Synthesis of Norbornenes Containing Tin(II), Tin(IV), Lead(II), and Zinc(II) and Their Polymerization To Give Microphase-Separated Block Copolymers

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The new ligands *trans*-2,3-bis(*tert*-butylamidomethyl)norborn-5-ene (bTAN) and *trans*-2,3-bis[(trimethylsilyl)amidomethyl]norborn-5-ene (bSAN) have been synthesized in order to prepare metal-containing monomers that can be polymerized by living ring-opening metathesis polymerization. Reaction of Li_2(bTAN) with $SnCl_4(THF)_2$ yields Sn(bTAN)Cl_2, whose molecular structure has been determined by X-ray crystallography (space group $P2_1/c$, $Z = 4$, $a = 11.741$ (3) Å, $b = 10.160$ (3) Å, $c = 17.352$ (5) Å, $\beta = 105.19$ (3)°, $V = 1998$ (2) Å^3, $R = 0.051$, $R_w = 0.049$). The key feature is a relatively rigid Sn-containing seven-membered ring annulated to the norbornene skeleton. Crystalline M(bSAN) (M = Sn, Pb) complexes were prepared by reacting Li_2(bSAN) with MCl_2 and are believed to have structures similar to that of Sn(bTAN)Cl_2. Reaction of diphenylzinc with $bTANH_2$ provided $(ZnPh)_2$(bTAN) in high yield. Sn(bTAN)Cl_2 can be polymerized by M(CHR)(NAr)(O-*t*-Bu)$_2$ (M = W or Mo, R = *t*-Bu or CMe_2Ph, Ar = 2,6-C_6H_3-*i*-Pr_2). [Sn(bTAN)Cl_2]$_{25}$/[norbornene]$_{120}$ was found by transmission electron microscopy (TEM) to exhibit a lamellar morphology (interdomain spacing $D \approx 190$ Å). Sn(bSAN), Pb(bSAN), and $(ZnPh)_2$(bTAN) were cleanly polymerized by W(CHR)(NAr)(O-*t*-Bu)$_2$. [Sn(bSAN)]$_{25}$/[MTD]$_{177}$ (MTD = methyltetracyclododecene) was shown to have a lamellar morphology with $D \approx 210$ Å, and [Pb(bSAN)]$_{20}$/[MTD]$_{176}$ a lamellar morphology with $D \approx 125$ Å (characterized by TEM and scanning transmission electron microscopy (STEM)). Small (25 (5) Å) particles were visible in the microdomains of the latter. [$(ZnPh)_2$(bTAN)]$_{80}$/[MTD]$_{250}$ gave a film exhibiting lamellar morphology ($D \approx 340$ Å) which contained a 0.97 ± 0.04 S:Zn ratio within the microdomains after treatment with H_2S (1 atm, 21 h), as measured by STEM.

Introduction

Intense research in the past few years has been directed toward the synthesis and study of metallic[1] and semiconducting[2] materials of such small dimensions (typically 10–110 Å) that electronic structure and properties are intermediate between those of an atom or molecule and those of the bulk material. If electronic properties can be predicted and selected by varying and controlling the size of these materials, then novel opticoelectronic properties may be in the offing.[3] Although such "nanoclusters" have received attention from both theoretical[2n-s] and experimental[2t-z] standpoints, the greatest challenge at the present time is devising effective methods for synthesizing them.[4] Current methods utilize zeolites,[2a,b] borosilicate glass,[2c] colloids,[2d,e] hydrophobic/hydrophilic random copolymers,[2h,i] molecular precursors,[2j-m] and inverse micelles.[2f,g] The reason synthesis is such a challenge is that a sample must be close to monodisperse in order that phenomena characteristic of a given size cluster may be observed. Self-assembly to give a structure bearing regular features of appropriate dimensions, against which cluster growth may be patterned, should provide a means of synthesizing such materials. For example, the best method at present for preparing monodisperse metal chalcogenide clusters on the nanometer scale employs inverted micelles as the medium for cluster growth in solution.[2f,g] We are pursuing a method that involves diblock copolymer microdomains[5] in solid films as the medium for patterning cluster growth, which is essentially a solid-state analogue of the solution micelle method. Block copolymer microdomains are thermodynamically driven to be essentially monodisperse,[6] their dimensions and shapes can be controlled by varying molecular weight and composition of the diblock,[7] and they frequently exhibit long-range three-dimensional order,[8] a feature that may be of value in

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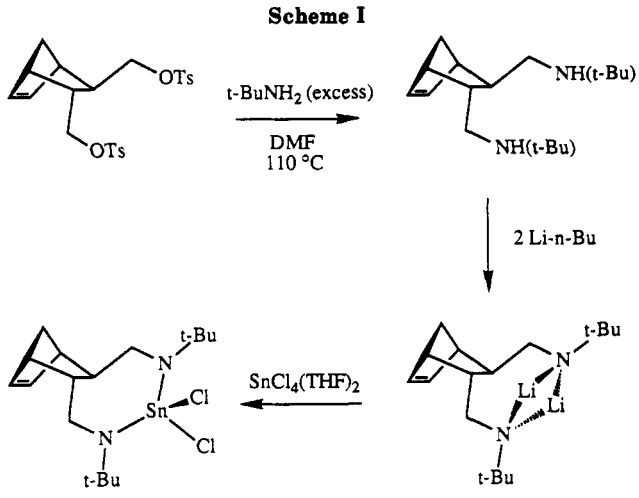
Scheme I



preparing well-defined cluster assemblies. If the block copolymer approach is successful, it may provide a more general route to a wider variety of size-selected materials dispersed in a transparent polymer host matrix.

The block copolymer approach is made possible through living ring-opening metathesis polymerization (ROMP) of norbornene and substituted norbornadiene derivatives using mild initiators of the type M(CHR)(NAr)(O-*t*-Bu)$_2$ (M = W or Mo, R = *t*-Bu or CMe_2Ph, Ar = 2,6-C_6H_3-*i*-Pr_2) to give homopolymers and block copolymers with a very low polydispersity.[9] If a metal is attached to one of the monomers in a block copolymer, then the number of metals in a microdomain will equal the number of monomers in one of the blocks times the number of chain ends in the microdomain. If the microdomain is spherical, then the number of metals could be controlled to give a narrow distribution about the mean. This approach contrasts sharply with cluster syntheses where a precursor metal complex is introduced (often by "soaking") into the film of random copolymer,[1c,d,2h,i] since all such techniques inherently lead to a relatively broad distribution of metal-containing domains. By attaching one or two metals to each repeat unit in one block of a *diblock* copolymer *prior* to microdomain formation, full advantage can be taken of the self-assembly process.

In a recent communication we outlined a new approach to the synthesis of lead sulfide that consisted of forming a diblock copolymer from a monomer containing organic lead and norbornene.[10] The lead-containing monomer that was chosen is inherently problematic since each lead was attached to *two* polymerizable norbornenes, i.e., each lead-containing monomer was a potential cross-linking agent, thereby complicating and possibly hindering well-defined microdomain formation in the resulting diblock copolymer film. In this paper we report two variations of a new type of ligand that bears *one* polymerizable double bond per metal and establish that these ligands can be attached to Sn(IV), Sn(II), Pb(II), or Zn(II), that block copolymers can be prepared, and that microphase separated materials can be synthesized. A complete study of the morphologies of the materials containing Sn(IV) appears elsewhere.[11]

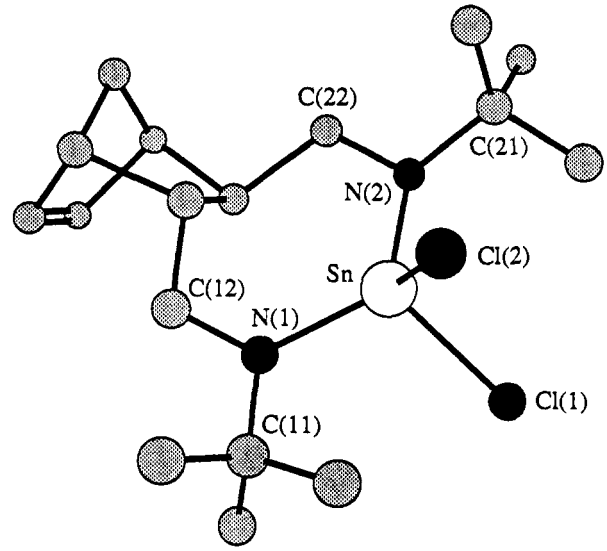


Figure 1. View of Sn(bTAN)Cl_2 structure as determined by X-ray diffraction.

