Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: Daniel J. Sandman , James C. Stark , Lewis A. Acampora , Lynne A. Samuelson , Gregory W. Allen , Susan Jansen , M. Thomas Jones & Bruce M. Foxman (1984): Synthetic, Structural, and Electrical Aspects of Molecular and Polymeric Selenium and Tellurium Materials, Molecular Crystals and Liquid Crystals, 107:1-2, 1-17

To link to this article: http://dx.doi.org/10.1080/00268948408072068

Mol. Cryst. Liq. Cryst. 1984, Vol. 107, pp. 1-17
0026-8941/84/1072-0001/$18.50/0

SYNTHETIC, STRUCTURAL, AND ELECTRICAL ASPECTS OF MOLECULAR AND POLYMERIC SELENIUM AND TELLURIUM MATERIALS[1]

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Abstract. The physical and structural concepts concerning organochalcogen-based anisotropic organic metals are summarized, and the rationales which motivate synthetic activity in new selenium and tellurium materials are presented. An overview of our approach to new aromatic molecular and polymeric materials involving direct thermal reaction of new alkali chalcogenide reagents with unactivated aromatic halides is given, and recent applications to the synthesis of tetraselenonaphthalene (TSeN) and new transition metal diselenolenes based on *o*-benzenediselenolate (bds) are noted. The crystal and molecular structures of TSeN and $(nC_4H_9)_4N^+$ $Ni(bds)_2^-$ have been determined, as well as their electronic absorption and electron spin resonance spectra and cyclic voltammetric behavior. The reaction of *cis*-dichloroethylene and sodium diselenide leads to a polymer to which the repeat sequence $\leftarrow$Se-CH=CH-CH=CH-Se$\rightarrow$ is assigned, based on elemental analysis and infrared spectrum.

INTRODUCTION

Beginning with the studies of TTF-TCNQ, the prototype quasi-one-dimensional organic metal, the class of ion-radical solids which are organic metals provides an impressive example of the use of new synthetic chemistry to control the details of crystal structure, and hence the electronic structure and physical properties, of the resultant solid. From a kinetic perspective,[5] the role of the chalcogen atom in the formation of the uniform segregated stack crystal structures of these organic metals is a crucial one in that it provides not only a rationale for phase formation but also outlines the approach to materials with improved metallic properties. In the course of a metal-to-insulator transition, as observed in TTF-TCNQ, the dielectric constant diverges. This situation requires that the ratio of molar refractivity (R) to molar volume V be unity in the Clausius-Mossotti relationship:[6]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{R}{V} \qquad (1)$$

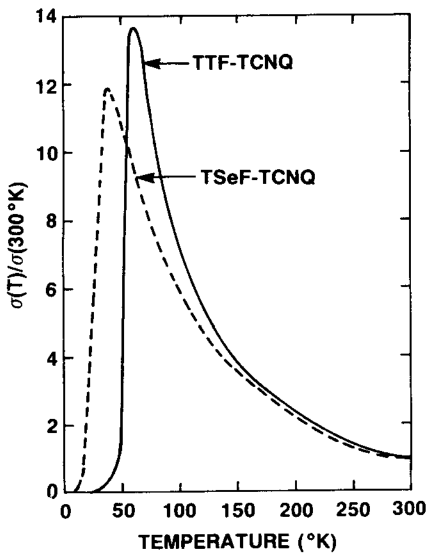
Since R relates to the polarizability α by

$$R = \frac{4}{3} L\pi\alpha, \qquad (2)$$

where L is Avogadro's number, it is important for organic metals to achieve maximum α with minimum V. For the case of conducting organochalcogen materials, since α increases $S < Se < Te$, it follows that if an organosulfur compound has metallic character, this property should be enhanced with progression down Group VI, if crystal structure is maintained and factors such as conduction band population do not change significantly.[7] The studies of the TCNQ salt of tetraselenafulvalene, i.e. TSeF-TCNQ, with a crystal structure isomorphous to that of TTF-TCNQ, provided the first demonstration of that situation.[8] Figure 1 exhibits representative b-axis single crystal dc conductivity data for these materials.

