) 3.60 (3 H, s, O*Me*), 5.64 (1 H, dd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10.5 Hz), 6.39 (1 H, d, H_A, J_{AB} = 15 Hz, J_{ASe} = 14.5 Hz), 6.55 (1 H, ddd, H_B, J_{BA} = 15 Hz, J_{BC} = 10.5 Hz, J_{BD} = 0.75 Hz, J_{BSe} = 11 Hz), 6.65 (1 H, d, H_D, J_{DC} = 12.5 Hz), 7.23–7.27 (3 H, m), 7.43 (2 H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR) 367 (s). Anal. Calcd for $C_{11}H_{12}OSe$: C, 55.24; H, 5.06. Found: C, 55.44; H, 5.04.

(*E*,*Z*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene (5c). As outlined in general procedure 2, **4c** (75 mg, 0.22 mmol) was mixed with *N*-PSP (67 mg, 0.22 mmol) to yield a pale yellow oil **5c** (47 mg, 90%): IR (film) 3054, 2928, 2837, 1635, 1573, 1475, 1433, 1219, 1107, 926, 732, 690 cm^{-1}; λ_{max} (hexane) 270 nm (ϵ 15 900); δ (CD_2Cl_2, 400 MHz, ^1H NMR) 3.66 (3 H, s, O*Me*), 5.11 (1 H, ddd, H_C, J_{CB} = 10.5 Hz, J_{CD} = 6 Hz, J_{CA} = 0.5 Hz), 5.96 (1 H, ddd, H_D, J_{DC} = 6 Hz, J_{DB} = 1 Hz, J_{DA} = 0.5 Hz), 6.52 (1 H, ddd, H_A, J_{AB} = 15.5 Hz, J_{AC} = J_{AD} = 0.5 Hz, J_{ASe} = 15.5 Hz), 6.89 (1 H, ddd, J_{BA} = 15.5 Hz, J_{BC} = 10.5 Hz, J_{BD} = 1 Hz, J_{BSe} = 10 Hz), 7.27 (3 H, m), 7.46 (2 H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR) 374 (s). Anal. Calcd for $C_{11}H_{12}OSe$: C, 55.24; H, 5.06. Found: C, 55.28; H, 5.00.

(*E*)-1-(Phenylseleno)-2-(1-cyclohexen-1-yl)ethene (5d). As outlined in general procedure 2, **4d** (75 mg, 0.21 mmol) was mixed with *N*-PSP (64 mg, 0.21 mmol) to yield a pale yellow oil **5d** (55 mg, 95%): IR (film) 3034, 2928, 2854, 2830, 1630, 1577, 1476, 1437, 949, 740, 690, 668 cm^{-1}; λ_{max} (hexane) 280 (ϵ 15 500), 270 (ϵ 14 900), 284 nm (ϵ 15 000); δ (CD_2Cl_2, 400 MHz, ^1H NMR) 1.39 (4 H, m), 1.88 (4 H, m), 5.48 (1 H, m, H_C), 6.48 (1 H, dd, H_A, J_{AB} = 15.5 Hz, J_{AC} = 0.75 Hz, J_{ASe} = 15.5 Hz), 6.65 (1 H, d, H_B, J_{BA} = 15.5 Hz, J_{BSe} = 10 Hz), 6.95–7.01 (3 H, m), 7.48 (2 H, m); δ ($CDCl_3$, 76.3 MHz, ^{77}Se NMR) 369 (s). Anal. Calcd for $C_{14}H_{16}Se$: C, 63.88; H, 6.13. Found: C, 64.13; H, 6.17.

Photolysis of (*E*)-1-(Phenylseleno)-1,3-butadiene (5a). A solution of (*E*)-1-(phenylseleno)-1,3-butadiene (**5a**; 30 mg, 0.14 mmol) in 0.5 mL of C_6D_6 was placed in a capped NMR tube under nitrogen. The pale yellow solution was then irradiated with fluorescent light for 2 h. ^1H and $^{77}Se\{^1H\}$ NMR spectra of the solution after photolysis indicated that isomerization of **5a** had taken place to give a 2:1 mixture of *E*/*Z* isomers. Addition of (*E*)-1-(phenylseleno)-1,3-butadiene to the 2:1 *E*/*Z* mixture resulted in a change in this ratio, which was reestablished after a further 2 h of irradiation with fluorescent light. Continued irradiation up to 24 h gave no change in the *E*/*Z* ratio. ^1H and $^{77}Se\{^1H\}$ NMR data, taken from the spectrum of the mixture, of (*Z*)-1-(phenylseleno)-1,3-butadiene were: δ (C_6D_6, 400 MHz, ^1H NMR) 5.04 (1 H, dd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz), 5.11 (1 H, dd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz), 6.35 (1 H, dd, H_B, J_{BA} = 9 Hz, J_{BC} = 10 Hz), 6.40 (1 H, d, H_A, J_{AB} = 9 Hz), 6.71 (1 H, ddd, H_C, J_{CD} = 17 Hz, J_{CB} = J_{CE} = 10 Hz), 6.93 (2 H, m), 7.33 (2 H, m); δ ($CDCl_3$, 76.3 MHz, $^{77}Se\{^1H\}$ NMR) 341 (s).

