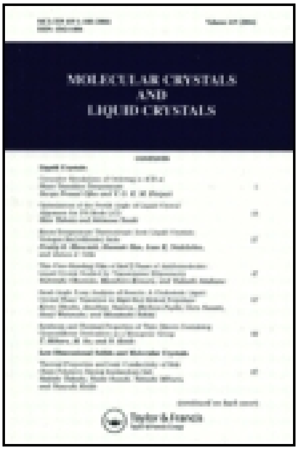

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An Approach to the Synthesis of TMTTeF

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AN APPROACH TO THE SYNTHESIS OF TMTTeF*

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Abstract An approach to the synthesis of tetramethyltetratellurafulvalene (TMTTeF) *via* an organosilicon intermediate is presented.

INTRODUCTION

Examination of the structural and electronic trends in the complex salts of sulfur, selenium and tellurium containing organic π-donors has revealed several important trends as the atomic number of the chalcogen is increased. For example, the conduction bandwidth is increased, the interchain interaction is also increased (more two- and three-dimensional character) and the molecules are more polarizable thus reducing the on-site coulomb repulsion. All three factors improve the electrical properties of the complex salts derived from the organic π-donors. These trends along with the fact that a large number of superconducting salts have been prepared from TMTSF indicate that the preparation of TMTTeF ought to have a high priority. To date, only four tellurium analogs of TTF have been prepared (see Figure 1). The HMTTeF was prepared by Wudl and Aharon-Shalom,[1] the TTeT was prepared by Sandman, Stark and Foxman,[2] while the DBTTeF and the

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BDMT-TTeF were prepared by Lerstrup, Cowan and co-workers.[3,4] Three of these compounds, HMTTeF, DBTTeF and BDMT-TTeF were prepared in a similar multistep sequence which is outlined for BDMT-TTeF in Figure 2. This set of reactions, which are described in more detail in another paper in this conference,[5] provides beautiful bronze-colored crystals (by reflected light) of BDMT-TTeF in 75% yield. Cyclic voltammetry performed on BDMT-TTeF in CH_2Cl_2 with Bu_4NBF_4 as the electrolyte, a platinum button working electrode and a saturated calomel reference electrode showed two one-electron oxidations at $E_{pa}(1) = 0.78$ V and $E_{pa}(2) = 1.2$ V. Only the first oxidation was entirely reversible under the conditions examined. The molecular structure, deduced by X-ray diffraction methods, indicates that the molecule has an unusual boat-like structure in the solid state. The dihedral angles between the tetratelluraethylene core and the exterior dimethylthienoditellura planes are quite different, 47.1(3) and 16.0(3)°. Some of the deviation from planarity is most likely due to the presence of dimer units which are coupled together with short intermolecular Te•••Te contacts inasmuch as the molecular structure of HMTTeF is almost planar.[6]

STRATEGY FOR THE SYNTHESIS OF TMTTeF

There are problems in trying to extend this method to the synthesis of TMTTeF since should one attempt the metal halogen exchange as in Figure 2, with an acyclic dibromide, the product will be an acetylene (elimination of LiBr). In fact, this reaction even takes place with small ring compounds at elevated temperatures.[7] To circumvent this problem, we propose to use a small ring structure which can be converted to methyl groups later in the synthetic sequence. One potential intermediate is the organosilicon compound shown in Figure 3. Three routes to this intermediate have been conceived. The first shown in Figure 4