Further consequences of the general perspective summarized by equations 1 and 2 are as follows.[7] If an organosulfur material has quasi-one-dimensional properties, its selenium and tellurium analogs will be less one-dimensional, as interchain coupling will be increased in the latter materials. Intermolecular forces increase

QUASI-ONE-DIMENSIONAL ORGANIC METALS



TTF-TCNQ { U. of PENNSYLVANIA
JOHNS HOPKINS U.
MONSANTO CO.

TSeF-TCNQ, E. ENGLER (IBM)

TTeF-TCNQ ?

CHARGE TRANSFER	
TTF-TCNQ	0.59
TSeF-TCNQ	0.63

FIGURE 1

$S < Se < Te$. It is also useful to recognize that R/V in (1) will differ for different classes of organochalcogen donors, e.g. tetrachalcogenofulvalenes and tetrachalcogenoacenes. It is anticipated that a fuller understanding of this class of materials will result from the study of new Se and Te donors with nonbonded interactions significantly different from presently known materials.[9]

A BROADLY APPLICABLE APPROACH TO NEW SELENIUM AND TELLURIUM MATERIALS

The major impetus for our work in new selenium and tellurium chemistry was provided by the observation of low-temperature metallic states in ion-radical solids of stoichiometry $D_2^{+}X^{-}$, where D represents the donors tetraselenotetracene (TSeT) and tetramethyltetraselenafulvalene (TMTSF), and X is a monovalent anion. In this regard, the observation of ambient pressure superconductivity in $(TMTSF)_2^{+}ClO_4^{-}$ (T_c ca. 1°K) is particularly noteworthy.[10] Pursuant to the discussion in the introduction above, the synthesis and detailed study of the tellurium analogs of these and related donors are of obvious interest.

A broader view of selenium and tellurium systems is provided by reference to Figure 2 which displays molecular structures of organochalcogen molecular and polymeric systems of interest for their chemical, structural, electrical, and magnetic properties. The dashed line in Figure 2 separates those types of materials which were known at the beginning of our investigations from those which were unknown. It is the latter substances which provide a meaningful challenge to chemists interested in the synthesis and characterization of such novel materials.

Over the last several years, we have developed a new pattern of selenium and tellurium chemistry which may be summarized as a two-step procedure.[11] In the first step, we react an alkali metal with elemental Se or Te in either a 1:1 or 2:1 atomic ratio in a dipolar aprotic solvent to form in situ an alkali chalcogenide reagent. The second step involves direct thermal reaction of an unactivated aromatic halide with the alkali chalcogenide reagent. This approach to Se and Te materials may be used to prepare both new and previously reported molecular and polymeric materials. Our studies of the synthetic and qualitative mechanistic aspects of this chemistry have been summarized.[7]

