(200 MHz) δ 1.1 (d, 3 H), 1.2 (t, 3 H), 2.35 (q, 1 H), 2.6 (m, 1 H), 3 (m, 3 H), 3.3 (dd, 1 H), 3.5 (dt, 1 H), 7–7.6 (m, 10 H).

1-Ethyl-3,4-diphenyl-2-methyl-2,5-dihydropyrrole (26a). *N*-Oxide **1b** (0.268 g, 2.6 mmol) and diphenylacetylene (13) (0.463 g, 2.6 mmol) were treated with LDA at –78 °C for 4 h. A crude mixture (0.593 g) was obtained after workup. Preparative TLC (CH_2Cl_2–MeOH (90/10)) afforded **13** (0.27 g, 1.56 mmol, 60%) and **26a** (0.272 g, 1.03 mmol, 39%): MS *m/e* 263, 262, 249, 186, 167, 124; ^{1}H NMR (200 MHz) δ 1.12 (d, 3 H, $J = 7$ Hz), 1.18 (t, 3 H), 2.6 (dq, 1 H, $J_{gem} = 13$ Hz), 3.0 (dq, 1 H), 3.60 (dd, 1 H, $J_{gem} = 14$ Hz, $J = 4$ Hz), 4.02 (m, 1 H), 4.39 (dd, 1 H), $J_{gem} = 14$ Hz, $J = 4$ Hz), 7.16 (m, 10 H). Picrate: mp 99–100 °C (EtOH). Anal. Calcd for $C_{25}H_{24}H_4O_7$: C, 60.98; H, 4.88. Found: C, 60.71; H, 4.83.

1-Ethyl-3,4-diphenyl-2-methylpyrrole (26b). Pyrroline **26a** (0.030 g, 0.11 mmol) was treated with 5% Pd/C at room temperature in methanol for 50 h to yield **26b** quantitatively: MS *m/e* 261; ^{1}H NMR (200 MHz) δ 1.39 (t, 3 H), 2.18 (s, 3 H), 3.86 (dq, 2 H), 6.73 (s, 1 H), 6.86 (m, 10 H).

3-Ethyl-5,5-diphenyl-4-methylthiazolidine (27a) and 3-Ethyl-5,5-diphenyl-2-methylthiazolidine (27b). *N*-Oxide **1b** (0.55 g, 0.5 mmol) and thiobenzophenone (14) (0.099 g, 0.5 mmol) were treated with LDA at 0 °C for 2 h. A crude mixture (0.159 g) was obtained after workup. VPC analysis revealed the presence of **27a** and **27b** in a 1.6 ratio. Preparative TLC (hexane–CH_2Cl_2 (80/20)) afforded the two isomers. **27a** (0.029 g, 0.1 mmol, 22%): MS *m/e* 283, 210, 181, 164, 85; ^{1}H NMR (200 MHz) δ 0.90 (d, 3 H, $J = 7$ Hz), 1.20 (t, 3 H), 2,56 (m, 1 H), 2.89 (m, 1 H), 3.86 (d, + q, 2 H, $J = 7$ Hz), 4.29 (d, 1 H, $J = 7$ Hz), 7.78 (m, 10 H). **27b** (0.011 g, 0.038 mmol, 8%): MS *m/e* 283, 268, 211, 165, 85; ^{1}H NMR (200 MHz) δ 1.1 (t, 3 H), 1.50 (d, 3 H, $J = 6$ Hz), 2.36 (m, 1 H), 2.73 (m, 1 H), 3.36 (d, 1 H, $J = 11$ Hz), 4.09 (d, 1 H, $J = 11$ Hz), 4.32 (q, 1 H, $J = 6$ Hz), 7–7.8 (m, 10 H).

