COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Novel multi-chalcogen ring systems with three different chalcogen atoms: synthesis, structure and redox property of five-membered trichalcogenaheterocycles†

Satoshi Ogawa,*[a] Satoko Yoshimura,[a] Noriyoshi Nagahora,[a] Yasushi Kawai,[b] Yuji Mikata[c] and Ryu Sato*[a]

[a] *Department of Chemical Engineering, Faculty of Engineering, Iwate University, Morioka 020-8551, Japan. E-mail: ogawa@iwate-u.ac.jp; Fax: +81-19-621-6327; Tel: +81-19-621-6934*
[b] *Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*
[c] *KYOUSEI Science Center, Nara Women's University, Nara 630-8506, Japan*

Received (in Cambridge, UK) 6th June 2002, Accepted 17th July 2002
First published as an Advance Article on the web 29th July 2002

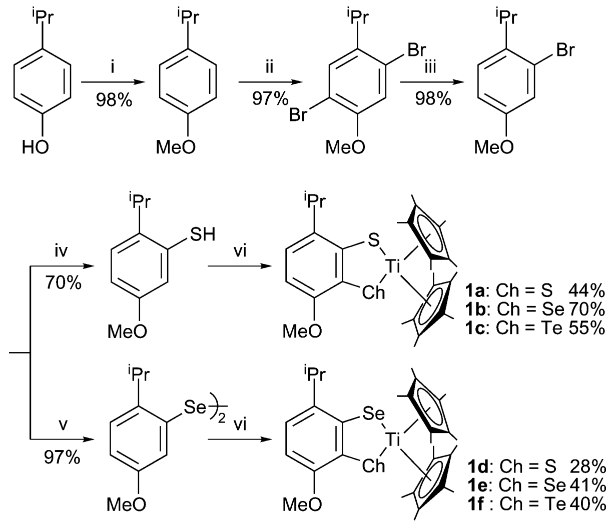
The molecular structure of novel five-membered trichalcogenaheterocycles with three different chalcogen atoms, sulfur, selenium and tellurium, has been determined by crystallographic studies.

The unusual 7π electron structure of certain five-membered rings has allowed the construction of a unique, reversible one-electron redox system.[1] Recently, we reported reversible one-electron redox responses by the use of 4,7-disubstituted benzotrichalcogenoles containing sulfur and/or selenium atoms and found by EPR spectroscopy that their radical cation salts obtained on treatment with one-electron oxidant had unusual 7π frameworks.[2] However, to date, five-membered trichalcogenoles with a tellurium atom or atoms have not been obtained due to their instability and/or to synthetic limitations.[3] On the other hand, incorporation of a tellurium atom in the five-membered ring is expected to significantly enhance their electron-donating ability and lead to a new field of molecular device.[4] Herein we present the synthesis and structural determination by X-ray crystallographic analysis on the novel trichalcogenoles containing different chalcogen atoms with multi-chalcogen linkages.

An elegant approach to the synthesis of trichalcogenoles containing a heavier chalcogen, tellurium, consisted of the transmetallation of titanacycle having two Cp* units as the synthetic intermediate. We synthesized 2-isopropyl-5-methoxybenzenethiol, which has two *ortho*-directing groups, methoxy and mercapto groups, at appropriate positions by a sequence of methylation, double bromination, selective mono-debromination and sulfurization of commercially available 4-isopropylphenol. 2,2-Bis(η^5-pentamethylcyclopentadienyl)-4-isopropyl 7-methoxy-1,3,2-benzothiatelluratitanole, a synthetic equivalent of unstable *ortho*-benzenedichalcogenol with sulfur and tellurium, was prepared in moderate yield by *ortho*-lithiation, addition of elemental tellurium and protection with the corresponding titanocene dichloride with two Cp* units (Scheme 1). Although the physical and spectroscopic data for titanacycles **1a**–**f** are in perfect agreement with those of the proposed structures, one of the solid-state structures, **1b**, was confirmed by X-ray crystallographic analysis (Fig. 1).‡

Transformation into trichalcogenole **2a**–**d** was successfully carried out, namely, by the reaction of the titanole with electrophiles containing one sulfur or selenium unit, sulfur dichloride or selenium oxychloride (Scheme 2). The successful incorporation of sulfur–tellurium and selenium–tellurium linkages is significant since the tellurium-containing five-membered trichlcogenoles have not been isolated.

