interesting classes of substrates are represented in this series. Epoxidation of 2,2-dimethylchromene derivatives (entries 3 and 4) is extremely selective and provides access to important classes of biologically active compounds with high optical purity.[5] Epoxy ketals (entry 5) are versatile chiral building blocks that may be regioselectively opened to either α- or β-hydroxy ketals.[6] The epoxidation of *cis*-methyl cinnamate (entry 6) is to our knowledge the first example of epoxidation of an α,β-unsaturated carbonyl compound via oxo transfer,[7] and this methodology provides access to valuable optically active erythro-glycidic esters which are otherwise difficult to prepare.[8] For this substrate, addition of substoichiometric amounts of 4-phenylpyridine *N*-oxide was observed to improve both catalyst selectivity and turnover numbers.[9]

The use of an unhindered diamine precursor opens a quadrant to olefin approach (approach d) in which stereochemical communication between ligand and incoming substrate is maximized. High selectivity with **5** results not from a highly dissymmetric ligand, but rather from limitation of competing substrate approaches such that substrate interaction with the asymmetric environment is maximized. The effectiveness of **5** rules out the possibility (that existed with **1**) that π-stacking plays a role in directing substrate approach. Consistent with the side-on approach model, trans olefins tend to be poor substrates for this catalyst, being epoxidized slowly and with very low selectivity.[10] Terminal olefins such as styrene are generally epoxidized with higher enantioselectivities (60–75% ee) than previously reported with other catalyst systems,[11] although ee's still fall short of synthetically useful levels.[12]

Complex **5** is prepared in two simple steps in >90% overall yield from di-*tert*-butylsalicylaldehyde and 1,2-diaminocyclohexane.[13] The diamine is very inexpensive[14] and is resolved in a single crystallization with tartaric acid;[15] both pure enantiomers are also commercially available.[16] The felicitous combination of optimal catalyst design with a highly available chiral auxiliary should lead to widespread applicability of catalysts such as **5**.

Acknowledgment. This work was supported in part by the National Institutes of Health (GM-43214-01A1), a National Science Foundation PYI Award (CHE-9057740) to E.N.J., and generous contributions from the Monsanto Corporation, ICI Pharmaceuticals, Merck and Co., and Rohm and Haas.

Supplementary Material Available: Experimental and physical data for **2–5** and their precursors (4 pages). Ordering information is given on any current masthead page.

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(4) The following procedure for alkene epoxidation is general. A solution of commercial household bleach (Clorox) was diluted to approximately 0.55 M in NaOCl with 0.05 M Na_2HPO_4, and the pH of the resulting buffered solution was adjusted to pH = 11.3 by addition of a 1 M NaOH solution. To this solution was added a solution of **5** (159 mg, 0.25 mmol) and 2,2-dimethylchromene (2.01 g, 12.5 mmol) in 12.5 mL of CH_2Cl_2. The two-phase mixture was stirred at 4 °C, and the reaction progress was monitored by TLC. After 6 h, 12.5 mL of CH_2Cl_2 was added to the mixture and the brown organic phase was separated, washed twice with 50 mL of H_2O and once with 50 mL of saturated NaCl solution, and then dried (Na_2SO_4). After solvent removal, the residue was purified by flash chromatography on silica gel to afford 1.59 g of pure epoxide (72% isolated yield). The ee of the product was determined to be 97.6% by GC analysis (see footnote *c* in Table II).

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Extended Orthogonally Fused Conducting Oligomers for Molecular Electronic Devices[1]

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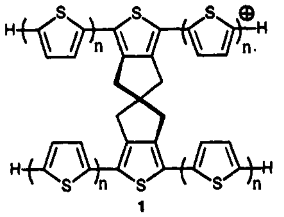
Since the time of the first room-filling computers, there has been a tremendous drive to compress the size of computing instruments. In order to bring this desire to its extreme, it was conceived that one may be able to construct single molecules that could each function as a self-contained electronic device.[3] Here we outline the convergent and flexible synthesis of two different macromolecules that approach the size necessary for molecular switch testing. Hence, the feasibility of molecular electronic devices, whether the architectures be of single molecule or ensemble arrangements, may soon be experimentally addressed.