Results and Discussion

Synthesis and Characterization of bTAN Complexes of Tin, Lead, and Zinc. The bTAN ligand (bTAN = *trans*-2,3-bis(*tert*-butylamidomethyl)norborn-5-ene) can be synthesized as shown in Scheme I. The ditosylate is prepared in three steps:[12] (i) a Diels–Alder reaction between cyclopentadiene and a fumaric acid derivative; (ii) $LiAlH_4$ reduction to the *trans*-diol; (iii) treatment of the diol with tosyl chloride in pyridine. The crucial synthetic step is conversion of the ditosylate to the diamine. It was found that both tosylates could be displaced completely by *tert*-butylamine in a 2:1 mixture of dimethylformamide and *tert*-butylamine over a period of 21 h at ~110 °C. The diamine thus obtained is a light-amber liquid that may be purified by vacuum distillation but is usually pure enough (>95% by ^1H NMR) to be lithiated directly by butyllithium in pentane. The dilithiodiamide is a white, microcrystalline solid formed in good yield.

Tin(IV) was chosen as the metal for initial studies on the basis of a relatively extensive chemistry of Sn(IV) complexes containing amido ligands and their thermal stability. Addition of the dilithiodiamide to $SnCl_4(THF)_2$ in cold ether gave Sn(bTAN)Cl_2 in moderate yield (~50%); it crystallizes as yellow prisms from pentane. An X-ray study of Sn(bTAN)Cl_2 revealed the structure shown in Figure 1. Selected bond distances and angles are listed in Table I in the supplementary meterial (see paragraph at end of paper). The most important feature is the ex-

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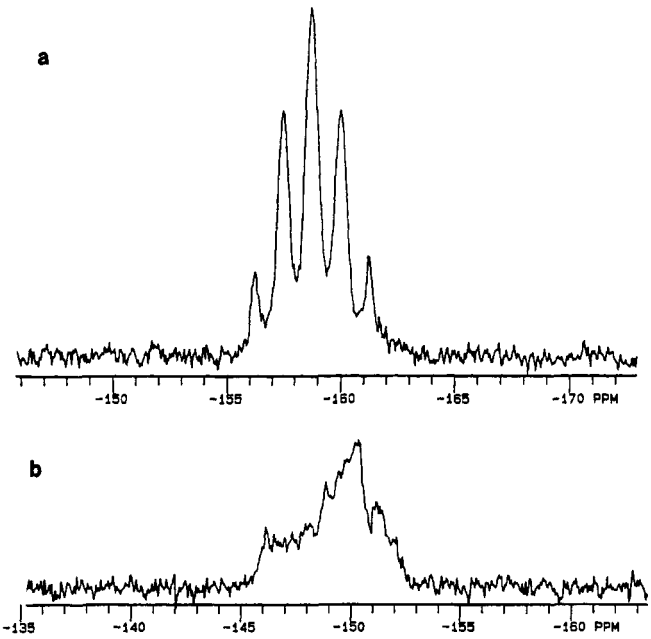
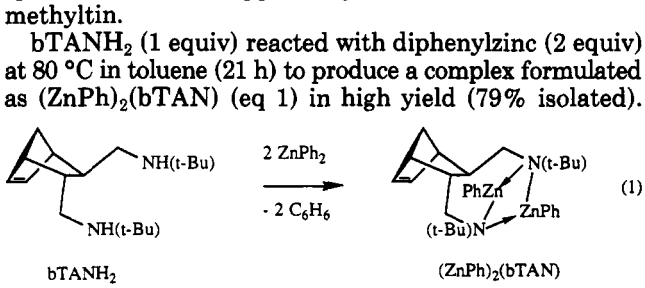


Figure 2. (a) ^{119}Sn NMR spectrum of $Sn(bTAN)Cl_2$ (proton coupled); (b) $^{119}Sn\{^1H\}$ NMR spectrum of $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$.

pected, relatively rigid seven-membered ring containing the tin. Note that the N–Sn–N angle is opened up from a tetrahedral value to 123.2 (2)°, while the Cl–Sn–Cl angle is closed down to 101.82 (8)°, relative to what one would expect in an analogue containing two monoamido ligands. The average Sn–N distance of 1.980 (6) Å is slightly shorter than that reported in $Sn(NMe_2)_4$ (2.045 Å).[13] In both $Sn(NMe_2)_4$ and $Sn(bTAN)Cl_2$ the nitrogen atoms are essentially planar, indicative of sp^2 hybridization at nitrogen and a significant amount of π bonding between nitrogen and tin.

NMR studies of $Sn(bTAN)Cl_2$ are totally consistent with its structure. In the proton NMR spectrum two *tert*-butyl resonances (δ 1.39, 1.35) and two olefinic doublet of doublets (δ 5.91, 5.77) are observed along with ten other unique proton resonances, identified through COSY experiments.[14] Three methylene carbon resonances (δ 53.40, 52.60, 47.53), four methine carbon resonances (δ 49.51, 47.41, 45.14, 42.33), two olefinic carbon resonances (δ 137.38, 135.41), two quaternary carbon resonances (δ 58.74, 58.59), and two methyl carbon resonances (δ 30.86, 30.79) were identified in a DEPT experiment.[15] Satellite resonances ~140 Hz apart are observed in the proton NMR spectrum flanking the nitrogen methylene resonances due to coupling to ^{119}Sn. One quintet resonance ($^3J_{SnH}$ = ~140 Hz) was observed in the proton-coupled ^{119}Sn NMR spectrum at δ −158 ppm (Figure 2a) relative to tetramethyltin.

$bTANH_2$ (1 equiv) reacted with diphenylzinc (2 equiv) at 80 °C in toluene (21 h) to produce a complex formulated as $(ZnPh)_2(bTAN)$ (eq 1) in high yield (79% isolated).



$bTANH_2$ $(ZnPh)_2(bTAN)$ (1)

Inequivalent phenyl groups and *tert*-butyl groups are observed by ^1H NMR, and integrations are consistent with the proposed formulation. The tendency of ZnR_2 reagents to lose only one molecule of RH per zinc atom upon treatment with a weakly acidic proton donor, such as a secondary amine, is well-documented,[16] as is the propensity of RZnX reagents to increase their coordination number to three or four via bridging of the X group when X is electronegative and bears a lone pair.[17]

The bTAN ligand was designed with several specific purposes and properties in mind. It should be bulky enough to form stable amido complexes that do not readily attack the metal alkylidene catalyst. It should be a versatile ligand, applicable to a variety of metals by routes analogous to those usually employed for synthesizing metal dialkylamides of both transition and main-group metals.[18] Its bidentate nature should significantly decrease the possibility of amido ligand-exchange reactions, which would be a method of cross-linking within a polymer. The chelate effect is probably enhanced, relative to a 1,4-bis(amido)butane, because four of the carbon atoms in the seven-membered metal-containing ring are locked into position by fusion to the norbornene skeleton. The *tert*-butyl groups not only have an important steric effect but also impart solubility to the metal complexes (and derived polymers) in hydrocarbon solvents, a critical property if solution-cast films are to be prepared. The 2,3-trans disposition of the amide substituents on the norbornene skeleton places the complexed metal as far as possible from the exo face of the norbornene double bond, which is where the alkylidene catalyst attacks. Finally, metal amides are highly susceptible, in general, to cleavage by protic reagents,[18] such as hydrogen sulfide or selenide, a reaction that could be exploited in carrying out further chemistry within the microdomain.

It was possible to synthesize M(bTAN) complexes (M = Sn, Pb) by treating MCl_2 with $Li_2(bTAN)$, but these species were unstable and could be characterized only by NMR spectroscopy. The Pb complex (red in solution and yellow in the solid state) decomposed completely within 10–20 min to give a Pb mirror and $bTANH_2$ as the only recognizable organic product. Although a bit more robust, yellow-orange Sn(bTAN) could not be isolated as a solid, and samples always contained significant amounts of $bTANH_2$ (according to proton NMR).