Photolysis of (*E*,*E*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene (5b). A solution of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5b**; 32 mg, 0.13 mmol) in 0.5 mL of CD_2Cl_2 was photolyzed with fluorescent light for 1.5 h. ^1H and $^{77}Se\{^1H\}$ NMR spectra of the solution after photolysis indicated that isomerization of **5b** had taken place to give a 41(±2):13(±1):36(±2):10(±1) mixture of *Z*,*E*/*Z*,*Z*/*E*,*E*/*E*,*Z* isomers. These ratios were determined, from the ^1H NMR spectrum, by integration of the O*Me* resonances. That these were representative of the equilibrium composition of these isomers was determined by continuing the photolysis for a further 24 h, during which time the ratios did not change beyond those values stated above. When the equilibrium was disturbed by addition of (*E*,*E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene, further photolysis (~1.5 h) reestablished the equilibrium values. ^1H and $^{77}Se\{^1H\}$ NMR data, taken from the spectrum of the mixture, were as follows. (*Z*,*E*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene: δ (CD_2Cl_2, 400 MHz, ^1H NMR) 3.62 (3 H, s, O*Me*), 5.63 (1 H, ddd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10.5 Hz, J_{CA} = 0.75 Hz), 6.22 (1 H, ddd, H_A, J_{AB} = 9 Hz, J_{AC} = J_{AD} = 0.75 Hz), 6.52 (1 H, ddd, H_B, J_{BC} = 10.5 Hz, J_{BA} = 9 Hz, J_{BD} = 0.5 Hz), 6.78 (1 H, d, H_D, J_{DC} = 12.5 Hz), 7.20–7.32 (3 H, m), 7.42–7.51 (2 H, m); δ ($CDCl_3$, 76.3 MHz, $^{77}Se\{^1H\}$ NMR) 310 (s). (*Z*,*Z*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene; δ (CD_2Cl_2, 400 MHz, ^1H NMR) 3.69 (3 H, s, O*Me*), 5.31 (1 H, ddd, H_C, J_{CB} = 11 Hz, J_{CD} = 6.5 Hz, J_{CA} = 1 Hz), 6.11 (1 H, ddd, H_D, J_{DC} = 6.5 Hz, J_{DA} = 1.5 Hz, J_{DB} = 1 Hz), 6.34 (1 H, ddd, H_A, J_{AB} = 9 Hz, J_{AD} = 1.5 Hz, J_{AC} = 1 Hz), 6.92 (1 H, ddd, H_B, J_{BC} = 11 Hz, J_{BA} = 9 Hz, J_{BD} = 1 Hz), 7.20–7.32 (3 H, m), 7.42–7.51 (2 H, m); δ ($CDCl_3$, 76.3 MHz, $^{77}Se\{^1H\}$ NMR) 323 (s).

Photolysis of (*E*,*Z*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene (5c). A solution of (*E*,*Z*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5c**; 31 mg, 0.13 mmol) in 0.5 mL of CD_2Cl_2 was photolyzed with fluorescent light for 1.5 h. By ^1H and ^{77}Se NMR, an isomeric mixture identical to that described above for the photolysis of **5b** was observed.

Preparation and Photolysis of a 65:35 *E*/*Z* Mixture of 1-(Phenylseleno)-2-(1-cyclohexen-1-yl)ethene (5d). A solution of (*E*)-chloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) (**4d**; 80 mg, 0.22 mmol) in 0.5 mL of C_6D_6 was photolyzed with fluorescent light in a sealed (under nitrogen) 5-mm NMR tube for 19 h. The ^1H NMR indicated the formation of a 65:35 *E*/*Z* mixture of chloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV). The orange solution (initially yellow) was then reacted with *N*-PSP (66 mg, 0.22 mmol) according to general procedure 5. Workup yielded a yellow oil (48 mg, 83%) which by ^1H NMR spectroscopy was identified as a 65:35 *E*/*Z* mixture of 1-(phenylseleno)-2-(1-cyclohexen-1-yl)ethene (**5d**). Photolysis of this mixture with fluorescent light, for up to 18 h, gave a 95:5 *E*/*Z* mixture of **5d**. (*E*)-1-(Phenylseleno)-2-(1-cyclohexen-1-yl)ethene did not isomerize under the same photochemical conditions. (*Z*)-Chloro[2-(1-cyclohexen-1-yl-ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV): δ (C_6D_6, 400 MHz, ^1H NMR) 1.54–1.71 (4 H, m), 2.00 (2 H, m), 2.16 (2 H, m), 5.47 (1 H, m, H_C), 5.98 (10 H, s, Cp), 6.13 (1 H, d, H_A, J_{AB} = 13 Hz), 7.24 (1 H, d, H_B, J_{BA} = 13 Hz). (*Z*)-1-(Phenylseleno)-2-(1-cyclohexen-1-yl)ethene: δ ($CDCl_3$, 400 MHz, ^1H NMR) 1.55–1.75 (4 H, m), 2.14 (2 H, m), 2.32 (2 H, m), 5.80 (1 H, m, H_C), 6.39 (2 H, AB_q, H_A/H_B), 7.25–7.35 (3 H, m), 7.56 (2 H, m).