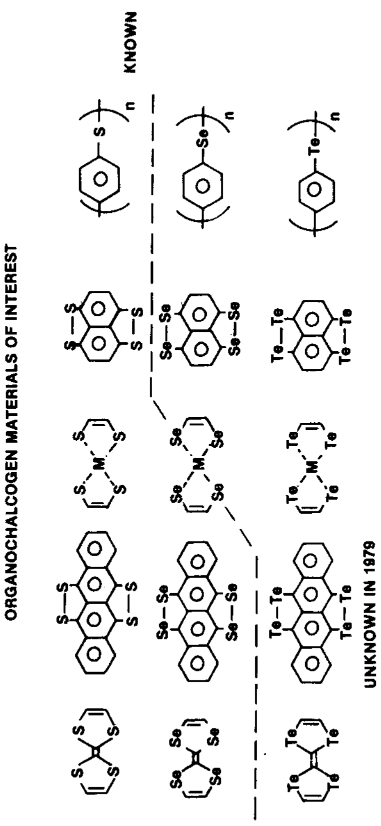

ORGANOCHALCOGEN MATERIALS OF INTEREST
KNOWN
UNKNOWN IN 1979
S
Se
Te
M
n

FIGURE 2

We have used this new pattern of chemistry to prepare new polymers, such as poly-p-phenylene selenide,[12] of interest for their potential thermal and electrical properties,[7,13] new peri-dichalcogenide derivatives of polyacenes, such as tetratellurotetracene[14] (TTeT) and tetraselenonaphthalene (TSeN),[15] of interest as precursors to low-temperature organic metals, and new dichalcogenide polymers which are useful as precursors to molecular reagents.[7] In this article, we summarize our recent studies of TSeN, new transition metal diselenolenes, and some initial results of our studies of the reactions of vinylic halides with selenium and tellurium nucleophiles.

1,4,5,8-TETRASELENONAPHTHALENE

Interest in the electronic structure of the peri-dichalcogenides of aromatic hydrocarbons[16] and in donors with nonbonded interactions other than those in the $(TMTSF)_2X$ class of ion-radical solids[7,9] motivated us to synthesize TSeN early in 1982. The sulfur analog of TSeN, i.e. TTN, interacts with TCNQ to give a highly conducting ion-radical solid with a uniform segregated stack crystal structure.[17] Solids of the type $(TTN)_2X$ have not been reported to date.

In N,N-dimethylformamide (DMF), sodium diselenide reacts with 1,4,5,8-tetrachloronaphthalene (TClN) to give TSeN and 1,8-diseleno-4,5 -dichloronaphthalene as minor and major products, respectively.[15] TSeN was purified by gradient sublimation to give a black solid, mp > 350°. The properties observed for our purified TSeN are at variance with those claimed in a recent report[18] of its synthesis.

Mass spectrometric analysis of the solids isolated from reaction of TClN with sodium ditelluride revealed the presence of the tellurium analogs of the two products isolated in the previous paragraph.

The intense visible absorption maximum of TSeN is observed at 441 nm (bromobenzene solution) compared to 420 nm for TTN. The ESR spectrum of $TSeN^{\dot{+}}$ is characterized by its 10.4 gauss line width and its isotropic g value, 2.0425. The increased linewidth and g value in $TSeN^{\dot{+}}$ compared to $TTN^{\dot{+}}$ (0.3 gauss, g = 2.0094)[17] are attributed to increased spin-orbit coupling in the selenium compound. The tetrachalcogenotetracenes[19] and naphthalene-1,8-dichalcogenides[20] behave similarly, exhibiting a linear relationship between g-value and chalcogen spin-orbit interaction parameter.

Analogously to TTN,[17] TSeN exhibits tow reversible one-electron steps at +0.15 and +0.54 V vs. Ag/Ag$^+$ in benzonitrile using 0.10 M TEAP as support electrolyte. The cyclic voltammogram for TSeN is displayed in Figure 3. The 0.39 V potential difference for the two electron transfers of TSeN is similar to that of TTN (0.38 V)[17] and that of the tetrachalcogenotetracenes (0.36 - 0.38 V).[19]

The crystal and molecular structure of TSeN have been determined using single crystals grown in chlorobenzene solution.[15] TSeN is monoclinic, space group $P2_1/c$, *a* = 7.722(2)Å, *b* = 4.226(1)Å, *c* = 15.305(4)Å, β = 102.15(3)°, V = 488Å^3, Z = 2. Solved by Patterson and difference-Fourier syntheses to R = 0.037, R_w = 0.048, the structure reveals linear chains of TSeN molecules stacked along *b* with interstack Se···Se contacts of 3.626Å and 3.534Å. The carbon atoms of the TSeN molecule form a plane with no deviations greater than ±0.007(6)Å. One of the selenium atoms deviates from this plane by 0.101(1)Å.

