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Reactivity of Chalcogenostannate Salts: Unusual Synthesis and Structure of a Compound Containing Ternary Cluster Anions $[Co_4(\mu_4\text{-}Se)(SnSe_4)_4]^{10-}$**

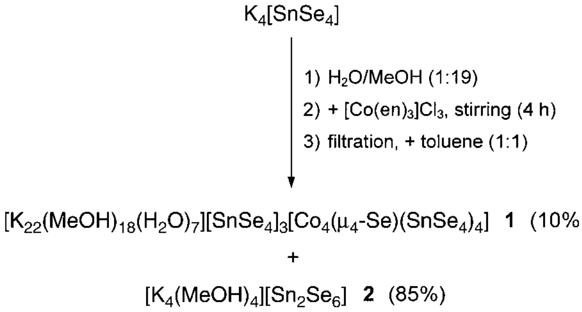
Christian Zimmermann, Maike Melullis, and Stefanie Dehnen*

Dedicated to Professor Dieter Fenske
on the occasion of his 60th birthday

The stabilization of binary aggregates of main group elements $[E'_xE_y]^{q-}$ in the coordination sphere of transition-metal ions M^{n+} (E′ or E = Group 13–15 or 16 element), and thus the formation of structures that contain ternary heavy atom frameworks, is an area of increasing research activity.[1–16] Besides diverse range of molecular and crystal structures, the synthesis of some ternary M/E′/E systems that show polymeric anion substructures representing “open solid-state structures”, as found in $Rb_3[AgGe_4Se_{10}]\cdot 2H_2O$[10] or $K_2[MnSnS_4]$,[11] have recently attracted attention. Such compounds combine both zeolite-type and semiconducting properties. If binary alloys or salts of binary anions are used for the construction of the E′/E aggregates instead of separate components, the investigations additionally serve to study the reaction behavior and stability of these systems in the presence of transition-metal compounds. However, most reports on the latter deal with binary reactants of Groups 15/16,[1,13–16] for example the synthesis of $[PPh_4]_2[Mn(CO)_3(As_3Se_3)_5]$ by using $[As_4Se_4]$.[13b] Only most recently, were some results published that considered the surfactant-templated solvothermal synthesis of mesoporous solids like $(C_{16}H_{33}NC_5H_5)_x[Pt_ySn'_4Se_{10}]$ ($x = 1.9$–2.8; $y = 0.9$–1.6).[12]

One of our current aims is to generate coordination compounds by reacting binary anions of Groups 14 and 16. However, reactions under conditions similar to those for the binary reactants from Groups 15 and 16—that is reactions with organometallic complexes in aprotic solvents—led to the reductive decomposition of the Sn–E framework under E^{2-} donation to the transition-metal ion.[17,18]

By employing protic solvents and another type of transition-metal complex, it was possible to synthesize a compound by completely transferring the binary anionic structures into the coordination sphere of the transition-metal ions. Scheme 1 depicts the reaction of $K_4[SnSe_4]$[19] and $[Co(en)_3]Cl_3$ (en = 1,2-diaminoethane) in a water/methanol mixture that yielded compounds **1** and **2**.[20,21] Compounds **1** and **2** were structurally characterized by single-crystal X-ray diffraction,[22] and the formal oxidation state of the cobalt centers in **1** was additionally checked by quantum-chemical investigations. Compound **1** crystallizes as black cubes in the cubic space group $Ia\bar{3}$. It is an ionic compound that features complex, ternary anions $[Co_4(\mu_4\text{-}Se)(SnSe_4)_4]^{10-}$ that are embedded in the crystal lattice by K···Se interactions to MeOH- or H_2O-coordinated potassium cations.The composition of the C_3 symmetric anion suggests that the $[SnSe_4]^{4-}$ ions of the starting material have acted as both a ligand and—in a well-known manner—as an Se^{2-} donor. This is additionally confirmed by the formation of compound **2** which can be viewed as a dimer of $[SnSe_3]^{2-}$ ions generated by removal of Se^{2-} ions from the tetraselenostannate anions $[SnSe_4]^{4-}$. Under the assumption that the formal oxidation state of the tin atoms in **1** remains +4, the cluster anion emerges as a Co^{II} compound. Thus, in contrast to the reactions in aprotic solvents, one observed a reduction of the transition metal ions by partially released Se^{2-} ions.[23] Figure 1 gives the molecular structure of the ternary anion.