The crystal structures of thiaselenetellurole **2b** and diselenatellurole **2d** were confirmed by X-ray crystallographic analyses.‡ Fig. 2 shows the ORTEP view of **2b** that has three different chalcogen atoms, sulfur, selenium and tellurium. The sulfur and tellurium atoms at the 1- and 3-positions are almost coplanar with the benzene ring, while the selenium atom at the



Scheme 1 *Reagents and conditions*: i, (a) K_2CO_3, acetone (b) MeI; ii, Br_2–Fe, CCl_4; iii, (a) n-BuLi, Et_2O (b) H^+/H_2O; iv, (a) Mg, THF (b) S_8 (c) H^+/H_2O; v, (a) Mg, THF (b) Se (c) H^+/H_2O; vi, (a) n-BuLi, TMEDA (b) S_8, Se, or Te (c) $Cp^*_2TiCl_2$, THF.

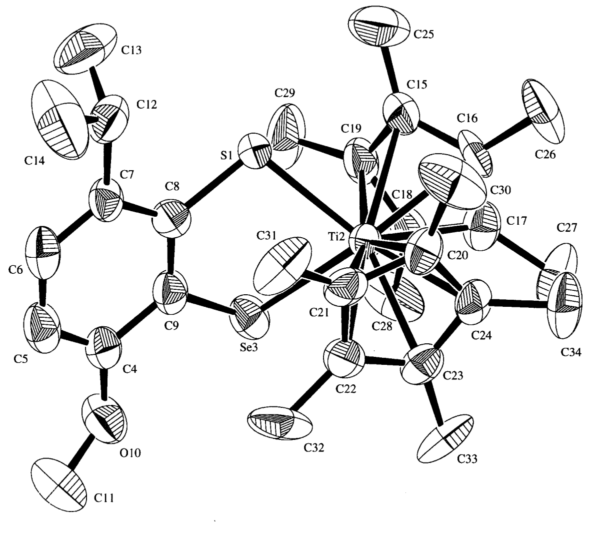
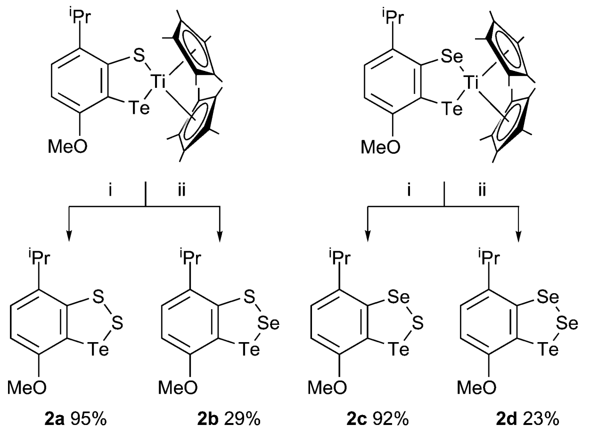


Fig. 1 Molecular structure of **1b** (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): Ti(2)–Se(3) 2.553(2), Ti(1)–S(1) 2.428(3), S(1)–C(8) 1.77(1), Se(3)–C(9) 1.89(1); Se(3)–Ti(2)-S(1) 81.80(9), Ti(2)–Se(3)–C(9) 94.9(4), Ti(2)–S(1)–C(8) 103.4(4); Ti(2)–Se(3)–C(9)–C(8) 32.3(10), Ti(2)–S(1)–C(8)–C(9) −28.5(9).

