Synthesis of 1-Stannacyclopent-3-enes and Their Pyrolysis to Stannylenes

Dong Zhou,^{†,#} Clemens Reiche,[†] Mrinmoy Nag,[†] John A. Soderquist,[‡] and Peter P. Gaspar^{*,†}

Department of Chemistry, Washington University, St. Louis, Missouri 63130-4899, and Department of Chemistry, University of Puerto Rico-Rio Piedras, Box 23346, UPR Station, San Juan, Puerto Rico 00931-3346

Received June 10, 2008

1,1-Diorgano-1-stannacyclopent-3-enes have been synthesized by condensation in THF of magnesium complexes of 1,3-dienes and dichlorodiorganostannanes. 1,1-Dimethyl-, 1,1-di-*n*-butyl-, 1,1-di-*tert*-butyl-, and 1,1-diphenyl-1-stannacyclopent-3-enes and 1,1,3,4-tetramethyl-, 1,1-di-*tert*-butyl-3,4-dimethyl-, and 3,4-dimethyl-1,1-diphenyl-1-stannacyclopent-3-enes were prepared. Kinetic studies of the pyrolysis at temperatures as low as 75 °C of several of these stannacyclopent-3-enes resulted in their first-order disappearance, consistent with a unimolecular dissociation to the corresponding stannylene and diene. Activation parameters are reported. Trapping of dimethylstannylene by dienes was overwhelmed by oligomerization of Me₂Sn:, but for *t*-Bu₂Sn: a high yield of diene adduct was obtained. The dimethylstannylene oligomer(s) functioned as stannylenoids and were responsible for several reactions previously attributed to free Me₂Sn:. *cyclo*-(*t*-Bu₂Sn)₄ may also function as a stannylenoid.

Introduction

The number of stannacyclopent-3-enes reported in the literature is surprisingly small,¹ and this has delayed their adoption as precursors for the generation of stannylenes, R_2Sn . In previous work the extrusion of dimethylsilylene Me_2Si : and dimethylgermylene Me_2Ge : from the corresponding heterocyclopent-3-enes **1** under pyrolysis conditions² led to the expectation that stannacyclopent-3-enes would be useful stannylene precursors (Scheme 1).

Indeed the 7-stannanorbornene **2** prepared by Neumann, the only previously well-established precursor to dimethylstannylene Me₂Sn: (**3**), is a substituted stannacyclopent-3-ene that undergoes unimolecular thermal dissociation (Scheme 2).³

(2) (a) Dimethylsilylene: Lei, D.; Gaspar, P. P. *Organometallics* **1985**, 4, 1471. (b) Dimethylgermylene: Lei, D.; Gaspar, P. P. *Polyhedron* **1991**, *10*, 1221.

The low thermal stability of this stannanorbornene makes it an inconvenient stannylene precursor, and variation of its substituents on tin is not straightforward.

The finding that 1,1-dimethyl-1-stannacyclopent-3-ene (4) can be handled at room temperature was encouraging for the prospects of using simple stannacyclopentenes as stannylene precursors. Soderquist and Leon synthesized a 1:1 mixture of 4 and 1,1-dimethyl-1-stannacyclopent-2-ene (5) by the route in Scheme 3.^{1e}

The promise held by 1-stannacyclopent-3-enes as precursors for the generation of stannylenes R_2Sn ; molecules containing divalent and dicoordinate tin atoms, and the absence from the literature of general methods for the preparation of such stannacyclopentenes led to this study of their synthesis and pyrolysis.

Previous Pyrolysis Studies of Molecules Proposed As Stannylene Precursors. Previous studies of precursor pyrolysis and trapping experiments have provided limited support for the thermal generation of free stannylenes. Stannanorbornene 2 prepared from the Diels-Alder reaction of 1,1-dimethyl-2,3,4,5tetraphenylstannole and tetracyanoethylene (Scheme 2) decomposed above -20 °C with a half-life of 17 min at -10 °C in a first-order process giving a quantitative yield of 1,1,2,2tetracyano-3,4,5,6-tetraphenylcyclohexa-3,5-diene.³ Formation of free Me₂Sn: (3) in a concerted extrusion was suggested, since the alternative stepwise decomposition via a diradical intermediate was expected to give rise to CIDNP signals, which were not observed; nor could an intermediate be trapped.³ Oligomers of Me₂Sn: (3) were obtained, but an adduct of unknown structure was found when stannanorbornene 2 was allowed to decompose in the presence of dimethylacetylenedicarboxylate. Attempts to trap $Me_2Sn:$ (3) from this precursor by means of 1,3-dienes failed.4

^{*} Corresponding author. Phone: (314) 935 6568. Fax: (314) 935 4481. E-mail: gaspar@wustl.edu.

[†] Washington University.

^{*} University of Puerto Rico-Rio Piedras.

[#]Current affiliation: Mallinckrodt Institute of Radiology, Washington University School of Medicine, St. Louis, MO 63110.

⁽¹⁾ A search of Chemical Abstracts files located only 17 distinct structures, of which all but three (1d, 1e, and 1j) resulted from stannylene addition to dienes:(a) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. J. Organomet. Chem. 2004, 689, 1337. (b) Neale, N. R.; Tilley, T. D. J. Am. Chem. Soc. 2002, 124, 3802. (c) Setaka, W.; Sakamoto, K.; Kira, M.; Power, P. P. Organometallics 2001, 20, 4460. (d) Fañanás, F. J.; Granados, A.; Sanz, R.; Ignacio, J. M.; Barluenga, J. Chem.-Eur. J. 2001, 7, 2896. (e) Soderquist, J. A.; Leon, G. Tetrahedron Lett. 1998, 39, 2511. (f) Saito, M.; Tokitoh, N.; Okazaki, R. Organometallics **1996**, *15*, 4531. (g) Saito, M.; Tokitoh, N.; Okazaki, R. Chem. Lett. **1996**, 265; (h) Weidenbruch, M.; Stilter, A.; Schlaefke, J.; Peters, K.; von Schnering, H. G. J. Organomet. Chem. 1995, 501, 67. (i) Saito, M.; Tokitoh, N.; Okazaki, R. Organometallics 1995, 14, 3620. (j) Wrackmeyer, B.; Klaus, U.; Millius, W. Chem. Ber. 1995, 128, 679. (k) Tokitoh, N.; Saito, M.; Okazaki, R. J. Am. Chem. Soc. 1993, 115, 2065. (1) Gruetzmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. M. Angew. Chem., Int. Ed. Engl. 1992, 31, 437. (m) Weidenbruch, M.; Schaefer, A.; Kilian, H.; Pohl, S.; Saak, W.; Marsmann, H. Chem. Ber. 1992, 125, 563-566. (n) Marx, R.; Neumann, W. P.; Hillner, K. Tetrahedron Lett. 1984, 25, 625.

⁽³⁾ Grugel, C.; Neumann, W. P.; Schriewer, M. Angew. Chem., Int. Ed. Engl. 1979, 18, 543.

⁽⁴⁾ Neumann, W. P. Chem. Rev. 1991, 91, 311.



The extrusion of dialkylstannylenes by α -elimination from 1,2-dihalotetraalkyldistannanes, a process whose silicon analogue is well known in silylene chemistry,⁵ was first proposed in 1974 for the pyrolysis of 1,2-dichlorotetrabutyldistannane (**6**) in the range 120–130 °C (Scheme 4).⁶

The formation of products expected from the insertion of stannylene 7 into C-X bonds of benzyl, allyl, propargyl, and allenyl halides and the Sn-Sn bond of hexamethyldistannane and a lack of acceleration of the reactions in the presence of trapping agents were taken as evidence for the formation of the free stannylene (but see below). The products of formal insertion were formed in yields of 15% to 25%, together with one or more oligometrs of the stannylene $[(n-Bu)_2Sn]_n$. The oligometric material was found to be stable under the reaction conditions, so its decomposition was believed not to contribute to the formation of the products attributed to the free stannylene. Adducts of (n-Bu)₂Sn: (7) to substituted 1,3-dienes (1,4diphenyl-, 2,3-dimethyl-, and 1,2,3,4-tetraphenyl-) were not found; polystannanes were the only products obtained. Results presented below suggest that 1,1-dialkyl-1-stannacyclopent-3enes are unstable at the temperatures employed for 1,2dichlorotetrabutyldistannane pyrolysis, so their absence as products is understandable and leaves open the question whether they were formed.

Addition of Persistent Stannylenes to Butadienes. Lappert reported the formation of a 1-stannacyclopent-3-ene from the addition of bis(bisyl)stannylene 8 [where bisyl = bis(trimethylsiyl)methyl, (Me₃Si)₂CH] to 2,3-dimethylbutadiene in 1976 (Scheme 5).⁷ In an important series of experiments reported in 1984, Neumann examined effects of substituents on, and the stereochemistry of addition of several stannylenes to, substituted 1,3-dienes. Addition of the stannylenes studied to the mesoand *dl*-isomers 9 and 10, respectively, of a diallene 2,7diphenylocta-2,3,5,6-tetraene gave products 11a and 11b, and 12, respectively, compatible with an exclusively disrotatory linear chelotropic process (Scheme 6).¹ⁿ With trans,trans-1,4disubstituted-1,3-dienes 13 the Lappert bis(bisyl)stannylene (8) underwent addition only with strongly electron-withdrawing substituents CO₂Me or CN; no adduct was obtained with substituents Ph, Me, NHCO₂Et, or OMe (Scheme 7). This result was interpreted as indicating that the dominant frontier orbital interaction was stannylene HOMO-diene LUMO, the stannylene thus acting as a nucleophile. For substituents in the 2and 3-positons of the diene, sterics apparently plays a dominant role, with 2,3-diphenylbutadiene undergoing addition by 8 more slowly than 2,3-dimethylbutadiene. The order of reactivity toward 8 was 2,3-dimethyl \geq *trans,trans*-1,4-carbomethoxy > 2,3-diphenyl > *trans,trans*-dicyano > *meso*-2,7-diphenylocta-2,3,5,6-tetraene.

Weidenbruch reported in 1991 that bis(2,4,6-triisopropylphenyl)stannylene undergoes addition to 2,3-dimethylbutadiene, yielding the corresponding 1-stannacyclopent-3-ene.⁸ It had earlier been proposed by Masamune and Sita that this stannylene mediates the equilibrium between its cyclotristannane "trimer" and its distannene "dimer".⁹ Weidenbruch obtained the 1-stannacylopent-3-ene by heating the cyclotristannane in the presence of diene and assumed that addition occurred by free stannylene from dissociation of the cyclotristannane. NMR evidence for the presence of free stannylene was presented, but the possibility that the stannacyclopentene resulted from direct reaction of the cyclotristannane or the distannene with 2,3-dimethylbutadiene was not considered.

The first dialkylstannylene monomeric in the solid state was synthesized by Kira in 1991.¹⁰ It is 2,2,5,5-tetrakis(trimethyl-silyl)-1-stannacyclopentane-1-diyl (14), whose addition to 2,3-dimethylbutadiene in hexane solution at room temperature yielded the corresponding 1-stannacyclopent-3-ene quantitatively (Scheme 8, A).¹¹ A related but more crowded persistent stannylene, **15**, prepared by Eaborn¹² failed to react with several substituted butadienes (Scheme 8, B).¹³ Two other persistent stannylenes, **16** (Scheme 8, C)¹⁴ and **17** (Scheme 8, D),¹⁵ have been found to add smoothly to 2,3-dimethylbutadiene at room temperature.

Results and Discussion

Synthesis. Separation of the stannacyclopentene isomers synthesized by the method of Soderquist and Leon^{1e} was not successful, so a new route to stannacyclopent-3-enes was developed employing magnesium-butadiene complexes. Richter reported high yields of 1,1-diorgano-1-silacyclopent-3-enes, with no indication of the formation of the silacyclopent-2-ene isomers, from the condensation of magnesium-butadiene¹⁶ with organodichlorosilanes.¹⁷ Richter employed toluene solvent, but we had employed ethereal solvents for this reaction,¹⁸ and THF proved useful in the preparation of stannacyclopent-3-enes (Scheme 9).

Yields as low as 10% provided useful quantities of stannacyclopent-3-enes, because they were the only monomeric products and could be isolated in high purity. This was not the case with 3-phenylstannacylopent-3-enes, whose yields were <10% and could not be separated from side products.

While elemental analysis and mass spectrometric precise mass determination was not possible for all the stannacyclopent-3enes formed, the combination of ¹H, ¹³C{¹H}, and ¹¹⁹Sn{¹H} NMR spectra led to unambiguous structure determinations. Vinyl ¹H signals at 6.1 to 6.7 ppm with J_{H-Sn} in the range 117 to 131 Hz, SnCH₃ ¹H signals at 0.1 ppm with J_{H-Sn} in the range 54 to 57 Hz, and ring SnCH signals at 1.4 to 1.8 ppm with J_{H-Sn} in the range 35 to 42 Hz were characteristic, as were ¹¹⁹Sn signals in the range -2 to 77 ppm. Vinylic ¹³C signals for alkyl-

(8) Weidenbruch, M.; Schäfer, A.; Kilian, H.; Pohl, S.; Saak, W.; Marsmann, H. *Chem. Ber.* **1991**, *125*, 563.