Scheme 1. Synthesis of the compounds **1** and **2**.

In the cluster anion, four barrelane-type $[SnCo_3Se_4]$ cages are linked by a μ_4-bridging selenium atom that centers an inner $[SeCo_4]$ fragment (barrelane = bicyclo[2,2,2]octane). In addition, the anion contains four terminal selenido ligands, which form the corners of a large tetrahedron with Se···Se edges of 1057.7(4)–1071.3(3) pm. Each of the metal atoms is almost tetrahedrally surrounded by selenido ligands. The narrow range of the observed bond lengths allows a deviation from ideal T_d symmetry by at most 1.1 pm.

Some cluster complexes are known that are topologically identical to **1**. These are chalcogenido- or pnictido-bridged clusters of the d^{10} elements, for example $[M^{II}_8(\mu_4\text{-}E)$-

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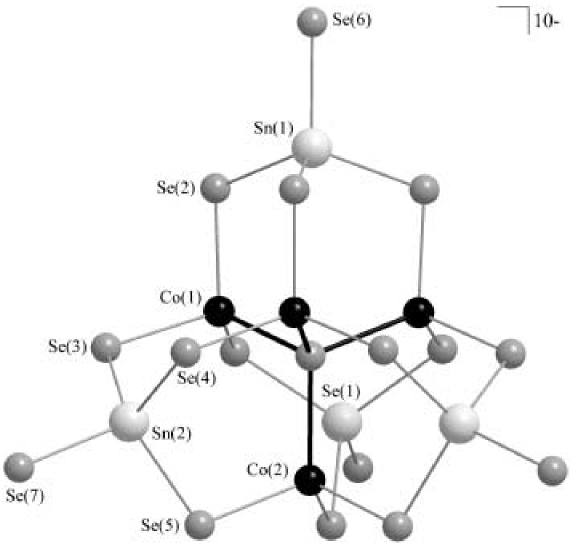

Figure 1. Structure of the cluster anion in **1**. Selected distances [pm] and angles [°]: Sn–Se_t 247.8(2)–249.0(1), Sn–(μ_2-Se) 250.9(1)–252.8(1), Co–(μ_2-Se) 242.6(2)–244.8(1), Co–(μ_4-Se) 243.5(2)–244.9(3), Co···Co 394.5(4)–402.1(5); Se_t-Sn-Se 105.29(4)–109.37(4), (μ_2-Se)-Sn-(μ_2-Se) 109.20(4)–112.59(4), (μ_4-Se)-Co-Se 109.13(5)–113.33(6), (μ_2-Se)-Co-(μ_2-Se) 105.92(5)–107.49(5), Co-(μ_4-Se)-Co 108.15(4)–110.76(4).

(μ_2-EPh)$_{12}$Cl$_4$]$^{2-}$ (M^{II} = Zn: E = Se, Te;[24] M^{II} = Cd: E = S,[25a] Se[26]) or [Cd_8(μ_4-S)(μ_2-SPh)$_{16}$]$^{2-}$.[25b] In contrast to all known M_8 clusters, the ternary anion in **1** contains two different sorts of metal atoms. Moreover, the cluster anions in **1** are the first ligand-free examples of this type, as they do not covalently bind to any ligand molecules at the μ_2-bridging or at the terminal selenium atoms. Finally, the twelve μ_2-bridging selenido ligands form a slightly distorted cubooctahedron rather than a Se_{12} icosahedron which has been observed for all the analogous species characterized so far.