***N*-(Phenylseleno)phthalimide-d_5 (*N*-PSP-d_5).** *N*-(Phenylseleno)phthalimide-d_5 was prepared according to literature procedure[33,34] starting from benzene-d_6 to yield white crystals (3.23 g, 64% over 4 steps). The following data were recorded for this compound: IR (Nujol) 2274, 1774, 1720, 1343, 1280, 1066, 710, 676 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 7.73 (2 H, m), 7.90 (2 H, m). Anal. Calcd for $C_{14}H_4D_5NO_2Se$: C, 54.73; H, 2.95; N, 4.56. Found: C, 55.00; H, 3.00; N, 4.49.

***N*-[(*p*-Chlorophenyl)seleno]phthalimide (*N*-ClPSP).** *N*-[(*p*-Chlorophenyl)seleno]phthalimide was prepared according to literature procedures[16,34] using bis(*p*-chlorophenyl) diselenide (2.5 g, 6.60 mmol) to yield pale yellow microcrystalline material (2.87 g, 75%): IR (Nujol) 1775, 1725, 1344, 1277, 1064, 1011, 731, 711 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 7.31 (2 H, m), 7.76 (2 H, m), 7.81 (2 H, m), 7.91 (2 H, m). Anal. Calcd for $C_{14}H_8ClNO_2Se$: C, 49.95; H, 2.40; N, 4.16. Found: C, 50.12; H, 2.44; N, 4.14.

(*E*)-1-(Phenylseleno)-1,3-butadiene-2-*d* (5a-d_1). As outlined in general procedure 2, (*E*)-1,3-butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV)-2-*d* (**4a**-d_1) (75 mg, 0.24 mmol) was reaced with *N*-PSP (73 mg, 0.24 mmol) to yield a pale yellow oil of **5a**-d_1 (43 mg, 85%): IR (film) 3075, 2985, 1617, 1578, 1475, 1215, 996, 737, 690 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 5.06 (1 H, dd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.75 Hz), 5.13 (1 H, dd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.75 Hz), 6.34 (1 H, b dd, H_A, J_{CD} = 17 Hz, J_{CE} = 10 Hz), 6.70 (1 H, b t, H_A, J_{Ad} = 2.5 Hz), 7.30 (3 H, m), 7.51 (2 H, m); *m*/*e* (relative intensity) 51 (25.2), 77 (25.3), 78 (24.7), 129 (41.1), 130 (100), 131 (28.3), 134 (29.7), 211 (M^+, 25.4); exact mass calcd for $C_{10}H_9{}^2H^{80}Se$ 211.0011, found 211.0007.

(*E*,*E*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene-2-*d* (5b-d_1). As outlined in general procedure 2, (*E*,*E*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV)-2-*d* (**4b**-d_1) (75 mg, 0.22 mmol) was reacted with *N*-PSP (67 mg, 0.22 mmol) to yield a pale yellow oil of **5b**-d_1 (48 mg, 91%): IR (film) 3060, 2932, 2832, 1632, 1577, 1478, 1219, 1145, 968, 734, 691 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 3.64 (3 H, s, O*Me*), 5.64 (1 H, b d, H_C, J_{CD} = 12.5 Hz), 6.41 (1 H, b t, H_A, J_{Ad} = 2.5 Hz), 6.66 (1 H, d, H_D, J_{DC} = 12.5 Hz), 7.27 (3 H, m), 7.48 (2 H, m); *m*/*e* (relative intensity): 51 (30.0), 77 (44.6), 78 (24.5), 116 (52.8), 117 (38.3),

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145 (36.6), 146 (21.9), 157 (41.0), 160 (87.9), 161 (100), 241 (M^+, 71.7); exact mass calcd for $C_{11}H_{11}{}^2HO^{80}Se$ 241.0116, found 241.0117.