1-Ethyl-3,4-diphenyl-5-methylimidazolidine (28a) and 1-Ethyl-3,4-diphenyl-2-methylimidazolidine (28b). *N*-Oxide **1b** (0.32 g, 3.10 mmol) and benzalaniline (**15**) (0.641 g, 3.41 mmol) were treated with LDA at 0 °C for 3 h. A crude mixture (0.880) was obtained after workup. **28a,b** were formed in 65% yield as determined by NMR. VPC analysis showed the presence of **28a** and **28b** in a 0.1 ratio. Preparative TLC (CH_2Cl_2) afforded **28b** (0.350 g, 1.50 mmol, 42%) and **28a**. **28b**: MS *m/e* 266, 251, 195, 194, 181, 85; HRMS calcd for $C_{18}H_{22}N_2$: 266.1789, found 266.1778; ^{1} H NMR (400 MHz) δ 1.08 (t, 3 H), 1.54 (d, 3 H), 2.04 (m, 1 H), 2.73 (m, 1 H), 3.15 (m, 1 H), 3.19 (m, 1 H), 4.45 (q, 1 H), 4.71 (dd, 1 H), 6.3–7.5 (m, 10 H). **28a**: ^{1}H NMR (400 MHz) δ 1.18 (t, 3 H), 1.22 (d, 3 H), 2.28 (q, 1 H), 2.59 (m, 1 H), 2.93 (m, 1 H), 6.3–7.5 (m, 10 H).

1-Ethyl-2-methyl-3-phenyl-4-(trimethylsilyl)-2,5-dihydropyrrole (29a) and 1-Ethyl-2-methyl-4-phenyl-3-(trimethylsilyl)-2,5-dihydropyrrole (29b). *N*-Oxide **1b** (0.164 g, 1.6 mmol) and protected phenylacetylene **16** (0.278 g, 1.6 mmol) were treated with LDA at 0 °C for 4 h. A crude mixture (0.461 g) was obtained after workup. VPC analysis revealed the presence of **29a** and **29b** in a 0.25 ratio. Preparative TLC (CH_2Cl_2–MeOH (97/3)) afforded **29a** (0.027 g, 0.1 mmol, 6.5%) and **29b** (0.280 g, 1.08 mmol, 68%). **29a**: MS *m/e* 259, 257, 244, 186, 73; ^{1}H NMR (200 MHz) δ 0 (s, 9 H), 1.22 (t,3 H), 1.32 (d, 3 H), 2.64 (dq, 1 H), 2.94 (dq, 1 H), 3.6–4.4 (m, 2 H), 7–8 (m, 10 H). **29b**: HRMS calcd for $C_{16}H_{25}NSi$ 259.1770, found 259.1769; ^{1}H NMR (200 MHz) δ 0 (s, 9 H), 1.20 (d, 3 H), 1.29 (dd, 3 H, $J = 7.5$ Hz) 2.66 (dq, 1 H, $J = 12$ Hz), 3.07 (dq, 1 H), 3.47 (dd, 1 H, $J_{gem} = 13$ Hz, $J = 5$ Hz), 3.93 (dq, 1 H, $J = 5$ Hz), 4.2 (dd, 1 H, $J = 4$ Hz), 7 (m, 5 H).

1-Ethyl-2-methyl-3-phenylpyrrolidine (30a and 30b) and 1-Ethyl-2-methyl-4-phenylpyrrolidine (30c and 30d). *N*-Oxide **1b** (0.309 g, 3 mmol) and styrene (0.260 g, 2.5 mmol) were treated with LDA at 0 °C for 3 h. A crude mixture (0.387 g) was obtained after workup. VPC analysis showed the presence of **30c**, **30a** + **30b**, and **30b** in a 1:4.2:1 ratio; **30a**/(**30b** + **30c** + **30d**) was shown by NMR analysis to be equal to 1.2. Preparative TLC (CH_2Cl_2–MeOH (97/3)) afforded 0.323 g (1.85 mmol, 74%) of various fractions in which **30a–c** were obtained in pure form. The stereochemistry was not attributed to **30c,d**. MS *m/e* 189, 175, 85. Picrate: Anal. Calcd. for $C_{19}H_{22}N_4O_7$: C, 54.54; H, 5.26; N, 13.39. Found: C, 54.26; H, 5.31; N, 13.20. **30a**: ^{1}H NMR (200 MHz) δ 0.75 (d, 3 H, $J = 6.5$ Hz), 1.27 (t, 3 H, $J = 7.5$ Hz), 2.23 (m, 2 H), 2.53 (m, 1 H), 2.72 (m, 1 H, $J_{Gem} = 7$ Hz), 3.0 (m, 1 H), 3.15 (m, 1 H), 3.33 (m, 1 H), 3.57 (dt, 1 H, $J = 8$ Hz), 7.36 (m, 5 H). **30b**: ^{1}H NMR (200 MHz) δ 1.12 (t, 3 H, $J = 8$ Hz), 1.17 (d, 3 H, $J = 6.6$ Hz), 1.37–1.73 (m, 1 H, $J_{gem} = 8$ Hz), 2.04–2.24 (m, 1 H, $J_{gem} = 12$ Hz), 2.24–2.46 (m, 1 H), 2.46–2.59 (m, 1 H, $J = 6.6$ Hz), 2.59–2.83 (dd, 1 H, $J = 11.5$ Hz), 2.83–3.09 (m, 1 H), 3.09–3.56 (m, 2 H), 7.16–8.0 (m, 5 H). **30c**: ^{1}H NMR (200 MHz) δ 1.18 (t, 3 H), 1.25 (d, 3 H), 1.9–2.2 (m, 2 H), 2.2–2.4 (m, 2 H), 2.5–2.9 (m, 1 H), 2.9–3.2 (dt, 1 H), 3.4–3.5 (m, 1 H), 3.4–3.6 (m, 1 H).