Synthesis and Characterization of M(bSAN) (M = Sn, Pb) Complexes. The instability of Sn(bTAN) and Pb(bTAN) could be ascribed to the fact that the amides in bTAN are relatively strong electron donors and therefore may place too much electron density on Sn(II) and Pb(II), ultimately leading to reduction of the metal. Replacing the *tert*-butyl group by a trimethylsilyl group should render the amide significantly less electron-donating without sacrificing many of the steric advantages of the bTAN ligand outlined above. The bSAN ligand (bSAN = *trans*-2,3-bis[(trimethylsilyl)amidomethyl]norborn-5-ene) may be synthesized as outlined in Scheme II. M(bSAN) complexes (M = Sn, Pb) were prepared straightforwardly by treating MCl_2 with $Li_2(bSAN)$ in THF at 25 °C. They were isolated as pure crystalline solids (white when M = Sn, yellow when M = Pb) from cold

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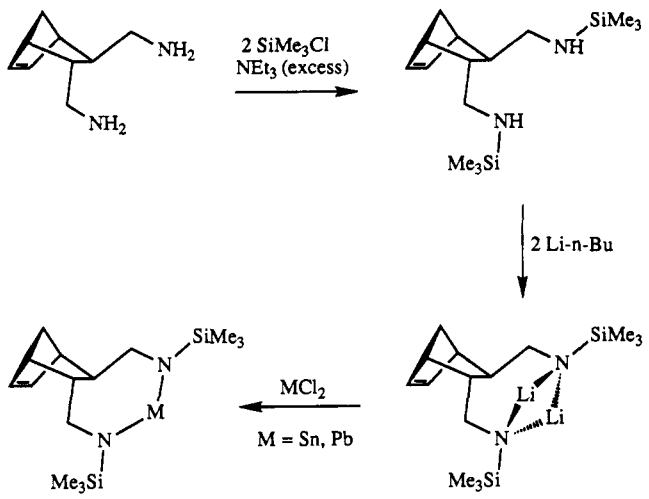
Scheme II

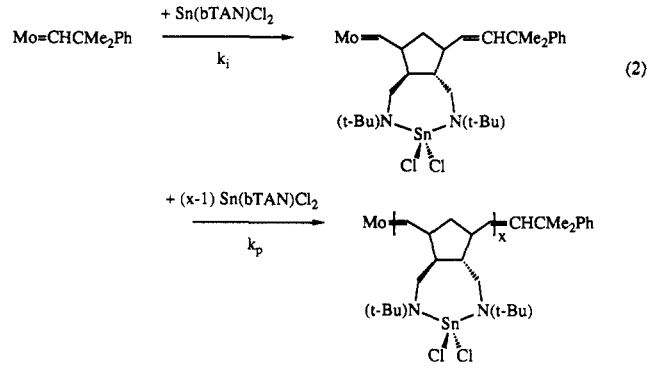


pentane solution and are stable indefinitely at 25 °C in solution in the absence of air and water.

NMR spectra of M(bSAN) complexes are analogous to those of Sn(bTAN)Cl_2. An anomalous downfield shift is observed for the NCH_2 protons in Pb(bSAN), analogous to that observed in Pb(bTAN) (see Experimental Section). The shift is most pronounced for the equatorial protons (δ 6.28 and 6.15, versus δ 3.92 and 3.51 for axial protons). The seven-membered ring PbN_2C_4 may be strained because of the long Pb–N bonds (cf. a Pb–N distance of 2.24 Å for Pb[N($SiMe_3$)$_2$]$_2$),[19] and the Pb atom therefore may be forced into the proximity of the methylene carbons. A gated ^{13}C NMR spectrum showed normal chemical shifts and $^1J_{CH}$ coupling constants for the methylene carbon atoms (δ 61.79, 132 Hz; δ 57.78, 133 Hz), indicating that they are sp^3 hybridized and that the attached protons therefore are not interacting with the Pb atom in any unusual way. The ^{119}Sn NMR spectrum of Sn(bSAN) exhibits a broad resonance at δ 457 with respect to tetramethyltin.

Although the silylamides M[N($SiMe_3$)$_2$]$_2$ (M = Sn, Pb) have been shown to be monomeric both in the vapor phase and in the crystal,[19] crystals of Sn[(*t*-BuN)$_2$$SiMe_2$] display both monomeric and dimeric forms in the unit cell.[20] The bSAN ligand might be less sterically demanding than two N($SiMe_3$)$_2$ ligands, perhaps roughly comparable to (*t*-BuN)$_2$$SiMe_2$, so M(bSAN) complexes could perhaps be dimeric in the solid state. In solution, however, there is no evidence for formation of dimers of either complex that are intact on the NMR time scale (several diastereomeric dimers would be possible, and close in energy, since the bSAN ligand is chiral but racemic). In fact the spectra are directly analogous to those obtained for monomeric Sn(bTAN)Cl_2. Therefore we propose that the M(bSAN) complexes are monomeric in solution.

Polymerization of bTAN and bSAN Complexes of Tin, Lead, and Zinc. An NMR experiment showed that 4 equiv of Sn(bTAN)Cl_2 in THF-d_8 is consumed rapidly and completely by Mo($CHCMe_2Ph$)(NAr)(O-*t*-Bu)$_2$[9f] at room temperature. Approximately half (45%) of the initiator is converted into a living polymer that has alkylidene proton resonances at 11.61 (d, $^3J_{HH}$ = 8 Hz) and 11.53 (d, $^3J_{HH}$ = 8 Hz) ppm (eq 2). A value of k_p/k_i = 24 can be calculated[9a] by integrating the alkylidene H_α resonance for unreacted initiator (at 11.27 ppm) versus the



(2)

alkylidene H_α resonance in the propagating alkylidene complexes at 11.61 and 11.53 ppm. The NMR sample retained a light yellow color and was homogeneous. Living poly-Sn(bTAN)Cl_2 does not decompose in THF-d_8 to any appreciable extent in 12 h at 25 °C. Addition of norbornene to it (4 equiv) caused the resonances at 11.61 and 11.53 ppm to disappear, and a new doublet characteristic of the alkylidene proton in living polynorbornene to appear at δ 11.60 ppm. These experiments suggest that the catalyst is stable to Sn(bTAN)Cl_2 and that living diblock copolymers should be preparable from norbornene and Sn(bTAN)Cl_2. Addition of Sn(bTAN)Cl_2 to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ also leads to stable living poly-Sn(bTAN)Cl_2 on the basis of similar proton NMR experiments.

To synthesize the best block copolymers, it was necessary to develop a clean method of terminating the living polymer. ROMP polymerizations by catalysts such as W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ normally are terminated by adding an aldehyde, which cleaves the polymer from the metal in a Wittig-like reaction.[9g] Benzaldehyde is often used because it is especially reactive and does not possess an enolizable proton. Unfortunately, Sn(bTAN)Cl_2 reacts rapidly with benzaldehyde to give a complex mixture of products. Benzophenone is an alternative cleavage agent, but it does not react efficiently with dilute living poly-Sn(bTAN)Cl_2. On the other hand, *trans*-1,3 pentadiene is known to react readily with living polynorbornene to yield a polymer chain capped with a methylene fragment and a thermally stable yet relatively reactive vinyl alkylidene complex (eq 3, P = polymer).[21] Control experiments

$$M{=}CHP + CH_3CH{=}CHCH{=}CH_2 \rightarrow M{=}CHCH{=}CHCH_3 + PCH{=}CH_2 \quad (3)$$

verify that Sn(bTAN)Cl_2 does not react with either *trans*-1,3-pentadiene or benzophenone (24 h, concentrated solution, 25 °C), and that polynorbornene (PDI ~ 1.05) can be obtained using 1,3-pentadiene as the cleavage reagent. Therefore the combination of 1,3-pentadiene (to cleave the polymer from the metal) followed by benzophenone (to react with the vinylalkylidene complex) was chosen as the method of cleaving poly-Sn(bTAN)Cl_2 from the metal. In the absence of benzophenone there is a significant possibility of secondary metathesis reactions by vinylalkylidene complexes during the time required to cast films.

The diblock copolymer [Sn(bTAN)Cl_2]$_{25}$/[NBE]$_{120}$ (the subscripts refer to the number of monomer equivalents added; NBE = norbornene) was prepared on a 0.5-g scale in benzene by adding first norbornene and then, after it was consumed, Sn(bTAN)Cl_2 to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, followed by terminating the reaction with 1,3-pen-

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Figure 3. Bright-field TEM of $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$; bar = 1000 Å.

tadiene as described above. A sample of living polynorbornene was removed before adding $Sn(bTAN)Cl_2$, quenched with benzaldehyde, and analyzed by GPC (PDI = 1.08 refractometer, 1.03 UV–vis; M_n 21 000 with respect to polystyrene standards). A portion of the diblock $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$ was precipitated by adding a benzene solution dropwise to pentane. The translucent, pale yellow sample of $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$ thus obtained was dried in vacuo. It dissolved readily again in benzene or toluene.

NMR studies of $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$ revealed no surprises. In the proton NMR spectrum, in addition to the usual resonances for polynorbornene, a strong resonance is observed at δ 1.40 that corresponds to the *t*-Bu groups in the poly-$Sn(bTAN)Cl_2$ block of $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$. Weak resonances are also observed at 3.2 and 2.6 ppm that can be assigned to the NCH_2 protons. All integrals are consistent with the formulation $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$. The shift of 1.40 ppm for the *t*-Bu groups strongly suggests that the Sn coordination sphere is essentially unchanged, since for $Sn(bTAN)Cl_2$ the *t*-Bu resonances appear at 1.39 and 1.35 ppm, but in $bTANH_2$, a likely decomposition or hydrolysis product, they appear at 1.04 and 1.07 ppm. In the ^{13}C NMR spectrum resonances are observed at δ 31.4 for the *t*-Bu methyl groups (cf. δ 30.86 and 30.79 for $Sn(bTAN)Cl_2$) and at δ 58.9 and 51.0 (broadened) for the carbon atoms bound to nitrogen (respectively δ 58.74 and 58.59, 53.40 and 52.60 ppm in $Sn(bTAN)Cl_2$). In the $^{119}Sn\{^1H\}$ NMR spectrum of $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$ a manifold of resonances extends from δ −145 to −153 (Figure 2b; cf. the well-defined resonance at −158 ppm for $Sn(bTAN)Cl_2$ in Figure 2a); no other resonances were observed in the region from δ 500 to −350 ppm. All evidence supports the contention that $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$ is a well-defined diblock copolymer with a narrow distribution about the expected number of monomer units in each chain.