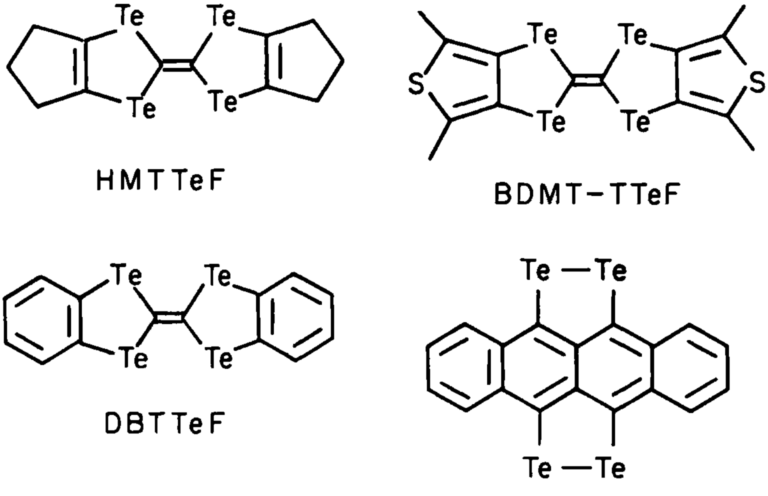

FIGURE 1

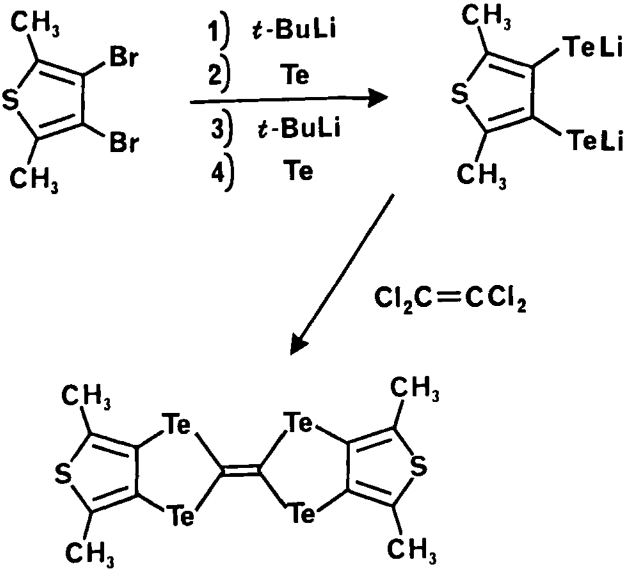

FIGURE 2

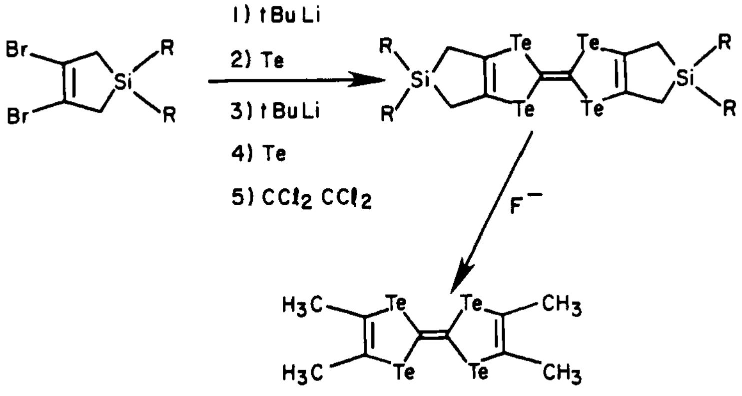

FIGURE 3

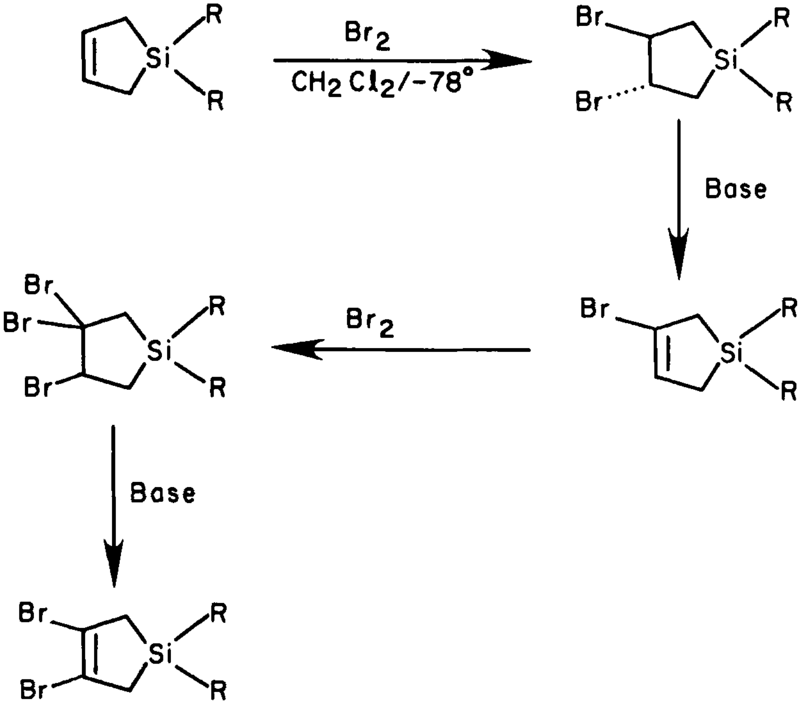

FIGURE 4

starts with the known halogenation of 1-sila-3-cyclopentene.[8] The remainder of the sequence, dehydrohalogenation, halogenation and dehydrohalogenation can be performed when the silicon is replaced by carbon. This is the type of classic procedure used by Wittig[7] to prepare 1,2-dibromocyclopentene. We considered the possibility that the basic elimination could form silacyclopentadiene or more likely its dimer but found no evidence for the formation of this compound.[9,10,11] However, neither did we find any evidence for the formation of the substituted 3-bromo-1-sila-3-cyclopentene. We suspect that reactions similar to those shown in Figure 5 take place. To date, four sets of conditions for this reaction have been tried: (1) $tBuO^-/tBuOH$, (2) $LiNH_2/Et_3N/Ph\text{-}H$, (3) $Na/NH_3(\ell)$, and (4) DBN [1,5-diazobicyclo[4.3.0]non-5-ene]/Ph-H.

A second potential route to the desired intermediate, 3,4-dibromo-1-sila-3-cyclopentene, is shown in Figure 6. 1-Sila-3-cyclopentenes can be prepared in 40-70% yields from the appropriate butadiene.[12,13] However, the mechanism of this reaction (Figure 7) involves the formation of a radical anion of the butadiene and this species could also be an intermediate in the formation of the vinyl Grignard. If the vinyl Grignard reagent is formed, then we expect elimination of magnesium bromide and the formation of an allene. The conditions which favor the formation of the vinyl Grignard are also those that favor the formation of the silacyclopentene (THF, HMPT), so it was not very surprising to find that the reaction did not produce the desired 3,4-dibromo-1-sila-3-cyclopentene.

A third route still under investigation is shown in Figure 8, and is based on the work of Manuel, Mazerolles and Florence.[14] They obtained a 60% yield of 1,1-dimethyl-1-sila-3-cyclopentene by allowing to react dichlorodimethylsilane, magnesium and *cis*-1,4-dibromo-1-butene in ether. A similar reaction with the tetrabromide shown in Figure 8 should afford the desired silacyclo-