1,2-Diphenyl-1,5,6,7,8,8a-hexahydroindolizine (31). *N*-Oxide **1c** (0.23 g, 2 mmol) and diphenylacetylene (**13**) (0.36 g, 2 mmol) were treated with LDA at 0 °C for 4 h. A crude mixture (0.627 g) was obtained after workup. Preparative TLC (ether) afforded **31** (0.362 g, 1.32 mmol, 66%): MS *m/e* 275, 233, 199; ^{1}H NMR (200 MHz) δ 1–2 (m, 6 H), 2.5–2.7 (m, 1 H, $J = 12$ Hz), 3–3.3 (m, 1 H, $J = 12$ Hz), 3.3–3.6 (m, 1 H), 3.63 (dd, 1 H, $J_{gem} = 12$ Hz, $J = 5$ Hz), 4.20 (dd, 1 H, $J_{gem} = 12$ Hz, $J = 3$ Hz), 6.7–7.8 (m, 10 H); mp 90 °C (MeOH). Anal. Calcd for $C_{20}H_{21}N$: C, 87.27; H, 7.64. Found: C, 87.16; H, 7.68.

1-Aza-1,2-diphenyloctahydroindolizine (32). *N*-Oxide **1c** (0.28 g, 2.43 mmol) and benzalaniline (**15**) (0.484 g, 2.67 mmol) were treated with LDA at –78 °C for 3 h. A crude mixture (0.800 g) was obtained after workup. Preparative TLC (CH_2Cl_2–MeOH (99/1) afforded **32** (0.480 g, 1.72 mmol, 71%): MS *m/e* 278, 277, 249, 222, 201, 97; ^{1}H NMR (200 MHz) δ 1.58 (m, 4 H), 1.9 (d, 1 H, $J = 10$ Hz), 2.36 (dt, 1 H), 2.46 (d, 1 H), 2.95 (dd, 1 H, $J_{gem} = 7$ Hz), 3 (m, 2 H), 3.58 (d, 1 H), 4.5 (d, 2 H), 6.6–7.7 (m, 10 H); mp 115 °C (CH_2Cl_2). Anal. Calcd for $C_{19}H_{22}N_2$: C, 82.01; H, 7.91; N, 10.07. Found: C, 81.77; H, 7.93; N, 9.80.

Generation of Diatomic Sulfur from Organometallic Precursors[1]

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Diatomic sulfur, generated from different titanium and zirconium pentasulfides (**5a,b**), has been successfully trapped by dienes.

The first chemical generation of diatomic sulfur ($^1S_2$) was achieved in 1984 by the decomposition of a germanium trisulfide species (1) with triphenylphosphine dibromide (2).[2a] Evidence for the existence of S_2 was accomplished

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[1] Organosulfur Chemistry. Part 57. For Part 56, see: Harpp, D. N.; Bodzay, S. J. *Sulfur Lett.* 1988, 7, 81.