Recently, Aviram of the IBM Corporation suggested that molecules ~50 Å long that contain a proconducting (nondoped or nonoxidized system, hence insulating) chain that is fixed at a 90° angle via a nonconjugated σ bonded network to a conducting (doped or oxidized system) chain should exhibit properties that would make them suitable for interconnection into future molecular electronic devices. These devices may be useful for the memory, logic, and amplification computing systems.[4] **1**, in doped form, is an example of a proconducting/σ/conducting molecule. To date, all experimental studies on orthogonal systems have dealt only with the spiro core of related molecules, and no synthetic approach demonstrated incorporation of the oligomeric chains.[5,6]



1

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(1) Presented at the 201st National Meeting of the American Chemical Society, Atlanta, GA, April 1991; Division of Polymeric Materials: Science and Engineering.

(2) Recipient of an Office of Naval Research, Young Investigator Award (1989–92) and National Science Foundation Presidential Young Investigator Award (1991–96).

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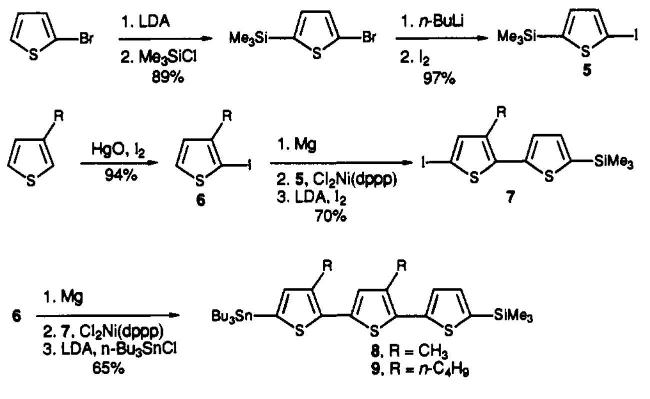
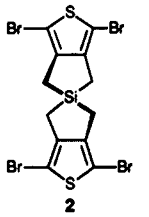
Scheme I



We recently described a facile approach to the core of two molecules which fit the general class of systems necessary for this electronic model.[7] The thiophene-based core (**2**) was synthesized in two steps from the tetraalkyne (**3**) by treatment with $Cp_2Zr(n\text{-}Bu)_2$ and S_2Cl_2 followed by bromodesilylation with Br_2. The phenylene-based core (**4**) was prepared in a four-step sequence from 2-aminobiphenyl.[7,8] In a single operation, we hoped to introduce the four branches onto the core units. In order to keep the final products soluble, it was necessary to use 3-alkylthiophenes as the branching units. Alkylated phenylenes have inferior conductivities due to the severe out-of-plane distortions of the consecutive aryl units.[9-11]



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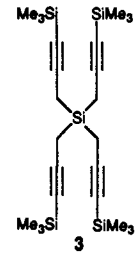

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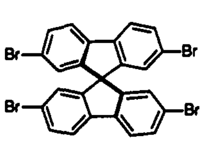
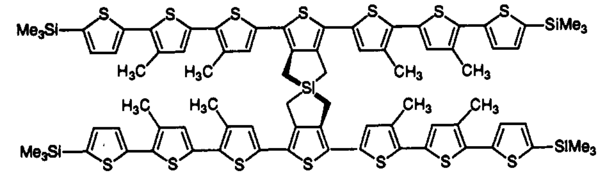


4

Functionalized and alkylated thiophene trimers were synthesized as shown in Scheme I (yields listed for R = CH_3).[12-14] When the silylated thiophene unit in **8** had a 3-methyl substituent, desilylation was rapid upon silica gel chromatography (even with amine-washed silica gel). Carbocationic character was sufficiently stabilized in the trimer (not the monomer or dimer) by both the β-silicon and α-methyl to allow for this rapid protodesilylation. Thus we chose to keep the terminal thiophene unit free of an alkyl substituent. These trimers possess several of the desired properties, namely (1) a terminal tributylstannyl substituent for attachment to the cores, (2) alkyl groups for maintaining the solubility, and (3) a terminal trimethylsilyl group for future chemoselective modification of the final orthogonal oligomers to permit adhesion to nanolithographic probes.[15]