---

† Electronic supplementary information (ESI) available: satisfactory characterizing data for all the new compounds. Typical experimental procedure, physical and spectroscopic data of all the new compounds and ORTEP view of **2d**. See http://www.rsc.org/suppdata/cc/b2/b205445k/

DOI: 10.1039/b205445k



Scheme 2 *Reagents and conditions*: i, SCl_2, THF; ii, $SeOCl_2$, THF.

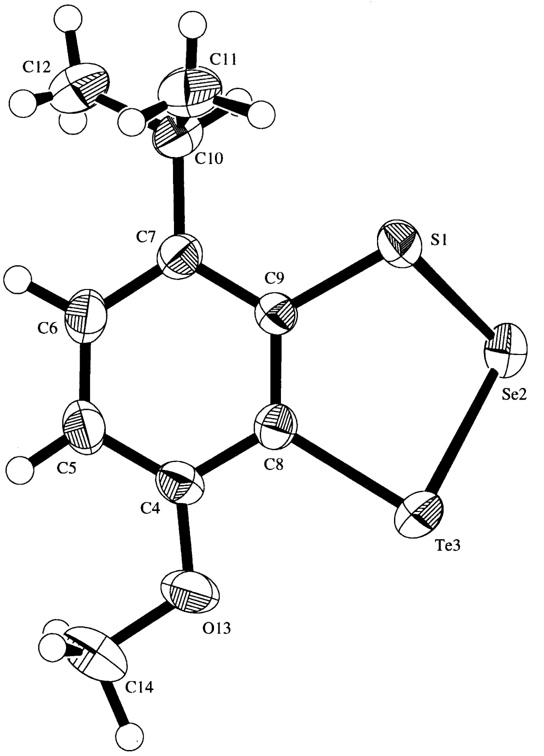


Fig. 2 Molecular structure of **2b**. Selected bond distances (Å) and angles (°): Te(3)–Se(2) 2.5306(5), Se(2)–S(1) 2.2218(9), Te(3)–C(8) 2.101(3), S(1)–C(9) 1.779(3); Se(2)–Te(3)–C(8) 86.16(8), Se(2)–S(1)–C(9) 99.68(10), Te(3)–Se(2)–S(1) 90.54(3), Te(3)–C(8)–C(9) 121.2(2), S(1)–C(9)–C(8) 119.6(2); S(1)–Se(2)–Te(3)–C(8) 35.98(7), Te(3)–Se(2)–S(1)–C(9) −42.83(9), Se(2)–S(1)–C(9)–C(8) 36.8(2), Se(2)–Te(3)–C(8)–C(9) −25.8(2), Te(3)–C(8)–C(9)–S(1) −4.4(3).

2-position lies out of this plane (S(1)–Se(2)–Te(3)–C(8) 35.98(7), Te(3)–Se(2)–S(1)–C(9) −42.83(9)). The distorted geometry of the five-membered ring implies the presence of lone-pair–lone-pair repulsion of three divalent chalcogen atoms. The sulfur–selenium and selenium–tellurium bond lengths are similar to those of acyclic molecules.[5]

Analysis of the cyclic voltammetric responses is diagnostic for an essentially electrochemically reversible anodic step. Cyclic voltamograms of **2b** and **2d** in acetonitrile at 20 °C under argon atmosphere exhibited quasi-reversible redox waves (**2b**: E_{pa} = 0.39 V, E_{pc} = 0.25 V; **2d**: E_{pa} = 0.36 V, E_{pc} = 0.26 V) *versus* Ag/0.01 mol dm^{-3} $AgNO_3$ (scan rate 100 mV s^{-1}). As expected, incorporation of a heavier chalcogen, tellurium, lowered oxidation peaks compared with sulfur or selenium analogues,[2] which could be explained by the ionization potential arising from energy of the highest occupied molecular orbital.[6]

In conclusion, we have shown that new redox active trichalcogenaheterocycles with sulfur, selenium and tellurium can be prepared from dichalcogenatitanacycles. Further studies on reactions of mixed chalcogen ring systems are under way.