Being a purely inorganic, discrete anion, the cluster in **1** differs from all Co/E′/E systems reported to date (E′ = Ge, Sn; E = chalcogen); for [{(CO)$_4$Co}$_4$Sn$_2$E$_2$],[4b] or [(Cp*Co)$_2$(μ_3-E)$_2${Sn{CH(SiMe$_3$)$_2$}$_2$}] (E = S, Se),[5a] such compounds are either protected by an organic ligand shell,[4,5] or they feature polymeric anionic networks such as the phases mentioned at the outset.[10–12] To our knowledge, only one further type of complex has been reported that contains ligand-free, discrete anions of the combination transition metal/tetrel/chalcogen: [PPh$_4$]$_4$[E′$_2$(WSe$_4$)$_4$] (E′ = Sn, Pb),[9] which was generated from E′Cl$_2$ and [NH$_4$]$_2$[WSe$_4$].

The Sn–Se bond lengths in **1** (Sn–Se_t 247.8(2), 249.0(1) pm, Sn–(μ_2-Se) 250.9(1)–252.8(1) pm) correspond with those of the adamantane-type selenostannate(IV) anion in [2,2,2-crypt-K]$_4$[Sn$_4$Se$_{10}$][27] (2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane). The Co–(μ_2-Se) and Co–(μ_4-Se) distances are very similar (Co–(μ_2-Se) 242.5(2)–244.8(1) pm; Co–(μ_4-Se) 243.6(1), 245.0(2) pm). They range within the upper values of bond lengths reported for the few known cobalt–selenide compounds with similar structural characteristics (tetrahedral coordination of Co^{III} and/or Co^{II} centers, μ_4-bridging Se^{2-} ligands),[28] which corroborates the formal oxidation state of +2 assigned to the cobalt atoms in **1**.

All investigations of re-dissolved **1** (NMR spectroscopy, cyclic voltammetry measurements, ESI mass spectrometry) were frustrated by instantaneous decomposition of the compound in solution; therefore we are currently undertaking solid-state measurements to ascertain the formal charge of the cobalt centers as well as to exclude the existence of $(OR)^-$ groups (R = H, Me). To get an impression of whether the structural parameters observed in the cluster anion in **1** might indeed be in accord with the assigned total charge, that is whether the assumed reduction by Se^{2-} ions turns out to be plausible, we performed density functional theoretical (DFT)[29] investigations on the cluster anions [Co$_4$(μ_4-Se)(SnSe$_4$)]$^{q-}$ (q = 6–10; program system Turbomole[30]). Simulation of mirror charges[31] allowed the theoretical treatment of the highly charged molecules. The calculated Sn–Se distances in the Co/Sn/Se cluster anions tended to be larger than the experimentally observed ones; a comparable situation was found for the results of calculations on the [Sn$_4$Se$_{10}$]$^{4-}$ ion[27] (Sn–Se_t: +4 to +5 pm, Sn–(μ_2-Se): +7 to +10 pm with respect to the crystallographically determined values). In contrast, the computed Co–Se bond lengths in the ternary anions were all somewhat shorter than the experimental ones, which likewise was in accordance with the results of calculations on the adamantane-type anion [{Co(SPh)}$_4$(μ_2-SPh)$_6$]$^{2-}$[32] (Co–S: −3 to −4 pm with respect to the crystallographically determined values). The best agreement between calculated and experimentally determined structural parameters—within the limits of the methods used—was observed for the ternary anion with the charge 10− (Sn–Se_t 255.0–255.2, Sn–(μ_2-Se) 259.2–259.8, Co–(μ_4-Se) 239.3–241.9, Co–(μ_2-Se) 242.1–244.3 pm), whereas deviation and divergence of the interatomic distances increased with decreasing total charge of the ternary anion (minimum 6−, corresponding to four Co^{III}).

In the crystal lattice, the high charge of the ternary anions is compensated by interactions with neighboring potassium ions. By coordinating to oxygen atoms of the solvent molecules and to selenido ligands of both the Co/Sn/Se anions and the additional [SnSe$_4$]$^{4-}$ units, potassium ions obtain coordination numbers of six ([KO$_n$Se$_{6-n}$], n = 0–4) or seven ([KO$_n$Se$_{7-n}$], n = 1, 2; K···Se 319.6(2)–376.9(3), K···(μ_1-, μ_2-O) 234.0(9)–327.4(10) pm). The terminal selenido ligands of the cluster anion show coordination numbers of five to seven by interacting with adjacent potassium ions or, through hydrogen bonds, with three adjacent oxygen atoms (Se(6)···O 325.4(4) pm). The coordination environment of the ternary anion is shown in Figure 2.