A pale yellow, transparent film of $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$ was prepared by slowly evaporating a 2 wt % benzene solution in an inert atmosphere, and a thin section (ca. 200 Å) was prepared by ultramicrotomy in air. The sample consists of randomly oriented, approximately square micron-sized patches of highly uniform parallel lamellae (Figure 3), as often observed for a diblock copolymer with approximately equal volumes of the two blocks.[5a,7] X-ray fluorescence data via STEM show that oxygen also is present in alternating lamellar regions, suggesting that although the Sn centers in $[Sn(bTAN)Cl_2]_{25}/[NBE]_{120}$ apparently have at least been partially hydrolyzed during microtoming, any tin oxide or hydroxide formed in this process evidently does not migrate out of the microphase in which it is formed to any significant degree at 25 °C.

Addition of either W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ or Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ to 50 equiv of Sn(bSAN) in THF results in the complete conversion of monomer to polymer, as evidenced by the proton NMR spectrum in C_6D_6 of a reaction mixture after removal of the THF in vacuo. The resonances due to what is nominally $[Sn(bSAN)]_{50}$ are broader using Mo as the initiator instead of W. Another difference is found on examining the alkylidene resonances that result from adding 10 equiv of Sn(bSAN) to the Mo and W initiators. In the case of Mo, the living alkylidene proton resonances are distributed

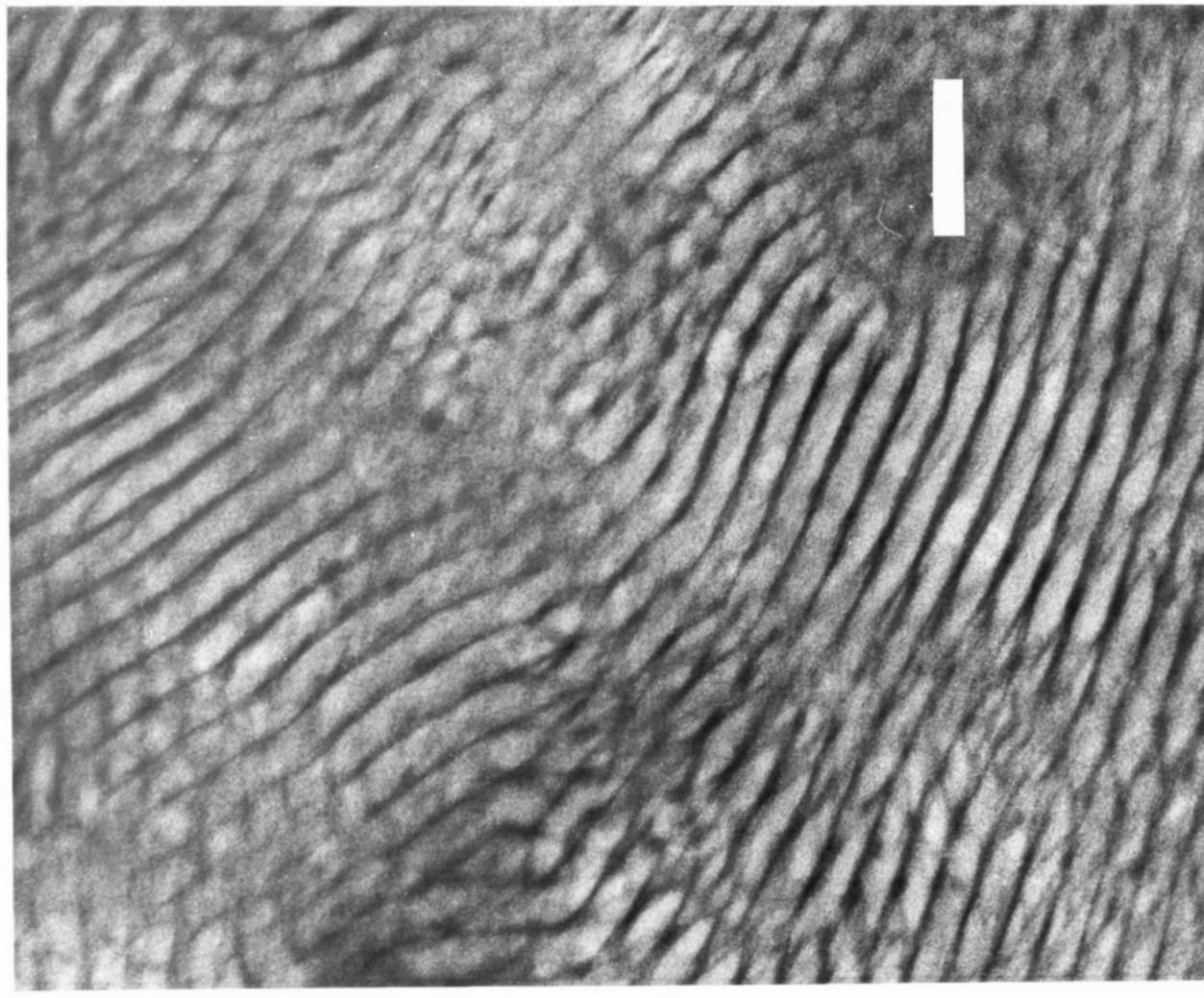

Figure 4. Bright-field TEM of $[Sn(bSAN)]_{25}/[MTD]_{177}$; bar = 1000 Å.

between δ 9.5 and 11.5, while in the case of W, the living alkylidene resonances appear centered at δ 8.5 with a spread of only ~0.5 ppm to either side. Subsequent addition of norbornene to the tungsten sample leads to replacement of the living alkylidene resonances by those attributable to living polynorbornene, as expected for a living system.

A diblock copolymer, nominally $[Sn(bSAN)]_{25}/[MTD]_{177}$ (25 wt % Sn(bSAN)), was prepared employing the W initiator. (MTD is methyltetracyclododecene, the norbornene derivative prepared from propylene and 2 equiv of cyclopentadiene.) A film that was cast and sectioned as described above exhibited a lamellar morphology (Figure 4) with an interdomain spacing of ~210 Å and domain width of ~40 Å.

Films of several analogous diblock copolymers prepared by employing the Mo catalyst showed no microdomains. The only observable feature was a speckled background, a typical phenomenon for many polymers.[22] Apparently the Mo initiator is in some way incompatible with Sn(bSAN), even though Sn(bSAN) appears to give rise to living alkylidene H_α resonances according to NMR studies. The fact that the "living alkylidene" resonances are spread over a wider range than when the W catalyst is employed and the fact that no morphology is observed both suggest that the Sn(bSAN)/Mo combination in fact is not satisfactorily living. Formation of regular microdomains suggests that diblocks are formed when the W catalyst is employed, since there is no alternative way of explaining microdomain formation. The reason the Mo catalyst does not work is not obvious to us at this juncture.

All the results mentioned above for Sn(bSAN) are mirrored for Pb(bSAN). Use of the Mo initiator and Pb(bSAN) and MTD as comonomers apparently did not yield high-quality diblocks since no microdomains were observed by TEM in static cast films. However, the W initiator again was successful. Microdomains formed that are comprised nominally of $[Pb(bSAN)]_{20}/[MTD]_{176}$ diblocks (Figure 5). The microdomains are ~25 Å thick and separated by ~120 Å. Close inspection of the micrograph in Figure 5 reveals small clusters lined up like beads within each of the microdomains. That the microdomains contain Pb is confirmed by STEM X-ray fluorescence analysis; Figure 6 gives an annular dark-field STEM image for a ~1000 $Å^2$ portion of the sample (regions of high density appear bright) and corresponding X-ray fluorescence maps for Pb, Si, and O. A 1:1 correspondence is observed between the Pb map and the dark-field image, showing that the Pb is indeed domain-confined. We propose that extensive hydrolysis has occurred to give domain-localized clusters of as yet unidentified lead compounds, possibly oxide or hydroxide.