(9) Masamune, S.; Sita, L. R. J. Am. Chem. Soc. 1985, 107, 6390.

(10) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. J. Am. Chem. Soc. **1991**, 113, 7785.

(11) Kira, M.; Ishida, S.; Iwamoto, T. Chem. Rec. 2004, 4, 243.

(12) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Patel, D.; Smith, J. D.; Zhang, S. *Organometallics* **2000**, *19*, 49.

(13) Asadi, A.; Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Meehan, M. M.;
 Smith, J. D. *Organometallics* **2002**, *21*, 2430.

(14) Saito, M.; Tokitoh, N.; Okazaki, R. Organometallics 1996, 15, 4531.
 (15) Setaka, W.; Sakamoto, K.; Kira, M.; Power, P. P. Organometallics 2001, 20, 4460.

(16) Fujita, K.; Ohnuma, Y.; Yasuda, H. J. Organomet. Chem. 1976, 113, 201.

(17) Richter, W. J. Synthesis 1982, 12, 1102.

(18) Jiang, P.; Gaspar, P. P. J. Am. Chem. Soc. 2001, 123, 8622.

^{(5) (}a) Atwell, W. H.; Weyenberg, D. R. J. Organomet. Chem. 1966, 5, 594. (b) J. Am. Chem. Soc. 1968, 90, 3438.

⁽⁶⁾ Schröer, U.; Neumann, W. P. Angew. Chem., Int. Ed. Engl. 1975, 14, 246.

⁽⁷⁾ Cotton, J. D.; Davidson, P. J.; Lappert, M. F. J. Chem. Soc., Dalton Trans. 1976, 2275.

Me₂Si

[9-BBN-H]₂

CI(nBu)2Sn-Sn(nBu)2CI

[(Me₃Si)₂CH]₂Sn:

6

Me₂Sn



(nBu)2SnCl2



When 1,1-dimethyl- and 1,1,3,4-tetramethyl-1-stannacyclopent-3-ene (**4** and **18**) were pyrolyzed in benzene- d_6 or cyclohexane- d_{12} , the only products detectable by NMR were the corresponding butadiene and dimethylstannylene oligomers, formed in yields in the range 70% to 100%. Formation of dimethylstannylene oligomers was indicated by both ¹H and ¹¹⁹Sn NMR spectroscopy. At the beginning of the pyrolysis a single broad peak was observed at 0.6 ppm (¹H) assigned to *cyclo*-(Me₂Sn)₆.²⁰ In the course of the pyrolysis several single sharp peaks were observed near 0.5 ppm whose formation occurred at the expense of the 0.6 ppm peak. These were attributed to *cyclo*-(Me₂Sn)_n (n = 5, 7, 8).²¹ Neumann reported the transformation of the cyclic hexamer to a mixture containing the pentamer, heptamer, and octamer in benzene solution even at 20 °C.²⁰

When a larger scale pyrolysis of 1,1-dimethyl-1-stannacyclopent-3-ene (4) was carried out in toluene, peaks at ppm 0.61 (broad) and 0.51 (sharp) were attributed to cyclo-(Me₂Sn)_n, n = 6 and n = 5, respectively (lit.²⁰ ppm 0.63 and 0.53, respectively). In the ¹¹⁹Sn NMR spectrum, several peaks were observed in the -230 to -250 ppm range in addition to the peak at 56.37 ppm due to the stannacyclopentene. A single broad peak at -231.13 ppm was attributed to cyclo-(Me₂Sn)₆ (lit.²⁰ ppm 231.04 [broad]). A large sharp peak at -241.51 ppm with satellites (J = 85.5, 750.7, 1175.1) was assigned to cyclo- $(Me_2Sn)_5$ (lit.²¹ ppm -241.40, J = 83, 755, 1176), while the peaks at -243.47 and -245.11 could be attributed to cyclo-(Me₂Sn)₇ and cyclo-(Me₂Sn)₈, respectively (lit.²¹ ppm -243.40 and -244.99, respectively. A peak at -233.37 ppm was also observed by Neumann²⁰ as an unidentified peak (-233.22 ppm) in a mixture of equilibrating cyclostannanes.

An authentic mixture of dimethylstannylene oligomers was prepared according to Neumann's procedure²⁰ and displayed the same NMR spectra. A similar mixture of dimethylstannylene oligomers was obtained in 92% (¹H NMR) yield when 1,1,3,4tetramethyl-1-stannacyclopent-3-ene (**18**) was subjected to pyrolysis in benzene- d_6 at 373 K for 4 h. The conversion was

substituted stannacyclopent-3-enes fell in the narrow range of 131 to 133 ppm. In the case of 1,1-dimethyl-1-stannacyclopent-3-ene (4), agreement was found with the spectroscopic data of Soderquist and Leon.^{1e}

Scheme 3

Scheme 4

Scheme 5

Hexane

Δ

PhCH=O

(*n*Bu)₂Sn:

7

f(Me₂Si)₂CH₂S

No stannacyclopent-3-ene was detected when the magnesium complex of *trans,trans*-1,4-diphenylbutadiene was reacted with dichlorodimethylstannane. As was the case with the reactions from which low but useful yields of stannacyclopent-3-enes were obtained, as given above, the major product was believed to be one or more oligomers of the stannylene. In some cases, e.g., *cyclo*-(Ph₂Sn)₆, unambiguous characterization of the oligomer resulted from comparison of its ¹¹⁹Sn NMR spectrum with that of an authentic sample. A characteristic of all the diorganotin oligomers was their rapid air-oxidation to insoluble organotin oxides.

Kinetic Studies of the Pyrolysis of 1-Stannacyclopent-3enes. As a first step in determining whether pyrolysis of simple 1-stannacyclopent-3-enes would be a useful route to the generation of sterically unencumbered stannylenes, the kinetics of the thermal decomposition of several stannacyclopent-3-enes was examined.

Pyrolysis of 1,1-dimethyl-1-stannacyclopent-3-ene (4) in benzene and in cyclohexane was cleanly first-order. Figure 1 is a representative first-order kinetic plot for the disappearance of the stannacyclopentene over three half-lives in benzene- d_6 at 373.1 K. Plotting these data as a second-order process led to distinct curvature (plot not shown). The products were butadiene and oligomers of dimethylstannylene $(Me_2Sn)_n$ formed in yields above 70% and often approaching 100%, as determined by NMR analysis. Table 1 indicates that the first-order rate constant for pyrolysis of 4 varies with solvent, increasing by a half from cyclohexane- d_{12} to benzene- d_6 , both considered to be inert solvents in this reaction. 2,3-Dimethylbutadiene is not inert toward dimethylstannylene, suggested to be an intermediate in the pyrolysis (vide infra), but the 30% rate enhancement in neat 2,3-dimethylbutadiene compared with cyclohexane- d_{12} is likely to be due to a solvent effect, rather than a sign of a direct reaction between the diene and stannacyclopentene 4. Induced decomposition of 4 by reaction with $Me_2Sn:$ (3) would have led to a decrease in the pyrolysis rate when cyclohexane was replaced by a solvent, 2,3-dimethylbutadiene, capable of reacting with 3. Again, first-order kinetics was observed, but the reaction was followed for only two half-lives.

⁽¹⁹⁾ Becerra, R.; Gaspar, P. P.; Harrington, C. R.; Leigh, W. J.; Vargas-Baca, I.; Walsh, R.; Zhou, D. J. Am. Chem. Soc. **2005**, 127, 17469.

⁽²⁰⁾ Watta, B.; Neumann, W. P.; Sauer, J. Organometallics 1985, 4, 1954.

⁽²¹⁾ Dräger, M.; Mathiasch, B.; Ross, L.; Ross, M. Z. Anorg. Allg. Chem. 1983, 506, 99.



Scheme 7

41%, and a 90% yield of 2,3-dimethylbutadiene was observed by 1 H NMR.

When reaction mixtures containing mixtures of dimethylstannylene oligomers were exposed to air, white solids precipitated that were no longer soluble in common organic solvents. These were presumed to be oligomers of dimethylstannylene oxide $(Me_2SnO)_n$, observed as oxidation products of dimethylstannylene oligomers by Neumann.³

Pyrolysis of 1,1-diphenyl-1-stannacyclopent-3-ene in benzened₆ in the range 355.5 to 403.2 K also led to first-order disappearance of the stannacyclopentene. Doubling its concentration did not alter the first-order rate constant. ¹H NMR yields of butadiene declined from 100% at the beginning of the pyrolysis to ca. 80% at the end (3 half-lives). The insolubility of the bulk of the oligomers of diphenylstannylene led to the observation of only a trace of $(Ph_2Sn)_6$ by ¹¹⁹Sn NMR spectroscopy as a peak at -216 ppm (lit. [CDCl₃]²¹ -208 ppm).

1,1-Di-tert-butyl-1-stannacyclopent-3-ene possesses much higher thermal stability than the corresponding methyl and phenyl compounds; no thermal decomposition was noted after 24 h at 100 °C (373.1 K) in toluene solution. First-order disappearance was observed in the range 414.5 to 448.6 K. No cyclo-(t-Bu₂Sn)₄, the only known cyclic oligomer of t-Bu₂-Sn:²² was detected by ¹¹⁹Sn NMR in the reaction mixtures, but it was found that cyclo-(t-Bu₂Sn)₄ was unstable under these reaction conditions. Heating a suspension of authentic cyclic tetramer in toluene (insoluble at room temperature) at 414.5 K for 65 min led to marked decomposition: the reaction mixture turned black, and insoluble products were formed. The reaction mixtures containing the di-tert-butylstannacyclopentene also turned black and deposited precipitates as well as a tin mirror. Butadiene yields were ca. 70% at the beginning of the pyrolysis, but fell to 15-20% at the end, due to self-condensation of the butadiene. Addition of a scavenger for carbon-centered radicals, 2,6-di-tert-butyl-4-hydroxytoluene (BHT), did not alter the rate of pyrolysis or of the loss of butadiene.

Activation parameters for the pyrolysis of several of the 1-stannacyclopent-3-enes were determined in a series of experiments in which the temperature dependence of the first-order rate constants, presented in Tables 2, 3, and 4, was measured. The E_a and log A activation parameters were obtained from the slope and intercept, respectively, of Arrhenius plots of the observed rate constants vs 1/T. The ΔH^{\ddagger} and ΔS^{\ddagger} activation parameters were computed from the slope and intercept, respectively, of Eyring plots of $\ln(k_{obs}/T)$ vs 1/T. Representative Arrhenius and Eyring plots are shown in Figures 3 and 4, respectively, and the others are included in the Supporting Information.

The first-order loss of 1,1-disubstituted-1-stannacyclopent-3-enes observed upon their heating in an inert solvent, together with a high yield of butadiene product, is compatible with a stannylene extrusion mechanism. The small effect observed of BHT radical scavenger and 2,3-dimethylbutadiene on the diphenyl and di-tert-butyl systems suggests a limited role for carbon-centered free-radical intermediates. In the diphenyl and di-tert-butyl cases, for which the diene can compete for the stannylene with oligomerization (vide infra), the modest reduction in the pyrolysis rate in the presence of 2,3-dimethylbutadiene may be due to induced decomposition, but the small effect of BHT and 2,3-dimethylbutadiene on the activation parameters suggests that unimolecular decomposition is the major pathway for the loss of the 1-stannacyclopent-3-enes studied upon heating. The rate reduction in the presence of 2,3-butadiene may also be a sign of readdition to butadiene in the absence of a trapping agent for *t*-Bu₂Sn:.

Product Studies of the Pyrolyses of 1-Stannacyclopent-3enes in the Presence of Dienes. 1,1-Dimethyl-1-stannacyclopent-3-ene (4). 1,1-Dimethyl-1-stannacyclopent-3-ene (4) was subjected to pyrolysis at 100 °C in neat 2,3-dimethylbutadiene, and the reaction was monitored by ¹H NMR spectroscopy. After 4 h, conversion was 32%, and the products observed were butadiene, (Me₂Sn)₆, and stannylene adduct 1,1,3,4-tetramethyl-1-stannacyclopent-3-ene (18) in absolute yields of 70%, 50%, and 12%, respectively. After 9 h the conversion was 62% and the product yields were 92%, 42%, and 9%, respectively. Exposure of the reaction mixture to air resulted in the formation of white solids from oxidation of the tin oligomer (see Scheme 10).