The results presented herein reveal for the first time that complete orthochalcogenostannate anions can be transferred into the coordination sphere of transition metal ions to give highly charged, purely inorganic, ternary cluster complexes. Decisive for the retention of the Sn–E bonds was the use of a Co^{III} complex with weaker coordinating en ligands instead of CO, PR$_3$, or Cp^R, and the presence of donor solvents H_2O and MeOH that enabled the design of a suitable aggregation of the counterions, embedding and thus stabilizing the anionic cluster molecules. Future investigations will focus on the synthesis and characterization of further M/Sn/E aggregates, containing other transition metal ions and/or other chalcogenostannate groups.

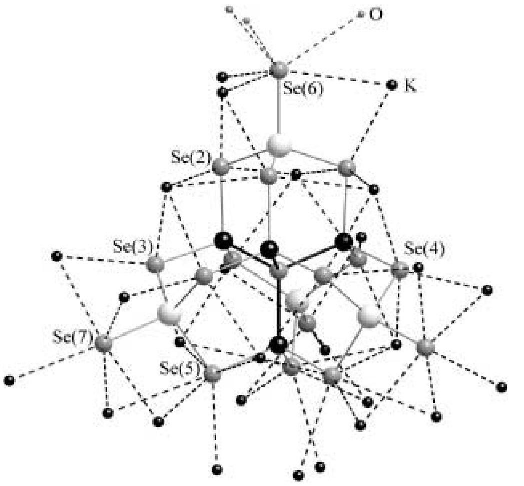

Figure 2. Embedding of the cluster anion in **1** in the coordination sphere of adjacent potassium ions and oxygen atoms (Co: black, Se: medium gray, Sn: light gray). Interatomic distances within the coordination sphere [pm]: K···Se 319.6(2)–376.9(3), Se···O 325.4(4). Structural parameters of the additional $[SnSe_4]^{4-}$ unit (not shown) [pm; °]: Sn-Se 250.8(1)–252.9(1); Se-Sn-Se: 105.56(4)–112.67(5).

Experimental Section

All synthesis steps were performed under exclusion of air and external moisture (N_2 atmosphere at a high-vacuum, double-manifold Schlenk line, or Ar atmosphere in a glove box). Methanol and toluene were dried and freshly distilled prior to use; water was degassed by applying dynamic vacuum (10^{-3} Torr) for several hours.

Synthesis of **1** and **2**: $K_4[SnSe_4]$ (0.201 g, 0.34 mmol)[19] was added to a suspension of $[Co(en)_3]Cl_3$ (0.115 g, 0.33 mmol) in H_2O/methanol (0.5/9.5 mL), whereupon the reaction mixture immediately turned dark brown. After the mixture had been stirred for 4 h, an insoluble, black precipitate was removed by filtration. The remaining solution was layered with toluene (10 mL). In the course of one week, the solution brightened under formation of black, cubic crystals of **1** and large quantities of **2**. Yields: **1**: 0.024 g (0.005 mmol, 10% with respect to $[SnSe_4]^{4-}$), **2**: 0.144 g (0.145 mmol, 85% with respect to $[SnSe_4]^{4-}$). C,H analyses (%): **1**: calcd: C 4.39, H 1.76; found: C 4.41, H 1.75; **2**: calcd: C 4.83, H 1.64; found: C 4.86, H 1.62.

Quantum-chemical investigations: Density functional (DFT) calculations[29] were performed by using the program system Turbomole[30] (RIDFT program;[33] Becke–Perdew functional (B-P-86);[34] basis sets of SV(P) quality;[35] relativistically corrected effective core potentials (ECP) for Sn atoms (ECP-46)[36]). Compensation of the negative charges of all calculated molecules was achieved by simulating mirror charges;[31] accordingly, negative values were obtained for all orbital energies and structural parameters were better than those from the computation of free anions. All geometry optimizations were performed without symmetry restrictions (C_1 symmetry), therefore convergence into local minimum structures can be assumed.

