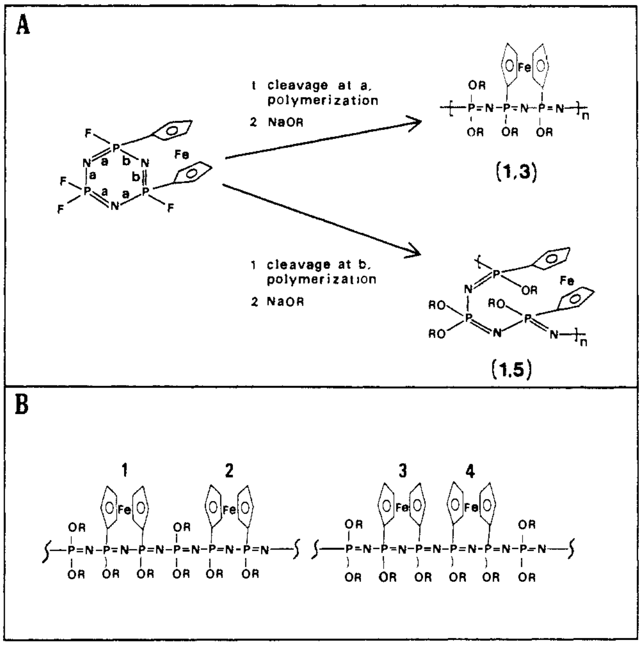

Figure 2. (A) Polymerization schemes for polyphosphazene III; OR = OCH_2CF_3. (B) Arrangements of ferrocene units on the polyphosphazene backbone.

potentials more than 1 V negative of oxidation. The nature of this reaction is still not understood.[4] However, the oxidized polymer undergoes a quantitative reduction upon scan reversal, whereas the oxidized trimer does not at similar scan rates.

Cyclic voltammetry obtained with polymer II (Figure 1B) is typical of that obtained from surface immobilized ferrocenyl compounds.[5,6] The peak potentials for oxidation and reduction remain unchanged over a range of moderate scan rates, and the voltammetric waves are symmetrical. The expected linear relationship[2] between $(i_p)_{anod}$ and v is observed for this polymer (correlation coefficient = 0.998, $n = 4$).

Figure 1C shows cyclic voltammetry of polymer III. As with II, the peak potentials for oxidation and reduction do not vary with changing scan rate, and plots of $(i_p)_{anod}$ versus v are linear (correlation coefficient = 0.9994, $n = 5$). The most striking and unique feature of the voltammetry of this polymer is the presence of two closely associated surface waves. This suggests the presence of two different types of ferrocene electron-transfer sites within the polymer. We have previously shown that different structural configurations and different amounts and types of substituents on the phosphazene affect the electrochemistry of ferrocene-substituted phosphazenes.[1] The voltammetric behavior of III might be rationalized by the presence of different microstructures of the polymer produced by different, competing polymerization routes.

Polymerization routes via cleavage of the cyclic trimer at two different sites forming a 1,3- and 1,5-type polymer can be envisioned (Figure 2A). While the oxidation peak potentials of these two different polymer types are nearly identical with those of the analogous 1,3- and 1,5- cyclic tetramers,[1] no spectroscopic (^{19}F and ^{31}P NMR) evidence for the 1,5-polymerization route has been found.[7] A more likely possibility is that the polymerization route forms a 1,3-polymer, but the ring-opened trimers link up in a head-to-tail as well as a head-to-head arrangement (Figure 2B). Here, a ferrocene unit in an arrangement as ferrocene 1 would have a slightly greater oxidation potential than ferrocene 4 because it is surrounded by more trifluoroethoxy groups.[1] A random arrangement of these two different ferrocene groups would result in a 1:1 ratio of these species.