We have initiated the preparation of ion-radical solids derived from TSeN as well as the study of their structural, electrical, and magnetic properties. $(TSeN)_2Br$ has been prepared by anodic electrocrystallization. TSeN and iodine interact in chlorobenzene solution to give a crystalline gray solid of composition $C_{10.7}H_{6.6}Se_{4.0}I_{2.1}$ by elemental analysis. This solid has a conductivity, measured on compacted material, of 10^{-5}(ohm-cm)$^{-1}$, and its x-ray powder pattern reveals that it is not contaminated with neutral TSeN and elemental selenium.

NEW TRANSITION METAL DISELENOLENES

The transition metal dithiolenes are multistage redox systems that have received considerable attention over the last twenty years for aspects of their unusual chemical bonding as well as their structural, electrical, and magnetic properties.[21] While the number of square planar dithiolenes which have been prepared is very large, the analogous selenium substances, the diselenolenes, are comparatively rare, and the tellurium compounds are unknown at present. In 1970, Davison and Shawl[22] reported

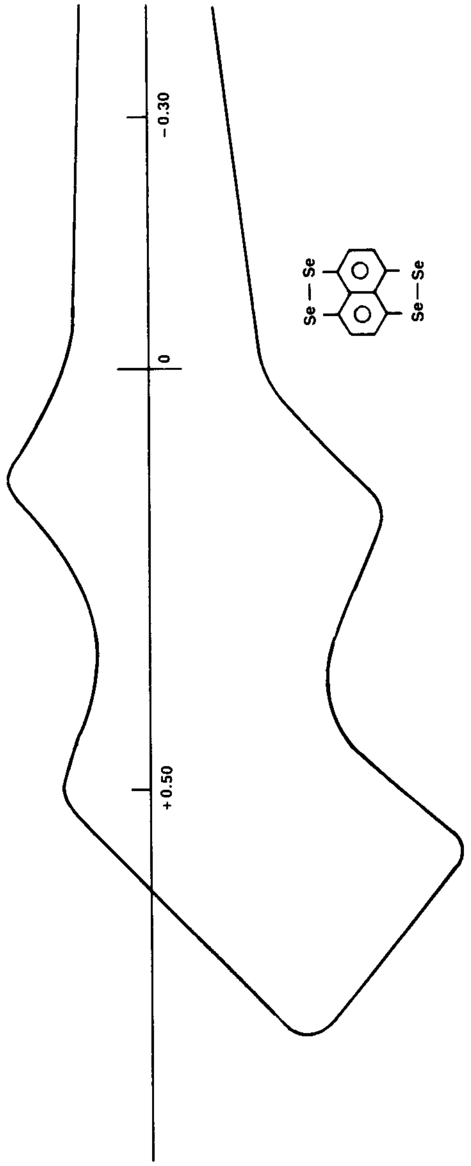


FIGURE 3

the preparation of metal diselenolenes from bis(trifluoromethyl)-1,2-diselenetene. More recently, examples of new metal diselenolenes have been provided by Rauchfuss,[23] Coucouvanis,[24] and Vollhardt[25] and their coworkers. While the crystal and molecular structure of a tris-molybdenum diselenolene has been reported,[26] no structural studies of bis-metal diselenolenes have been published to date.

In the summer of 1982, G. Allen prepared poly-o-phenylenediselenide and -ditelluride, and successfully converted the former, via the chemistry in Figure 4, to the tetra-n-butylammonium salt of o-benzenediselenolate nickel ($Ni(bds)_2^-$). The properties of $Ni(bds)_2^-$ are compared to those reported for the sulfur analog $Ni(bdt)_2^-$[27] and the mixed sulfur-selenium material[28] in Table 1.[29] When the chemistry of Figure 4 is repeated using poly-o-phenyleneditelluride, the Te material corresponding to $(n\text{-}C_4H_9)_4N^+$ $Ni(bds)_2^-$ is found to be markedly less stable than the Se material.