When 1,1-dimethyl-1-stannacyclopent-3-ene (4) was subjected to pyrolysis under similar conditions for 4 h at 100 °C in C_6D_6 (0.082 M in 4 containing a lower concentration, 0.11 M, of 2,3-dimethylbutadiene), the conversion was 43%, and a 51% yield of dimethylstannylene oligomers was observed in the ¹H NMR spectrum as broad peaks at 0.4–0.8 ppm. Spectral interference from the 2,3-dimethylbutadiene prevented the determination of the butadiene yield. None of the stannylene adduct, 1,1,3,4-tetramethyl-1-stannacylopent-3-ene (18), was observed by ¹H NMR, but GC/MS analysis of the reaction mixture revealed its formation in <1% yield. The stannylene

⁽²²⁾ Neumann, W. P.; Pedain, J.; Sommer, R. Ann. Chem. 1966, 694, 9.

Scheme 8







oligomers precipitated as white solids when the reaction mixture was dissolved in dry hexane and exposed to air.

Upon pyrolysis of 1,1,3,4-tetramethyl-1-stannacyclopent-3ene (**18**) in neat 1,3-butadiene at 100 °C for 4 h, ¹H NMR assay of the residue after evaporation of butadiene indicated a 5% yield of 1,1-dimethyl-1-stannacyclopent-3-ene (**4**) and a 31% yield of *cyclo*-(SnMe₂)₆, some of which was lost by oxidation during the workup.

Control Experiments for 1,1-Dimethyl-1-stannacyclopent-3-ene (4). In a control experiment (see Supporting Information) the presence of MeI led at most to a small depression of the conversion of **4** upon pyrolysis, the yield of stannylene oligomers, the rate of $Me_2Sn:$ (3) extrusion, and the yield of the formal adduct of $Me_2Sn:$ (3) to 2,3-dimethylbutadiene.



Figure 1. First-order kinetic plot for the pyrolysis of 1,1-dimethyl-1-stannacyclopent-3-ene (4) in benzene- d_6 at 373.1 K.

Radical intermediates scavengeable by MeI do not seem to play a significant role in this chemistry.

Authentic *cyclo*- $(Me_2Sn)_6^{20}$ was employed to examine the role of dimethylstannylene oligomers in the pyrolysis of 1,1dimethyl-1-stannacyclopent-3-enes (see Supporting Information). When 1,1-dimethyl-1-stannacyclopent-3-ene (**4**) was subjected to pyrolysis in neat 2,3-dimethylbutadiene for 8 h or less, greater than 80% of the 1,1,3,4-tetramethyl-1-stannacyclopent-3-ene (**18**) product arises from addition of free Me₂Sn: (**3**). The presence of dimethylstannylene oligomers does not affect the rate of decomposition of **4** but does reduce the rate of formation of the Me₂Sn: (**3**) adduct 1,1,3,4-tetramethyl-1stannacyclopent-3-ene (**18**) by competition between the dimethylstannylene oligomer and 2,3-dimethylbutadiene for free stannylene **3**. The oligomer is ca. 130 times as reactive as 2,3dimethylbutadiene toward stannylene **3**.

Pyrolysis of 1,1-Dimethyl-1-stannacylopent-3-ene (4) in the Presence of Other Potential Stannylene Trapping Agents. As previously mentioned, the formation of products expected from the insertion of *n*-Bu₂Sn: into carbon-halogen bonds of several alkyl halides was taken as support for the intermediacy of the free stannylene in the pyrolysis of Cl(n-Bu₂Sn)₂Cl in 1:6 mixtures with the alkyl halide at 120-130 $^{\circ}C.^{6}$ The rate of loss of the Cl(*n*-Bu₂Sn)₂Cl was unaffected by the presence of alkyl halide. The stability under the reaction conditions of the dibutyltin oligomers that were also formed was believed to preclude their participation in product formation.⁶ Similar evidence was cited for the formation of Et₂Sn: and Me₂Sn: (3) in the pyrolysis of Et₃SnSnEt₂Br (100 °C), Me₃SnSnMe₂Br (20 °C), and ClMe₂SnSnMe₂Cl (50 °C), respectively.²³ All these halodistannane decompositions were reported as being accelerated by light.

With the thermal extrusion of free dimethylstannylene (3) from 1,1-dimethyl-1-stannacyclopent-3-enes 4 and 18 having been placed on a firm footing by the kinetic studies reported here, it was decided to examine the reactions of free Me_2Sn : (3) with several haloalkanes.

CDCl₃. 4 was heated in neat CDCl₃ for 6 h at 100 °C, and the reaction was monitored by ¹H NMR; 42% conversion led to a 75% yield of butadiene and a 76% yield of dimethylstannylene oligomers. No NMR peaks attributable to the C–Cl insertion product from Me₂Sn: (**3**), (CH₃)₂Sn(CDCl₂)Cl, were observed. Authentic (CH₃)₂Sn(CHCl₂)Cl was synthesized and

⁽²³⁾ Grugel, C.; Neumann, W. P.; Seifert, P. Tetrahedron Lett. 1977, 18, 2205.

Table 1. First-Order Rate Constants for Pyrolysis of 1-Stannacyclopent-3-enes at 373.1 K

		rate constant (s ⁻¹) at 373.1 K	
substrate	cyclohexane- <i>d</i> ₁₂	2,3-dimethylbutadiene	benzene-d ₆
1,1-dimethyl-1-stannacyclopent-3-ene (4)	$2.01 \pm 0.02 \times 10^{-5}$	$2.60 \pm 0.02 \times 10^{-5}$	$3.12 \pm 0.02 \times 10^{-5}$
1,1,3,4-tetramethyl-1-stannacyclopent-3-ene (18)	$2.52 \pm 0.03 \times 10^{-5}$	$2.75 \pm 0.02 \times 10^{-5}$	$3.79 \pm 0.04 \times 10^{-5}$

Table 2. Temperature Dependence of First-Order Rate Constants (units: 10⁻⁵ s⁻¹) and Activation Parameters (units: kcal·mol⁻¹, cal·mol⁻¹·K⁻¹, s⁻¹) for the Pyrolysis of 1,1-Dimethyl-1-stannacyclopent-3-ene (4) in Benzene-*d*₆ and

Cycloboyano d

Cyclonexane-u ₁₂				
	rate constants	$(\times 10^{-5} \text{ s}^{-1})$		
T, °C	in C ₆ D ₆	in C ₆ D ₁₂		
87.4	0.73 ± 0.02			
88.0		0.46 ± 0.01		
100.0	3.12 ± 0.02	2.01 ± 0.02		
110.6	9.29 ± 0.08	5.52 ± 0.20		
126.0	43.8 ± 1.3	27.3 ± 0.9		
E_a	30.1 ± 0.2	30.2 ± 0.3		
log A	13.2 ± 0.3	13.0 ± 0.8		
ΔH^{\ddagger}	29.4 ± 0.2	29.4 ± 0.3		
ΔS^{\ddagger}	0.9 ± 0.5	-1.6 ± 0.8		

Table 3. Temperature Dependence of First-Order Rate Constants(units: $10^{-5} s^{-1}$) and Activation Parameters (units: kcal·mol⁻¹,
cal·mol⁻¹·K⁻¹, s⁻¹) for the Pyrolysis of

1,1-Diphenyl-1-stannacyclopent-3-ene in Benzene-d₆

	rate	rate constants ($\times 10^{-5} \text{ s}^{-1}$)			
<i>T</i> , °C	in C ₆ D ₆	in C ₆ D ₆ ^a	in C ₆ D ₆ ^b		
82.2	2.74 ± 0.07				
82.4		2.26 ± 0.05			
82.6			2.59 ± 0.31		
100.0	20.03 ± 0.70	16.35 ± 0.32	13.80 ± 1.07		
110.4		51.27 ± 1.55	75.08 ± 10.26		
110.6	57.17 ± 2.34				
130.1		189.21 ± 1.37	194.09 ± 10.13		
130.4	335.88 ± 1.40				
E_a	28.3 ± 0.1	25.6 ± 0.1	25.8 ± 0.7		
log A	12.8 ± 0.2	11.2 ± 0.2	11.3 ± 0.9		
ΔH^{\ddagger}	27.5 ± 0.1	28.2 ± 0.3	25.0 ± 0.7		
ΔS^{\ddagger}	-2.2 ± 0.2	-0.8 ± 0.8	-9.4 ± 1.7		

 a Solution contains BHT. b Solution contains BHT and 2,3-dimethylbutadiene.

shown to be stable at 100 °C for 4 h in C₆D₆. A mixture of the stannacyclopentene **4** and $(CH_3)_2Sn(CHCl_2)Cl$ heated at 100 °C for 4 h in C₆D₆ led to a 10% loss of the latter compound and 42% decomposition of stannacyclopentene **4** with a 100% yield of butadiene and a 64% yield of dimethylstannylene oligomers. These control experiments suggested that thermally generated Me₂Sn: was not trapped by CDCl₃ under the conditions employed.

CH₂Cl₂. 4 was similarly heated in neat CH₂Cl₂ at 100 °C for 6 h and monitored by ¹H NMR; 45% conversion led to yields of butadiene and dimethylstannylene oligomers of 100% and 77%, respectively. Absence of other ¹H NMR signals suggested that thermally generated Me₂Sn: (**3**) was not trapped by CH₂Cl₂, but stability studies were not carried out on the known authentic insertion product (CH₃)₂Sn(CH₂Cl)Cl.

EtBr. 4 was similarly heated in neat EtBr at 100 °C for 4 h and monitored by ¹H NMR; 42% conversion led to yields of butadiene and dimethylstannylene oligomers of 84% and 65%, respectively. No other products were observed by ¹H NMR, and neither EtMe₂SnBr nor any other products containing Br were observed by GC/MS analysis. Me₂Sn: (**3**) does not appear to be trapped by EtBr under the conditions employed. Since the reaction mixture was shielded from light, it was also found that dimethylstannylene oligomers do not react with EtBr in the absence of light under these conditions.

 Table 4. Temperature Dependence of First-Order Rate Constants (units: 10⁻⁵ s⁻¹) and Activation Parameters (units: kcal·mol⁻¹, cal·mol⁻¹·K⁻¹, s⁻¹) for the Pyrolysis of 1,1-Di-*tert*-butyl-1-stannacyclopent-3-ene in Toluene-d₈

	rate	rate constants ($\times 10^{-5} \text{ s}^{-1}$)			
<i>T</i> , °C	in C ₇ D ₈	in C ₇ D ₈ ^a	in C ₇ D ₈ ^b		
141.4	2.35 ± 0.09	2.15 ± 0.04	1.89 ± 0.06		
155.6	10.23 ± 0.24	9.27 ± 0.10	10.19 ± 0.33		
163.1	22.34 ± 0.33	20.02 ± 0.75	18.81 ± 0.37		
175.5	73.70 ± 3.31	61.51 ± 2.40	64.03 ± 1.50		
E_a	37.5 ± 0.6	36.4 ± 0.4	37.7 ± 0.4		
$\log A$	15.1 ± 0.6	14.5 ± 0.5	15.2 ± 0.5		
ΔH^{\ddagger}	36.6 ± 0.6	35.6 ± 0.4	36.9 ± 0.4		
ΔS^{\ddagger}	8.0 ± 0.6	5.3 ± 0.9	8.7 ± 1.0		

 a Solution contains BHT. b Solution contains BHT and 2,3-dimethylbutadiene.



Figure 2. First-order kinetic plot for the pyrolysis of 1,1,3,4-tetramethyl-1-stannacyclopent-3-ene (**18**) in 2,3-dimethylbutadiene at 373.1 K.

Control experiments (see Supporting Information) indicated that at longer times (100 °C, 14 h) dimethylstannylene oligomers react with EtBr to give the product of formal stannylene insertion into the C–Br bond of EtBr, EtMe₂SnBr. When the reaction mixture is exposed to light, the reaction of oligomer with EtBr is rapid even at room temperature.

MeI. When solutions 0.25 M in **4** and 2.1 M in MeI, degassed, sealed, and protected from light were heated at 100 °C for 5 h in C_6D_6 or cyclohexane- d_{12} , conversions of 48% and 33% respectively led to 84% and 100% yields of butadiene, respectively, and 73% and 79% yields of dimethylstannylene oligomers, as determined by ¹H NMR. No Sn–I insertion product Me₃SnI was detected, although it is stable under these conditions. When a 0.25 M solution of **4** in neat MeI was subjected to the same reaction conditions, 55% conversion led to the observation of butadiene and Me₃SnI in 90% and 31% yields, respectively, but no dimethylstannylene oligomer was observed. It appeared that direct reaction of dimethylstannylene oligomers with MeI contributed to the formation of Me₃SnI in the latter experiment.

Control experiments (see Supporting Information) with authentic dimethylstannylene oligomers indicated that the oligomers react with MeI forming the product of formal C–I bond



Figure 3. Arrhenius plot for the pyrolysis of 1,1-dimethyl-1stannacyclopent-3-ene (**4**) in benzene- d_6 solution in the temperature range 87.4 to 126.0 °C.