Chronoamperometry was used to evaluate the rate of electron transport through films of II and III (Table I). The behavior of II is nearly identical for oxidation versus reduction of the ferrocene sites, and the values for $D_{ct}^{1/2}C$ are similar to the values reported for plasma polymerized films of vinylferrocene in acetonitrile.[6]

Chronoamperometric data for the oxidation step of III (0.0 V to 1.3 V) do not show the characteristic Cottrell $t^{-1/2}$ dependence[8] for the decay current, whereas the reduction step (1.3 V to 0.0 V) is well behaved. Two current domains are apparent for the oxidation step: $t < 25$ and $t > 25$ ms. Plots of i versus $t^{-1/2}$ yield two nonparallel linear regions (correlation coefficient > 0.990). A comparison of values for $D_{ct}^{1/2}C$ (Table I) shows that the initial oxidation process is significantly slower than either the second oxidation domain or subsequent reduction step.

These trifluoroethoxy-substituted polymers permit a unique comparison of the rate of charge diffusion in ferrocene-containing polymer films with ferrocene both in a freely moving (II) and bound (III) configuration. All values of $D_{ct}^{1/2}C$ for III are larger than those for II. This is interesting since the pendent ferrocene polymer (II) would be expected to display greater mobility and, hence, a greater through-space electron cross exchange rate. The greater rate of charge transport observed with the rigid bridged ferrocene polymer might indicate a mechanism which involves both electron cross exchange and "metallic-like" conduction in the partially oxidized III which results in larger $D_{ct}^{1/2}C$ values for this structure.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. BNS-8705777 (A.G.E.) and the U.S. Army Research Office (H.R.A). A.G.E. is a recipient of an N.S.F. Presidential Young Investigator Award (CHE-8657193).

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A Catalytic Reductive Cyclization of 1,6-Diynes

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Intramolecular carbametalations are proving to be a useful strategy for ring construction.[1] The cyclization of diynes to generate dialkylidenecycloalkanes according to eq 1, path a, using stoichiometric amounts of low valent titanium and/or zirconium complexes represents a particularly intriguing reaction because of the utility of the 1,3-dienes in subsequent cycloadditions.[2,3] In this communication, we wish to report a general catalytic approach (eq 1, path b) for the preparation of 1,2-dialkylidenecyclopentanes from diynes and its extension to multiple ring construction.

The strategy and perceived complications are outlined in eq 2, based upon a novel catalyst presumed to be a hydridopalladium carboxylate.[5] Success requires (1) regioselective hydropalladation