The ESR spectrum of polycrystalline samples of $(n\text{-}C_4H_9)_4N^+$ $Ni(bds)_2^-$ exhibits an anisotropic signal suggesting a paramagnetic site which possesses axial symmetry. At 23°, $g_1 = g_2 = 2.1723$ and $g_3 = 2.0765$. Our studies of the temperature dependence of the ESR spectrum will be reported elsewhere.[30] ESR signals have not been observed to date in the copper and cobalt analogues of $(n\text{-}C_4H_9)_4N^+$ $Ni(bds)_2^-$.

Crystals of $(n\text{-}C_4H_9)_4N^+$ $Ni(bds)_2^-$ are orthorhombic, space group $Pbc2_1$, Z = 4, with $\underline{a} = 9.904(3)$, $\underline{b} = 16.954(5)$, and $\underline{c} = 19.106(6)$Å. Full matrix least-squares refinement of positional and thermal parameters for all nonhydrogen atoms, using 1029 data for which $F > 3.92\sigma(F)$, led to $R = 0.065$, $R_w = 0.068$. The $NiSe_4$ unit is square planar within experimental error, with an average Ni-Se distance of 2.259Å. The packing of the molecular anions and cations is shown in Figure 5. The anions are well-separated; there are no short Ni···Se contacts (cf. Ni···S distance of 3.531Å in $\{N(CH_3)_3C_6H_5\}^+\{Ni(C_4N_2S_2)_2\}$).[31] Further, there are no Se···Se contacts at distances less than 5.0Å.

PREPARATION AND REACTION OF o- DISELENOBENZENE DIANION

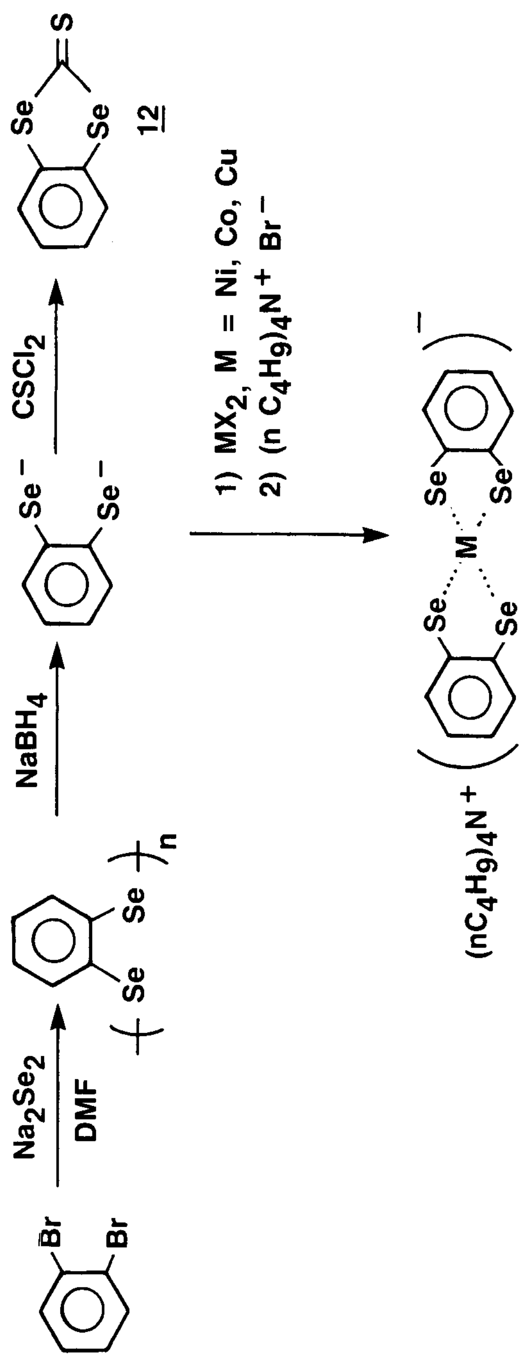
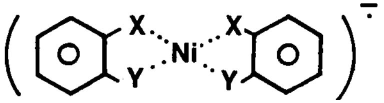