(*E,Z*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene-2-*d* (5c-*d*$_1$). As outlined in general procedure 2, (*E,Z*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV)-2-*d* (**4c-*d*$_1$**) (75 mg, 0.22 mmol) was reacted with *N*-PSP (67 mg, 0.22 mmol) to yield a pale yellow oil of **5c-*d*$_1$** (44 mg, 83%): IR (film) 2935, 2830, 1628, 1577, 1476, 1437, 1213, 1109, 929, 736, 688 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 3.61 (3 H, s, O*Me*), 5.06 (1 H, b d, H_C, J_{CD} = 6 Hz), 5.87 (1 H, dd, H_D, J_{DC} = 6 Hz, J_{DA} = 0.5 Hz), 6.46 (1 H, b t, H_A, J_{Ad} = 2.5 Hz), 7.22 (3 H, m), 7.42 (2 H, m); *m/e* (relative intensity) 51 (21.0), 77 (38.1), 78 (32.3), 116 (42.6), 117 (25.5), 118 (24.2), 129 (38.1), 130 (34.6), 145 (28.6), 146 (16.3), 155 (19.1), 160 (74.8), 161 (100), 241 (M^+, 54.9); exact mass calcd for $C_{11}H_{11}{}^2HO^{80}Se$ 241.0166, found 241.0119.

(*E*)-1-(Phenylseleno)-2-(1-cyclohexen-1-yl)ethene-2-*d* (5d-*d*$_1$). As outlined in general procedure 2, (*E*)-chloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV)-2-*d* (**4d-*d*$_1$**; 75 mg, 0.21 mmol) was reacted with *N*-PSP (64 mg, 0.21 mmol) to yield a pale yellow oil of **5d-*d*$_1$** (52 mg, 93%): IR (film) 1628, 1578, 1477, 1438, 829, 733, 690, 669 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 1.62 (2 H, m), 1.70 (2 H, m), 2.17 (4 H, m), 5.79 (1 H, m, H_C), 6.51 (1 H, b s), 7.25–7.34 (3 H, m), 7.50 (2 H, m); *m/e* (relative intensity) 51 (58.1), 65 (22.0), 77 (75.2), 78 (94.2), 80 (99.6), 106 (50.0), 141 (21.4), 142 (100), 143 (30.1), 156 (25.8), 184 (67.8), 186 (34.3), 188 (61.0), 265 (M^+, 54.4); exact mass calcd for $C_{14}H_{15}{}^2H^{80}Se$ 265.0480, found 265.0481.

(*E*)-1-(Phenylseleno)-1,3-butadiene-*d*$_5$ (5a-*d*$_5$). As outlined in general procedure 2, (*E*)-1,3-butadienylchlorobis(η^5-cyclopentadienyl)zirconium(IV) (**4a**; 75 mg, 0.24 mmol) was reacted with *N*-PSP-*d*$_5$ (74 mg, 0.24 mmol) to yield a pale yellow oil of **5a-*d*$_5$** (42 mg, 82%): IR (film) 2288, 2274, 1620, 1568, 1545, 1341, 1215, 993, 936, 900, 806, 641 cm^{-1}; ^1H NMR was identical to **5a** with the absence of the aromatic resonances; *m/e* (relative intensity) 54 (41.9), 82 (37.3), 83 (38.0), 131 (28.0), 132 (37.1), 133 (100), 215 (M^+, 20.2); exact mass calcd for $C_{10}H_{15}{}^2H_5{}^{80}Se$ 215.0261, found 215.0264.

(*E,E*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene-*d*$_5$ (5b-*d*$_5$). As outlined in general procedure 2, (*E,E*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) (**4b**; 75 mg, 0.22 mmol) was reacted with *N*-PSP-*d*$_5$ (68 mg, 0.22 mmol) to yield a pale yellow oil of **5b-*d*$_5$** (45 mg, 84%): IR (film) 2290, 2276, 1630, 1578, 1542, 1222, 1145, 965, 827, 628 cm^{-1}; ^1H NMR was identical to **5b** with the absence of the aromatic resonances; *m/e* (relative intensity) 54 (25.4), 82 (38.9), 119 (29.9), 120 (32.4), 121 (23.8), 132 (24.8), 133 (22.5), 134 (35.1), 149 (25.2), 160 (25.8), 162 (50.5), 163 (54.8), 164 (34.8), 165 (100), and 245 (M^+, 87.7); exact mass calcd for $C_{11}H_7{}^2H_5O^{80}Se$ 245.0367, found 245.0362.