Figure 4. Eyring plot for the pyrolysis of 1,1-di-*tert*-butyl-1-stannacyclopent-3-ene in benzene- d_6 solution containing 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) radical scavenger and 2,3-dimeth-ylbutadiene stannylene trapping agent in the temperature range 141.4 to 175.5 °C.



insertion by stannylene **3**, Me₃SnI, in quantitative yield under both thermal (100 $^{\circ}$ C, 14 h) and daylight-induced (rt, 5 min) conditions. In the absence of light the reaction of the oligomer with MeI was slow at room temperature.

3-Hexyne. Trapping reactions of Me₂Ge: with alkynes are known to produce adducts containing two units of the germylene, 1,1,4,4-tetramethyl-1,4-digermacyclohexa-2,5-dienes.²⁴ Seeking an analogous reaction of dimethylstannylene **3**, 0.25 M solutions of **4** in C₆D₆ containing 1.7 M 3-hexyne were subjected to pyrolysis at 100 °C for periods of 4 and 8 h. The formation of butadiene and dimethylstannylene oligomers in high yield was revealed by ¹H NMR, but neither NMR nor GC/ MS analysis of the reaction mixture gave any indication of the formation of the expected stannylene-alkyne adduct 2,3,5,6-tetraethyl-1,1,4,4-tetramethyl-1,4-distannacyclohexa-2,5-diene. A pair of similar pyrolysis experiments with **4** in neat 3-hexyne gave similar results.

Trimethyltin Hydride, Me₃SnH. Having found that Me₂Sn: (3) photochemically generated from 4 was trapped by insertion into the H-Sn bond of Me₃SnH,¹⁹ it was expected that thermally generated 3 would also undergo this trapping reaction. The results, however, were ambiguous. When a 0.29 M solution of 4 in Me₃SnH was heated at 89.0 °C, 29% conversion after 14 h and 50% after 26 h were found. No butadiene coproduct nor dimethylstannylene oligomers were detected. The reaction mixture had not been shielded from ambient light. Analysis of the volatiles by GC/MS led to the detection of Me₃SnSnHMe₂, Me₃SnSnMe₃, and Me₃SnSnMe₂SnMe₃ in a ratio of 1.3:1:1.6. These products in ratio 1:4.5:2.8 were also formed when a 0.67 M solution of dimethylstannylene oligomers in Me₃SnH was prepared. The oligomers were largely insoluble until the suspension was exposed to daylight. Then they dissolved within 2 h, and within 5 h the yellow color associated with the oligomers in solution disappeared. The volatiles were analyzed by GC/MS. Under these conditions oligomerization of any free $Me_2Sn:$ (3) formed from 4 and reaction of the oligomers with Me₃SnH is indicated as the major source of the volatile tin products. The absence of the butadiene coproduct of stannylene extrusion may be due to its consumption by radical chain processes involving the tin hydrides.

Pyrolysis of 1,1-Diphenyl-1-stannacyclopent-3-ene and 1,1-Di-tert-butyl-1-stannacyclopent-3-ene in the Presence of Trapping Agents. Diphenyldisulfide, Ph₂S₂. Neumann reported that Me₂Sn: (3) from the pyrolysis of ClMe₂SnSnMe₂Cl at 37 °C in a benzene solution of Ph2S2 gave a quantitative yield of the S-S insertion product Me₂Sn(SPh)₂.²³ With t-Bu₂S₂, only dimethylstannylene oligomers were obtained.³³ We decided to determine whether Ph₂Sn: upon thermal extrusion from a stannacyclopent-3-ene would undergo reaction with Ph₂S₂. A C₆D₆ solution containing 0.031 M 1,1-diphenyl-1-stannacyclopent-3-ene and 0.5 M Ph2S2 was heated at 100 °C and monitored by NMR spectroscopy. The loss of the stannacyclopent-3-ene followed a first-order rate law with a rate constant 15% greater than in the absence of Ph_2S_2 . After 45 min conversion was 48% and the butadiene yield was ca. 60%. Ph₂Sn(SPh)₂ was found in >90% yield, as gauged by ¹H NMR, but no diphenylstannylene oligomer was found.

When a similar pyrolysis experiment was carried out with 1,1-di-*tert*-butyl-1-stannacyclopent-3-ene at 140 °C, 53% conversion was observed at the end of 1.6 h, and the formal S–S insertion product t-Bu₂Sn(SPh)₂ was formed in >95% yield as determined by ¹H NMR, with a butadiene yield of ca. 60%, but the first-order rate constant was significantly enhanced (by a factor of 5) above that observed in the absence of Ph₂S₂. No (*t*-Bu₂Sn)₄, the only known oligomer of *t*-Bu₂Sn:, was observed. It appears that at 140 °C, direct reaction of the trapping agent with the 1,1-di-*tert*-butyl-1-stannacyclopent-3-ene takes place.

2,3-Dimethylbutadiene. In the kinetic studies of the pyrolysis of 1,1-diphenyl- and 1,1-di-*tert*-butyl-1-stannacyclopent-3-ene, those carried out in the presence of 2,3-dimethylbutadiene led to the formation of the corresponding 3,4-dimethyl-1-stanna-

^{(24) (}a) Billeb, G.; Neumann, W. P.; Steinhoff, G. *Tetrahedron Lett.* **1988**, 29, 5245. (b) Johnson, F.; Gohlke, R. S.; Nasulavicus, W. A. *J. Organomet. Chem.* **1965**, *3*, 233. (c) Vol'pin, M. E.; Struchkov, Yu.T.; Vilkov, L. V.; Mastryukov, V. S.; Dulova, V. G.; Kusanov, D. N. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1963**, 2067. (d) Johnson, F.; Gohlke, R. S. *Tetrahedron Lett.* **1962**, 1291.

⁽²⁵⁾ Dewar, M. J. S.; Friedheim, J. E.; Grady, G. L. Organometallics 1985, 4, 1784.

cyclopent-3-ene, characterized by comparison with the authentic compounds. Solutions of 0.031 M of the diphenylstannacyclopentene in C_6D_6 containing 5% (0.44 M) 2,3-dimethylbutadiene were heated at 82.6, 100.0, 110.6, and 126.0 °C, and the kinetic measurements are reported in Table 3. Yields determined by ¹H NMR were butadiene, 60% to 90%, and 3,4-dimethyl-1,2-diphenyl-1-stannacyclopent-3-ene adduct, characterized by comparison with authentic material, ca. 30%. Oligomer (Ph₂Sn)₆ was formed, but its yield could not be determined.

Solutions of 0.035 M of 1,1-di-tert-butyl-1-stannacyclopent-3-ene in toluene- d_8 containing 5% (0.44M) 2,3-dimethylbutadiene were heated at 141.4, 155.6, 163.1, and 175.5 °C, and the kinetic measurements are reported in Table 4. Yields determined by ¹H NMR were butadiene, decreasing from 85% at the beginning of the reaction to ca. 30%, and 1,1-di-tertbutyl-3,4-dimethyl-1-stannacyclopent-3-ene adduct, characterized by comparison with authentic material, 75% to 83%. The presence of the dimethylbutadiene led to <10% change in the measured first-order rate constants, as shown in Table 4. The cyclic tetramer cyclo-(Sn-t-Bu₂)₄, the only known oligomer of di-tert-butylstannylene, is unstable under the conditions that 1,1-di-tert-butyl-1-stannacyclopent-3-ene underwent pyrolysis. When a solution (initially a suspension) of cyclo-(Sn-t-Bu₂)₄ in toluene-d₈ containing 5% (0.44 M) 2,3-dimethylbutadiene was heated at 140 °C, decomposition was noted within 4 h as indicated by the formation of insoluble material and the darkening of the reaction mixture. At 4.38 h, a 43% yield of the stannylene-diene adduct was recorded by ¹H NMR, and this rose to 56% after 19.5 h. Thus it is possible that oligomer did form during the stannacyclopentene pyrolysis and its decomposition under the reaction conditions contributed to the high yield of stannylene-diene adduct observed upon stannacyclopentene pyrolysis.

The increasing yield of formal 1,4-adducts with increasing steric congestion at the tin atom, Me < Ph < t-Bu, is understandable in light of the finding¹⁹ that oligomerization of Me₂Sn: is initiated by a second-order dimerization. Reduction of the dimerization rate, second-order in stannylene concentration, is expected to be greater than the reduction in the rate of reaction with 2,3-dimethylbutadiene, which is first-order in stannylene concentration. Thus addition competes with oligomerization more effectively, the larger the substituent. Tetramethyldistannene, Me₂Sn=SnMe₂, has been found <u>not</u> to dissociate to Me₂Sn: (**3**) at room temperature,¹⁹ so it is unlikely that the steric effect is exerted on distannene dissociation.

Mechanism of Stannylene Extrusion from 1-Stannacyclopent-3-enes and the Reverse Process, Addition of Stannylenes to Butadiene. Neither the mechanism of stannylene extrusion from 1,1-stannacyclopent-3-enes nor the reverse process, the addition of stannylenes to 1,3-dienes, has received much attention. Neumann reported in 1984 that reaction of five stannylenes in solution with a pair of diasteromeric bis(allenes), shown in Scheme 6, was compatible with a stereospecific chelotropic process, concerted 1,4-addition.¹ⁿ Shortly thereafter Dewar reported that MNDO semiempirical calculations on the 1,4-addition of SnBr₂ to butadiene predicted a synchronous process via a symmetrical transition state.²⁵ An activation barrier of 19.5 kcal/mol was predicted.



Figure 5. Transition structure from ref 26 for the extrusion of $Me_2Sn:$ (3) from 1,1-dimethyl-1-stannacyclopent-3-ene (4) calculated at B3LYP/6-31G(d,p)/LANL2DZ (for Sn).



Reaction coordinate

Figure 6. Predicted B3LYP energy profile from ref 26 for addition of $Me_2Sn:$ (**3**) to 1,3-butadiene and the retro-addition, extrusion of $Me_2Sn:$ (**3**) from 1,1-dimethyl-1-stannacyclopent-3-ene (**4**).

Our recent computational studies²⁶ point to asynchronous concerted 1,4-addition and retroaddition as the exclusive pathways connecting Me₂Sn: (3) and butadiene with 1,1dimethylstannacyclopent-3-ene (4). The transition structure for the extrusion of Me₂Sn: (3) from stannacyclopent-3-ene 4 calculated at B3LYP/6-31G(d,P) for C and H, LANL2DZ for Sn is shown in Figure 5. An energy profile is shown in Figure 6, and B3LYP predictions of the energies²⁶ are included in the Supporting Information. The ball-and-stick models shown with the structures of the stationary states along the reaction coordinate are representations of the theoretical predictions. The favored concerted pathway is comprised of Sn1 = 4; Sn2, the transition structure for extrusion of 3 from 4; Sn3, an association complex between 3 and butadiene leading to 1,4-addition; and Sn4 = 3 plus butadiene. The disfavored stepwise pathway is comprised of Sn1 = 4; Sn5, the transition structure for the rearrangement connecting 4 and vinvlstannirane Sn6: Sn7, the transition structure for 1,2-addition and retroaddition of 3 and butadiene; Sn8, an association complex of 3 and butadiene leading to 1,2-addition, differing in structure from but isoenergetic with Sn3; and Sn4 = free 3 plus butadiene.

According to our calculations,²⁶ 1,1-dimethyl-2-vinylstannirane is a local minimum on the potential surface, but it is highly unstable, protected from dissociation to the corresponding stannylene and butadiene by a barrier of less than 1 kcal/mol. Its barrier for rearrangement to the stannacyclopentene is ca.

⁽²⁶⁾ Nag, M.; Gaspar, P. P. A computational study of the mechanism of addition of singlet carbene analogs to 1,3-butadiene to form 1,1-dimethyl-1-metallacylopent-3-enes [*cyclo*-Me₂MCH₂CH=CHCH₂, M = Si, Ge, Sn] and its reverse retro-addition reaction. *Organometallics*, in preparation.

⁽²⁷⁾ Gross, L. W.; Moser, R.; Neumann, W. P.; Scherping, K. H. Tetrahedron Lett. 1975, 23, 635.

Synthesis of 1-Stannacyclopent-3-enes

22 kcal/mol. The intrinsic reaction coordinate (irc) calculated for the extrusion of $Me_2Sn: (3)$ from stannacyclopent-3-ene (4) does not traverse a vinylstannirane structure.

The pathway favored by these calculations is a concerted but asynchronous 1,4-addition and retroaddition with barriers of 2 and 31.8 kcal/mol, respectively. The computationally predicted gas phase enthalpy barrier (see Supporting Information) of 31.75 kcal/mol calculated at 106 °C (average temperature used in pyrolyses experiments) is in reasonable agreement with the experimental values of 29.4 ± 0.2 (C₆D₆) and 29.2 ± 0.3 (C₆D₁₂) reported here.