Treatment of the core **2** with excess **8** in the presence of 8 mol % of $Pd(PPh_3)_4$ afforded the target orthogonal thiophene system **10** in 86% yield.[16,17] Similarly, the core **4** was treated with **9** and 8 mol % of $Pd(PPh_3)_4$ to give the mixed phenylene-thiophene spiro-fused octamer **11** in 60% yield.[18] Compounds **10** and **11** are approximately 25 and 30 Å in length (excluding the trimethylsilyl substituents), respectively, as determined by MMX with extended π Hückel parameters.[19] Both **10** and **11** are soluble in many organic solvents which will allow simple processing; however, without the alkyl substituents, these materials are intractable. Interestingly, while most fast atom bombardment mass spectra (FAB/MS) resemble chemical ionization spectra in providing primarily even-electron cations or anions (i.e., M + H),[20] both **10** and **11** readily showed M^+ data in 3-nitrobenzyl alcohol (NBA) and *o*-nitrophenyloctyl ether (ONPOE) matrices, respectively.[17,18] This is an indication of the ease of oxidation of these oligomers which was confirmed in cyclic voltammetry studies on **10** that showed two redox processes with anodic peak potentials (E_{pa}) at 0.68 and 1.05 V.[21,22]



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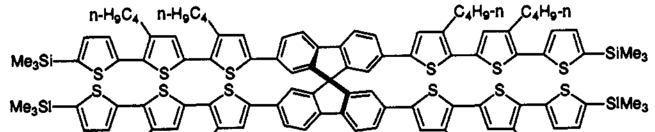

11

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(17) Spectral data for **10**: UV ($CHCl_3$) λ_{max} 456 nm, ϵ_{max} 2.94 × 10^4, tailing edge 545 nm; IR (KBr) 2950, 1132, 991, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.19 (1/2 ABq, J = 2.5 Hz, 4 H), 7.15 (1/2 ABq, J = 2.5 Hz, 4 H), 6.99 (s, 4 H), 6.93 (s, 4 H), 2.40 (s, 12 H), 2.37 (s, 12 H), 2.33 (s, 8 H), 0.31 (s, 36 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.94, 141.22, 140.61, 134.82, 134.80, 134.60, 134.58, 134.25, 131.34, 130.78, 129.60, 128.64, 128.44, 126.77, 17.08, 16.12, 16.00, 0.31; FAB/MS (NBA) calcd relative isotopic intensities for $C_{80}H_{84}S_{14}Si_5$ (M^+) 1632 (64%), 1633 (80%), 1634 (100%), 1635 (83%), 1636 (83%), 1637 (40%), 1638 (23%), found 1632 (77%), 1633 (96%), 1634 (100%), 1635 (94%), 1636 (79%), 1637 (56%), 1638 (45%).

(18) Spectral data for **11**: UV ($CHCl_3$) λ_{max} 418 nm, ϵ_{max} 2.91 × 10^5, tailing edge 495 nm; IR (thin film) 2955, 2927, 1458, 1250, 990 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 4 H), 7.65 (dd, J = 8.1, 1.6 Hz, 4 H), 7.14 (1/2 ABq, J = 3.4 Hz, 4 H), 7.13 (1/2 ABq, J = 3.4 Hz, 4 H), 6.98 (s, 4 H), 6.95 (d, J = 1.4 Hz, 4 H), 6.89 (s, 4 H), 2.71 (t, J = 7.7 Hz, 8 H), 2.67 (t, J = 8.1 Hz, 8 H), 1.65–1.52 (m, 16 H), 1.36 (sext, J = 7.7 Hz, 16 H), 0.91 (t, J = 7.5 Hz, 12 H), 0.87 (t, J = 7.4 Hz, 12 H), 0.31 (s, 36 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 141.8, 141.6, 141.2, 140.8, 140.0, 134.8, 134.47, 134.45, 131.0, 130.7, 128.8, 127.3, 126.9, 126.2, 121.4, 121.1, 66.4, 33.2, 33.1, 29.8, 29.5, 23.2, 23.1, 14.39, 14.38, 0.4; FAB/MS in (ONPOE) calcd relative isotopic intensities for $C_{117}H_{136}S_{12}Si_4$ (M^+) 2037 (51%), 2038 (83%), 2039 (100%), 2040 (89%), 2041 (67%), 2042 (43%), 2043 (25%), 2044 (13%), 2045 (6%), found 2037 (61%), 2038 (88%), 2039 (100%), 2040 (93%), 2041 (72%), 2042 (50%), 2043 (34%), 2044 (21%), 2045 (11%). Anal. Calcd for $C_{117}H_{136}S_{12}Si_4$: C, 68.96; H, 6.68. Found: C, 68.14; H, 6.86.

