Acknowledgment. This work was supported by a grant from the National Institutes of Health (PHS-GM 33589). The National Institutes of Health has provided a predoctoral training agent for D.C.Y. (GM 07151). Some of the mass spectral data were obtained at the Midwest Center for Mass Spectrometry, an NSF Regional Instrument Facility (CHE-8211164). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (CA-14599).

Supplementary Material Available: Spectral data for compounds **2a,b**, **11**, **12**, **13c**, **16a-f**, **17**, **19a,b**, **20a,b**, **21a,b**, **22a,b**, **26**, and **28** (8 pages). Ordering information is given on any current masthead page.

Approaches to Orthogonally Fused Conducting Polymers for Molecular Electronics[1]

James M. Tour,*[2] Ruilian Wu, and Jeffry S. Schumm

Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

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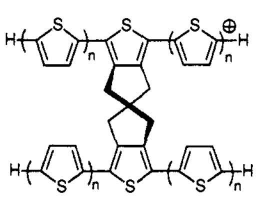
Molecular electronics based computing instruments possess tremendous technological potential. There is the hope of developing single molecules that could each function as a self-contained electronic device. Thus, one can envision computing systems with molecular-sized electronic elements and operational efficiencies far exceeding those of present systems.[3] Recently, Aviram of the IBM Corporation has suggested that molecules that contain a proconducting (nondoped or nonoxidized system, hence insulating) polymer that is fixed at a 90° angle via a nonconjugated σ-bonded network to a conducting (doped or oxidized system) should exhibit properties that would make it suitable for interconnection into future molecular electronic devices.[4] These devices may be useful for memory, logic, and amplification computing systems. Molecule **1** (in doped form) is an example of this proconducting/σ/conducting type of molecule.



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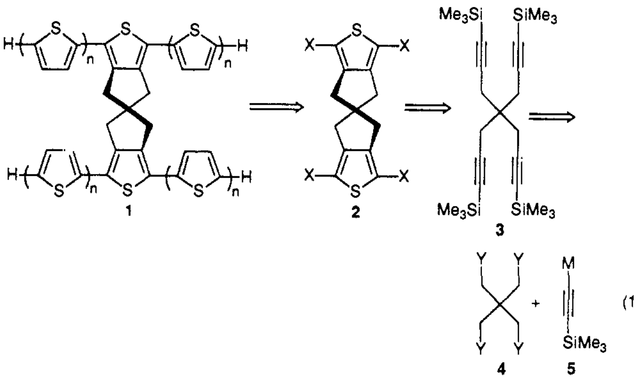
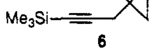
We have undertaken the synthesis of several molecules that fit the structural requirements of this electronic model. From the synthetic standpoint, several aspects are challenging. First, there must be one spiro-fused junction separating two potentially conducting chains with a tetrahedral bonding atom at the center to maintain the 90° angle via a σ-bonded network. Secondly, all four conducting chains originating from the central segment must be *identical* in length. These requirements prohibit the use of any random polymerization methods. Initial reports suggested that conducting chains $\sim$50 Å long (from end to end rather than from end to core) would fulfill the model.[4]

Our initial approach to these systems involved the synthesis of the key spiro core **2** from which we envisioned selective oligomerization to the target molecule **1**. A retrosynthetic analysis is shown in eq 1.



(1)

Though substitutions on pentaerythrityl tetrahalides involve reactions on a neopentyl system, exhaustive substitution has been accomplished using oxygen, nitrogen, and sulfur nucleophiles.[5] Attempted formation of **3** using 1-metallo-2-(trimethylsilyl)acetylenes **5** and pentaerythrityl tetrahalides and tosylates **4** proved to be very difficult even though we tried numerous coupling procedures (M = MgBr, Li, ZnCl, Cu, and AlR_2 with and without Pd and Ni catalysis). In several cases, we obtained the cyclopropyl system **6**.[6] In an effort to overcome these difficulties while maintaining the required σ-bonded tetrahedral spiro junction, we turned our attention to the use of silicon as the central atom. Accordingly, treatment of $SiCl_4$ with the silyl-protected propargyl Grignard reagent cleanly afforded the tetraalkyne **7**.[6] Treatment of **7** with a zirconocene equivalent, generated in situ from zirconocene dichloride and butyllithium, and quenching with sulfur monochloride afforded the trimethylsilyl spiro core **8** (eq 2).[6,7]