Summary

Condensation of magnesium-1,3-diene complexes and dichlorodiorganostannanes in THF produces stannacyclopent-3-enes that can, in favorable cases, be separated in high purity from their polystannane coproducts, thus rendering their modest yields preparatively useful. The pyrolyses of 1,1-dimethyl, 1,1diphenyl, 1,1-di-tert-buyl, and 1,1,3,4-tetramethyl-1-stannacyclopent-3-enes were all first-order processes whose rates were independent of stannacyclopentene concentration, compatible with unimolecular thermal extrusion of the corresponding diorganostannylene. A small effect of carbon-centered radical scavenger and diene trapping agent on the reaction rate suggests no more than a minor role for radical intermediates. In the case of the smallest substituent, addition of Me₂Sn: (3) to butadiene and 1,3-dimethylbutadiene to form stannacyclopent-3-enes 4 and 18 was much slower than oligomerization, with addition yields of ca. 5% compared with >40% yields of dimethylstannylene oligomers. The oligomerization had been found in kinetic spectroscopy experiments to be initiated by dimerization at nearly the diffusion-controlled rate.¹⁹

The oligomers are themselves stannylenoids, but, when protected from light, they make at most minor contributions to the formation of stannylene-diene adducts. The dimethylstannylene oligomers compete with dienes for free $Me_2Sn: (3)$ but do not induce decomposition of stannacylopent-3-enes. In the absence of light, substrates previously believed to trap diorganostannylenes, e.g., chloroform, methylene chloride, ethyl bromide, and methyl iodide, were found not to undergo reaction with thermally generated Me_2Sn : (3), but dimethylstannylene oligomers were found to react with EtBr and MeI. Me₃SnH was found previously to undergo H-Sn insertion by photochemically generated $Me_2Sn:$ (3), but under thermal reaction conditions reaction of dimethylstannylene oligomers with Me₃SnH was the major source of the volatile tin-containing products, including Me₃SnSnHMe₂, Me₃SnSnMe₃, and Me₃SnSnMe₂SnMe₃. Insertion of Ph₂Sn: into the S-S bond of Ph₂S₂ previously suggested by Neumann²⁷ was confirmed.

Concerted 1,4-addition of several stannylenes to 1,3-dienes had been suggested on the basis of the stereospecificity experimentally observed and theoretically predicted by semiempirical molecular orbital calculations. The mechanism of Me₂Sn: (3) addition to 1,3-butadiene has been probed by hybrid density functional calculations that supported a concerted asynchronous 1,4-addition mechanism with vinylstannirane intermediates playing a negligible role due to their low thermal stability.

Experimental Section

General Instrumentation. ¹H NMR spectra were recorded on a Varian Unity-300 (300 MHz), a Varian Unity-500 (500 MHz), or a Varian Unity-600 (600 MHz) NMR spectrometer. Unless 500 or 600 MHz is specified, the spectrum was recorded at 300 MHz. Benzene- d_6 or chloroform-d was used as the solvent. The small amount of protiated benzene impurity in benzene- d_6 was used as an internal standard (δ 7.15 ppm). In the case of chloroform-d, the peak from CHCl₃ at δ 7.25 ppm was used as an internal standard. All coupling constants (J) are given in hertz (Hz). Splitting patterns are typically described as follows: s, singlet; d, doublet; t, triplet; m, multiplet. ¹³C NMR spectra were recorded on a Varian Unity-300 (75.4 MHz), a Varian Unity-500 (125 MHz), or a Varian Unity-600 (150 MHz) NMR spectrometer. Unless otherwise indicated, they are proton decoupled. Unless 125 or 150 MHz is specified, the spectrum was recorded at 75.4 MHz. Benzene- d_6 or chloroform-d was used as solvent. The peaks from benzene- d_6 at δ 128.0 ppm or the peak from chloroform-d at δ 77.0 ppm was used as the internal standard in that solvent. All ¹H and ¹³C chemical shifts were reported as parts per million (ppm) downfield from tetramethylsilane (TMS). 119Sn NMR spectra were recorded on a Varian Unity-300 (111.9 MHz) NMR spectrometer employing Me₄Sn as the external standard. All spectra were recorded with proton decoupling, and all chemical shifts were reported as ppm downfield from Me₄Sn. All NMR spectra were recorded at room temperature.

High-resolution mass spectra data were recorded on a VG ZAB-SE mass spectrometer in the Washington University MS Facility; GC/MS data were recorded on an HP 5890A instrument coupled with a HP integrator or on a Thermo Finnigan QIT GC/MS. The GC/MS data are all 70 eV EI spectra. Ultraviolet spectral data were recorded on a Varian Cary 219 spectrometer with baseline correction. Uncorrected melting points were measured on a Thomas-Hoover capillary melting point apparatus. The preparative GC was constructed in this laboratory with dual rhenium tungsten filaments as the thermal conductivity detector.

Materials. Unless otherwise indicated, all chemicals used for the reactions were reagent grade quality. Liquid compounds were distilled before use, and solids were used as supplied or dried as appropriate. Diethyl ether, benzene, and tetrahydrofuran were distilled from a blue solution of the benzophenone sodium ketyl under nitrogen and used immediately. Pentane and hexane were distilled from calcium hydride under nitrogen. Methylene chloride was distilled from phosphorus pentoxide under nitrogen. Preparative reactions were carried out under dry N2.

2,3-Dimethylbutadiene (99%), 3-hexyne (99%), n-Bu₂O (anhydrous, 99.3%), LiAlH₄ (95%), MgCl₂ (99.9%, anhydrous), Li powder (99%, Na 0.5%), MeI (99.5%), Na (99%), 1,3-butadiene (99+%), Mg turnings (98%), Me₄Sn (95%), Ph₂SnCl₂ (96%), 1,4diphenyl-1,3-butadiene (98%), 9-borabicyclo[3.3.1]nonane (98%), CH2=CHBr (98%), (Me3Si)2CHCl (97%), Me2NH (99.5%), and n-BuLi (1.6 M, hexanes) were obtained from Aldrich Chemicals, Me_2SnCl_2 (98+%) was obtained from TCI America, *n*-Bu₂SnCl₂ and Me₃SnCl were obtained from Gelest, and SnCl₂ (98%) was obtained from Fisher Scientific.

Me₃SnH, Me₂SnH₂ were synthesized by the method of Finholt et al.28

Me₂Sn(NEt₂)₂ was synthesized by the method of Jones and Lappert.30

Dimethylstannylene oligomers (Me₂Sn)_n were synthesized by the method of Watta, Neumann, and Sauer.²⁰

Detailed experimental procedures for the preparation of the above compounds can be found in the Supporting Information.

Magnesium-butadiene complex from magnesium turnings (MgBD) was synthesized by the method of Fujita et al.³³ To a 250 mL heavy duty Schlenk flask with a magnetic stirring bar was added 20 g (0.83 mol) of magnesium turnings, which were flame dried in the flask under vacuum. Then 125 mL of freshly dried and distilled

⁽²⁸⁾ Finholt, A. E.; Bond, A. C.; Wilzbach, K. E.; Schlesinger, H. J. Am. Chem. Soc. 1947. 69. 2692.

⁽²⁹⁾ Birchall, T.; Pereira, A. R. J. Chem. Soc., Dalton Trans. 1975, 1087. (30) Jones, J.; Lappert, M. F. J. Chem. Soc. 1965, 1944.

THF was transferred to the Schlenk flask via a cannula, and 0.3 mL of 1,2-dibromoethane was added by syringe. The flask was cooled in a dry ice—acetone bath so that butadiene (12 g, 0.22 mol), condensed and weighed in a 50 mL Schlenk flask containing ca. 4 g of P_2O_5 as drying agent, could be transferred and condensed under vacuum. The flask was closed and heated in a 37 °C water bath while the mixture was being stirred rapidly. The reaction mixture became cloudy within hours, and a quantity of slightly yellow solids was formed overnight. After 3 days, so much solid had formed that the reaction mixture was difficult to stir, and the reaction was stopped.

The suspension of magnesium-butadiene complex in THF was transferred to a 250 mL Schlenk flask via a cannula. The solids settled, and the top layer was removed via a cannula. Two potions of 50 mL of THF were used to wash the solids. The washed yellow solids were stored in THF as a dispersion before use.

The yield of magnesium-butadiene complex was estimated to be almost 100% based on the magnesium consumed and the butadiene added. The complex was tested by reaction with Ph_2SiCl_2 in THF to form 1,1-diphenyl-1-silacyclopent-3-ene as the only product observed by GC/MS.¹⁷

Caution. Magnesium-butadiene complex is <u>EXTREMELY</u> <u>FLAMMABLE</u>; it must be kept in THF with the exclusion of air. Dry magnesium-butadiene complex may burn in air.

Magnesium-2,3-dimethylbutadiene complex (Mg*DMB) from activated Mg was synthesized by the method of Rieke.³⁴ Activated magnesium (Mg*) from 0.29 g (42 mmol) of lithium wire, 5.9 g (46 mmol) of naphthalene, and 2.0 g (21 mmol) of anhydrous MgCl₂ were added to 40 mL of freshly distilled THF. Then 1.64 g (20 mmol) of 2,3-dimethylbutadiene was dried in a Schlenk flask containing 5 g of P₂O₅ as drying agent; DMB was transferred to the flask containing Mg* and THF by using a cannula. The reaction mixture was stirred at ambient temperature, and the black Mg* became gray within 30 min. Stirring was continued for 4 to 8 h. The complex was tested by reacting with Ph₂SiCl₂ in THF to form 1,1-diphenyl-2,3-dimethyl-1-silacyclopent-3-ene as the only product observed by GC/MS.¹⁷

1,1-Dimethyl-1-stannacyclopent-3-ene (4). In a 1000 mL flamedried three-neck flask, equipped with a mechanical stirrer, a nitrogen inlet/outlet, and a septum, were added 7 g (31.9 mmol) of Me₂SnCl₂ and 700 mL of freshly distilled THF. MgBD dispersion, ca. 10 g (44 mmol) in 150 mL of THF in another flask, while being stirred, was added dropwise via a cannula over 4 to 8 h, while the Me₂SnCl₂ solution was being stirred rapidly at ambient temperature. Once the MgBD was added to the solution of Me₂SnCl₂, the solid complex disappeared immediately. The reaction mixture was checked by moistened pH paper when the reaction was close to completion. When the reaction mixture was neutral, addition of the MgBD was stopped, and stirring was continued for 15 min.

While stirring continued, saturated NH₄Cl solution was added by syringe, the reaction mixture became cloudy, and white solids formed. More NH₄Cl solution was added until the supernatant became clear while further white solids formed. MgSO₄ drying agent was added. Solids were removed by filtration, and a clear solution was obtained. The volume was reduced to ca. 25 mL; then 50 mL of hexane was added and more white solids formed. Separation (15% yield) was achieved by passing the mixture through a silica gel column (3 × 5 cm), and the silica gel was washed with hexane to collect any product left on it. ¹H NMR (C₆D₆, 300 MHz): δ 0.10 (s, 6H, J_{H-Sn} = 54.6 Hz, SnCH₃), 1.47 (s, 4H, J_{H-Sn} = 35.1 Hz, SnCH₂), 6.27 (s, 2H, J_{H-Sn} = 113.1 Hz, HC=CH) (lit:³⁵ (CDCl₃): δ 0.36 (s, 6H, J_{H-Sn} = 54.4 Hz), 1.56 (s, 4H), 6.2 (s, 2H)). ¹³C NMR (C₆D₆, 75.4 MHz): δ -10.3 (SnCH₃), 13.56 (SnCH₂), 133.03 (CH=CH) (lit:³⁵ (CDCl₃): δ -10.6 (SnCH₃), 13.3 (SnCH₂), 132.7 (HC=CH)). ¹¹⁹Sn NMR (C₆D₆, 111.9 MHz): δ 57.43. MS (EI) *m/e* (relative intensity): 204(6), 202(6), 200(5) (M⁺⁺), 189(11), 187(8), 185(6) (M⁺ - 15), 165(16), 163(11), 161(9), 150(82), 148(53), 146(35), 135(100), 133(71), 131(41), 120(8), 118(7), 116(5), 54(13), 53(19). HRMS: calcd for C₆H₁₂Sn 203.9961; found 203.9956.