In the case of $(ZnPh)_2$(bTAN), NMR experiments again indicated that only the W initiator yielded living alkylidenes and completely consumed the monomer to give polymer. A diblock, nominally $[(ZnPh)_2(bTAN)]_{80}/[MTD]_{250}$, was synthesized, and a film prepared as de-

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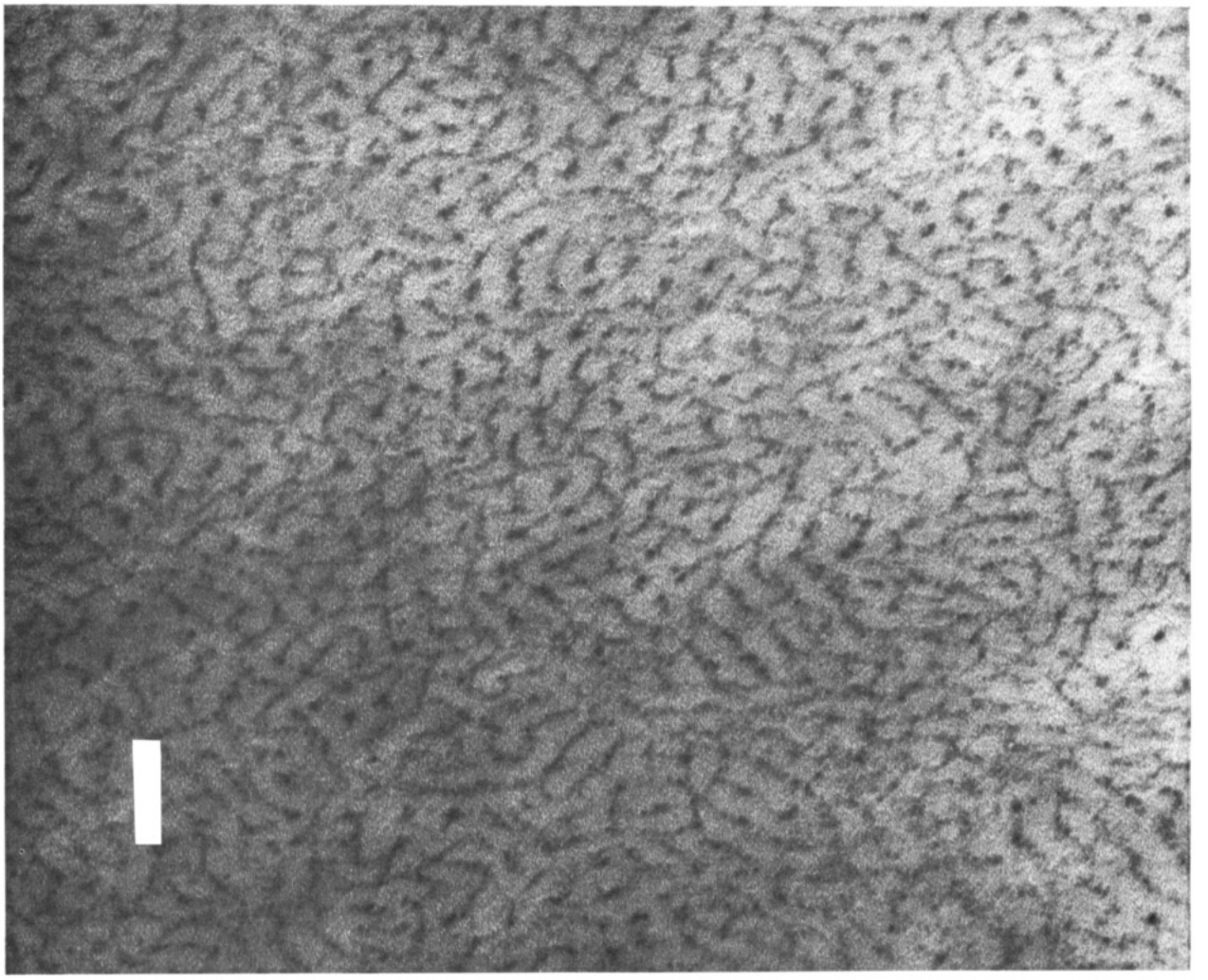

Figure 5. Bright-field TEM of $[Pb(bSAN)]_{20}/[MTD]_{176}$; bar = 500 Å.

scribed above was shown by TEM to consist of lamellar microdomains with a periodic spacing of 340 Å (Figure 7). This nearly colorless film turned yellow upon treating it with H_2S for 21 h at 25 °C. STEM investigation after this treatment revealed that the lamellar microdomains now contained sulfur and zinc in a 0.97 ± 0.04 ratio, consistent with reaction of one H_2S per zinc.

Conclusions

It is possible to prepare bidentate diamide ligands and complexes of them that are suitable for living ring-opening metathesis polymerization by the proper catalyst under the proper conditions. Since the block copolymers that have been prepared are not air-stable and therefore not amenable to GPC analysis, microdomain formation (as determined by TEM) comprises the most conclusive proof that the expected block copolymers have been prepared. TEM and STEM results indicate that metal complexes within a given microdomain are protolyzed readily. Therefore the ROMP block copolymer approach should be applicable to the synthesis of a variety of metal-containing morphologies in which further metal-based chemistry (e.g., formation of semiconductor materials) should be possible. Future studies will be aimed toward the synthesis and characterization of such materials.

Experimental Section

General Procedures. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques, unless otherwise stated. Reagent grade diethyl ether, tetrahydrofuran (THF), and toluene were distilled from purple sodium benzophenone ketyl under nitrogen. Benzene and THF for polymerization reactions were vacuum transferred immediately prior to use. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from purple sodium benzophenone ketyl under nitrogen. Deuterated benzene and tetrahydrofuran were vacuum transferred from purple sodium benzophenone ketyl. ^{13}C and ^{1}H NMR data are listed in parts per million downfield from TMS; ^{119}Sn NMR data are listed in parts per million downfield from tetramethyltin. Coupling constants are quoted in hertz. Obvious multiplicities and routine constants often are not listed. Spectra were recorded in benzene-d_6 at 25 °C unless otherwise noted. GPC analyses were performed at 25 °C on an instrument assembled from components (four Shodex columns and refractive index and variable-wavelength detectors). All columns were calibrated with polystyrene standards. Transmission electron microscopy was performed on a JEOL 200CX operating at 200-kV accelerating voltage. X-ray fluorescence elemental analysis was performed on a VG HB5 STEM (scanning transmission electron microscope) operating at 100-kV accelerating voltage.

Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ and Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$,[9f] W(NAr)(CH-*t*-Bu)(O-t-Bu)$_2$,[23] *endo,exo*-2,3-bis(tosylatomethyl)norborn-5-ene,[12] and diphenylzinc[24] were prepared as described in the literature.

Preparation of Compounds. trans-2,3-Bis((*tert*-Butylamino)methyl)norborn-5-ene (bTANH$_2$). A colorless solution containing the ditosylate (12.50 g, 27.0 mmol), dimethylformamide (115.13 g), and *tert*-butylamine (52.16 g, 713 mmol), was loaded

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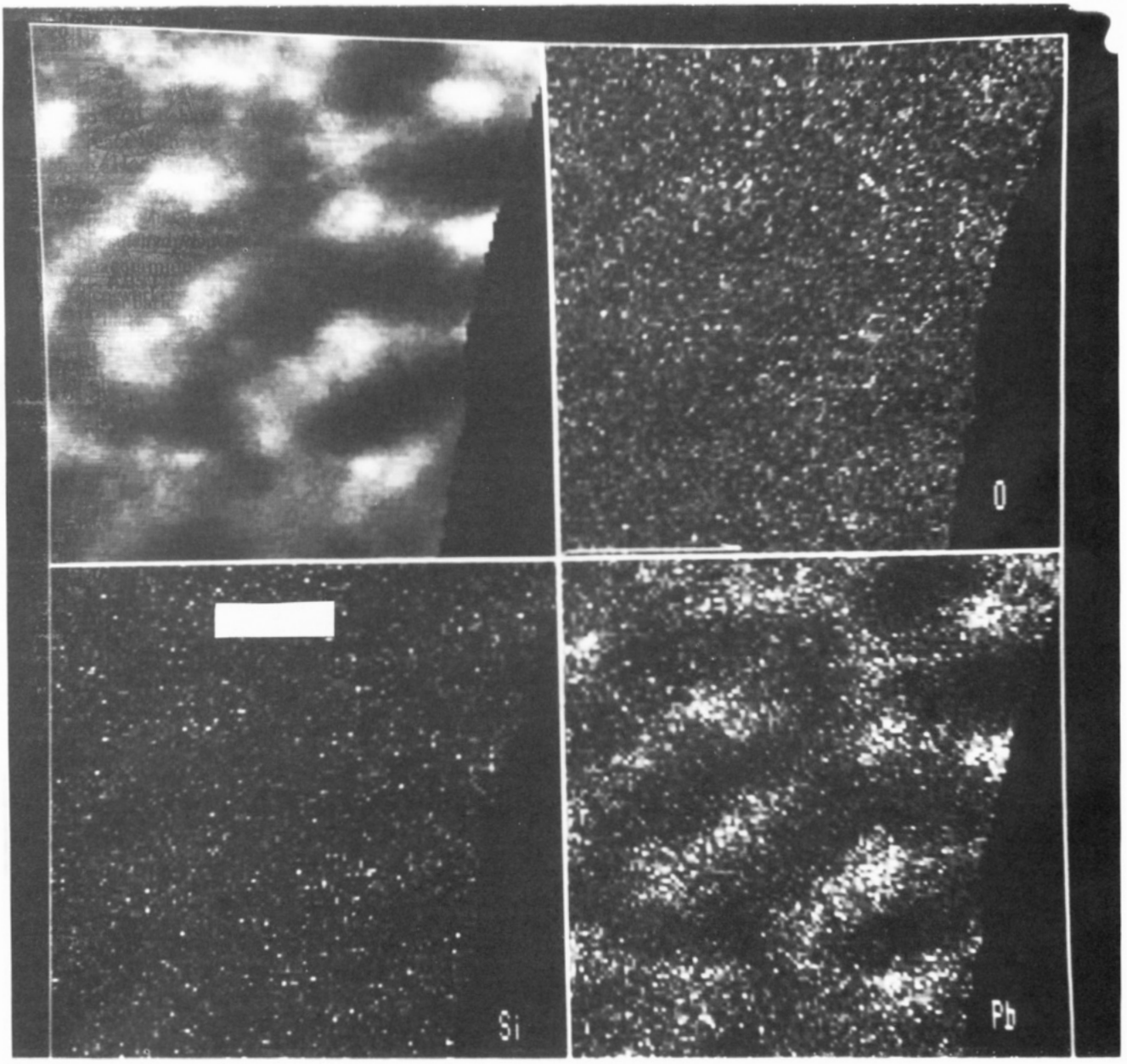