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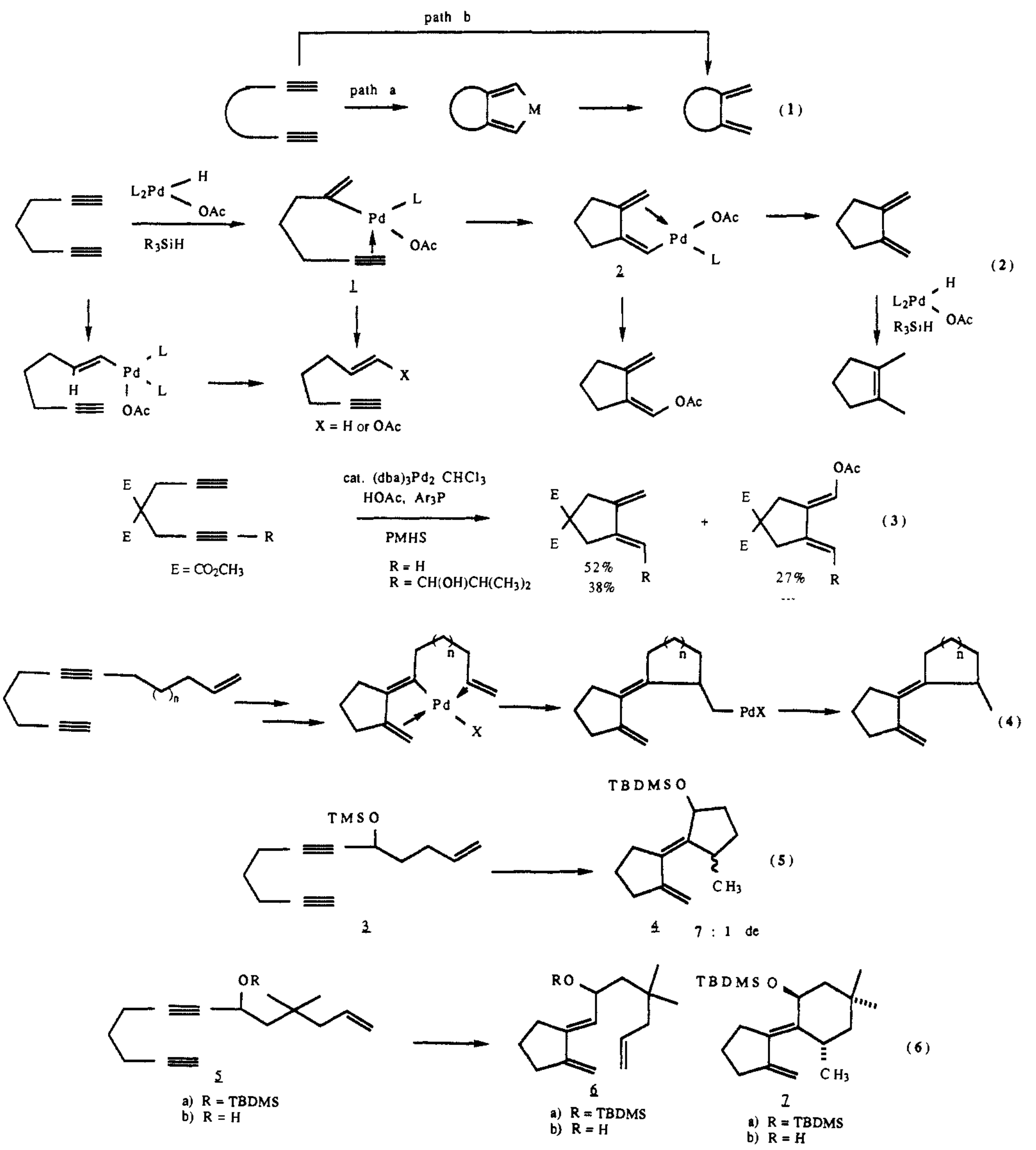
Scheme I



opposite the expected direction, (2) cyclization of the initial vinylpalladium intermediate **1** faster than reductive elimination to the vinyl acetate or reductive cleavage to the simple olefin, (3) reductive cleavage of the second vinylpalladium intermediate **2** faster than reductive elimination, and (4) reactions of the diyne starting materials being faster than those of the products. In the case of terminal acetylenes, oligomerization also occurs readily with such palladium catalysts. Initial attempts were somewhat disappointing, as shown in eq 10^3.[6]

The key proved to be the choice of silane. Replacing polymethylhydrosiloxane (PMHS) with triethylsilane led to a smooth cyclization procedure, as summarized in Table I. The following conditions were adopted as our standard protocol. To a solution of 2.5 mol% of $(dba)_3Pd_2{\cdot}CHCl_3$ and 10 mol% of tri-*o*-tolylphosphine which was stirred 3–5 min at room temperature was added 200 mol% of acetic acid and excess (up to 10-fold) triethylsilane in benzene. After having been stirred 5 min, the diyne was added all at once, and the reaction stirred at 0 °C to room temperature. Workup normally involved direct concentration in vacuo and chromatographic purification.

The examples demonstrate the great generality of this process. Its success with terminal triple bonds stands in contrast to the stoichiometric zirconium and titanium reactions.[2] Excellent chemoselectivity characterizes this reaction as shown by its compatibility with acid-sensitive functionality such as silylated triple bonds, silyl ethers, acetals, propargyl and allyl ethers (even tertiary ones), in addition to many other reactive functional groups, including esters, ketones, enones, alcohols, sulfones, olefins, and dienes. Due to the ease of synthesis, most substrates incorporated a fully substituted carbon in the chain connecting the two triple bonds; entry 2 reveals that this feature is not required.