1,1-Diphenyl-1-stannacyclopent-3-ene was synthesized by a similar procedure: 10 g (29.1 mmol) of Ph₂SnCl₂ in 300 mL of THF, 6.47 g (29.1 mmol) of MgBD in 150 mL of THF, and an addition time of 4 h were employed. When the reaction was complete, THF was removed under low pressure. The residue was shaken with 200 mL of dry hexane, and solids were removed by filtration. A clear hexane solution resulted, and crude product was obtained after hexane was removed under low pressure. The product was purified by silica gel chromatography (5 cm \times 4 cm, hexane, $R_f = 0.2$), and 1.2 g (13% yield) was obtained as a white crystalline solid: ¹H NMR (C₆D₆, 300 MHz): δ 1.76 (s, 4H, $J_{H-Sn} = 36.9$ Hz, SnCH₂), 6.31 (s, 2H, $J_{H-Sn} = 124.2$ Hz, HC=CH), 7.14 (m, 6H, Ph), 7.44 (m, 4H, Ph). ¹³C NMR (CDCl₃, 75.4 MHz): δ 13.39 (SnCH₂), 128.50, 128.93, 132.50, 136.78,138.56 (HC=CH, Ph). ¹¹⁹Sn{¹H} NMR (C₆D₆, 111.9 MHz): δ –1.95. Anal. (C,H): Calcd: C (58.77%), H (4.93%). Found: C (58.94%), H (4.99%).

1,1-Di-n-butyl-1-stannacyclopent-3-ene was synthesized by a similar procedure: 8.7 g (28.6 mmol) of n-Bu₂SnCl₂ in 300 mL of THF, 6.4 g (28.7 mmol) of MgBD in 150 mL of THF, and an addition time of 4 h were employed. When the reaction was complete, and THF was removed under low pressure, the residue was shaken with 200 mL of dry hexane, and solids were removed by filtration. A clear hexane solution resulted, and crude product was obtained after hexane was removed under low pressure. Purification by silica gel chromatography (5 cm \times 4 cm, hexane, $R_f = 0.5$) gave 1.2 g (15% yield) of product as a colorless liquid: ¹H NMR (CDCl₃, 300 MHz): δ 0.88 (t, 6H, J = 7.2 Hz, CH₃), 1.04 (t, 4H, J = 8.1 Hz, Sn-CH₂), 1.30 (m, 4H, CH₂), 1.44 (s, 4H, C=C-CH₂-Sn) 1.52 (m, 4H, CH₂), 6.12 (s, 2H, HC=CH, J_{H-Sn} = 131.7 Hz). ¹³C NMR (CDCl₃, 75.4 MHz): δ 10.09, 11.82, 13.69, 27.00, 29.29 (SnCH₂, SnCH₂CH₂CH₂-CH₃), 132.97 (C=C). ¹¹⁹Sn NMR (CDCl₃, 111.9 MHz): δ 58.62. MS (EI) *m/e* (relative intensity): 234 (15), 231(10), 229(6) (M⁺ - 54), 177(64), 175(51), 173(39), 147(14), 121(100), 120(91), 119(96), 53(4).

1,1-Di-tert-butyl-1-stannacyclopent-3-ene was synthesized from MgBD made from magnesium turnings. To a solution of 7 g (23) mmol) of t-Bu₂SnCl₂ dissolved in 700 mL of THF was added an excess of a suspension of MgBD in THF via a cannula over 4 h at ambient temperature until the pH of the reaction mixture reached 7. The mixture was heated at reflux for 1 h, and its volume was reduced to 50 mL by removing THF under vacuum. Hexane (250 mL) was added and solids were removed by filtration. Hexane was removed in vacuo, and the crude product was purified by flash column chromatography (silica gel, hexane eluent, $R_f = 0.88$), giving 1.7 g (25% yield) of product as a colorless liquid: ¹H NMR $(C_6D_6, 300 \text{ MHz})$: δ 1.18 (s, 18H, SnCMe₃), 1.46 (s, 2H, CH₂), 1.47 (s, 2H, CH₂), 6.32 (s, 2H, CH). ¹³C NMR (C₆D₆): δ 10.80 (s, CH₂), 26.98 (s, CMe₃), 31.37 (s, CMe₃), 133.11 (s, CH). ¹¹⁹Sn NMR (C_6D_6) : δ 78.00 (s). MS (EI): m/z (relative intensity) 288 (2) (M⁺), 234 (45) $(M^+ - C_4H_6)$, 177 (100) $(M^+ - C_4H_6)$, - CMe₃), 135(46), 121(46). HRMS: calcd for C₁₂H₂₄Sn 288.0900; found 288.0903; d = 1.215 g/mL.

1,1,3,4-Tetramethyl-1-stannacyclopent-3-ene (18) was synthesized by reacting Mg*DMB with Me₂SnCl₂. In a 250 mL Schlenk flask was placed 100 mL of freshly dried and distilled THF and 1.2 g (5.46 mmol) of Me₂SnCl₂; then this solution was cooled to -78 °C. While it was being stirred rapidly by a magnetic stir bar, Mg*DMB complex was added via a cannula dropwise for 4 h until the pH value was close to 7. Saturated NH₄Cl solution was added until the reaction mixture became clear. MgSO₄ was added to dry the solution, and solids were removed by filtration through

⁽³¹⁾ Kofron, W.; Baclawski, L. M. J. Org. Chem. 1976, 41, 1879.
(32) van den Berghe, E. V.; van der Kelen, G. P. J. Organomet. Chem.
1973, 61, 197.

a 5 cm silica gel column. After further purification by silica gel chromatography with pentane eluent ($R_f = 0.8$), 0.32 g of product (25% yield) was obtained as a colorless liquid: ¹H NMR (C_6D_6 , 300 MHz): δ 0.13 (s, 6H, $J_{H-Sn} = 57$ Hz, CH₃), 1.59 (s, 4H, $J_{H-Sn} = 42$ Hz, SnCH₂), 1.81 (s, 6H, C=C-CH₃). ¹³C NMR (C_6D_6 , 75.4 MHz): δ -11.56 (SnCH₃), 20.87 (SnCH₂), 130.91 (C=CCH₃). ¹¹⁹Sn NMR (C_6D_6 , 111.9 MHz): δ 21.65. MS (EI) *m/e* (relative intensity): 232(8), 230(7), 228(3) (M⁺⁺), 217(47), 215(40), 213(19) (M⁺ - 15), 165(27), 163(16), 161(12), 150(19), 148(18), 146(10), 135(100), 133(71), 131(46), 120(11), 82(15), 67(62), 65(29). HRMS: calcd for C₈H₁₆Sn 232.0259; found 232.0269.

3,4-Dimethyl-1,1-diphenyl-1-stannacyclopent-3-enene was synthesized by condensing 6.9 g (20 mmol) of Ph₂SnCl₂ with Mg*DMB using the same procedure described for the preparation of **18**. Pure product (1.5 g, 21% yield) was obtained after silica gel chromatography (hexane, $R_f = 0.56$) as a white solid: ¹H NMR (C₆D₆, 300 MHz): δ 1.80 (s, 6H, CCH₃), 1.896 (s, 2H, CH₂), 1.899 (s, 2H, CH₂), 7.1–7.3 (m, 6H, Ph_{0, p}), 7.4–7.6 (m, 4H, Ph_m). ¹³C NMR (C₆D₆, 75.4 MHz): δ 21.46 (s, C<u>C</u>H₃), 21.65 (s, CH₂), 108.42 (s, Ph), 128.69 (s, Ph), 128.99 (s, Ph), 137.10 (s, Ph), 138.69 (s, Ph). ¹¹⁹Sn NMR (C₆D₆, 111.9 MHz): δ –31.80 (s). MS (EI) *m/z* (relative intensity): 356 (11, M⁺), 274 (53, M⁺ – C₆H₁₀), 226 (100), 197 (43), 183 (38), 144 (37), 120 (54).

1,1-Di-*tert*-**butyl-3,4-dimethyl-1-stannacyclopent-3-ene** was synthesized by condensing 6.1 g (20 mmol) of *t*-Bu₂SnCl₂ with Mg*DMB using the same procedure described above. A 16% yield (1.0 g) of pure product was obtained after silica gel chromatography (hexane, $R_f = 0.92$) as a white solid: ¹H NMR (toluene- d_8 , 300 MHz): δ 1.31 (s, 18H, C(CH₃)₃), 1.65 (s, 2H, CH₂), 1.66 (s, 2H, CH₂), 1.92 (s, 6H, CCH₃). ¹³C NMR (toluene- d_8 , 75.4 MHz): δ 18.95 (s, CMe), 22.14 (s, CH₂), 26.61 (s, CMe₃), 31.49 (s, CMe₃), 131.95 (s, CMe). ¹¹⁹Sn NMR (C₆D₆, 111.9 MHz): δ 43.16 (s). MS (EI) *m*/*z* (relative intensity): 316 (4, M⁺), 259 (87), 234 (48, M⁺ - C₆H₁₀), 203 (73), 177 (100), 135 (49). HRMS: calcd for C₁₄H₂₈Sn 316.1213; found 316.1214.

2-Phenyl-1,3-butadiene magnesium complex (Mg*PhBD) was synthesized by the method of Jiang³⁶ from 1.0 g (7.7 mmol) of 2-phenyl-1,3-butadiene³⁷ and activated Mg*, from 0.18 g (25.94 mmol) of Li wire, 3.54 g (27.6 mmol) of naphthalene, and 1.24 g (13.0 mmol) of anhydrous MgCl₂. The reaction, usually complete within 3 h, was monitored by GC/MS on an aliquot of reaction mixture hydrolyzed with D₂O. Unreacted Mg* was removed by standing or filtration.

1,1-Dimethyl-3-phenyl-1-stannacyclopent-3-ene was obtained in low yield. Into a 500 mL Schlenk flask were combined 250 mL of freshly dried and distilled THF and 1.68 g (7.67 mmol) of Me_2SnCl_2 , and the resulting solution was cooled to -78 °C while stirred rapidly by a magnetic stirring bar. MgPhBD (7.68 mmol) was added via a cannula dropwise during 1 h, and the red color associated with MgPhBD disappeared upon addition to the reaction mixture. After warming slowly to ambient temperature overnight, THF was removed under low pressure, and the white residue was shaken with 250 mL of dry hexane, giving a clear solution after filtration. Hexane was then removed under low pressure, and white solids again appeared. Recrystallization from hexane at -30 °C failed. A yield of <10% was estimated from the NMR spectroscopic characterization: ¹H NMR (C₆D₆, 300 MHz): δ 0.09 (s, 6H, J_{H-Sn} = 54.0 Hz, SnCH₃), 1.6 (m, 2H, SnCH₂), 1.8 (m, 2H, SnCH₂), 6.7 (m, 1H, C=C-H), 7.20 (m, Ph), 7.60 (m, Ph). ¹¹⁹Sn NMR (C₆D₆, 111.9 MHz): δ 76.17.

1,1-Di-*n***-butyl-3-phenyl-1-stannacyclopent-3-ene** was obtained in low yield. Into a 500 mL Schlenk flask were added 200 mL of freshly distilled THF and 1.75 g (5.76 mmol) of *n*-Bu₂SnCl₂, and the resulting solution was cooled to -78 °C. With rapid stirring by a magnetic stirring bar, MgPhBD (7.52 mmol) in 40 mL of THF was added dropwise via a cannula. Addition was stopped when the pH of the reaction mixture neared 7. After warming slowly to ambient temperature, THF was removed under vacuum, and the white residue was extracted with 250 mL of dry Et₂O. A clear solution was obtained after filtration, Et₂O was removed under vacuum, and white solids again were formed. Crude product was analyzed by NMR and a <10% yield estimated: ¹H NMR (C₆D₆, 300 MHz): δ 0.86 (t, 6H, CH₃), 0.96 (t, 4H, SnCH₂), 1.26 (m, 4H, CH₂), 1.47 (m, 4H, CH₂), 1.75 (m, 2H, SnCH₂), 1.86 (m, 2H, SnCH₂), 6.75 (m, 1H, *J*_{H-Sn} = 117 Hz, C=CH), 7.24 (m, Ph), 7.56 (m, Ph). ¹³C NMR (C₆D₆, 300 MHz): δ 10.42, 13.79, 27.27, 29.45 (CH₂CH₂CH₂CH₃CH₃), 126–130, 143.57, 144.45 (Ph, C=CH). ¹¹⁹Sn NMR (C₆D₆, 111.9 MHz): δ 77.26.

Synthesis of Me₂SnCl(CHCl₂). To a 250 mL Schlenk flask with a magnetic stirring bar were added 40 mL of freshly dried and distilled THF and 2 mL (32 mmol) of dichloromethane; then the flask was cooled in a liquid nitrogen ethanol slush bath at -100°C. n-Butyllithium solution (13.3 mL, 1.50 M, 20 mmol) was added via syringe carefully along the cold flask wall during 20 min. Stirring was continued for 15 min at -100 °C. CHCl₂Li was formed as a white precipitate. Then this solution at -100 °C was transferred quickly to a -100 °C stirred THF solution of 6.6 g (30 mmol) of Me₂SnCl₂ via cannula. The reaction mixture turned clear quickly, and stirring was continued at -100 °C for 1 h; then the reaction mixture was allowed to warm to room temperature overnight. The reaction flask was placed in a 30 °C bath, and solvents were removed from the mixture under 0.1-0.2 Torr and trapped in liquid nitrogen. White crystals were obtained on the upper wall of the flask, which were stable at room temperature, as Me₂SnCl(CHCl₂) (10% yield) containing a small amount of Me₂SnCl₂. ¹H NMR: δ 1.2. ¹H NMR (C₆D₆, 300 MHz): δ 0.90 (s, 6H, $J_{H-Sn} = 59.4$ Hz; $J_{\text{H-Sn}} = 62.4 \text{ Hz}, \text{ SnCH}_3$, 5.70 (s, 1H, $J_{\text{H-Sn}} = 13.5 \text{ Hz}, \text{ SnCHCl}_2$). MS 70 eV *m/e* (relative intensity): 252(1), 230(1), 204(18), 185(100), 155(74), 135(24), 120(25), 83(9), 63(6), 48(6).