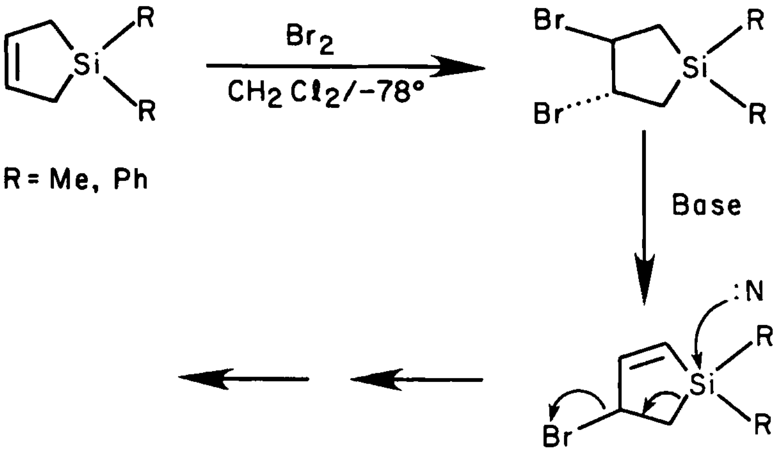

FIGURE 5

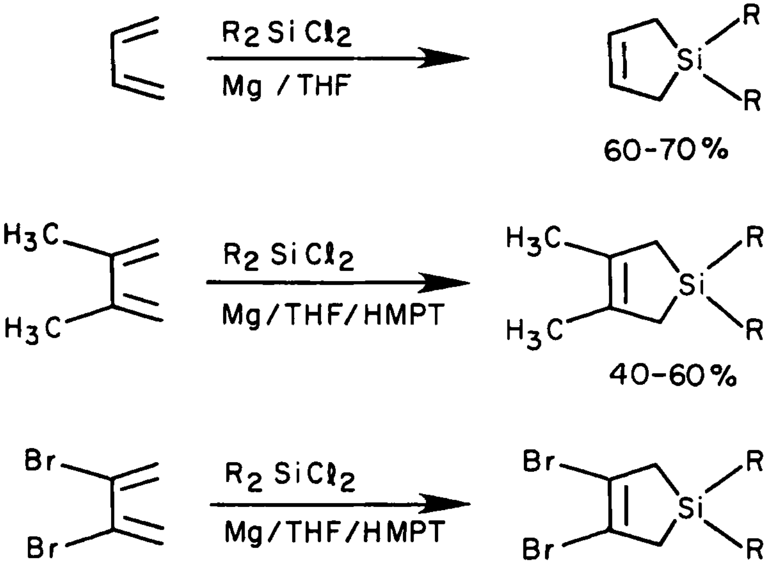

FIGURE 6

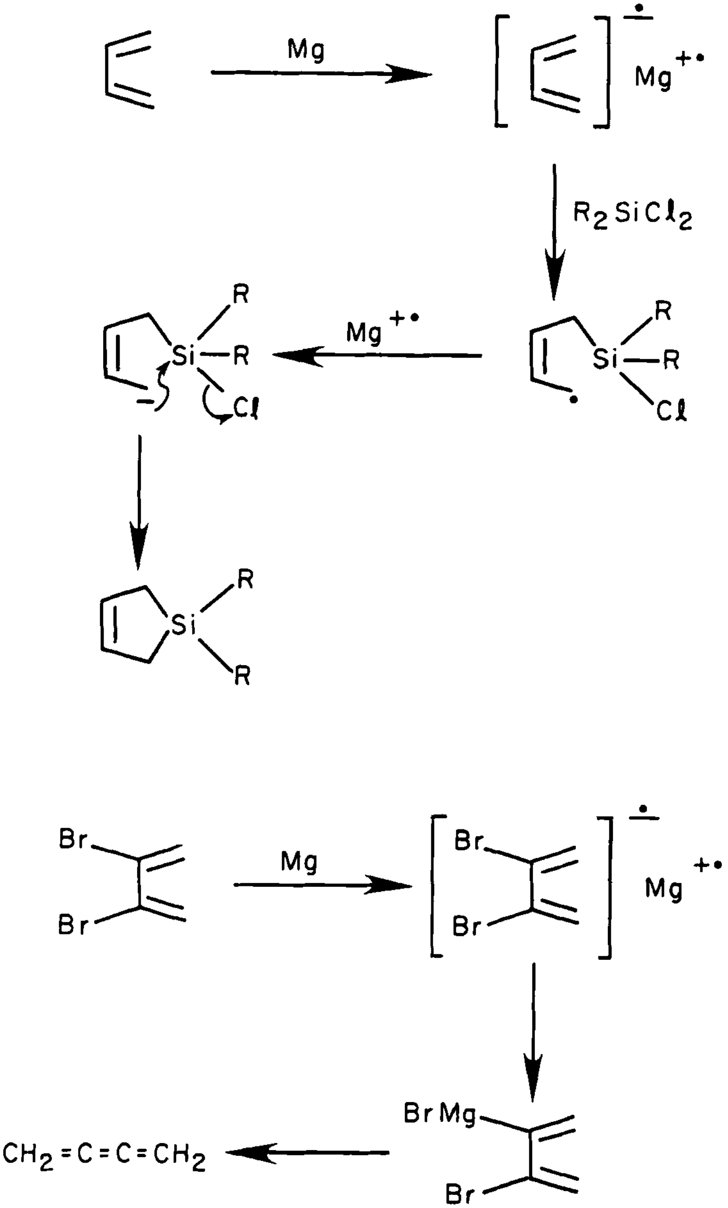

FIGURE 7

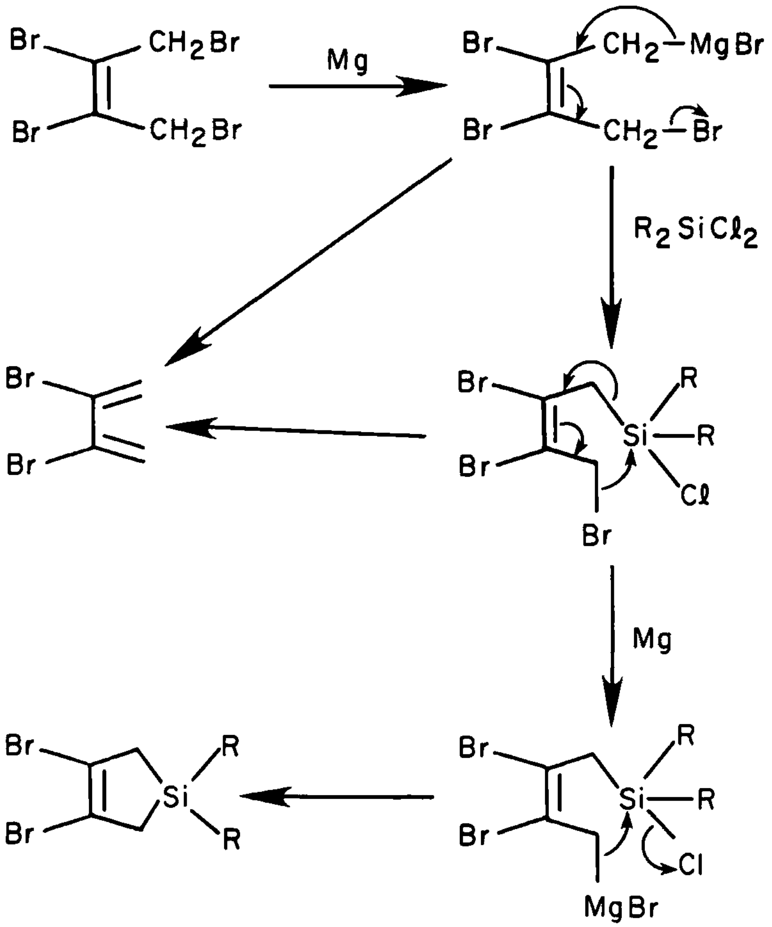
Br
CH2Br
Br
CH2Br
Mg
Br
CH2—MgBr
Br
CH2—Br
R2SiCl2
Br
Br
Br
R
Si
R
Cl
Br
Mg
Br
R
Si
R
Br
R
Br
Si
R
Cl
MgBr

FIGURE 8

pentene. However, the possibility of forming 2,3-dibromobutadiene in this reaction is also noted.

CONCLUDING REMARKS

We have proposed that it should be possible to prepare TMTTeF using the same type of reaction sequence used to prepare HMTTeF, DBTTeF and BDMT-TTeF providing the incipient methyl groups are part of a ring structure which is destroyed at the end of the synthetic scheme. To date, TMTTeF has eluded us, but we believe that this general synthetic strategy should ultimately yield this elusive compound.

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