DIRECT ELECTROCHEMICAL SYNTHESIS OF METAL PENTAFLUOROTHIOPHENOLATES

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The need for the development of new photoconductors, luminophors, and electroluminescent materials has created a need for improvements in the methods used to synthesize metal sulfides. These may be obtained from alkyl derivatives of the metals by decomposition in the presence of hydrogen sulfide, or metal mercaptides may be used as the starting material [1, 2]. In the synthesis of metal mercaptides as currently practiced classical methods are used extensively – methods in which the mercaptan is used as an extraction agent for aqueous or nonaqueous solutions of the corresponding metal salts [3-8].

As recently reported by Said and Tuck [9], zinc, cadmium, mercury, indium, thallium, tin, and lead thiolates have been synthesized by electrochemical dissolution of an anode of the corresponding metal in the presence of a mercaptan. In that paper it was noted that the electrochemical method is considerably simpler than the chemical method, since the reaction proceeds with a high yield, in a single stage. Moreover, it was shown that in the electrochemical reaction, not only mercaptans can be used, but also certain disulfides.

The chemical methods that have been reported for the synthesis of metal pentafluorothiophenolates [10-15] by the interaction of pentafluorothiphenol with aqueous or nonaqueous solutions of the salts of the corresponding metals are frequently complicated by the formation of bis(pentafluorophenyl)disulfide [10] as a result of oxidation by higher-valence metal cations.

In the work reported here, we accomplished the electrochemical synthesis of metal pentafluorothiophenolates; in developing this synthesis, we considered that the electrochemical reaction will involve not only pentafluorothiophenol, but also its disulfide.

DISCUSSION OF RESULTS

As had been assumed, in the anodic dissolution of metal electrodes in the presence of pentafluorothiophenol, metal pentafluorothiophenolates are formed with yields of 15-20%, depending on the anode material.

$$\underset{n=1-3}{C_6F_5SH} \xrightarrow[\text{Zn, Cd, Hg, Sn, Pb, Tl, Cu, Bi, Ni}]{\text{Anodic dissolution of electrodes of}} (C_6F_5S)_nM$$

In this electrochemical reaction, we were not successful in isolating bis(pentafluorophenyl)disulfide, which is reduced at the cathode to the pentafluorothiolate anion.

$$C_6F_5SSC_6F_5 \xrightarrow{\text{Cathodic reduction}} 2C_6F_5S^-$$

However, the pentafluorothiolate anion that is formed as a result of this reaction, the same as the anion formed by reduction of pentafluorothiophenol

$$C_6F_5SH \xrightarrow{\text{Cathodic evolution of hydrogen}} C_6F_5S^-$$

acting as a nucleophile, attacks the aromatic ring of the original thiophenol molecule to form bisthiophenylene. This process does not stop in the first stage, but continues, forming perfluoropolythiophenylenes that are insoluble in the electrolyte

$$C_6F_5SH \xrightarrow[-F^-]{+C_6F_5S^-} C_6F_5SC_6F_4SH \xrightarrow[-F^-]{+C_6F_5S^-} \ldots$$

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TABLE 1. Synthesized Metal Pentafluorothiolates, and Analytical Data

Anode	Product	Color	mp, °C	Found, %				Calculated, %		
				C	F	M*	H	C	F	M*
Zn	$Zn(C_6F_5S)_2$	White	>280	31,3	40,6	13,7	–	31,1	41,0	14,1
Cd	$Cd(SC_6F_5)_2$	Same	>280	27,6	36,6	22,3	–	28,2	37,2	22,0
Hg	$Hg(SC_6F_5)_2$	»	186	24,0	30,8	32,5	–	24,1	31,7	33,5
Sn	$Sn(SC_6F_5)_4$	Yellow	143	30,7	40,9	23,7	–	31,5	41,5	23,0
Pb	$Pb(C_6F_5S)_2$	Same	255	23,2	30,8	34,8	–	23,8	31,4	34,2
Tl	$Tl(SC_6F_5)$	»	280	17,2	23,0	48,9	–	17,9	23,6	50,7
Cu	$Cu(C_6F_5S)$	»	>280	27,5	36,5	24,5	–	27,4	36,2	24,2
Ni	$Ni(SC_6F_5)_2$	Claret	>280	31,6	41,9	13,1	–	31,5	41,6	12,9
Co	$Co(SC_6F_5)_2$	Dark green	>280	31,9	42,5	12,5	–	31,6	41,7	12,9
Bi	$Bi(SC_6F_5)_3$	Yellow	>280	26,5	35,0	N/a†	–	26,8	35,3	25,9
Al	Polymer	White		32,1	38,4	8,75	0,91			
Mg	Same	Same		30,75	38,0	N/a†	1,20			
Zr	»	»		35,0	37,20	N/a†	0,48			
Pt	$C_6F_5SSC_6F_5$	»	46	36,5	47,9	–	–	36,2	47,7	–
	Cathodic polymer	»		39,7	41,8	–				