Figure 6. STEM of $[Pb(bSAN)]_{20}/[MTD]_{176}$ with dark-field image and X-ray fluorescence maps for Pb, Si, and O; bar = 100 Å.

into a 350-mL thick-walled glass vessel which was then tightly closed with a Teflon stopcock. The vessel was then immersed in a 110 °C bath. The reaction mixture was stirred magnetically and maintained at 110 °C for 21 h. A white sublimate appeared at the top of the vessel; this was shaken back into the reaction mixture and redissolved. The homogeneous, amber solution was cooled to 25 °C and poured into a 1-L separatory funnel containing 1.33 M NaOH (250 mL), and the resulting mixture was extracted with 30–65 petroleum ether (3 × 200 mL). The combined petroleum ether extracts were then washed with water (6 × 300 mL) and dried over Na_2SO_4. Filtration followed by removal of the volatiles left the diamine as a light-amber liquid (5.69 g, 80%). Yields generally range between 80 and 90%: ^{1}H NMR ($CDCl_3$) δ 6.08 (dd, 1, olefinic C*H*), 5.88 (dd, 1, olefinic C*H*), 2.66 (bs, 1, bridgehead), 2.52 (dd, 1, NCH_2), 2.43 (bs, 1, bridgehead), 2.39 (dd, 1, NCH_2), 2.31 (dd, 1, NCH_2), 2.03 (dd, 1, NCH_2), 1.50 (ddd, 1, exo-methine), 1.35 (d, 1, C(7)H_2), 1.30 (d, 1, C(7)H_2), 0.87 (ddd, 1, endo methine), 0.98 (s, 9, C(CH_3)$_3$), 0.94 (s, 9, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$) δ 137.6 (olefinic *C*H), 133.3 (olefinic *C*H), 50.02 (N*C*Me$_3$), 49.99 (N*C*Me$_3$), 48.01, 47.05, 46.77, 46.67, 46.29, 46.25, 45.05, 28.84 (NC(*C*H$_3$)$_3$), 28.80 (NC(*C*H$_3$)$_3$).

Li_2(bTAN). Butyllithium (63.6 mmol, 2.2 equiv, 2.5 M in hexane) was added by syringe to a stirred −40 °C solution of $bTANH_2$ (7.64 g, 28.9 mmol) in pentane (100 mL) in a 250-mL round-bottom flask. A white, microcrystalline precipitate appeared immediately. The reaction mixture was allowed to warm to 25 °C, was stirred for 1.5 h, and then was cooled to −40 °C for 24 h. The white, microcrystalline product was then collected by filtration under dinitrogen on a frit and dried in vacuo; yield 5.97 g (75%); ^{1}H NMR (C_6D_6) δ 6.19 (dd, 1, olefinic C*H*), 6.13 (dd, 1, olefinic C*H*), 3.22 (dd, 1, NCH_2), 3.13 (dd 1, NCH_2), 2.80 (bs, 1, bridgehead), 2.72 (dd, 1, NCH_2), 2.61 (bs, 1, bridgehead), 2.32 (dd, 1, NCH_2), 1.10 (s, 9, CMe$_3$), 1.08 (s, 9, CMe$_3$), 1.61 (d, 1, C(7)H_2), 1.50 (d, 1, C(7)H_2), 1.11 (m, 2, endo and exo methines).

Sn(bTAN)Cl_2. $SnCl_4(THF)_2$ (732 mg, 1.809 mmol) was added to cold ether (−40 °C) to produce a white slurry, to which was added solid Li_2(bTAN) (500 mg, 1.809 mmol) in small portions over 15 min. After stirring the mixture for 2 h, the volatile components were removed in vacuo, and the residue was extracted with pentane (20 mL). The extract was filtered and stripped to dryness in vacuo. The resulting pale yellow solid was dissolved in ~10 mL of pentane, and the solution was filtered and chilled to −40 °C to yield Sn(bTAN)Cl_2 as translucent yellow prisms (420 mg, 0.929 mmol, 51%): ^{1}H NMR (C_6D_6) δ 5.91 (dd, 1, olefinic C*H*), 5.80 (dd, 1, olefinic C*H*), 3.18 (dd [5, 10], 1, NCH_2), 3.14 (dd [4, 9], 1, NCH_2), 2.45 (bs, 1, bridgehead), 2.42 (dd [10, 12], 1, NCH_2), 2.21 (bs, 1, bridgehead), 2.15 (dd [10, 12], 1, NCH_2), 1.70 (ddd, 1, exo methine), 1.39 (s, 9, CMe$_3$), 1.35 (s, 9, CMe$_3$), 1.25

Figure 7. Bright-field TEM of $[(ZnPh)_2(bTAN)]_{80}/[MTD]_{250}$; bar = 1000 Å.

(d, 1, C(7)H_2), 1.16 (d, 1, C(7)H_2), 1.09 (ddd, 1, endo methine); ^{13}C NMR (C_6D_6 δ 137.4 (olefinic *C*H), 135.4 (olefinic *C*H), 58.7 (N*C*Me$_3$), 58.6 (N*C*Me$_3$), 53.4 (N*C*H$_2$), 52.6 (N*C*H$_2$), 49.5 (methine *C*), 47.5 (*C*(7)H$_2$), 47.4 (methine *C*), 45.1 (methine *C*), 43.3 (methine *C*), 30.9 (NC(*C*H$_3$)$_3$), 30.8 (NC(*C*H$_3$)$_3$). Anal. Calcd for $C_{17}H_{30}Cl_2N_2Sn$: C, 45.17; H, 6.69; N, 6.20. Found: C, 45.21; H, 6.67; N, 6.42.

Sn(bTAN). Li_2(bTAN) (150 mg, 543 μmol) was added to $SnCl_2$ (103 mg, 543 μmol), in 10 mL of ether at −40 °C with stirring. The mixture turned bright yellow and a precipitate was observed as the mixture was stirred and warmed to 25 °C. After 40 min the volatile components were removed in vacuo, and the residue was extracted with pentane (10 mL). The orange extract was concentrated in vacuo to an orange oil, a portion of which was dissolved in C_6D_6: ^{1}H NMR (C_6D_6) δ 6.14 (dd, 1, olefinic C*H*), 6.05 (dd, 1, olefinic C*H*), 3.67 (dd [4,12], 1, NCH_2), 3.60 (dd [4, 12], 1, NCH_2), 2.64 (bs, 1, bridgehead), 3.02 (dd [12, 12], 1, NCH_2), 2.42 (bs, 1, bridgehead), 2.68 (dd [12, 12], 1, NCH_2), 2.10 (ddd, 1, exo-methine), 1.41 (s, 9, CMe$_3$), 1.37 (s, 9, CMe$_3$), 1.60 (d, 1, C(7)H_2), 1.50 (d, 1, C(7)H_2), 1.46 (ddd, 1, endo-methine); ^{13}C NMR (C_6D_6) δ 136.70 (olefinic *C*H), 135.59 (olefinic *C*H), 58.51 (N*C*Me$_3$), 58.51 (N*C*Me$_3$), 60.72 (N*C*H$_2$), 58.44 (N*C*H$_2$), 49.44, 47.94, 47.10, 45.96, 44.11, 33.91 (NC(*C*H$_3$)$_3$), 33.83 (NC(*C*H$_3$)$_3$). All attempts to crystallize the oil failed.