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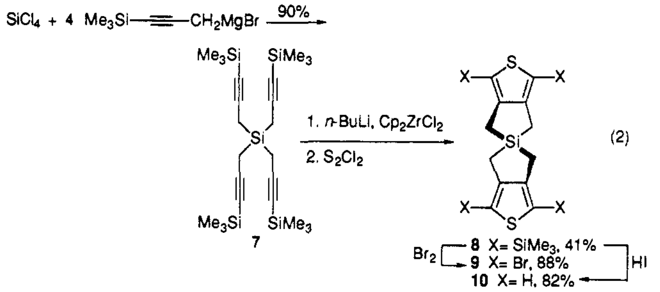

To our knowledge, use of this group IVA coupling procedure for a bisbicyclization has never before been demonstrated. The trimethylsilyl core (**8**) was converted to the tetrabromide (**9**) and parent core (**10**) under electrophilic substitution conditions.[6,8] Remarkably, no attack on the pseudoallylic central silicon atom was observed.

Likewise, we have synthesized another key core segment based on a *p*-polyphenylene[9] conducting unit which fits the general

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(1) Presented at the 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; Polymer Division.

(2) Recipient of the Office of Naval Research Young Investigator Award (1989–1992).

(3) (a) Bowden, M. J. In *Electronic and Photonic Applications of Polymers*; Bowden, M. J., Turner, S. R., Eds.; Advances in Chemistry 218; American Chemical Society: Washington, DC, 1988. (b) *Molecular Electronic Devices*; Carter, F. L., Ed.; Marcel Dekker: New York, 1982. (c) *Molecular Electronic Devices II*; Carter, F. L., Ed.; Marcel Dekker: New York, 1984. (d) Third International Symposium on Molecular Electronic Devices, Washington, DC, Oct 1986. Roland Etvos Physical Society, Satellite Symposium on Molecular Electronics, Budapest, Hungary, Aug 1987.

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(5) (a) Padias, A. B.; Hall, H. K., Jr.; Tomalia, D. A.; McConnell, J. R. *J. Org. Chem.* **1987**, *52*, 5305. (b) Fujihara, H.; Imaoka, K.; Furukawa, N. *J. Chem. Soc., Perkin Trans. 1* **1986**, 465.

(6) All new compounds were fully characterized spectroscopically, and the elemental composition was established by high-resolution mass spectrometry and/or combustion analysis. All reported yields pertain to isolated homogeneous materials which were purified by recrystallization or chromatography.

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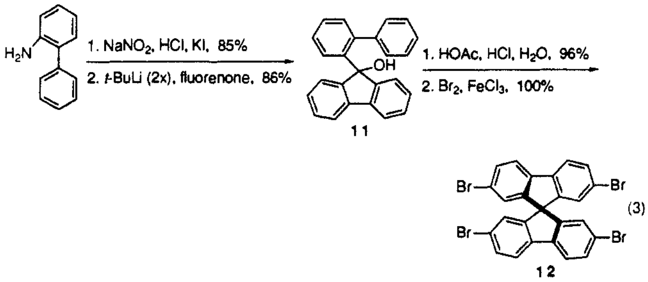
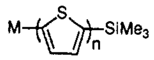
electronic architectural requirements. Conversion of 2-aminobiphenyl to the corresponding iodide under Sandmeyer[10] conditions followed by lithium halogen exchange and quenching with fluorenone afforded the alcohol **11**. Acid treatment to close the spiro system[11] followed by reaction with bromine and $FeCl_3$ gave the tetrabromide **12** in excellent yields (eq 3).[6] Bromination occurred only at the positions para to the second ring in the chain as one would expect by resonance stabilization arguments of the ionic intermediate. It is imperative that the bromination take place at the para position since a 4-substituted moiety is essential to afford a highly conducting system.[9]