FIGURE 4

PROPERTIES OF



	X = Y = S	X = S, Y = Se	X = Y = Se
MELTING POINT	173°	—	192°
ELECTROCHEMISTRY (vs. SCE)			
$NiL_2^- + e \rightleftharpoons NiL_2^{-2}$	−0.55v	−0.53v	−0.47
ELECTRONIC SPECTRUM			
ν_{MAX}, cm^{-1} (log ϵ)	11350 (4.12)	—	10360 (3.51), 11800 (3.68)
ESR <g>	2.0779	2.116	2.1404
X-RAY DIFFRACTION			
d, Å	9.44	—	9.58
	7.77		7.76
	4.84		4.90
	4.07		4.14

TABLE I

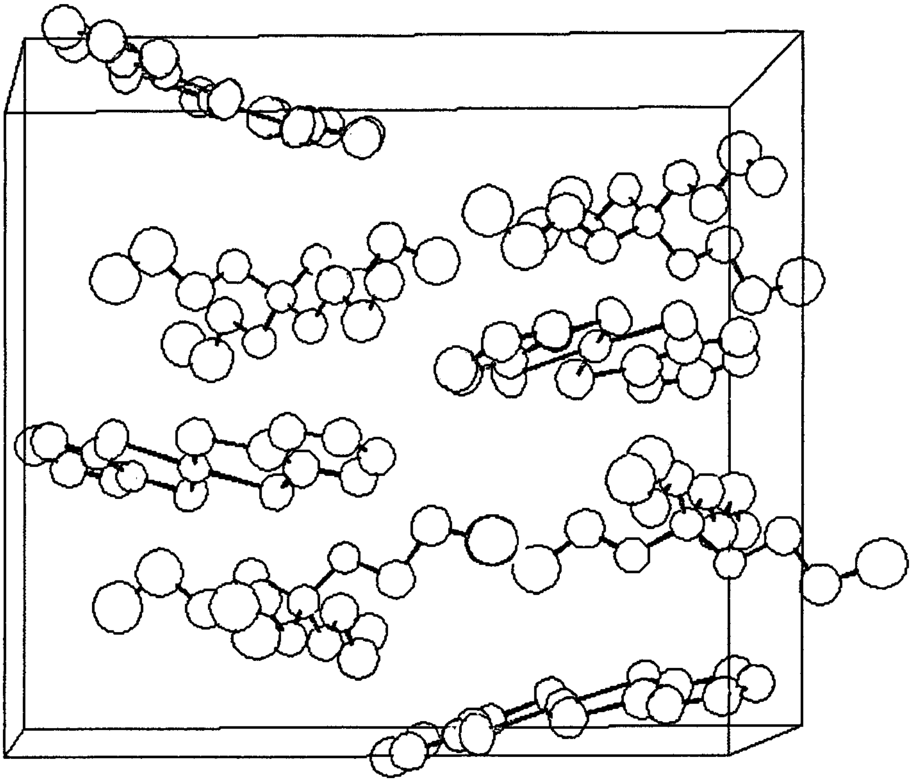


FIGURE 5 A perspective view of the contents of the unit cell of $(n\text{-}C_4H_9)_4N^+$ $Ni(bds^-)_2$ projected onto the bc plane.

REACTIONS OF VINYLIC HALIDES WITH SELENIUM AND TELLURIUM NUCLEOPHILES

Our motivating interest in the reactions of vinylic halides with Se and Te nucleophiles is summarized in Figure 6 which shows a projected synthesis of TSeF and TTeF derivatives via *cis*-vinylic dichalcogenide dianions prepared from reduction of a dichalcogenide polymer, a reaction sequence we demonstrated for ortho-aromatic dianions in the previous section. In 1981, J. Stark first isolated polymers from reaction of *cis*-dichloroethylene and Na_2Se_2 or Na_2Te_2. Interestingly, the reported syntheses of the hexamethylene[32] and dibenz[33] derivatives of TTeF involved vinylic displacements in tetrachloroethylene.