Pb(bTAN). Li_2(bTAN) (100 mg, 362 μmol) was added to a vial containing 8 mL of ether at −40 °C followed by (while stirring the solution) $PbCl_2$ (101 mg, 362 μmol). After the red reaction mixture was warmed to 25 °C and stirred for 40 min, the volatile components were removed in vacuo, and the residue was extracted with ~8 mL of pentane. The pentane was removed in vacuo, and the solid residue was quickly and carefully washed with a small portion of cold ether leaving some yellow, crystalline Pb(bTAN). The proton NMR spectrum of the pure material was recorded within 10 min, but lead metal already was observable as a mirror on the NMR tube wall. Decomposition was complete within ~20 min; $bTANH_2$ was the only identifiable organic compound: ^{1}H NMR (C_6D_6) δ 6.23 (dd, 1, olefinic C*H*), 6.14 (dd, 1, olefinic C*H*), 5.90 (dd [3,12], 1, NCH_2, 40 Hz J_{PbH}), 5.85 (dd [3, 12], 1, NCH_2, 40 Hz J_{PbH}), 2.87 (bs, 1, bridgehead), 4.27 (dd [12, 12], 1, NCH_2, 13 Hz J_{PbH}), 2.61 (bs, 1, bridgehead), 3.80 (dd [12, 12], 1, NCH_2, 13 Hz J_{PbH}), 2.23 (ddd, 1, exo-methine), 1.44 (s, 9, CMe$_3$), 1.38 (s, 9, CMe$_3$), 1.78 (d, 1, C(7)H_2), 1.55 (d, 1, C(7)H_2), 1.75 (ddd, 1, endo-methine).

$(ZnPh)_2$(bTAN). A solution of diphenylzinc (0.500 g, 2.27 mmol) and $bTANH_2$ (0.331 g, 1.25 mmol) in toluene (12 mL) was loaded into a glass pressure vessel which was then tightly sealed with a Teflon stopcock. The reaction mixture was stirred magnetically and heated at 80 °C for 21 h. After the mixture was cooled to 25 °C, the volatile components were removed under reduced pressure leaving a crude solid residue (638 mg, ~ quantitative), examination of which by ^{1}H NMR revealed the presence of only $(ZnPh)_2$(bTAN) and a small amount of $bTANH_2$. The crude product was recrystallized from a mixture of toluene and pentane to yield the pure compound as white needles (495 mg, 0.90 mmol, 79%): ^{1}H NMR (C_6D_6) δ 7.85 (~d, 2, ortho Ar*H*), 7.74 (~d, 2, ortho Ar*H*), 7.40 (~t, 2, meta Ar*H*), 7.37 (~t, 2, meta Ar*H*), 7.27 (~t, 2, overlapping para Ar*H*), 6.02 (dd, 1, olefinic C*H*), 5.76 (dd, 1, olefinic C*H*), 3.17 (dd, 1, NCH_2), 3.12 (dd, 1, NCH_2), 2.58 (bs, 1, bridgehead), 2.60 (dd, 1, NCH_2), 2.32 (bs, 1, bridgehead), 2.28 (dd, 1, NCH_2), 1.86 (ddd, 1, exo methine), (s, 9, CMe$_3$), (s, 9, CMe$_3$), 1.26 (1, C(7)H_2), 1.22 (1, C(7)H_2); ^{13}C NMR (C_6D_6) δ 153.5, 153.4, 139.1, 138.6, 138.4, 132.9, 127.2, 127.1, 54.4, 52.9,

52.8, 52.1, 51.8, 48.5, 48.0, 47.7, 30.7, 30.6. Anal. Calcd for $C_{29}H_{40}N_2Zn_2$: C, 63.63; H, 7.36; N, 5.12. Found: C, 62.59; H, 7.32; N, 4.99 (values reported are the average of three runs).

***trans*-2,3-Bis(aminomethyl)norborn-5-ene.** The Diels–Alder reaction between fumaronitrile and cyclopentadiene in MeOH at 0 °C gave *trans*-2,3-dicyanonorborn-5-ene in quantitative yield. A 1-L, three-neck flask was purged with argon and equipped with mechanical stirrer, reflux condenser with Ar inlet, and a 500-mL dropping funnel. Dry ether (200 mL) was added followed by $LiAlH_4$ (18.4 g, 485 mmol). The dinitrile (17.30 g, 120 mmol) was dissolved in 400 mL of ether, and the solution was transferred to the dropping funnel. The solution was added dropwise over a period of ~2.5 h. Toward the end of the addition stirring became difficult. After addition was complete the reaction was chilled to 0 °C and 18.4 g of water, 18.4 g of aqueous NaOH (15%), and 55.2 g of water were added sequentially and cautiously. The resulting white, granular precipitate was filtered off and washed with three 100-mL portions of ether. The product is immiscible with ether, so a fine emulsion results. The emulsion was dried with Na_2SO_4 and the volatile components were removed in vacuo to give the diamine as a colorless liquid (14.57 g, 95.7 mmol, 80%): ^{1}H NMR (D_2O) δ 6.08 (dd, 1, olefinic C*H*), 5.91 (dd, 1, olefinic C*H*), 2.57 (dd, 1, NCH_2), 2.41 (dd, 1, NCH_2), 2.29 (dd, 1, NCH_2), 2.08 (dd, 1, NCH_2), 2.68 (bs, 1, bridgehead), 2.45 (bs, 1, bridgehead), 1.43 (ddd, 1, exo methine), 1.27 (d, 1, C(7)H_2), 1.20 (d, 1, C(7)H_2), 0.73 (ddd, 1, endo-methine).

***trans*-2,3-Bis[(trimethylsilyl)aminomethyl)]norborn-5-ene (bSANH$_2$).** To 180 mL of vigorously stirred ether at −40 °C were added sequentially the diamine (3.34 g, 21.94 mmol), triethylamine (22.20 g, 219.4 mmol, 10 equiv), and trimethylchlorosilane (9.53 g, 87.76 mmol, 4 equiv), the latter two having been prechilled to −40 °C. A voluminous precipitate of $[HNEt_3]Cl$ formed. After 48 h the triethylamine hydrochloride was filtered off and washed with additional ether (100 mL). The ether was then removed in vacuo to give the product as a viscous, colorless liquid (6.02 g, 20.3 mmol, 93%): ^{1}H NMR (C_6D_6) δ 6.14 (dd, 1, olefinic C*H*), 5.98 (dd, 1, olefinic C*H*), 2.40–2.80 (m, 6, overlapping multiplets due to NCH_2 and bridgehead protons), 1.41 (ddd, 1, exo-methine), 1.34 (d, 1, C(7)H_2), 1.46 (d, 1, C(7)H_2), 0.86 (ddd, 1, endo-methine), 0.10 (s, 9, Si(CH_3)$_3$), 0.09 (s, 9, Si(CH_3)$_3$).

Li$_2$(bSAN). A 100-mL flask charged with pentane (50 mL) and H$_2$(bSAN) (5.79 g, 19.52 mmol) was chilled to −40 °C. The solution was stirred while *n*-BuLi (39.04 mmol, 2.5 M in hexane) was added by syringe; some of the white, microcrystalline product appeared during the addition. The reaction mixture was warmed to 25 °C, stirred for 2 h, and then chilled to −40 °C overnight. White Li$_2$(bSAN) (5.405 g, 17.52 mmol, 90%) was then collected on a frit.

Sn(bSAN). Li$_2$(bSAN) (2.00 g, 6.484 mmol) was dissolved in THF (100 mL), and solid $SnCl_2$ (1.230 g, 6.484 mmol) was added in portions over ~15 min at 25 °C while the reaction mixture was stirred. The solution was orange by the end of the addition. After 45 min the solvents were removed in vacuo, and the residue was extracted with pentane (50 mL). The pentane was removed from the filtrate in vacuo. Pentane (~10 mL) was added to the residue, and the solution was chilled to −40 °C to give beige crystals. The crystals were isolated by decanting the supernatant and dried in vacuo (2.00 g, 4.84 mmol, 75%). Freshly crystallized Sn(bSAN) produces yellow solutions when dissolved in ether or benzene, and solid Sn(bSAN) readily turns into an orange oil in the presence of trace impurities: ^{1}H NMR (C_6D_6) δ 6.09 (dd, 1, olefinic C*H*), 5.99 (dd, 1, olefinic C*H*), 3.86 (dd [4, 12], 1, NCH_2), 3.74 (dd [3, 12], 1, NCH_2), 2.59 (bs, 1, bridgehead), 3.03 (dd [12, 12], 1, NCH_2), 2.38 (bs, 1, bridgehead), 2.65 (dd [12, 12], 1, NCH_2), 1.82 (ddd, 1, exo-methine), 0.31 (s, 9, Si(CH_3)$_3$), 0.28 (s, 9, Si(CH_3)$_3$), 1.48 (d, 1, C(7)H_2), 1.42 (d, 1, C(7)H_2), 1.30 (ddd, 1, endo-methine); ^{13}C{^{1}H} NMR (C_6D_6) δ 136.96 (olefinic *C*H), 134.75 (olefinic *C*H), 60.22 (*N*CH$_2$), 57.52 (*N*CH$_2$), 50.85, 49.12 (2 *C*), 47.71, 47.23, 2.43 (Si(*C*H$_3$)$_3$), 2.31 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{15}H_{30}N_2Si_2Sn$: C, 43.59; H, 7.32; N, 6.78. Found: C, 43.68; H, 7.33; N, 6.59.