Having established the feasibility of intercepting the initially formed vinyl palladium intermediate **1** (eq 2) before its reduction led us to consider the feasibility of intercepting the second organopalladium intermediate **2** (eq 2) before its reduction, as outlined in eq 4. This process would require the proposed initial hydropalladation to be chemoselective for the terminal triple bond. In the event, the readily available enediyne **3**, upon treatment with 2.5 mol% of $(dba)_3Pd_2{\cdot}CHCl_3$, 10 mol% of tri-*o*-tolylphosphine, 200 mol% of acetic acid, and 10 equiv of polymethylhydrosiloxane, produced only the doubly cyclized product **4** as a 7:1 mixture of diastereomers in an astonishing 90% combined yield. The olefin geometry is assigned based upon mechanistic considerations and analogy. Furthermore, the very close agreement of the ^{13}C shifts for all olefinic carbons in the two isomers supports this contention. The major diastereomer, isolated pure in 79% yield, is tentatively assigned as cis with respect to the methyl and siloxy substituents,

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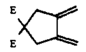
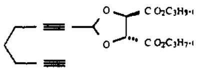
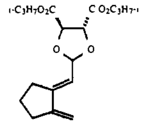
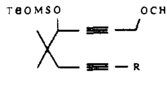
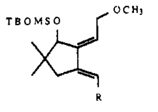
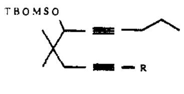
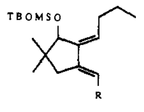
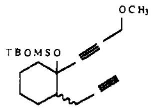
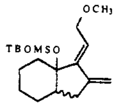
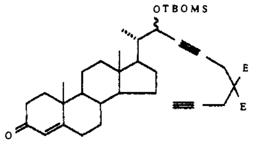
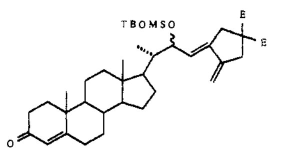
[5] Trost, B. M.; Rise, F. *J. Am. Chem. Soc.* **1987**, *109*, 3161. Upon the basis of reductive cyclization of enynes for which labeling studies support a hydropalladation mechanism, we prefer a similar mechanism for the reductive cyclization of the diynes. However, a mechanism invoking a palladacyclopentadiene cannot be eliminated at this time.

[6] This reaction was performed by F. Rise in these laboratories.

Table I. Catalytic Reductive Diyne Cyclizations

entry	substrate	time (min)	product[a]	isolated yield (%)
1		25		34
2		25		51
				
3 R = H		60		70
4 R = TMS		3		89
5 R = H		15		60
6 R = $\overset{\text{OMEM}}{\text{CHCH}_3}$		30		83
7 R = CO_2CH_3		20		95
8		15		86
9		90		84

[a] All new products have been fully characterized spectrally and elemental composition established by high resolutions mass spectroscopy and/or combustion analysis.

based upon the higher field shift for the carbon of the methyl group in the major (δ 17.3) compared to the minor (δ 19.3) isomer. The absence of any geminal disubstitution facilitating either ring formation should be noted.

To test the effectiveness of the capture of the vinylpalladium species, we examined the enediyne **5a** (eq 6). Using the same reaction conditions as above gave only the doubly cyclized product **7a** as a single diastereomer in 48% yield (eq 6). Difference NOE spectra establishes the geometry of the tetrasubstituted double bond as predicted and depicted in **7**. The trans stereochemistry assigned arises from the vicinal coupling constants of the two allylic methine protons (δ 4.60, dd, J = 4.6, 1.8 Hz; δ 2.88, d quint, J = 10, 7 Hz) which suggests that one is equatorial and the other axial. It is interesting to note that cyclization of the free alcohol **5b** gave a mixture of the mono- and bis-cyclized products **6b** and **7b**. Whether the difference between the two substrates derives from steric effects or a direct participation of the free hydroxyl group in the reaction with the silicon hydride cannot be discerned at present. The formation of **6b** also supports the proposed pathway (eq 4) whereby the initial hydropalladation occurs with the terminal triple bond rather than the double bond.