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[20] Two independent $[Sn_2Se_6]^{4-}$ ions are observed in the crystal structure of **2** (C_i symmetry; idealized D_{2h} symmetry, as observed for solvent-free $K_4[Sn_2Se_6]$);[21] Sn–Se_t 246.2(1)–248.3(1), Sn–(μ_2-Se) 259.0(2)–259.9(1) pm. K^+ ions show distorted octahedral coordination geometry (n O- and $6-n$ Se atoms; $n = 1, 2$; K···O 267.3(6)–291.7(6), K···Se 331.4(3)–365.8(3) pm). Terminal selenido ligands have coordination numbers five (Sn atom, $n\,K^+$ ions, $4-n$ hydrogen bonds to adjacent O atoms, $n = 2$–4; Se···O 330.0(6)–342.2(6) pm); bridging selenium atoms have coordination numbers four ($SeSn_2K_2$) or five ($SeSn_2K_3$). All O atoms are situated in a distorted tetrahedral coordination geometry by binding/coordinating to C and H atoms and two K^+ ions each.

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[22] Data of the X-ray structural analyses: $T = 203$ K, $Ag_{K\alpha}$ radiation ($\lambda = 0.56087$ Å), graphite monochromator, imaging plate detector STOE IPDS. Structure solution by direct methods, full-matrix least-squares refinement against F^2; used software: Shelxl-96,[37] shelxl-97.[38] $C_{18}H_{86}O_{25}Co_4K_{22}Se_{29}Sn_7$, **1:** cubic, space group $Ia\bar{3}$, $Z = 16$, $a = 3681.5(4)$ pm, $V = 49897(10) \times 10^6$ pm^3, $\rho_{calcd} = 2.619$ g cm^{-3}, $2\theta = 2$–42°, 8962 independent reflections ($R_{int} = 0.1579$), 6146 with $I > 2\sigma(I)$; $\mu(Mo_{K\alpha}) = 5.869$ mm^{-1}, 332 parameters (refinement of Sn, Se, and K atomic sites by employing anisotropic displacement parameters; one K atom threefold disordered, another K atomic site occupied to a 1/3; some of the C and O atoms twofold or threefold disordered; respective assignment of split positions; refinement of O and C atomic sites by employing isotropic displacement parameters; H atoms not calculated), residual electron density 1.541 $e^- \times 10^{-6}$ pm^{-3}. R values for reflections with $I > 2\sigma(I)$: $R_1 = 0.0533$, $wR_2 = 0.1156$. $C_4H_{16}K_4O_4Se_6Sn_2$, **2**: triclinic, space group $P\bar{1}$, $Z = 2$, $a = 1022.1(2)$, $b = 1084.7(2)$, $c = 1311.5(3)$ pm, $\alpha = 104.01(3)$, $\beta = 106.83(3)$, $\gamma = 108.60(3)$°, $V = 1226.1(4) \times 10^6$ pm^3, $\rho_{calcd} = 2.697$ g cm^{-3}, $2\theta = 3$–42°, 5005 independent reflections ($R_{int} = 0.0486$), 4177 with $I > 2\sigma(I)$; $\mu(Mo_{K\alpha}) = 6.137$ mm^{-1}, 209 parameters (refinement of Sn, Se, K, O, and C atomic sites by employing anisotropic displacement parameters; some H atoms localized from the Fourier map), residual electron denisty: 1.645 $e^- \times 10^{-6}$ pm^{-3}. R values for reflections with $I > 2\sigma(I)$: $R_1 = 0.0424$, $wR_2 = 0.1044$. CCDC-187775 (**1**) and CCDC-187776 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre,

12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[23] The pH value of the reaction mixture is ≈11; standard redox potentials under basic conditions: a) $[Co^{III}(en)_3]^{2+} \rightarrow [Co^{II}(en)_3]^{3+}$: −0.18; J. E. Huheey, E. A. Keiter, R. L. Keiter, *Anorganische Chemie: Prinzipien von Struktur und Reaktivität*, 2nd ed., de Gruyter, Berlin, **1995**, p. 477; b) $Se^{2-} \rightarrow 1/n\,Se_n$: −0.92 V; A. F. Hollemann, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 100th ed., de Gruyter, Berlin, **1985**, p. 543.