Pb(bSAN). An olive-drab reaction mixture formed when Li$_2$(bSAN) (1.165 g, 3.78 mmol) in THF (35 mL) at 25 °C was treated with portions of $PbCl_2$ (1.050 g, 3.78 mmol) over 5 min. After 1 h the THF was removed at reduced pressure, and the residue was extracted with pentane (20 mL). The pentane was removed from the yellow-gold filtrate and the residue was dissolved in a minimum of pentane (~7 mL). Cooling this solution to −40 °C yielded pale-yellow crystalline Pb(bSAN) (1.336 g, 2.66 mmol, 70%): ^{1}H NMR (C_6D_6) δ 6.19 (dd, 1, olefinic C*H*), 6.08 (dd, 1, olefinic C*H*), 6.28 (dd [2, 12], 1, NCH_2), 6.15 (dd [2, 12], 1, NCH_2), 2.80 (bs, 1, bridgehead), 3.92 (dd [12, 12], 1, NCH_2), 2.56 (bs, 1, bridgehead), 3.51 (dd [12, 12], 1, NCH_2), 2.15 (ddd, 1, exo-methine), 0.28 (s, 9, Si(CH_3)$_3$), 0.24 (s, 9, Si(CH_3)$_3$), 1.58 (d, 1, C(7)H_2), 1.42 (d, 1, C(7)H_2), 1.62 (ddd, 1, endo-methine); ^{13}C NMR (C_6D_6) δ 136.96 (olefinic *C*H), 135.02 (olefinic *C*H), 61.79 (*N*CH$_2$, $^1J_{CH}$ = 132 Hz), 57.78 (*N*CH$_2$, $^1J_{CH}$ = 133 Hz), 47.73 (*C*(7)), 52.75, 51.03, 50.68, 48.39, 2.03 (Si(*C*H$_3$)$_3$), 1.83 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{15}H_{30}N_2Si_2Pb$: C, 35.91; H, 6.03; N, 5.58. Found: C, 35.61; H, 6.31; N, 5.58.

Preparation of [Sn(bTAN)Cl$_2$]$_{25}$/[NBE]$_{120}$. W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (19 mg, 34 μmol) was added to a stirred solution of norbornene (380 mg, 4.036 mmol) in benzene (6.00 g) at 25 °C. After 5 min half the reaction mixture was removed and treated with benzaldehyde (17 μL, 168 μmol, 10 equiv). This solution was taken outside the drybox and added dropwise to 50 mL of rapidly stirred methanol. The resulting sample of white [NBE]$_{120}$ was collected by filtration and dried in vacuo. A solution of freshly recrystallized Sn(bTAN)Cl$_2$ (190 mg, 420 mmol, 25 equiv) in 1.74 g of benzene was added to the second half of the living poly-Sn(bTAN)Cl$_2$. After 5 min 1,3-pentadiene (252 μmol, 25 μL) and benzophenone (33 μmol, 6 mg) were added. Approximately 100 mg of the [Sn(bTAN)Cl$_2$]$_{25}$/[NBE]$_{120}$ sample was precipitated by adding part of the solution dropwise to 10 mL of rapidly stirred pentane; the [Sn(bTAN)Cl$_2$]$_{25}$/[NBE]$_{120}$ sample was dried in vacuo. The remaining solution containing [Sn(bTAN)Cl$_2$]$_{25}$/[NBE]$_{120}$ (ca. 280 mg) was diluted to ~2% (w/w) with benzene and transferred to a polyethylene cup. The benzene was allowed to evaporate slowly over a period of 4 days at 25 °C. The resulting transparent yellow film was placed in vacuo for 24 h prior to ultramicrotomy. GPC on [NBE]$_{120}$: PDI = 1.08 (refractometer), 1.03 (UV–vis); M_n = 21 000 (calibrated against polystyrene; CH_2Cl_2).

[Sn(bSAN)]$_{25}$/[MTD]$_{177}$. W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 μmol) was added to a rapidly stirred solution of MTD (300 mg, 1.72 mmol) in THF (6.00 g). After 15 min 2.00 g of the reaction mixture was removed and treated with benzaldehyde (32 μmol) in order to provide a sample of [MTD]$_{177}$ homopolymer for GPC analysis (PDI = 1.10; refractometer; THF). The remainder of the reaction mixture was treated with Sn(bSAN) (67 mg, 162 μmol) in THF (1.44 g). After 20 min 1,3-pentadiene (100 μmol) was added and the reaction mixture was stirred for 1 h. THF was then added in order to dilute the solution to 2% (w/w). This solution was transferred to a polyethylene cup in a foil-wrapped jar in the drybox that had five 3-mm holes in the cap. The solvent evaporated completely over 4–5 days to give a stiff, yellow, transparent film which was easily separated from the polyethylene container.

[Pb(bSAN)]$_{20}$/[MTD]$_{176}$. The procedure was identical to that described for [Sn(bSAN)]$_{25}$/[MTD]$_{177}$ using the following quantities: THF (5.06 g), MTD (253 mg, 1.451 mmol), W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (8 μmol), PhCHO (32 μmol), Pb(bSAN) (50 mg, 100 μmol), and 1,3-pentadiene (75 μmol), GPC for MTD$_{176}$: PDI = 1.14 (refractometer, THF).

[(ZnPh)$_2$(bTAN)]$_{80}$/[MTD]$_{250}$. The procedure was identical to that described for [Sn(bSAN)]$_{25}$/[MTD]$_{177}$ using the following quantities: THF (2.76 g), MTD (150 mg, 861 μmol), W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (3.4 μmol), PhCHO (30 μmol), (ZnPh)$_2$(bTAN) (50 mg, 91 μmol), and 1,3-pentadiene (45 μmol). GPC for MTD$_{176}$: PDI = 2.22 (refractometer, THF).

X-ray Structure of Sn(bTAN)Cl$_2$. A yellow prismatic crystal of approximate dimensions 0.30 × 0.40 × 0.25 mm was mounted in a glass capillary. Data were collected at 23 °C on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. A total of 5068 reflections were collected to a maximum 2θ value of 55°, of which 4839 were unique (R_{int} = 0.043); equivalent reflections were merged. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2780 observed reflections ($I > 3.00\sigma(I)$) and 199 variable parameters and converged (largest parameter shift was less than 0.009 times its esd) with unweighted and weighted agreement factors of R = 0.051 and R_w = 0.049. A final difference

Fourier map showed no chemically significant features. Crystal data are a = 11.741 (3) Å, b = 10.160 (3) Å, c = 17.352 (5) Å, β = 105.19 (3)°, V = 1998 (2) Å^3, space group $P2_1/c$, Z = 4, mol wt = 452.03, ρ(calcd) = 1.503 g/cm^3.

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Registry No. (±)-bTANH$_2$, 137124-40-4; (ZnPh)$_2$(bTAN), 137124-46-0; Li$_2$(bTAN), 137124-44-8; Sn(bTAN)Cl$_2$, 137124-42-6; ((±)-Sn(bTAN)Cl$_2$)(NBE), 137124-43-7; (±)-Sn(bTAN), 137124-45-9; (±)-bSANH$_2$, 137143-77-2; Li$_2$(bSAN), 137124-47-1; (±)-Sn(bSAN), 137124-48-2; (±)-Pb(bSAN), 137124-49-3; SnCl$_4$(THF)$_2$, 17362-82-2; SnCl$_2$, 7772-99-8; t-BuNH$_2$, 75-64-9; Li-n-Bu, 109-72-8; PbCl$_2$, 7758-95-4; fumaronitrile, 764-42-1; cyclopentadiene, 542-92-7; trimethylchlorosilane, 75-77-4; (±)-*trans*-2,3-bis(hydroxymethyl)-5-norbornene ditosylate, 79465-49-9; (±)-*trans*-2,3-bis(aminomethyl)norborn-5-ene, 137124-41-5.

Supplementary Material Available: Fully labeled ORTEP drawing, final positional parameters, final thermal parameters (15 pages) and final observed and calculated structure factors (31 pages) for Sn(bTAN)Cl$_2$. Ordering information is given on any current masthead page.