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* M = metal. The metal contents were determined by x-ray fluorescence spectroscopy for all of the metals except aluminum. The content of Al in the polymer was determined by complexometric titration.

† Not analyzed.

The formation of the polymeric product lowers the yield of the metal thiolates as a result of decomposition of the thiophenol, and it also contaminates the mercaptides, particularly those that are formed as precipitates. For this reason, the electrosynthesis of metal thiolates in an unpartitioned cell is accompanied by side cathodic process of decomposition of pentafluorothiophenol. Moreover, the reduction of acetonitrile soluble pentafluorothiophenolates of mercury, lead, bismuth, and tin leads to cathodic deposition of the metal on the electrode.

In order to eliminate the cathodic process of decomposition of the pentafluorothiophenol, we used an electrolysis cell with a ceramic filter separating the anode and cathode spaces. However, even the use of the ceramic membrane did not completely eliminate the formation of perfluoropolythiophenylenes in the anode section. Even so, at the initial moment of electrolysis, with a low yield relative to pentafluorothiophenol (20-30%) and a 60-70% yield relative to the current, we were able to synthesize pentafluorothiophenolates of zinc, cadmium, nickel, cobalt, thallium, tin, lead, mercury, copper, and bismuth. The use of aluminum, magnesium, or zirconium anodes, even in the case of a partitioned cell, led to the formation of a white precipitate, containing polymeric products, as indicated by IR spectroscopic data.

When using a platinum anode, the thiophenol is oxidized to bis(pentafluorophenyl) disulfide.

$$2C_6F_5SH \xrightarrow{\text{Oxidation on platinum anode}} C_6F_5SSC_6F_5 + 2H^+$$

When using an unpartitioned cell with two platinum electrodes, an insoluble polymeric product is formed on the cathode, containing an average of four phenyl rings as determined by elemental analysis.

The results obtained in the present work show that the electrochemical synthesis of metal pentafluorothiophenolates by anodic dissolution of metals in the presence of pentafluorothiophenol is possible in principle; however, in contrast to the electrochemical synthesis of the nonfluorinated analogs [7], this process is severely complicated by cathodic decomposition of the pentafluorothiophenol.

EXPERIMENTAL

The electrolysis was performed in the galvanostatic regime by means of a P-5848 potentiostat, in a glass cell with a 1-mm diameter platinum wire as the cathode and a strip of the particular test metal (area 1-2 cm^2) as the anode. In the synthesis of the mercury pentafluorothiophenolate, mercury on the bottom of the electrolyzer was used as the anode.

The electrolyte, consisting of 0.7 g pentafluorothiophenol, 0.1 g tetrabutylammonium tetrafluoroborate, and 10 ml absolute MeCN, was electrolyzed for 1 h with a current of 50 mA; the electrolyte was evaporated to