(*E,Z*)-1-(Phenylseleno)-4-methoxy-1,3-butadiene-*d*$_5$ (5c-*d*$_5$). As outlined in general procedure 2, (*E,Z*)-chlorobis(η^5-cyclopentadienyl)(4-methoxy-1,3-butadienyl)zirconium(IV) (**4c**, 75 mg, 0.22 mmol) was reacted with *N*-PSP-*d*$_5$ (68 mg, 0.22 mmol) to yield a pale yellow oil of **5c-*d*$_5$** (46 mg, 86%): IR (film) 2274, 1633, 1575, 1546, 1227, 1146, 962, 828, 630 cm^{-1}; ^1H NMR was identical to **5c** with the absence of the aromatic resonances; *m/e* (relative intensity): 54 (23.7), 82 (36.7), 119 (28.3), 120 (32.5), 121 (38.3), 149 (22.4), 160 (24.9), 162 (50.4), 163 (55.1), 165 (100), 245 (M^+, 74.3); exact mass calcd for $C_{11}H_{17}{}^2H_5O^{80}Se$ 245.0367, found 245.0364.

(*E*)-1-(Phenylseleno)-2-(1-cyclohexen-1-yl)ethene-*d*$_5$ (5d-*d*$_5$). As outlined in general procedure 2, (*E*)-chloro[2-(1-cyclohexen-1-yl)ethenyl]bis(η^5-cyclopentadienyl)zirconium(IV) (**4d**, 75 mg, 0.21 mmol) was reacted with *N*-PSP-*d*$_5$ (65 mg, 0.21 mmol) to yield a pale yellow oil of **5d-*d*$_5$** (51 mg, 91%): IR (film) 3027, 2991, 2928, 2274, 1630, 1578, 1544, 1435, 1339, 1022, 952, 764, 639 cm^{-1}; ^1H NMR was identical to **5d** with the absence of the aromatic resonances; *m/e* (relative intensity) 54 (30.5), 78 (44.8), 79 (100), 80 (21.7), 82 (36.9), 83 (40.9), 105 (41.3), 107 (25.7), 145 (36.9), 146 (65.6), 159 (19.5), 160 (19.9), 185 (27.4), 187 (54.8), 188 (45.2), 269 (M^+, 42.7); exact mass calcd for $C_{14}H_{11}{}^2H_5{}^{80}Se$ 269.0731, found 269.0736.

(*E*)-1-[(4-Chlorophenyl)seleno]-1,3-butadiene (6a). As outlined in procedure 2, **4a** (75 mg, 0.24 mmol) was reacted with *N*-ClPSP (81 mg, 0.24 mmol) to yield a pale yellow oil of **6a** (51 mg, 88%) which by ^1H NMR spectroscopy was ≥95% pure: IR (film) 1620, 1565, 1471, 1091, 1010, 812, 729 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 5.12 (1 H, ddd, H_E, J_{EC} = 10 Hz, J_{ED} = 1.5 Hz, J_{EB} = 0.75 Hz), 5.20 (1 H, ddd, H_D, J_{DC} = 17 Hz, J_{DE} = 1.5 Hz, J_{DB} = 0.75 Hz), 6.38 (1 H, ddd, H_C, J_{CD} = 17 Hz, J_{CB} = J_{CE} = 10 Hz), 6.52 (1 H, dddd, H_B, J_{BA} = 15.5 Hz, J_{BC} = 10 Hz, J_{BD} = J_{BE} = 0.75 Hz, J_{BSe} = 10 Hz), 6.68 (1 H, d, H_A, J_{AB} = 15.5 Hz, J_{ASe} = 15 Hz), 7.31 (2 H, m), 7.46 (2 H, m); *m/e* (relative intensity): 51 (42.6), 77 (30.1), 112 (32.2), 114 (11.3), 128 (100), 130 (22.9), 133 (53.1), 163 (52.3), 165 (17.4), 224 (M^+, 26.5); exact mass calcd for $C_{10}H_9{}^{35}Cl^{80}Se$ 243.9558, found 243.9557.

(*E,E*)-1-[(4-Chlorophenyl)seleno]-4-methoxy-1,3-butadiene (6b). As outlined in procedure 2, **4b** (75 mg, 0.22 mmol) was reacted with *N*-ClPSP (74 mg, 0.22 mmol) to yield a pale yellow oil of **6b** (52 mg, 87%) which by ^1H NMR spectroscopy was ≥95% pure: IR (film) 3013, 2935, 2837, 1634, 1577, 1474, 1218, 1089, 1011, 812, 728 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 3.62 (3 H, s, O*Me*), 5.62 (1 H, dd, H_C, J_{CD} = 12.5 Hz, J_{CB} = 10 Hz), 6.35 (1 H, d, H_A, J_{AB} = 15 Hz, J_{ASe} = 15 Hz), 6.55 (1 H, ddd, H_B, J_{BA} = 15 Hz, J_{BC} = 10.5 Hz, J_{BD} = 0.5 Hz, J_{BSe} = 10 Hz), 6.66 (1 H, d, H_D, J_{DC} = 12.5 Hz), 7.25 (2 H, m), 7.37 (2 H, m); *m/e* (relative intensity) 51 (37.1), 68 (25.3), 115 (77.8), 128 (15.3), 144 (28.9), 151 (40.6), 159 (51.0), 194 (100), 196 (31.8), 274 (M^+, 38.8); exact mass calcd for $C_{11}H_{11}{}^{35}ClO^{80}Se$ 273.9663, found 273.9665.