Notes and references

‡ *Crystal data* for **1b**: $C_{30}H_{42}OSSeTi$, M = 577.58, orthorhombic, a = 10.109(4), b = 14.855(4), c = 18.680(4) Å, V = 2805(1) $Å^3$, Z = 4, T = 296 K, space group $P2_12_12_1$ (no. 19), D_c = 1.367 g cm^{-3}, μ(Cu-Kα) = 49.04 cm^{-1}, 5630 reflections measured, 2852 unique (R_{int} = 0.107), 307 parameters, R = 0.055, R_w = 0.085 (on 1834 observed data [$I > 3\sigma(I)$]). CCDC 187544.

Crystal data for **2b**: $C_{10}H_{12}OSSeTe$, M = 386.82, monoclinic, a = 7.373(2), b = 16.563(3), c = 10.046(2) Å, β = 94.66(2)°, V = 1222.7(5) $Å^3$, Z = 4, T = 294 K, space group $P2_1/a$ (no. 14), D_c = 2.101 g cm^{-3}, μ(Mo-Kα) = 55.5 cm^{-1}, 2420 reflections measured, 2240 unique (R_{int} = 0.008), 176 parameters, R = 0.021, R_w = 0.037 (on 1926 observed data [$I > 1.50\sigma(I)$]). CCDC 187545.

Crystal data for **2d**: $C_{10}H_{12}OSe_2Te$, M = 433.72, monoclinic, a = 7.389(3), b = 16.581(3), c = 10.165(2) Å, β = 93.14(3)°, V = 1243.6(6) $Å^3$, Z = 4, T = 296 K, space group $P2_1/a$ (no. 14), D_c = 2.316 g cm^{-3}, μ(Mo-Kα) = 82.1 cm^{-1}, 2467 reflections measured, 2282 unique (R_{int} = 0.013), 176 parameters, R = 0.033, R_w = 0.039 (on 2192 observed data [$I > 0.00\sigma(I)$]). CCDC 187546.

See http://www.rsc.org/suppdata/cc/b2/b205445k/ for crystallographic data in .cif or other electronic format.

1 T. S. Cameron, R. C. Haddon, S. M. Matter, S. Parsons, J. Passmore and A. P. Ramirez, *J. Chem. Soc., Chem. Commun.*, 1991, 358; T. S. Cameron, R. C. Haddon, S. M. Matter, S. Parsons, J. Passmore and A. P. Ramirez, *J. Chem. Soc., Dalton Trans.*, 1992, 1563; G. Wolmershäuser and H. Heckmann, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 779; S. Ogawa, S. Nobuta, R. Nakayama, Y. Kawai, S. Niizuma and R. Sato, *Chem. Lett.*, 1996, 757; S. Ogawa, M. Kikuchi, Y. Kawai, S. Niizuma and R. Sato, *Chem. Commun.*, 1999, 1891.

2 S. Ogawa, T. Ohmiya, T. Kikuchi, A. Kawaguchi, S. Saito, A. Sai, N. Ohyama, Y. Kawai, S. Niizuma, S. Nakajo and R. Sato, *J. Organomet. Chem.*, 2000, **611**, 136.

3 D. Schröder, H. Schwarz, B. Löbrecht, W. Koch and S. Ogawa, *Eur. J. Inorg. Chem.*, 1998, 983.

4 K. Lerstrup, D. Tslha, A. Bloch, T. Poehler and D. Cowan, *J. Chem. Soc., Chem. Commun.*, 1982, 226; R. D. McCullough, G. B. Kok, K. A. Lerstrup and D. O. Cowan, *J. Am. Chem., Soc.*, 1987, **109**, 4115; G. Schukat, A. M. Richter and E. Fanghänel, *Sulfur Rep.*, 1987, **7**, 155; G. Schukat and E. Fanghänel, *Sulfur Rep.*, 1993, **14**, 245.

5 I. Hargittai and B. Rozsonzai, in *The Chemistry of organic selenium and tellurium compounds*, **Vol. 1,** eds. S. Patai and Z. Rappoport, John Wiley and Sons, 1986, pp. 63–155.

6 Unpublished results from our laboratory. The data will be discussed in a full paper.