This new approach for catalytic reductive cyclization provides an expeditious and unambiguous synthesis of dialkylidenecyclopentanes of defined geometry. Both steric and electronic factors apparently dictate which triple bond participates initially. Entry 7 suggests that the more electron-rich triple bond preferentially reacts, since hydropalladation of the ynoate should have occurred opposite of the orientation required for cyclization.[7] The double cyclizations of eq 5 and 6 require initial hydropalladation of the monosubstituted acetylene. These observations are in accord with a Pd(+2) species being the active catalyst as proposed. The ability to achieve multiple interceptions of the organopalladium intermediates to form several rings before termination may be considered the organometallic version of polycyclization processes involving radical[8] and cationic intermediates.[9] The formation of exocyclic tetrasubstituted double bonds of defined geometry is a major advantage of such a strategy.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

Registry No. 3, 116377-61-8; *cis*-**4**, 116377-62-9; *trans*-**4**, 116497-59-7; **5a**, 116377-63-0; **5b**, 116377-64-1; **6b**, 116377-66-3; **7a**, 116377-65-2; **7b**, 116377-67-4; $CH{\equiv}CCH_2C(CO_2CH_3)CH_2C{\equiv}CH$, 63104-44-9; $CH{\equiv}CCH_2C(CH_3)_2CH(TBDMSO)C{\equiv}CCH_2OCH_3$, 116377-44-7; $TMSC{\equiv}CCH_2C(CH_3)_2CH(TBDMSO)C{\equiv}CCH_2OCH_3$, 116377-45-8; $CH{\equiv}CCH_2C(CH_3)_2CH(TBDMSO)C{\equiv}C(CH_2)_2CH_3$, 116377-46-9; $CH_3CH(OMEM)C{\equiv}CCH_2C(CH_3)_2CH(TBDMSO)C{\equiv}C(CH_2)_2CH_3$, 116377-47-0; $MeOC(O)C{\equiv}CCH_2C(CH_3)_2CH(TBDMSO)C{\equiv}C(CH_2)_2CH_3$, 116377-48-1; $(dba)_3Pd_2{\cdot}CHCl_3$, 52522-40-4; $CH{\equiv}CCH_2C(CO_2CH_3)CH_2C{\equiv}CCH(OH)CH(CH_3)_2$, 116377-59-4; diisopropyl 2-(hepta-1,6-diynyl)-1,3-dioxa-4(*R*),5(*R*)-cyclopentanedicarboxylate, 116377-43-6; 1-(*tert*-butyldimethylsiloxy)-1-(3-methoxy-1-propynyl)-2-(2-propynyl)cyclohexane, 116377-49-2; 20(*S*)-methyl-21-(*tert*-butyldimethylsiloxy)-21-[4,4-bis(methoxycarbonyl)hepta-1,6-diynyl]-4-pregnen-3-one, 116377-50-5; 1,1-bis(carbomethoxy)-3,4-bis(methylidene)cyclopentane, 87185-05-5; diisopropyl 2-[2′,2′-(2″-methylidene)tetra-