Diphenyldiphenylthiostannane, **Ph₂Sn(SPh)**₂, was synthesized by the method of Schmidt, Dersin, and Schumann,³⁸ from 10.3 g (30 mmol) of Ph₂SnCl₂ and 6.6 g (60 mmol) of thiophenol. A 60% yield (8.0 g) was obtained: ¹H NMR (C₆D₆, 300 MHz): δ 6.84 (m, Ph), 7.04 (m, Ph). ¹¹⁹Sn NMR (C₆D₆, 111.9 MHz): δ -3.90.

Octa-*tert***-butylcyclotetrastannane**, *cycylo*-[(*t***-Bu**₂)**Sn**]₄, was synthesized by the method of Farrar and Skinner.³⁹ ¹H NMR (300 MHz) in (toluene-*d*₈): δ 1.71; in (C₆D₆): δ 1.60; in (CDCl₃): δ 1.51 [lit:⁴⁰ (C₆D₆): δ 1.61].

Kinetic Studies. Samples for NMR studies of rates of pyrolysis of 1-stannacyclopent-3-enes were prepared in small, sealed Pyrex tubes inserted into standard 5 mm NMR tubes for analysis or directly in sealed NMR tubes. The reaction mixtures were thermostatted by immersion in the vapors of boiling liquids of appropriate boiling points. Temperatures were periodically monitored using thermocouples mounted near the reaction mixtures. Two typical procedures are described:

1. A mixture of 10 mg of 1-stannacyclopent-3-ene and ca. 2 mg of tetramethylsilane internal standard in 1 mL of C_6D_6 was freeze-pump-thaw degassed and sealed in a 5 mm NMR tube that was suspended in the vapors of boiling *tert*-butanol (82.4 ° C), water (100 °C), toluene (110.4 °C), or 3-methyl-1-butanol (130.1 °C), respectively. For kinetic studies at higher temperatures 5 μ L of toluene internal standard and toluene- d_8 solvent were employed, and the vapor baths were di-*n*-butyl ether (141.4 °C), *n*-hexanol (155.6 °C), mesitylene (163.1 °C), or *p*-cymene (175.5 °C),

⁽³³⁾ Fujita, K.; Ohnuma, Y.; Yasuda, H.; Tani, H. J. Organomet. Chem. **1976**, *113*, 201.

⁽³⁴⁾ Rieke, R. D.; Xiong, H. J. Org. Chem. 1991, 56, 3109.

⁽³⁵⁾ Unpublished data of J. A. Soderquist.

⁽³⁶⁾ Jiang, P. Doctoral Dissertation, Washington University, St. Louis, 2002.

⁽³⁷⁾ Marvel, C. S.; Woolford, R. G. J. Org. Chem. 1958, 23, 1658.

⁽³⁸⁾ Schmidt, M.; Dersin, H. J.; Schumann, H. Chem. Ber. 1962, 95, 1428.

respectively. Temperatures were periodically checked with a thermocouple inserted near the reaction tube. The vapor bath apparatus, consisting of a boiling flask, a tube in which the reaction tube was suspended in such a way that refluxing liquid did not contact it, and a reflux condenser, was protected from the atmosphere by a slow stream of dry N_2 passing through a T-joint at the top of the condenser. The apparatus was wrapped in aluminum foil to protect it from light. The reaction tubes were periodically removed and immediately quenched for NMR analysis.

2. 16.0 μ L (0.10 mmol) of **4** and 25.6 μ L (0.24 mmol) of toluene as internal standard were dissolved in 1.2 mL of C_6D_6 , and 150 μ L of the solution was injected into a small tube (3 mm o.d.). After the solution was freeze-pump-thaw degassed to 10⁻⁴ Torr, the tube was sealed and heated at 85 °C. The reaction was monitored by ¹H NMR. The reaction tube was immersed in C_6D_6 in a normal NMR tube during an NMR experiment. The concentrations were calculated from the integral ratios of ¹H NMR peaks from 4, the products, and the toluene internal standard. In ¹H NMR, peaks from butadiene were observed at 4.90-5.10 and 6.10-6.20 ppm, and dimethylstannylene oligomers at 0.5-0.7 ppm as broad multiple peaks that formed gradually during pyrolysis. After 14 h at 85 °C, 28% 4 was depleted, with formation of butadiene in 78% yield and dimethylstannylene oligomers in 75% yield. When the tube was opened in the air, white solids precipitated gradually from the solution from oxidation of the oligomers.

Product Studies. Pyrolysis of 1-Stannacyclopent-3-enes in the Presence of Dienes. Pyrolysis of 4 in Neat 2,3-Dimethylbutadiene (**DMB**). All reaction mixtures were freeze-pump-thaw degassed to 10^{-4} Torr and sealed prior to pyrolysis.

To a 3 mm o.d. Pyrex tube was added 3.0 μ L (0.019 mmol) of 4, 5.0 μ L (0.047 mmol) of toluene internal standard (δ CH₃ 2.90 in neat DMB), and 150 µL (1.33 mmol) of DMB. The reaction tube was heated at 100 °C for 4 h and then immersed in C_6D_6 in an NMR tube for ¹H NMR analysis. Conversion of 4 was 32%. Butadiene was obtained in 70% yield. Oligomeric dimethylstannylene was observed in 50% yield as a single broad peak at 1.16 ppm. 1,1,3,4-Tetramethyl-1-stannacyclopent-3-ene (18) was formed in 12% yield. After 9 h of pyrolysis at 100 °C, 62% of 4 was consumed with the formation of butadiene in 92% yield, dimethylstannylene oligomers in 42% yield, and tetramethylstannacyclopentene 18 in 9% yield. When the reaction mixture was dissolved in dry hexane, white solids formed gradually and were removed before GC/MS analysis, which revealed a dimer of dimethylbutadiene as an additional product. 1,1,3,4-Tetramethyl-1-stannacyclopent-3-ene (18) was observed as the major product peak upon GC/ MS analysis.

1,1,3,4-Tetramethyl-1-stannacyclopent-3-ene (**18**) in neat DMB: ¹H NMR (300 MHz, DMB/C₆D₆): δ 0.88 (s, 6H, J_{H-Sn} = 55.8, 52.8 Hz, SnCH₃), 1.70 (s, 4H), C=C-CH₃ overlapping with CH₃ of DMB.

Pyrolysis of 4 in a Mixture of DMB and MeI. To an NMR tube were added 0.042 g (0.21 mmol) of **4**, 10.0 μ L (0.094 mmol) of toluene as internal standard (CH₃ δ 2.10 ppm), 370 μ L (2.9 mmol) of 2,3-dimethyl-1,3-butadiene, and 200 μ L (2.9 mmol) of MeI. A C₆D₆ capillary was placed in the NMR tube as locking agent. The tube was heated at 100 °C for 8 h. By ¹H NMR analysis, ca. 61% **4** was converted. 1,1,3,4-Tetramethyl-1-stannacyclopent-3-ene (**18**) (confirmed by GC/MS analysis), butadiene, and (Me₂Sn)_n were observed in yields of 4%, 48%, and 93%, respectively. When the reaction mixture was dissolved in dry hexane, white solids formed gradually, which were removed before GC/MS analysis, and a dimer of butadiene was observed in GC/MS.

Pyrolysis of 18 in Neat Butadiene. Into a thick-walled glass tube (7 mm o.d., 2.5 mm I.D.) were loaded, by bulb-to-bulb distillation on a vacuum line, 25.0 μ L (0.14 mmol) of **18** and 25 μ L (0.24 mmol) of toluene as internal standard. Then ca. 300 μ L of butadiene was condensed in the tube. The sealed tube was

wrapped in aluminum foil and heated behind a shield at 100 °C for 4 h and then cooled to 0 °C and opened. Most of the butadiene was evaporated slowly at 0 °C with slight reduction of pressure; white solids were observed during removal of butadiene. The residue was dissolved in C_6D_6 , and more white solids were observed. According to ¹H NMR, little toluene remained after removal of butadiene, so the extent of decomposition of the 1,1,3,4-tetramethyl-1-stannacyclopent-3-ene (**18**) was assumed to be 41% during 4 h in benzene at 100 °C. From the SnCH₃ ¹H NMR peak of **4** a 5% yield was estimated; the single broad peak for (Me₂Sn)₆ observed at 0.6 ppm corresponds to a 31% yield. ¹¹⁹Sn NMR confirmed the identity of the products, and GC/MS analysis also indicated that **4** was the major volatile product.

Pyrolysis of 4 in the Presence of Other Potential Stannylene Trapping Agents. CDCl₃. Yields are based on integral ratios in ¹H NMR analyses.

To a small tube (3 mm o.d.) were added 10.0 μ L (0.064 mmol) of 4, 10.0 μ L (0.095 mmol) of toluene as internal standard (δ 2.4 ppm in CDCl₃), and 150 μ L (1.78 mmol) of CDCl₃. The tube was heated at 100 °C for 6 h and then immersed in CDCl₃ in a normal NMR tube during ¹H NMR analysis. Conversion of 42% was found, and butadiene, observed at δ 5.12–5.27 and 6.37–6.48 ppm, was formed in 75% yield. Dimethylstannylene oligomers were observed in 76% yield at δ 0.36–0.56 ppm with a single broad peak with broad satellites at 0.41 ppm ($J_{H-Sn} = 20.7$ Hz). No other new peaks were observed in the ¹H NMR. 4 in neat CDCl₃: ¹H NMR (300 MHz, CDCl₃/CDCl₃): δ 0.34 (s, 6H, $J_{H-Sn} = 55.8$, 53.4 Hz, SnCH₃), 1.54 (d, 4H, J = 1.2 Hz, $J_{H-Sn} = 35.4$ Hz), 6.19 (s, 2H, $J_{H-Sn} = 113.4$ Hz).

CH₂Cl₂. To a small tube (3 mm o.d.) were added 10.0 μ L (0.064 mmol) of **4**, 10.0 μ L (0.0946 mmol) of toluene as internal standard (δ 2.3 ppm in CH₂Cl₂), and 150 μ L (2.34 mmol) of CH₂Cl₂. The tube was heated at 100 °C for 6 h and then immersed in CDCl₃ in an NMR tube during the ¹H NMR analysis. Conversion of 45% was found, butadiene was observed at 6.28–6.37 ppm in ca. 100% yield, and dimethylstannylene oligomers were observed in 77% yield at 0.36–0.48 ppm as a single broad peak with broad satellites at 0.40 ppm (J = 20.7 Hz). No other new peaks were observed in the ¹H NMR. **4** in neat CH₂Cl₂: ¹H NMR (300 MHz, CH₂Cl₂/CDCl₃): δ 0.24 (s, 6H, J_{H-Sn} = 56.1, 54.0 Hz, SnCH₃), 1.44 (s, 4H, J_{H-Sn} = 35.4 Hz, CH₂), 6.09 (s, 2H, CH).

EtBr. To a small tube (3 mm o.d.) were added 6.0 μ L (0.038 mmol) of **4**, 6.0 μ L (0.068 mmol) of toluene as internal standard (Ph-CH₃: δ 2.31 ppm), and 150 μ L (2.01 mmol) of EtBr. The tube was heated at 100 °C for 4 h and then immersed in C₆D₆ in an NMR tube during ¹H NMR analysis. Conversion of 42% was found, butadiene was observed at 5.1–5.3 and 6.3–6.4 ppm in 84% yield, and broad peaks, observed at 0.48 ppm, were assigned to dimethylstannylene oligomers formed in 65% yield. No other products were observed by ¹H NMR spectroscopy. White solids were formed when the reaction mixture was dissolved in dry hexane. No Me₂EtSnBr or other compounds containing bromine were observed by GC/MS analysis. **4** in neat EtBr: ¹H NMR (300 MHz, EtBr/C₆D₆): δ 0.27 (s, 6H, J_{H-Sn} = 56.1, 53.1 Hz, SnCH₃), 1.45 (s, 4H, CH₂), 6.07 (s, 2H, CH).