(*E,Z*)-1-[(4-Chlorophenyl)seleno]-4-methoxy-1,3-butadiene (6c). As outlined in procedure 2, **4b** (75 mg, 0.22 mmol) was reacted with *N*-ClPSP (74 mg, 0.22 mmol) to yield a pale yellow oil of **6c** (51 mg, 85%) which by ^1H NMR spectroscopy was ≥95% pure: IR (film) 2939, 2839, 1639, 1571, 1473, 1266, 1121, 1087, 1011, 811, 769 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 3.68 (3 H, s, O*Me*), 5.10 (1 H, ddd, H_C, J_{CB} = 10.5 Hz, J_{CD} = 6 Hz, J_{CA} = 0.5 Hz), 5.95 (1 H, ddd, H_D, J_{DC} = 6 Hz, J_{DB} = 1 Hz, J_{DA} = 0.5 Hz), 6.45 (1 H, ddd, H_A, J_{AB} = 15.5 Hz, J_{AC} = J_{AD} = 0.5 Hz, J_{ASe} = 15 Hz), 6.94 (1 H, ddd, H_B, J_{BA} = 15.5 Hz, J_{BC} = 10.5 Hz, J_{BD} = 1 Hz, J_{BSe} = 10 Hz), 7.23 (2 H, m), 7.38 (2 H, m); *m/e* (relative intensity) 75 (18.8), 77 (14.0), 115 (37.7), 144 (25.3), 159 (56.8), 194 (100), 196 (30.5), 274 (M^+, 43.8); exact mass calcd for $C_{11}H_{11}{}^{35}ClO^{80}Se$ 273.9663, found 273.9667.

(*E*)-1-[(4-Chlorophenyl)seleno]-2-(1-cyclohexen-1-yl)ethene (6d). As outlined in general procedure 2, **4d** (75 mg, 0.21 mmol) was reacted with *N*-ClPSP (71 mg, 0.21 mmol) to yield a pale yellow oil of **6d** (56 mg, 89%) which by ^1H NMR spectroscopy was ≥95% pure: IR (film) 3027, 2928, 2858, 2830, 1631, 1575, 1475, 1089, 1012, 952, 811 cm^{-1}; δ ($CDCl_3$, 400 MHz, ^1H NMR) 1.64 (2 H, m), 1.71 (2 H, m), 2.15 (4 H, m), 5.73 (1 H, m, H_C), 6.44 (1 H, d, H_A, J_{AB} = 15 Hz, J_{ASe} = 15 Hz), 6.60 (1 H, d, H_B, J_{BA} = 15 Hz, J_{BSe} = 10 Hz), 7.25 (2 H, m), 7.40 (2 H, m); *m/e* (relative intensity) 51 (32.6), 77 (64.6), 79 (100), 105 (35.3), 107 (20.6), 112 (21.4), 175 (60.4), 187 (43.8), 189 (16.2), 217 (34.6), 255 (11.9), 298 (M^+, 35.3); exact mass calcd for $C_{14}H_{15}{}^{35}Cl^{80}Se$ 298.0028, found 298.0027.

General Procedure 3: Crossover Experiments for Photochemical and Thermal Isomerization Process. A known ratio (approximately 1:1) of 1-(phenylseleno)-1,3-diene-*d*$_5$ **5a–d-*d*$_5$** (or 1-(4-chlorophenyl)seleno 1,3-diene **6a–d**) and 1-(phenylseleno) 1,3-diene-2-*d* **5a–d-*d*$_1$** were dissolved in 0.5 mL of $CDCl_3$ (C_6D_6 or C_7D_8 for thermolysis reactions) and placed in a capped (or sealed) 5-mm NMR tube. The mixture was then photolyzed (1.5 h with fluorescent light) or heated at 80 °C in the dark (48 h). Analyses for crossover products were performed by ^1H NMR and low-resolution mass spectrometry.

Effect of 1,4-Cyclohexadiene on Crossover. When crossover experiments (thermal and photochemical) were carried out according to general procedure 6, using 1,4-cyclohexadiene as the solvent instead of deuterated solvents, a reduction in the amount of crossover was observed by ^1H NMR and low-resolution mass spectrometry.

Effect of 2,6-Di-*tert*-butyl-4-methylphenol (BHT). Photolysis of a solution of (*E,E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene **5b** (29 mg, 0.12 mmol) in 0.5 mL of C_7D_8, containing BHT (2 equiv), showed a significant decrease in the rate of isomerization. It was necessary to photolyze the solution for 20 h before the *Z,E/Z,Z/E,E/E,Z* ratio approached the equilibrium value (see above).