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methylene-1′-vinyl]-1,3-dioxa-4(*R*),5(*R*)-cyclopentanedicarboxylate, 116377-51-6; 1-(*tert*-butyldimethylsiloxy)-2(*Z*)-(2′-methoxy)-ethylidene-5,5-dimethyl-3-methylidenecyclopentane, 116377-52-7; 1-(*tert*-butyldimethylsiloxy)-2-(*Z*)-(2′-methoxy)ethylidene-5,5-dimethyl-3(*E*)-(1′-trimethylsilyl)methylidenecyclopentane, 116377-53-8; 1-(*tert*-butyldimethylsiloxy)-2(*Z*)-butylidene-5,5-dimethyl-3-methylidenecyclopentane, 116377-54-9; 1-(*tert*-butyldimethylsiloxy)-2-butylidene-5,5-dimethyl-3-(2′-methoxyethoxymethoxypropylidene)cyclopentane, 116377-55-0; 1-(*tert*-butyldimethylsiloxy)-2(*Z*)-butylidene-3(*E*)-(carbomethoxymethylidene)-5,5-dimethylcyclopentane, 116377-56-1; 1-(*tert*-butyldimethylsiloxy)-9-(2′-methoxy)ethylidene-8-methylidenebicyclo[4.3.0]-nonane, 116377-57-2; 20(*S*)-methyl-21-(*tert*-butyldimethylsiloxy)-21-[[4,4-bis(carbomethoxy)-2-methylidene-1(*E*)-cyclopentylidene]-methyl]-4-pregnen-3-one, 116377-58-3; dimethyl 3(*E*)-(2-hydroxy-3-methylbutylidene)-4(*E*)-(acetoxymethylidene)cyclopropanedicarboxylate, 116377-60-7; dimethyl 3(*E*)-(2-hydroxy-3-methylbutylidene)-4-methylidenecyclopentanedicarboxylate, 116405-79-9.

Supplementary Material Available: Experimental procedures and spectral data (3 pages). Ordering information is given on any current masthead page.

Polymerization of α,α′-Bis(dialkylsulfonio)-*p*-xylene Dihalides via *p*-Xylylene Intermediates: Evidence for a Nonradical Mechanism

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Received May 4, 1988

Simple *p*-xylylenes (PX's) require fairly low-temperature conditions for direct solution state observations, although stabilization can be achieved through appropriate substitution.[1] Recent advances in polymer chemistry have increased interest in functionalized PX's as useful monomers,[1,2] which one may in principle generate as reactive monomers that polymerize in situ.[3] Wessling[3b,c] has postulated that basic treatment of bis(dialkylsulfonio) salt derivatives of **1** yield polymerization to **4** by the route indicated in Figure 1. Since the Wessling polymerization is of particular importance in current work involving the production of the important conducting polymer precursor poly(*p*-phenylenevinylene)[4] (PPV), understanding its mechanism is of much potential use in controlling efficient syntheses of various substituted PPV's. In the investigations described below, we spectroscopically observed PX's **3a–f** but found no direct evidence favoring intervention of radical intermediates. We propose a modified polymerization mechanism, whereby PX's under typical reaction conditions polymerize by an anionic chain rather than a radical chain mechanism.