MeI. To a small tube (3 mm o.d.) were added 6.0 μ L (0.038 mmol) of **4**, 6.0 μ L (0.068 mmol) of toluene as internal standard, 20.0 μ L (0.32 mmol) of MeI, and 150 μ L of C₆D₆. After the solution was freeze-pump-thaw degassed to 10⁻⁴ Torr, the tube was sealed and wrapped in aluminum foil and then heated at 100 °C for 5 h. The reaction tube was immersed in C₆D₆ (7.15 ppm) solvent in a normal NMR tube during ¹H NMR analysis. A 48% conversion was found, butadiene (84% yield) was observed at 4.9 and 6.2 ppm, and dimethylstannylene oligomers (73% yield) were observed at 0.4 to 0.6 ppm. No sharp signal was observed at 0.44 ppm corresponding to Me₃SnI superim-

posed on the broad peaks from dimethylstannylene oligomers found in that region.

The same procedure was employed with cyclohexane solvent: 6.0 μ L (0.038 mmol) of **4**, 6.0 μ L (0.068 mmol) of toluene as internal standard, 20.0 μ L (0.321 mmol) of MeI, and 150 μ L of C₆D₁₂. **4** was observed at 0.50, 1.72, and 6.31 ppm with a conversion of 33%, butadiene (100% yield) was observed at 6.48–6.58 and 5.23–5.41 ppm, and dimethylstannylene oligomers (79% yield) were observed at 0.64 to 0.78 ppm. No peak from Me₃SnI was observed.

The same procedure was used with neat MeI as reactant and solvent: 6.0 μ L (0.038 mmol) of 4, 6.0 μ L (0.068 mmol) of toluene as internal standard, and 150 μ L of MeI. Conversion of 55% was found, butadiene (90% yield) and Me₃SnI (31% yield) were observed by ¹H NMR analysis, but no peaks from dimethylstannylene oligomers were found. 4 in neat MeI: ¹H NMR (300 MHz, MeI/C₆D₆): δ -0.40 (s), 0.76 (s), 5.37 (s); Me₃SnI in neat MeI: ¹H NMR (300 MHz, MeI/C₆D₆): δ 0.20; butadiene in neat MeI: ¹H NMR (300 MHz, MeI/C₆D₆): δ 4.35–4.53 (m), 5.57–5.67 (m).

3-Hexyne. In Neat 3-Hexyne. To a small tube (3 mm o.d.) were added 6.0 μ L (0.038 mmol) of 4, 2.0 μ L of cyclohexane as internal standard (δ 2.01 ppm in 3-hexyne), and 150 μ L (132 mmol) of EtC=CEt. The tube was heated at 100 °C for 4 h and then immersed in C₆D₆ in a normal NMR tube during ¹H NMR analysis. A ca. 31% conversion was found, butadiene was observed at 5.57-5.82 and 6.83-6.93 ppm in 100% yield, and dimethylstannylene oligomers were observed in 76% yield as a single peak at 0.096 ppm. After 8 h of pyrolysis at 100 °C, 46% conversion was found, with the formation of butadiene in 86% vield and dimethylstannylene oligomers in 92% yield. When the reaction mixture was dissolved in dry hexane, white solids were formed gradually, which were removed before GC/MS analysis. None of the very small (relative to 4) peaks observed corresponded to 2,3,5,6-tetraethyl-1,4-distannacyclohexa-2,5-diene. 4 in neat diethylacetylene: ¹H NMR (300 MHz, 3-hexyne/C₆D₆): δ 0.84 (s, 6H, J_{H-Sn} = 55.5, 53.1 Hz, SnCH₃), 2.04 (s, 4H, CH₂), 6.64 (s, 2H, CH).

3-Hexyne in C₆D₆. A similar procedure was used with 6.0 μ L (0.038 mmol) of **4**, 2.0 μ L of cyclohexane as internal standard, 30.0 μ L (0.26 mmol) of 3-hexyne, and 150 μ L of C₆D₆. The solution was heated for 4 h at 100 °C, and 37% conversion was observed, with formation of butadiene in 85% yield and dimethylstannylene oligomers in 62% yield. After 8 h at 100 °C, the corresponding quantities were 58%, 86%, and 75%, respectively.

Trimethyltin Hydride, Me₃SnH. To a small tube (3 mm o.d.) were added 7.0 µL (0.044 mmol) of 4, 6.0 µL (0.068 mmol) of toluene as internal standard, and 150 µL (1.17 mmol) of Me₃SnH transferred to the tube under vacuum. The sealed tube was wrapped in aluminum foil and heated at 89.0 °C and then immersed in C₆D₆ (7.15 ppm) in an NMR tube during ¹H NMR analysis. Conversion of 29% was found after 14 h and 50% after 26 h at 89.0 °C. No peaks for butadiene were observed at 5 to 6 ppm, and no broad peaks for dimethylstannylene oligomers at 0.6 ppm. Volatile compounds were removed from the reaction mixture under vacuum, and the resulting solution was subject to GC/MS analysis. Me₃SnSnMe₂H (<10%), Me₃SnSnMe₃, and Me₃SnSnMe₂SnMe₃ were observed in the ratio 1.3:1:1.6, but these products comprised less than 40% of the compounds observed in GC/MS. The residue was dissolved in C_6D_6 , and in the ¹¹⁹Sn NMR spectrum peaks were observed at δ 57.37 (4), 2.469, -0.068, -3.029, -101.185, -103.191, -107.979, -234.32,-258.67, and -261.71.

Control Experiment: Dimethylstannylene Oligomers in Me₃-SnH with Daylight. In an O-ring tube was added 30 mg (0.20 mmol) of dimethylstannylene oligomers and 0.3 mL (2.3 mmol) of Me₃SnH transferred to the tube under vacuum. After warming from -178 °C, dimethylstannylene oligomers began to dissolve and the solution turned yellow. Ultrasound was used to help the dissolution of the oligomers. After 2 h, all dimethylstannylene oligomers were dissolved, and the color became slightly yellow. After 5 h, the yellow color was gone, and then Me₃SnH was removed from the reaction mixture at ambient temperature at 15 Torr. The residue was analyzed by ¹H and ¹¹⁹Sn NMR spectroscopy and GC/MS. ¹H NMR (300 MHz, C₆D₆): δ 0.035 (d, Me₃SnH) 0.2 to 0.6 (broad), 0.2 to 0.4 (several sharp peaks). 4.74 (m, Me₃SnH), 4.45 (septet, J = 3.1 Hz, Me₂SnH). ¹¹⁹Sn NMR (111.9 MHz, C₆D₆): δ -95.65, -96.53, -98.24, -101.2 $(Me_{3}SnH),\,-103.14,\,-107.92,\,-234.29,\,-249.3,\,-261.62\;(lit.^{42}$ ¹¹⁹Sn (33.55 MHz, CDCl₃): Me₃Sn-SnMe₃: δ -108.7; Me₃Sn-SnMe₂SnMe₃: δ -99.5, -261.7). Volatiles were removed from the mixture and trapped in liquid nitrogen under high vacuum. The residue comprised ca. half the reaction mixture and was identified by ¹H NMR as oligomers with only broad peaks observed at 0.2 to 0.8 ppm. In the analysis of the volatiles by GC/MS, Me₃SnSnMe₂H, Me₃SnSnMe₃, and Me₃SnSn-Me₂SnMe₃ were observed in the ratio 1:4.5:2.8 as 95% of the compounds containing tin and 90% of all compounds observed.

Pyrolysis of 1,1-Diphenyl-1-stannacyclopent-3-ene and 1,1-Di*tert*-butyl-1-stannacyclopent-3-ene in the Presence of Ph₂S₂. A degassed mixture of 10 mg (0.048 mmol) of 1,1-diphenyl-1stannacyclopent-3-ene, a 16-fold excess of diphenyldisulfide (150 mg, 0.77 mmol), and ca. 2 mg of Me₄Si internal standard in 1 mL of C₆D₆ was sealed in an NMR tube and pyrolyzed at 100 °C in a boiling water vapor bath. The mixture was monitored by NMR spectroscopy. After 45 min the conversion was 48%, butadiene was formed in 60% yield, and a 90% yield of Ph₂Sn(SPh)₂ was observed. ¹H NMR (300 MHz, C_6D_6): δ 1.76 (s, SnCH₂), 5.0-5.15 (m, C₄H₆), 6.1-6.2 (m, C₄H₆), 6.30 (s, HC=CH of 1,1-diphenyl-1-stannacyclopent-3-ene) 6.78-6.91 $(m, SPh of Ph_2S_2 and Ph_2Sn(SPh)_2), 7.11-7.14 (m, SnPh of 1,1$ diphenyl-1-stannacyclopent-3-ene), 7.34-7.41 (SnPh of 1,1diphenyl-1-stannacyclopent-3-ene and Ph₂Sn(SPh)₂) [authentic compounds vide supra Ph₂S₂: δ 6.78–6.85, 7.13, 7.36–7.40; 1,1-diphenyl-1-stannacyclopent-3-ene: δ 1.76 (s, SnCH₂), 6.31 (s, HC=CH), 7.14 (m, Ph), 7.44 (m, Ph); $Ph_2Sn(SPh)_2$: δ 6.82-6.92 (m, Ph), 7.35-7.39 (m, Ph)]. ¹¹⁹Sn NMR (111.9 MHz, C_6D_6): $\delta -2.10$ (1,1-diphenyl-1-stannacyclopent-3-ene), -3.92(Ph₂Sn(SPh₂) [authentic compounds, *vide supra* 1,1-diphenyl-1-stannacyclopent-3-ene: -1.95; Ph₂Sn(SPh)₂: -3.90]. The firstorder rate constant for loss of 1,1-diphenyl-1-stannacyclopent-3-ene in C₆D₆ at 100 °C in the presence of Ph₂S₂ was 22.7 \times 10^{-5} s^{-1} compared with $19.80 \pm 0.81 \times 10^{-5} \text{ s}^{-1}$ in the absence of Ph₂S₂. No diphenyltin oligomer (¹¹⁹Sn NMR at δ –216) was observed.

A similar reaction mixture of 10 mg (0.030 mmol) of 1,1di-*tert*-butyl-1-stannacyclopent-3-ene, 150 mg (0.77 mmol) of Ph₂S₂, and 5 μ L of toluene-H₈ internal standard in 1 mL of toluene-d₈ was similarly heated in a standard NMR tube at 140 °C. After 1.6 h, 53% conversion was found by ¹H NMR analysis, butadiene was formed in ca. 60% yield, and a product believed to be *t*-Bu₂Sn(SPh)₂ was formed in >95% yield. A first-order rate constant of 0.47 h⁻¹ was found (cf. 0.084 h⁻¹ in the absence of Ph₂S₂). ¹H NMR (300 MHz, toluene-d₈): δ 1.20 (s, *t*-Bu of *t*-Bu₂Sn(SPh)₂ 1.27 (s, *t*-Bu of stannacyclopentene), 2.20 (s, SnCH₂ of stannacyclopentene), 6.39 (s, HC=CH of stannacyclopentene), 5.0–5.15 (m, C₄H₆), 6.2–6.33 (m, C₄H₆), 6.39 (s, HC=CH of stannacyclopentene and *t*-Bu₂Sn(SPh)₂). ¹¹⁹Sn (111.9

⁽³⁹⁾ Farrar, W. V.; Skinner, H. A. J. Organomet. Chem. 1964, 1, 434.
(40) Adams, S.; Dräger, M. J. Organomet. Chem. 1985, 288, 295.

⁽⁴¹⁾ van den Berghe, E. V.; van der Kelen, G. P. J. Organomet. Chem. 1973, 59, 175.

2608 Organometallics, Vol. 28, No. 8, 2009

MHz, toluene- d_8): δ 57.75 (*t*-Bu₂Sn(SPh)₂), 78.16 (stannacyclopentene [authentic *vide supra* 78.00]; no *cyclo*-(*t*-Bu₂Sn)₄ was observed [authentic⁴⁰ ¹H (C₆D₆) δ 1.61, ¹¹⁹Sn (C₆D₆) δ 87.4]).

Acknowledgment. We are grateful for financial support from the National Science Foundation under grants CHE-9981759 and 0316124. This research was supported in part by the NSF through TeraGrid resources provided by NCSA under grant TG-CHE070050N. This work made use of the Washington University Computational Chemistry Facility, supported by NSF grant CHE-0443501. Supporting Information Available: Control experiments, ¹H NMR spectra of stannacyclopent-3-enes, Arrhenius and Eyring plots for all kinetic studies of stannacyclopent-3-ene pyrolysis, and energies of stationary points predicted by electronic structure calculations for the addition of $Me_2Sn:$ (3) to 1,3-butadiene are available free of charge via the Internet at http://pubs.acs. org.

OM800541F

⁽⁴²⁾ Mitchell, T. N.; Walter, G. J. Chem. Soc., Perkin Trans. 2 1977, 1842.