In DMF or liquid NH_3 at temperatures of -40° or lower, *cis*-dichloroethylene reacts immediately with Na_2Se_2 and Na_2Te_2 to give polymers which contain both dichalcogenide groups and carbon-carbon double bonds from infrared spectra. Since the polymer from the Na_2Se_2 reaction was found to be uncontaminated with elemental Se by x-ray diffraction, this material was characterized in detail. Complete elemental analysis revealed the atomic ratio $(C_{3.96}H_{5.31}Se_{2.00}Cl_{0.06})_x$ which is consistent with a $\left(C_4H_4Se_2\right)_x$ composition and $\left(Se\text{-}CH{=}CH\text{-}CH{=}CH\text{-}Se\right)_x$ atomic repeat sequence. Since the reaction sequence in Figure 6 requires a $(C_2H_2Se_2)_x$ composition, the polymers we have isolated in these initial experiments are not useful for the preparation of *cis*-1,2-ethylene dichalcogenide dianions.

ACKNOWLEDGEMENTS

The authors thank S. Meyler for technical assistance. P. Gagnè (1981 National Science Foundation Industrial Undergraduate Research Participant at GTE Laboratories) made preliminary studies of chemical transformations of the polymers isolated from reaction of *cis*-dichloroethylene with Na_2Se_2 and Na_2Te_2. The authors also thank Dr. G.D. Zoski for the use of the electrochemical apparatus. Dr. D. Dugger furnished mass spectra and M. Downey and J. Mullins provided x-ray powder diffraction data.

PROJECTED SYNTHESIS OF TETRACHALCOGENOFULVALENES

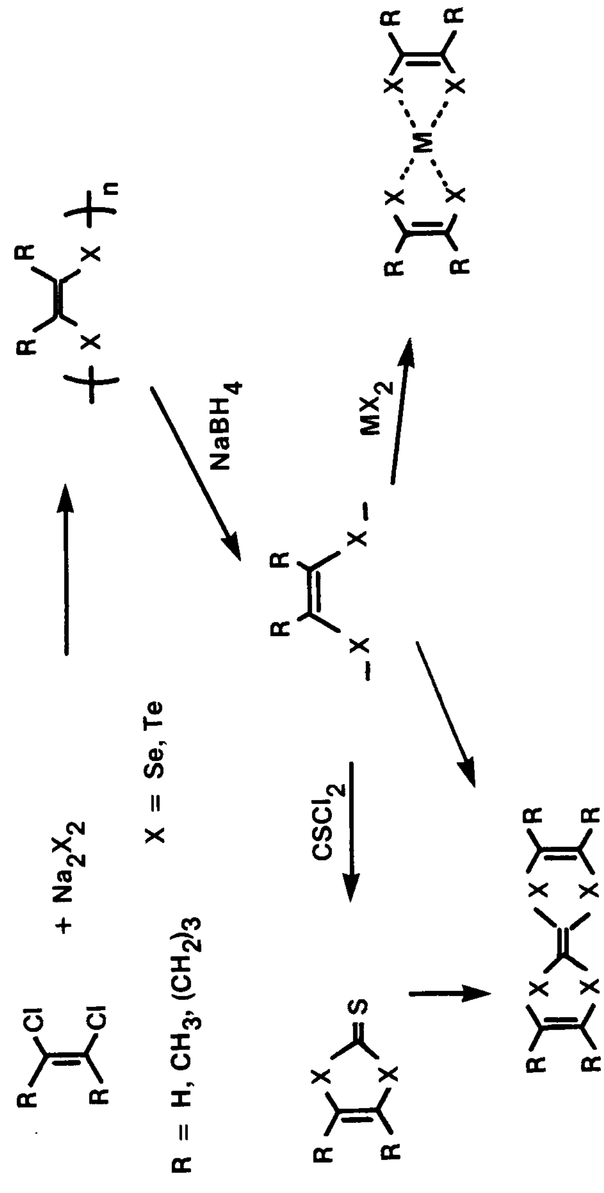


FIGURE 6

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