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The "Aryne" Route to Biaryls Featuring Uncommon Substituent Patterns[**]

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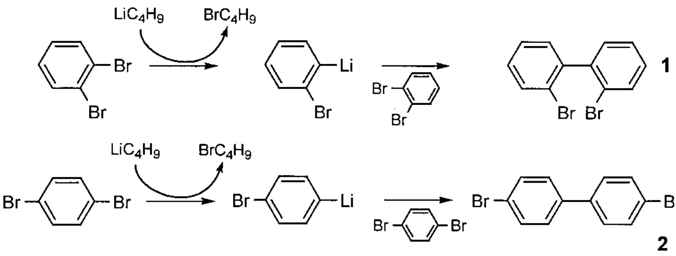
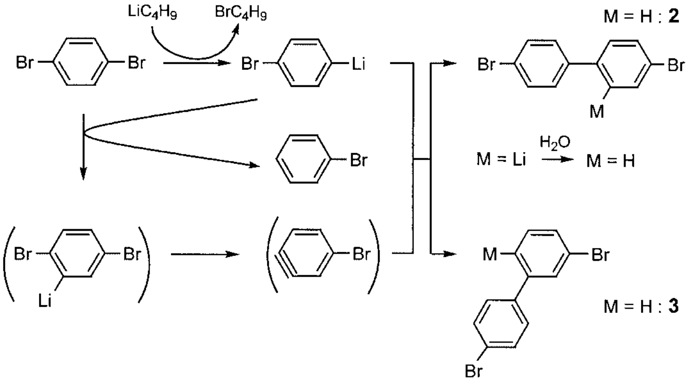
In 1957, Gilman and Gaj[1] disclosed a facile preparation of 2,2′-dibromobiphenyl (**1**) in 21% yield by treatment of 1,2-dibromobenzene with half a molar equivalent of butyllithium (Scheme 1). In support of the surmised condensation process between dibromobenzene and a phenyllithium intermediate derived from it by halogen–metal permutation, they analogously converted 1,4-dibromobenzene into 4,4′-dibromobiphenyl (**2**; 18%).[1] Effective aryl–aryl coupling in general requires the participation of transition elements. When Lau and co-workers[2] succeeded in raising the yield of 2,2′-dibromobiphenyl to 81% by a careful optimization of the reaction conditions, the condensation hypothesis had to be abandoned. It was tempting to base an alternative mechanism on the intermediacy of 1,2-didehydrobenzene (1,3-cyclohexadien-5-yne, the so-called "benzyne"). However, if such a species were really involved, 1,4-dibromobenzene would have to give rise not only to **2**, as reported,[1] but also to its 3,4′-isomer **3**. As revealed by gas chromatographic analysis, the isomers **2** (M = H; 41%) and **3**[3] (M = H; 21%) were indeed formed concomitantly with bromobenzene (14%; Scheme 2). These findings are in agreement with a metalation, elimination, addition sequence featuring 4-bromophenyllithium, 2,5-dibromophenyllithium, and 4-bromo-1,2-didehydrobenzene as transient entities.



Scheme 1. Reported[1] reaction of 1,2- and 1,4-dibromobenzene with butyllithium to form **1** or **2**, respectively.



Scheme 2. Postulated mechanism of the coupling of 1,4-dibrombenzene with butyllithium to account for the formation of a mixture of **2** and **3**.

The ensuing work developed in three stages. The first objective was to provide evidence for the suspected aryne intermediate in the 1,2-dibromobenzene transformation. Once the essential details of this reaction are understood, one should be able to make use of this knowledge to construct first symmetrical and eventually unsymmetrical biaryls. According to our hypothesis, the final step in the formation of **1** should be bromine abstraction from 1,2-dibromobenzene by the 2′-bromo-2-biphenylyllithium species resulting from the combination of 2-bromophenyllithium with 1,2-didehydrobenzene (Scheme 3). If the starting material were replaced with 1-bromo-2-iodobenzene, iodine transfer would have to occur. In fact, treatment of this dihalo compound with half a

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