(19) PC Model version 4.1 from Serena Software (Box 3076, Bloomington, IN 47402-3076) with MMX mode with extended π-Hückel calculations.

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(21) Recorded with a 1-mm Pt disc working electrode and SCE double junction reference electrode at a scan rate of 50 mV/s at 10^{-4} M in CH_2Cl_2 with 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte.

(22) An orthogonally fused thiophene trimer (see ref 7) exhibited only one oxidation peak with E_{pa} = 1.07 V. Thus the heptamer is considerably easier to oxidize.

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Supplementary Material Available: Experimental details for compounds listed in this paper (6 pages). Ordering information is given on any current masthead page.

Synthesis of an Air-Stable, Moisture-Stable, and Thermally Stable Tungsten(VI) Oxo Alkylidene Complex. Precursor to an Air- and Moisture-Stable ROMP Catalyst

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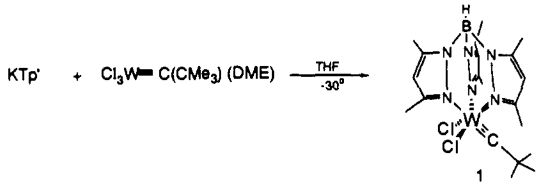
There has been considerable interest in the chemistry of high-valent tungsten alkylidyne[1,2] and alkylidene[1,3] complexes. Many such complexes have been demonstrated to be catalysts for acetylene[2,5] and olefin metathesis,[3,6] respectively. Tungsten imido alkylidenes have been shown to be extremely active catalysts for the ring opening metathesis polymerization (ROMP) of cyclic olefins[3a-c] and for the metathesis polymerization of acyclic dienes.[4] Until now, all well-characterized, molecular, high-valent tungsten alkylidynes and alkylidenes have proven to be air and moisture sensitive as well as thermally unstable at elevated temperatures.[7] We report here the synthesis and characterization of the first air-stable, moisture-stable, and thermally stable tungsten(VI) alkylidyne and alkylidene complexes and the conversion of the alkylidene complex to an air-stable ROMP catalyst.

Addition of 1 equiv of the tris-chelating monoanionic ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate[8] (Tp′) to a cold, stirring solution of $W[\equiv CC(CH_3)_3]Cl_3(DME)$[9] yielded the Tp′ alkylidyne dichloride **1**, eq 1. Compound **1** was recrystallized from toluene, producing small, fine purple needles.[10] The ^{1}H[11] and ^{13}C NMR spectra[12] were consistent with the proposed structure, with the alkylidyne α-carbon resonance appearing 335 ppm downfield of tetramethylsilane in the region characteristic for tungsten(VI) alkylidynes.[13] Remarkably, **1** has been found to be completely air and moisture stable both in the solid phase and in solution indefinitely.[14] No evidence of decomposition was observed when **1** was heated to 275 °C in an open capillary tube.[14b] Due to the extreme, unprecedented thermal stability of **1**, a very clean fragmentation pattern and intense molecular ion envelope (nominal parent ion mass 620.16) were detected by high-resolution mass spectroscopy.[15]



(1)