A solution of (*E,E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5b**; 27 mg, 0.11 mmol) in 0.5 mL of C_7D_8, containing BHT (2 equiv), gave an isomeric mixture of 15:4:69:12 *Z,E/Z,Z/E,E/E,Z*

after 48 h of thermolysis at 80 °C in the dark. This ratio shows a concentration of the *E,E* isomer far in excess of the equilibrium value. Subsequent photolysis of this solution, for 20 h with fluorescent light, gave the equilibrium ratios for the *Z,E/Z,Z/E,E/E,Z* isomeric mixture.

Effect of (4-Oxo-2,2,6,6-tetramethylpiperidinyl)oxy Radical (TEMPONE). Photolysis of a solution of (*E,E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5b**; 28 mg, 0.12 mmol) in 0.5 mL of C_7D_8, containing TEMPONE (1 mg, 5 mol %) showed little effect on the rate of isomerization. Equilibrium values of *Z,-E/Z,Z/E,E/E,Z* were reached within 2 h of photolysis with fluorescent light.

A solution of (*E,E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5b**, 27 mg, 0.11 mmol) in 0.5 mL of C_7D_8, containing TEMPONE (1 mg, 5 mol %), had little effect on the thermal isomerization process, with equilibrium values for *Z,E/Z,Z/E,E/E,Z* attained after 48 h at 80 °C in the dark.

Effect of 1,4-Cyclohexadiene. A solution of (*E*)-1-(phenylseleno)-1,3-butadiene (**5a**) (28 mg, 0.13 mmol) in 0.5 mL of 1,4-cyclohexadiene was photolyzed, in a capped 5-mm NMR tube, for 2 h with fluorescent light. A 9:1 *E/Z* mixture was observed by ^1H NMR, indicating significant retardation of the isomerization process.

A solution of (*E*)-1-(phenylseleno)-1,3-butadiene (**5a**; 28 mg, 0.13 mmol) in 0.5 mL of 1,4-cyclohexadiene was heated at 80 °C in a capped NMR tube for 48 h. A 20:1 *E/Z* mixture was observed by ^1H NMR, indicating significant retardation of the isomerization process.

A solution of (*E,E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5b**; 28 mg, 0.13 mmol) in 0.5 mL of 1,4-cyclohexadiene was photolyzed, in a capped NMR tube, for 1.5 h with fluorescent light. An isomeric ratio of 29:13:34:15 *Z,E/Z,Z/E,E/E,Z* was obtained, indicating a slight retardation of the isomerization process.

A solution of (*E,E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5b**; 30 mg, 0.13 mmol) in 0.5 mL of 1,4-cyclohexadiene was heated at 80 °C in a capped NMR tube for 48 h. An equilibrium ratio was obtained after 48 h, but a significant retardation in the initial stages was observed with 92% of *E,E* isomer remaining in solution after 24 h.

Effect of Diphenyl Diselenide-d_{10} [$(C_6D_5)SeSe(C_6D_5)$].[33] It was shown, by mass spectroscopy, that when 1:1 mixtures of $(C_6D_5)SeSe(C_6D_5)$ and PhSeSePh were photolyzed with fluorescent light in C_6D_6 significant quantities of $PhSeSe(C_6D_5)$ were produced. A similar result was seen on thermolysis (80 °C in the dark for 24 h) of such a mixture. A solution of (*E*)-1-(phenylseleno)-1,3-butadiene (**5a**; 26 mg, 0.12 mmol) in 0.5 mL of C_6D_6 (or (*E,E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5b**; 30 mg, 0.13 mmol) in $CDCl_3$) containing $(C_6D_5)SeSe(C_6D_5)$ (1 equiv) was photolyzed, in a capped 5-mm NMR tube, for 2 h with fluorescent light. Mass spectroscopy indicated the presence of significant amounts of 1-(phenylseleno)-1,3-butadiene-d_5 (or 1-(phenylseleno)-4-methoxy-1,3-butadiene-d_5] and $PhSeSe(C_6D_5)$. A similar result was observed on thermolysis (at 80 °C), in the dark, of these mixtures.

Thermal Isomerization of 1-Phenylseleno 1,3-Dienes. A solution of (*E*)-1-(phenylseleno)-1,3-butadiene (**5a**; 28 mg, 0.13 mmol) in 0.5 mL of C_6D_6 was placed in a capped NMR tube under nitrogen. The pale yellow solution was then heated in the dark at 80 °C for 48 h. ^1H NMR spectroscopy of the solution indicated that isomerization had taken place to give a 2:1 *E/Z* mixture of 1-(phenylseleno)-1,3-butadiene.

A solution of (*E,E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5b**; 30 mg, 0.13 mmol) in 0.5 mL of C_7D_8 was placed in a capped NMR tube under nitrogen. The pale yellow solution was then heated in the dark at 80 °C for 48 h. ^1H NMR spectrum of the solution indicated that isomerization had taken place to give a mixture of isomers (*Z,E/Z,Z/E,E/E,Z*) of the composition described above.