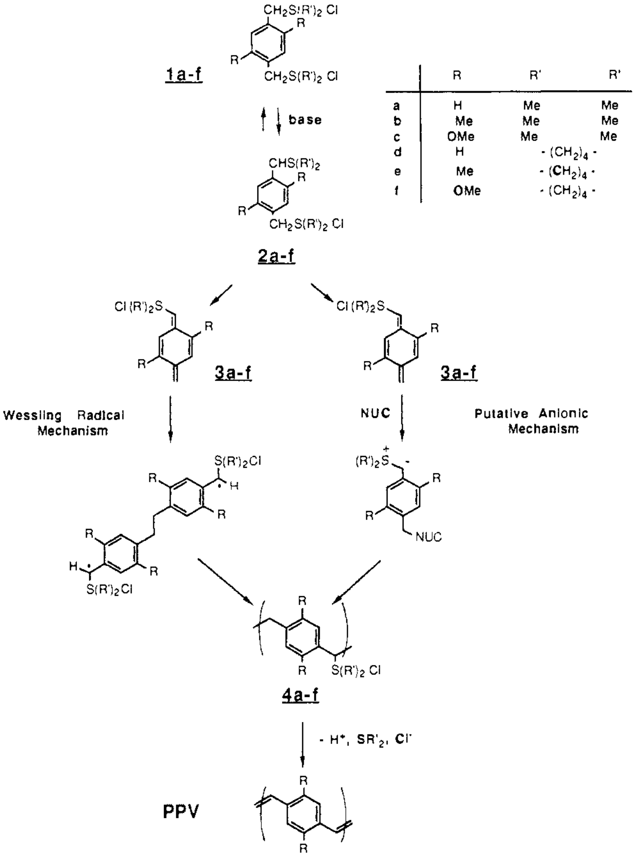

Figure 1. Two possible polymerization mechanisms forming poly(*p*-xylylenes) **4**. Wessling mechanism from ref 3c, anionic mechanism from this paper.

At −12 °C, treatment of **1a**[5] in basic methanol yields a new UV–vis band at 317 nm (Figure 2) that reaches maximum intensity within 10 min and then gradually fades within 1 h. Similar treatment of **1b**[5] and **1c**[5] yields transient UV–vis absorptions at 322 and 330 nm, in reasonable agreement with model INDO-CI[6] computations predicting transitions for **3a–c** at 293, 334, and 325 nm, respectively. Similar absorptions are observed upon similar treatment of **1d–f**[5] and analogous tetrafluoroborate salts. The common position and transience of absorbance in all these reactions is consistent with formation of PX's **3a–f**.

Line-broadening effects in the ^{1}H NMR spectrum ($CD_3OD/NaOCD_3$) show exchange deuteriation of the methylene positions in **1a** via ylid **2a** at −50 °C.[7a] At >−40 °C the spectrum

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(5) (a) Salts **1a–f** are obtained by boiling the corresponding 1,4-di(α-chloromethyl) compounds[5b] in a methanolic solution of the appropriate dialkyl sulfide. We thank Dr. Sharon Palmer for furnishing us with purified samples of the chloromethyl precursors of **1b–c,e,f**. Full experimental details of syntheses of **1a–f** and ^{1}H NMR spectral data for these compounds is described in the Supplementary Material. (b) Syntheses of the chloride precursors to **1a–f** that are not commercially available are described more fully by Lenz et al. (Lenz, R. W.; Han, C.-C.; Lux, M., submitted for publication).

(6) Zerner, M. C.; Ridley, J. E. *Theor. Chim. Acta* **1973**, *32*, 11; **1976**, *42*, 233.

(7) (a) In further support of this process, vacuum pyrolytic elimination of tetrahydrothiophene (THT) from **4d** produced from **1d** in CH_3OD/CH_3ONa yields unsubstituted PPV with an IR spectrum showing substantial deuterium incorporation at the vinyl positions (2229 cm^{-1} for C–D stretch, decreased intensity of vinyl C–H out-of-plane at 968 cm^{-1}, new band at 910 cm^{-1} assigned to vinyl C–D out-of-plane). Assignments were made in typical fashion, e.g., as in Dolphin and Wick (Dolphin, D.; Wick, A. E. *Tabulation of Infrared Spectral Data*; Wiley: New York, NY, 1977). (b) Polymers **4a,d** when synthesized under conditions similar to these have been characterized by ^{1}H NMR and IR spectroscopy (see Supplementary Material). The molecular weight (MW) of **4d** produced thusly is difficult to measure due to frequent clogging of GPC columns but is measured in the range 500 000–2 000 000. See: Machado, J. M.; Denton, F. R., III; Schlenoff, J. B.; Karasz, F. E.; Lahti, P. M. *J. Polym. Sci. Phys.*, in press. As a result of the difficulties in finding routine MW's for these polymers, investigation of the effects of anionic inhibitors, added inert nucleophile initiators, etc., upon the polymer MW remains for future mechanistic work.

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