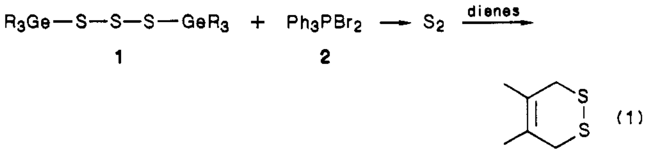
[2] (a) Steliou, K.; Gareau, Y.; Harpp, D. N. *J. Am. Chem. Soc.* 1984, *106*, 799. (b) Professor K. Steliou, private communication.

Table I. Reaction of 5 with 2 To Give S_2

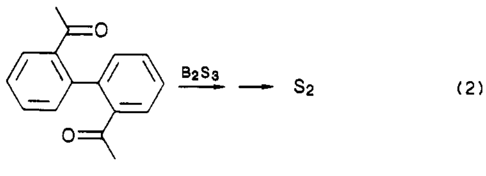
sulfane **5**	diene	% disulfide[a]
$(Cp)_2TiS_5$	**6**	21[b]
$(Cp)_2ZrS_5$	**9**	15[c]
$(Cp)_2ZS_5$	**6**	22
$(Cp)_2ZrS_5$	**8**	0
$(Cp)_2HfS_5$	**6**	0

[a] Isolated yields. [b] 31% polymer. [c] GC yield.

by Diels–Alder trapping with various dienes to afford cyclic disulfides (eq 1) in isolated yields ranging from 20% to 50%.



In 1987, Steliou and co-workers reported an improved method for S_2 production using a biphenyl precursor (**3**) in the presence of generated B_2S_3[3] (eq 2). These efforts



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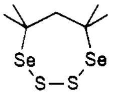
have stimulated considerable interest in this subject, and during the past year or so a variety of groups have investigated aspects of diatomic sulfur chemistry, paralleling the remarkably rapid development of singlet oxygen chemistry that began nearly 25 years ago.[4]

Recently, Schmidt found[5] that 1,2-dithia-3,7-diselena-4,4,6,6-tetramethylcycloheptane (**4**) thermally decomposes to afford modest yields of trapped disulfide by way of an ejected S_2 species. Ando has implicated S_2 production



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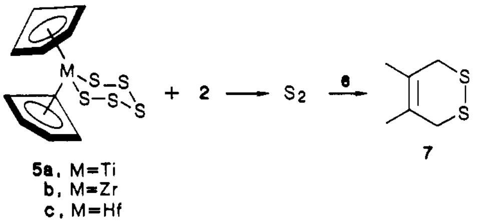
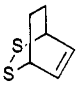
from unisolated 9,10-epidithio-9,10-dihydroanthracene (anthracene endodisulfide).[6] Finally, there have been other recent suggestions as to S_2 formation in a variety of decomposition reactions but in none of these cases was it authenticated by trapping experiments.[7]

Our own work during this period centered on inducing a variety of organometallic pentasulfides **5** to fragment in the presence of dibromide **2**[8] (Table I). The Ti, Zr, and Hf pentasulfides were prepared and treated with **2** in the presence of diene trap 2,3-dimethyl-1,3-butadiene (**6**). In the case of both **5a** and **5b**, reaction took place at room temperature to afford a purple-red solid. Extraction with pentane followed by chromatography and sublimation gave modest isolated yields (21% and 22%, respectively) of cyclic disulfide **7**. This compound was identical in all respects with an authentic sample.[2]



The same reaction procedure was applied to the hafnium derivative **5c**; however, only starting materials were recovered. Efforts to use 1,4-diphenyl-1,3-butadiene (**8**) as a trap for S_2 from zirconium pentasulfide **5b** failed and only triphenylphosphine sulfide and unreacted diene were isolated. Steliou has noted[3] that higher reaction temperatures result in better yields of trapped S_2 with an isomeric diene; the implication is that **8** is a less sensitive trap for S_2 than diene **6**. Zirconium pentasulfide (**5b**) was decomposed by **2** in the presence of 1,3-cyclohexadiene (**9**) to give the highly volatile bicyclic disulfide **10**. While great care was taken to isolate **10** (sublimation), it had volatility roughly comparable to that of solvent.

The sensitivity of the product disulfides toward polymerization reduced the yields of monomer. The likely electrophilic nature of the $(Cp)_2MBr_2$ (**11**) product also lowered yields of disulfide. In a control experiment with the stable disulfide, thiane (**12**), less than half of **12** survived a room temperature treatment with the chloro analogue of **11** (M = Ti); the remainder of the disulfide gave ^1H NMR bands associated with polymerized disulfide.