TABLE 2. IR Spectra of Compounds Obtained (ν, cm^{-1})*

$Pb(SC_6F_5)_2$	$Tl(SC_6F_5)$	$Cd(SC_6F_5)_2$	$Cu(SC_6F_5)$	$Ni(SC_6F_5)_2$	$Zn(SC_6F_5)_2$	$Sn(SC_6F_5)_4$	$Co(SC_6F_5)_2$
							410 br
445 br	444 m		442 br		445 br	443 br	
489 br		489 vbr		489 m			470 br
513 br	510 m	512 m	511 br	515 br	513 br	513 br	510 m
586 br	582 m		588 m				
623 s	620 m			624 m		622 m	628 vbr
628 s		631 s	627 s	635 s	629 m		
		693 vbr					
714 m	712 m	711 vbr	713 in	708 m	712 m	711 m	707 m
718 m	718 m	719 m	718 m	718 m	721 m	718 in	722 in
858 s	856 vs	859 vs	855 vs	852 s	855 vs	859 vs	865 in
865 s			860 in		860 in		872 s
963 vs	967 vs						
973 s		976 vs	972 vs	979 s	970 vs	974 vs	985 vs
	992 m		977 vs				
1010 m		1020 m	1010 m		1014 s	1016 m	1012 m
1077 m	1078 s	1084 s	1088 s	1087 s	1080 vs	1088 vs	1098 vs
1086 m		1090 s	1097 s		1094 s		
1130 br	1125 m	1134 m	1143 m	1143 m	1145 m	1144 br	1140 br
							1265 br
		1290 br		1292 br	1285 m	1286 vbr	1290 br
		1305 br	1298 m		1293 m	1293 br	
1340 m		1340 m	1341 m		1344 m	1346 br	
				1390 br			1396 br
			1442 in				1405 m
			1462 s				
1477 vs	1472 vs	1480 vs	1475 s	1482 vs	1478 vs	1480 vs	1488 vs
			1482 in				1487 in
							1498 s
1513 s	1506 s	1508 vs	1514 s	1511 s	1508 s	1508 s	1510 s
			1526 in		1538 m	1523 br	
1628 br	1609 m	1621 m	1623 m	1621 m	1626 m	1626 m	1619 m
1634 br		1632 m	1632 m		1634 m		1636 m

$Hg(SC_6F_5)_2$	$Bi(SC_6F_5)_3$	$C_6F_5SSC_6F_5$	Cathodic polymer	Polymer from Al	Polymer from Mg	Polymer from Zr
403 br			418 br	408 br		414 br
				428 br		436 br
442 br	442 br	443 br				
		488 br				
512 m	513 br		511 br		514 br	512 br
591 br	587 br	588 br	592 br		590 br	599 m
639 m	627 m	639 m				635 m
			653 br	655 vbr	652 br	652 vs
712 br	718 m	724 m				722 m
720 in	720 m	728 m	718 m			734 m
			808 m	812 vs	814 vs	812 s
860 vs	855 vs	856 vs	859 m	855 m	865 s	862 s
				892 m	904 m	
	968 vs		955 vs	962 s	960 vbr	960 vs
974 vs		973 vs	975 vs	980 s	974 s	978 vs
1019 m	1010 m	1022 m		1018 in	1010 in	1022 m
1031 m	1025 in					
1091 s	1079 s	1089 vs	1092 s	1092 vs	1094 s	1092 s
1104 in	1096 in	1100 in				
1140 m	1130 br	1146 br		1149 in	1145 m	
				1170 br	1181 m	
		1250 br	1245 br	1245 s	1245 s	1248 vs
		1271 br	1253 m	1256 s		
1284 br	1285 br	1283 m		1288 m		1284 m
1293 br						
1338 m	1339 m					
1400 m	1379 m	1398 m		1375 s		1385 m
				1418 m	1429 m	1410 m
				1452 m	1468 s	1452 s
1480 vs	1472 vs	1489 vs	1474 s	1466 s	1462 s	1468 s
				1481 s	1482 s	1485 s
				1495 s	1493 s	1492 m
1510 vs	1505 vs	1511 vs	1510 s	1508 s	1514 s	1512 s
1539 in						
1626 m	1622 m	1618 br	1618 br	1624 s	1614 s	1614 s
1634 m		1633 m	1635 br	1636 br	1636 m	1636 s

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*m = medium intensity; br = broad signal; vs = very strong; s = strong; vbr = very broad; in = inflection.

TABLE 3. ^{19}F NMR Spectra of Synthesized Metal Pentafluorothiophenolates in Ether Solution, Relative to CF_3COOH External Standard

Compound	o-Fluoro	m-Fluoro	p-Fluoro
$Zn(C_6F_5S)_2$	55,8	88,7	87,6
$Cd(C_6F_5S)_2$	55,3	86,7	83,9
$Hg(C_6F_5S)_2$	55,2	87,6	83,2
$Pb(C_6F_5S)_2$	55,5	87,8	85,4
$Bi(C_6F_5S)_3$	52,8	85,1	83,2
$C_6F_5SSC_6F_5$	56,4	85,2	73,6

Notes. The o-fluorine atoms correspond to signals in the form of a complex triplet and doublet due to splitting on m- and p-fluorine atoms. The signals corresponding to the m-fluorine atoms are a complex triplet and doublet. The signals corresponding to the p-fluorine atoms consist of a triplet with a splitting constant on the m-fluorine atoms amounting to ~ 20 Hz for all compounds.

dryness under vacuum, and the residue was extracted with ether, after which the soluble metal pentafluorothiophenolate was recovered. The insoluble metal pentafluorothiophenolate, together with the perfluoropolythiophenylene, were filtered from the electrolyte and washed with MeCN and ether. The presence of the metal pentafluorothiophenolate and perfluoropolythiophenylene was registered by IR spectroscopy.