A solution of (*E,Z*)-1-(phenylseleno)-4-methoxy-1,3-butadiene (**5c**; 29 mg, 0.12 mmol) in 0.5 mL of C_7D_8 was placed in a capped NMR tube under nitrogen. The pale yellow solution was then heated in the dark at 80 °C for 48 h. ^1H NMR spectrum of the solution indicated that isomerization had taken place to give a mixture of isomers (*Z,E/Z,Z/E,E/E,Z*) of the composition described above for the thermolysis of **5b**.

Thermolysis at 80 °C of a solution of (*E*)-1-(phenylseleno)-2-(1-cyclohexen-1-yl)ethene (**5d**; 34 mg, 0.13 mmol) in 0.5 mL of C_6D_6 in the dark showed no isomerization after 4 days.

Thermolysis, at 80 °C in the dark, of a solution of 1-(phenylseleno)-1,3-butadiene (**5a**; 27 mg, 0.13 mmol) in 0.5 mL of C_6D_6 in a sealed tube under nitrogen for 48 h resulted in no isomerization. When the experiment was repeated (same concentration of **5a**) with the tube sealed under dry air (air was passed through a 20 × 2 cm column of Drierite) or under nitrogen in an acid-washed tube (tube was soaked in 12 M HCl for 3 h, then dried at 120 °C for 3 h) the same results were obtained: no isomerization.

A solution of **5a** (35 mg, 0.17 mmol) in 0.5 mL of C_6D_6 containing azobisisobutyronitrile (AIBN) (2 mg, ~5 mol %) when heated at 80 °C in the dark for 3 h resulted in a 2:1 *E/Z* mixture of stereoisomers.

Thermolysis, at 80 °C in the dark, of a solution of 1-(phenylseleno)-4-methoxy-1,3-butadiene (**5b**; 29 mg, 0.12 mmol) in 0.5 mL of C_7D_8 contained in a sealed tube under nitrogen for 48 h resulted in only limited isomerization (less than 30% conversion of the *E,E* isomer of **5b**). When the experiment was repeated (same concentration of **5b**) with a tube sealed under dry air or under nitrogen in an acid-washed tube, both reactions gave rise to preequilibrium isomeric mixtures (~40% conversion of the *E,E* isomer of **5b**).

A solution of **5b** (33 mg, 0.14 mmol) in 0.5 mL of C_7D_8 containing azobisisobutyronitrile (AIBN) (2 mg, ~5 mmol) when heated at 80 °C in the dark for 3 h resulted in an equilibrium mixture of *E,Z/Z,Z/E,E/Z,E* stereoisomers.

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Registry No. **3a**, 689-97-4; **3b**, 3685-20-9; **3c**, 3685-19-6; **3d**, 931-49-7; **4a**, 107860-75-3; **4a**-d_1, 137008-14-1; **4b**, 107913-11-1; **4b**-d_1, 137008-13-0; **4c**, 107860-77-5; **4c**-d_1, 137008-12-9; **4d**, 107860-76-4; **4d**-d_1, 137008-11-8; **5a**, 84509-73-9; **5a**-d_1, 137007-99-9; **5a**-d_5, 137008-03-8; **5b**, 108189-82-8; **5b**-d_1, 137008-00-5; **5b**-d_5, 137008-04-9; **5c**, 108189-83-9; **5c**-d_1, 137008-01-6; **5c**-d_5, 137008-05-0; **5d**, 108189-84-0; **5d**-d_1, 137008-02-7; **5d**-d_5, 137008-06-1; **6a**, 137008-07-2; **6b**, 137008-08-3; **6c**, 137008-09-4; **6d**, 137008-10-7; *N*-PSP, 71098-88-9; *N*-PSP-d_5, 137007-96-6; *N*-ClPSP, 137007-97-7; $Cp_2Zr(H)Cl$, 37342-97-5; $Cp_2Zr(D)Cl$, 80789-51-1; (*Z*)-chloro[2-(1-cyclohexen-1-ylethenyl)]bis(η^5-cyclopentadienyl)zirconium(IV), 137119-53-0; (*Z*)-1-(phenylseleno)-1,3-butadiene, 108189-85-1; (*Z,E*)-1-(phenylseleno)-4-methoxy-1,3-butadiene, 108189-86-2; (*Z,Z*)-1-(phenylseleno)-4-methoxy-1,3-butadiene, 108189-87-3; (*Z*)-1-(phenylseleno)-2-(1-cyclohexen-1-yl)ethene, 137007-98-8.

Supplementary Material Available: ^1H NMR spectra (400 MHz) for compounds **6a–d** (8 pages). Ordering information is given on any current masthead page.