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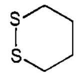

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While the isolated yields of trapped disulfides were not high in any of the reactions, ^1H NMR evidence suggests that the decomposition/trapping processes were essentially complete; this tends to corroborate[2,3] that S_2 (unlike "activated elemental sulfur"[6a,7]) does not yield episulfides or thiophene derivatives. These latter products (as compared with disulfides) do not appear to be consistent with a diatomic sulfur precursor and indicate that product type in reactions that incorporate sulfur atom(s) may well reflect the identity of the parent intermediate. It is also possible that the reverse process (sulfur-loss reactions) may reveal clearly defined intermediates as well.[8] Research is progressing in these areas.

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(3) Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* 1987, *109*, 926.

(4) For leading references, see: *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic: New York, 1979.

(5) Schmidt, M.; Görl, U. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 887.

(6) Ando, W.; Sonobe, J.; Akasaka, T. *Tetrahedron Lett.* 1987, *28*, 6653. Unfortunately, it is not clear from this report whether the diene-trapped products were actually isolated or detected in the reaction mixture; yields were inferred from isolated byproducts. This anthracene approach was tried unsuccessfully some years ago: (a) Smith, D. L. University Microfilms, Ann Arbor, MI, 77-11,451. (b) K. Steliou, University of Montreal, private communication. In addition, in no case (using Ando's substrates 1–3 and 5), in experiments where S_2 is produced and trapped in high yield, were any episulfides or thiophene derivatives detected; MacDonald, J. G.; Bernstein, M.; Williams, C.; Harpp, D. N., unpublished results; K. Steliou, private communication. These products are reminiscent of products from "activated sulfur" where sulfur fragments (possibly including S_2) are implicated; cf. ref 7a.

(7) (a) Efforts to trap diatomic sulfur were unsuccessful (or not reported) in the following recent articles implicating S_2: Bartlett, P. D.; Ghosh, T. *J. Org. Chem.* 1987, *52*, 4937. (b) Ando, W.; Kumamoto, Y.; Tokitoh, N. *Tetrahedron Lett.* 1987, *28*, 4833. (c) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Carroll, P. J. *J. Am. Chem. Soc.* 1987, *109*, 3801. (d) Orahovatz, A.; Levinson, M. I.; Carroll, P. J.; Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* 1985, *50*, 1550.

(8) Harpp, D. N. *Perspectives in the Organic Chemistry of Sulfur*; Zwanenburg, B., Klunder, A. J. H., Eds.; Elsevier: Amsterdam, 1987; pp 1–22.

While this particular route to S_2 is reliable, other pathways to this fascinating intermediate are actively being pursued in our laboratory.

Experimental Section

All melting points and boiling points are uncorrected. The infrared spectra were determined on a Perkin-Elmer 580 spectrophotometer. The proton magnetic resonance spectra were determined at 60 MHz using $CDCl_3$ as an internal standard with a Varian Associates T-60A spectrometer. Mass spectra were obtained on a DuPont 21-492B mass spectrometer, using a direct insertion probe.

Generation of S_2 from Bis(η-cyclopentadienyl)titana(IV)cyclohexasulfane (5a) and Triphenylphosphine Dibromide (2). To a suspension of 0.82 g (2.44 mmol) of bis(η-cyclopentadienyl)titana(IV)cyclohexasulfane(**5a**)[9] and 0.60 g (7.32 mmol) 2,3-dimethyl-1,3-butadiene in 20 mL of dry CH_2Cl_2 under a nitrogen atmosphere at room temperature was slowly added 1.03 g (2.44 mmol) of triphenylphosphine dibromide (**2**) in 5 mL of dry CH_2Cl_2. The resultant mixture was stirred at room temperature in the dark for 2 h. The solvent was then removed carefully under reduced pressure to leave a purple-red solid, which was extracted with pentane (2 × 35 mL). Removal of the pentane left a light yellow oil. Purification of the crude product was achieved by either neutral alumina chromatography (10% ethyl acetate in hexane as eluent) or sublimation at room temperature under water aspirator vacuum onto a water-cooled cold finger. Chromatography gave 50 mg (7%) and sublimation 150 mg (21%) of a light yellow oil whose structure was assigned as the cyclic disulfide **7** from the following spectroscopic data: ^{1}H NMR 1.78 (s, 6 H), 3.21 (s, 4 H); MS *m/e* 146 (M^+), 82. These spectra were consistent with literature values.[2] In the chromatography of the crude product a second fraction was isolated (220 mg, 31%) of a light yellow oil whose structure is assigned as a "polymer" of the cyclic disulfide unit: ^{1}H NMR 1.84 (s), 3.64 (s).