When using the glass electrolyzer with a ceramic membrane separating the anode and cathode sections, the anode section was charged with 0.7 g pentafluorothiophenol and 0.05 g tetrabutylammonium tetrafluoroborate in 5 ml of absolute MeCN. The cathode section was filled with the same electrolyte, but without the pentafluorothiophenol. Electrolysis with a current of 50 mA was continued for 1 h, after which the anolyte was evaporated to dryness under vacuum. The residue was extracted with ether, subsequently recovering the soluble metal pentafluorothiolate. In cases in which products insoluble in MeCN were formed, the electrolyte was filtered to remove the precipitate. The precipitate was washed with MeCN and ether.

^{19}F NMR spectra in ether solutions were taken in a Perkin–Elmer R-32 spectrometer with an external standard; IR spectra were taken in a UR-20 instrument in KBr tablets.

The elementary analyses and the ^{19}F NMR and IR spectra of the compounds that were obtained are given in Tables 1-3.

CONCLUSIONS

1. Zinc, cadmium, mercury, tin, lead, tallium, copper, nickel, cobalt, and bismuth pentafluorothiophenolates have been synthesized electrochemically by anodic dissolution of the corresponding metal in an electrolyte containing pentafluorothiophenol.

2. Anodic oxidation of pentafluorothiophenol on a platinum electrode leads to the formation of bis(pentafluorophenyl) disulfide.

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ORGANOBORON COMPOUNDS

COMMUNICATION 409. 2-(2-THIENYL)-1-BORAADAMANTANE PYRIDINATE

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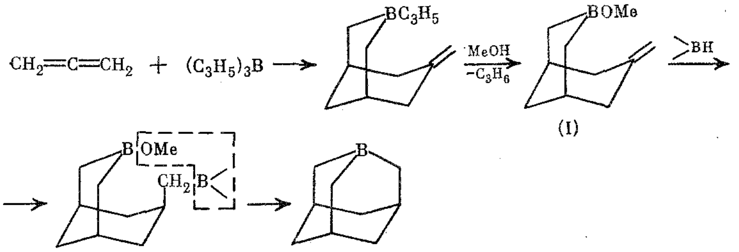
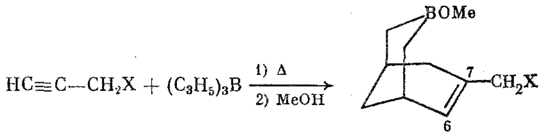
In the condensation of allylboranes with allenes, derivatives of 3-borabicyclo[3.3.1]nonene are formed with a methyl grouping in position 7 (I) [1], these derivatives being used to obtain 1-boraadamantane compounds [2]. This synthesis is based on the reaction of hydroboranation with subsequent intramolecular cyclization of the resulting diboron compounds, which had been observed previously in a number of acyclic diboron [3] and triboron [4] systems.

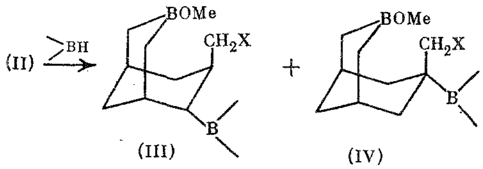


It appeared extremely attractive to use this cyclization reaction for the synthesis of functionally substituted 1-boraadamantane derivatives, starting with the corresponding 7-substituted 3-borabicyclo[3.3.1]non-6-ene (II), obtained by the condensation of acetylenic compounds with allylboranes in accordance with the scheme [5]



(II)

It should be expected that in the hydroboranation of compounds of the type of (II), the boron atoms will add to the carbon atoms 6 and 7, forming compounds (III) and (IV)



The subsequent fate of (III) and (IV) was determined by the capability of the boron atom for migrating along the carbon chain; in the case of compound (IV), the fate was also determined by its susceptibility to elimination reactions that are characteristic for β-functional derivatives of alkylboranes [6].

The isomerization of (III) to (IV) and migration of the boron atom in (IV) into the side chain to form the borane (V) would lead, through cyclization, to the 2-substituted 1-boraadamantane (VI)

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* Deceased.

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