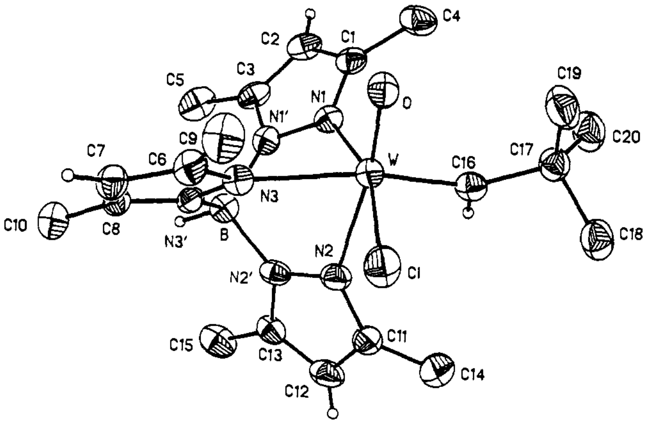


Figure 1. The structure of $Tp'W{=}C(H)CMe_3(O)Cl$ (**2**), showing 50% thermal ellipsoids and the atom-labeling scheme. Selected bond distances (Å): W–Cl, 2.363 (2); W–O, 1.685 (8); W–C(16), 1.949 (8); W–N(1), 2.174 (5); W–N(2), 2.359 (9); W–N(3), 2.285 (6). Selected bond angles (deg): Cl–W–O, 96.2 (2); Cl–W–N(1), 161.2 (2); O–W–N(1), 96.8 (3); Cl–W–N(2), 85.1 (2); O–W–N(2), 172.7 (2); N(1)–W–N(2), 80.3 (3); Cl–W–N(3), 85.0 (2); O–W–N(3), 94.5 (3); N(1)–W–N(3), 80.5 (2); N(2)–W–N(3), 78.4 (3); Cl–W–C(16), 96.6 (2); O–W–C(16), 99.8 (4); N(1)–W–C(16), 94.5 (3); N(2)–W–C(16), 87.2 (4); N(3)–W–C(16), 165.3 (4).

Although **1** proved to be stable to protonation by triflic acid, tetrafluoroboric acid, and hydrochloric acid, it was quantitatively converted to an oxo alkylidene monochloride, **2**, in essentially quantitative yield by stirring with neutral, activity 1 alumina,[16] eq 2. After filtration from alumina, **2** was pure (by ^{1}H NMR) and was dried under reduced pressure, giving a bright yellow, air-stable powder. Compound **2** also has remarkable thermal stability since it can be heated to reflux in cyclooctene solution

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(10) Calculated for $C_{20}H_{31}BCl_2N_6W$: C, 38.08; H, 5.05; N, 13.57. Found: C, 38.34; H, 4.94; N, 13.34. Yield, 49%. Complete experimental details can be found in the supplementary material.

(11) ^{1}H NMR data (300 MHz) for **1** (C_6D_6, 22 °C): δ 5.58, 5.38 (each s, 1:2 H, Tp' ring H's); 2.76, 2.61, 2.09, 1.83 (each s, 3:6:3:6 H, Tp′CH_3's); 1.56 (s, 9 H, $C(CH_3)_3$].

(12) ^{13}C NMR data (300 MHz) for **1** (C_6D_6, 22 °C): δ 335.33 [$^{1}J_{CW}$ = 212, *C*$C(CH_3)_3$]; 153.09, 152.40, 145.86, 141.62 (substituted Tp′ ring C's); 107.49 (unsubstituted Tp′ ring C's, overlapping); 47.69 [C*C*$(CH_3)_3$]; 33.30 [CC(*C*$H_3)_3$]; 19.30, 13.56, 12.16, 11.62 (Tp′ CH_3's).

(13) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342. See also ref 1, pp 135–136.

(14) (a) No change in the physical appearance or ^{1}H NMR spectrum of **1** could be detected after 3 months' storage of the solid in air or 3 weeks' stirring in THF or C_6D_6 solution. (b) There was no change in the ^{1}H NMR spectrum of the sample following heating of the sample to 275 °C.

(15) The complex mass envelopes generated for each peak are a consequence of the large number of atoms in **1** with relatively abundant isotopes. Modeling calculations accounting for five tungsten isotopes, two boron isotopes, and the usual carbon, hydrogen, and chlorine isotopes have successfully reproduced the parent ion envelope and the envelope around 551.082 which corresponds to loss of alkylidyne. Further analysis of the fragmentation pattern is currently underway.

(16) (a) The reaction of **1** with alumina was facilitated by the presence of undried solvents. Such reactivity has precedent for group VI Tp′ compounds, but has not been reported for high-valent alkylidenes. Trofimenko, S. *Inorg. Chem.* **1971**, *10*, 504. (b) The transformation of **1** to **2** can also be carried out by using 1 equiv of H_2O and NEt_3 in THF solvent, but the transformation is very slow (only 34% conversion after 5 days at 25 °C). No reaction was observed between **1** and LiOH in THF at 25 °C after 2 days.

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