Generation of S_2 from Bis(η-cyclopentadienyl)zircona(IV)cyclohexasulfane (5b) and Triphenylphosphine Dibromide (2). The method described for the titanium system was repeated except that 0.93 g (2.33 mmol) of bis(η-cyclopentadienyl)zircona(IV) cyclohexasulfane (**5b**) was used. Workup and purification were the same to yield 70 mg (10%) by chromatography and 155 mg (22%) by sublimation of a light yellow oil whose structure was assigned as the cyclic disulfide **7** by identical spectral data as above. This experiment was repeated except that 1,4-diphenyl-1,3-butadiene was used (0.50 g, 2.44 mmol) as a trapping agent; only starting materials were detected by ^{1}H NMR.

Treatment of Bis(η-cyclopentadienyl)hafna(IV)cyclohexasulfane (5c) with Triphenylphosphine Dibromide (2) in the Presence of 2,3-Dimethyl-1,3-butadiene. The method described for the titanium system was repeated here except that 1.15 g (2.44 mmol) of sulfane **5c** was used. ^{1}H NMR analysis of the crude reaction mixture indicated no sign of cyclic disulfide and only the presence of starting materials.

Generation of S_2 from Bis(η-cyclopentadienyl)zircona(IV)cyclohexasulfane (5b) and Triphenylphosphine Dibromide (2). The method used above employing 2,3-dimethyl-1,3-butadiene was repeated except that 0.60 g (2.44 mmol) of 1,3-cyclohexadiene was used as the diene trap. Careful removal of the solvent at room temperature under reduced pressure left a yellow residue, which was extracted with pentane (2 × 15 mL). Removal of the pentane left a light yellow oil. The crude product was partially purified by sublimation at room temperature under water aspirator vacuum to yield a light yellow oil whose structure was assigned as the highly volatile bicyclic disulfide **10** on the basis of its spectral data and by comparison with an authentic sample.[2] The yield was 103 mg (15%) as estimated from ^{1}H NMR; there was some contamination with diene **9**. ^{1}H NMR 5.80 (m, 2 H), 4.88 (m, 2 H), 1.6–2.0 (m); MS *m/e* 80.

Reaction of Bis(η-cyclopentadienyl)titanium Dichloride with 1,2-Dithiane (12). A solution containing 0.18 g (1.5 mmol) of 1,2-dithiane and 0.37 g (1.5 mmol) of bis(cyclopentadienyl)titanium dichloride in 20 mL of dry THF under a nitrogen atmosphere was stirred at room temperature for 48 h. The solvent was removed under reduced pressure to yield a red powder. This was subjected to silica gel chromatography, using a 50% ethyl acetate–hexane solution as eluent. The major fraction of the column, 60 mg, had broad ^{1}H NMR peaks indicating polymer. Extraction of the column with chloroform afforded 80 mg of recovered 1,2-dithiane.

Acknowledgment. We thank the National Sciences and Engineering Research Council of Canada and the Ministère de l'Education du Québec for financial support. In addition, we are grateful to Professor Kosta Steliou (University of Montreal) and Professor Alan Shaver (McGill University) for helpful discussions.

Registry No. **2**, 5758-24-7; **5a**, 12116-82-4; **5b**, 75213-09-1; **5c**, 75213-10-4; **6**, 513-81-5; **7**, 18655-88-4; **7** homopolymer, 115018-96-7; **8**, 886-65-7; **9**, 592-57-4; **10**, 115018-95-6; **12**, 505-20-4; **12** homopolymer, 33087-70-6; $(Cp)_2TiCl_2$, 1271-19-8; S_2, 23550-45-0.

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[9] McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37. J. M. McCall, Ph.D. Thesis, McGill University, 1983.