With two key core units in hand, we then addressed methods to selectively and equally extend the chains in all four directions. Coupling **9** and **12** with **13** and **14**, respectively, using transition-metal catalysis[12] would allow for the selective introduction of a known number of units.[13] Additionally, the terminal trimethylsilyl group in **13** and **14** would allow for selective bromination at those sites and, hence, a position for further coupling if necessary.[8a] Accordingly, treatment of **9** with **13** ($M = Bu_3Sn$, $n = 1$) in the presence of catalytic $Pd(PPh_3)_4$ afforded **15** in 41% yield. Likewise, treatment of **12** with **14** ($M = ClZn$, $n = 1$) under similar catalytic conditions afforded **16** in 40% yield.[6] Use of 3-substituted thiophenes for connection to both **9** and **12** is also being investigated to help in solubilizing these systems.[13,14]



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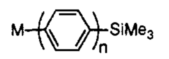

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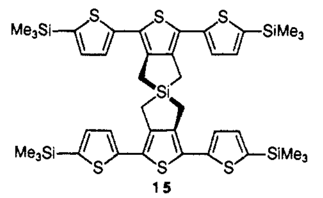
M= R_3Sn, XZn, XMg



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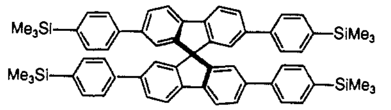

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Clearly, the efficiency of these coupling reactions must be optimized and the chain lengths further extended. However, these synthetic approaches demonstrate the power of modern synthetic methods to allow for the construction of macromolecules with the extremely specific architectural requirements necessary for the construction of the future molecular electronics based computing machine.

Acknowledgment. This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Program (N00014-89-J-3062), the National Science Foundation EPSCoR program (RII-8922165), and the University of South Carolina Venture Fund.

Supplementary Material Available: Detailed synthetic procedures for compounds **7-9**, **11**, **12**, **15**, and **16** (6 pages). Ordering information is given on any current masthead page.

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C-H Bond Activation as the Initial Step in the Co^+-Mediated Demethanation of Propane: The Critical Role of Angular Momentum at the Rate-Limiting Transition State

Petra A. M. van Koppen,* J. Brodbelt-Lustig, and
Michael T. Bowers

Department of Chemistry, University of California
Santa Barbara, California 93106

David V. Dearden and J. L. Beauchamp

Arthur Amos Noyes Laboratory of Chemical Physics[†]
California Institute of Technology
Pasadena, California 91125

Ellen R. Fisher and P. B. Armentrout

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

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Exothermic reactions of transition-metal ions with alkanes have in many instances been shown to be facile in the gas phase.[1] Reactions mainly result in the loss of molecular hydrogen and small alkanes to yield metal ion-olefin complexes. A variety of experimental techniques have provided thermochemical, kinetic, dynamic, and mechanistic information for these reactions, with an important focus being the identification of the initial activation step. The question of C-H versus C-C bond activation as the initial step in the formation of C-C bond cleavage products has yet to be resolved.[2]

We have measured reaction cross sections and kinetic energy release distributions for the exothermic reactions of Co^+ with propane, propane-*2*-d_1, propane-*2,2*-d_2, propane-*1,1,1*-d_3, propane-*1,1,1,3,3,3*-d_6, and propane-d_8. Both dehydrogenation and demethanation pathways are observed in all systems, although the emphasis here is on the demethanation reaction. Our observations demonstrate that this system is sensitive to the small perturbations induced by isotopic substitutions, and these provide insight into the fundamental question of initial C-H versus C-C bond activation for the demethanation process. Many exothermic gas-phase ion-molecule reactions occur near the collision rate at thermal energy due to the electrostatic attraction between the ion and the neutral.[3] In these cases the chemical activation provided

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[†] Contribution No. 8113.

(1) For recent reviews see: (a) Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; pp 34 and 628 and references therein. (b) Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russel, D., Ed.; Plenum: New York, 1989; p 1.

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