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Synthesis and characterization of germanium (IV) and silicon (IV) complexes derived from 9-hydroxyphenalenone: X-ray crystal and molecular structure of tris-(9-oxophenalenone)-germanium (IV) and silicon (IV) salts

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Abstract

The germanium (IV) and silicon (IV) complexes, tris-(9-oxophenalenone)-germanium (IV) tetrakis[3,5-bis(trifluoromethyl) phenyl] borate ($7^{+}TFPB^{-}$) and tris-(9-oxophenalenone)-silicon (IV) tetrakis[3,5-bis(trifluoromethyl) phenyl] borate ($8^{+}TFPB^{-}$), derived from 9-hydroxyphenalenone have been synthesized and characterized by elemental analyses, infrared spectra and as well as by single crystal X-ray study. The crystal structure of $7^{+}TFPB^{-}$ and $8^{+}TFPB^{-}$ shows a one-dimensional chain like structure and π -overlap between the neighbouring phenalenyl planes. The cyclic voltammograms of $7^{+}TFPB^{-}$ and $8^{+}TFPB^{-}$ show three reversible one-electron reduction steps due to the formation of the radical, anion and dianion as each phenalenyl moiety accepts an electron. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Phenalenone; Cyclic voltammetry; Germanium (IV) complex; Silicon (IV) complex; Neutral radical; X-ray crystal and molecular structure

1. Introduction

Neutral radicals, and the phenalenyl system in particular, have been proposed for the preparation of intrinsic molecular conductors [1]. Sulfur–nitrogen radicals were the first class of neutral radicals to show conductivity based on this principle [2]. We have recently reported the first phenalenyl-based neutral radical conductor [3] and more recently, the first one-dimensional phenalenyl-based neutral radical molecular conductor [4]. Although these compounds differ only in the alkyl groups (**R**, for **6** Benzyl), they show significantly different physical properties. For example, hexyl radical **5** exists as monomers in the solid state with the highest conductivity at room temperature ($\sigma_{RT} = 0.05$ S/cm) of any neutral organic compound reported. Radicals **1** and **3** involve face-to-face π - π interactions, with mean plane separations around 3.33 Å at high temperature and about 3.16 Å at low temperature and this change is accompanied by a magnetic phase transition from the paramagnetic π -dimer form to the diamagnetic π -dimer form, while their conductivities increase by about two orders of magnitude when the diamagnetic state is formed [5]. Radical **6** forms a one-dimensional π -step structure along the *y*-direction. Nevertheless, its conductivity ($\sigma_{RT} = 1.4 \times 10^{-3}$ S/cm) is comparable with that of the previously reported radicals (**1**, **3**, **5**) and greater

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than that of the propyl (2) and pentyl (4) radicals [6,7] (see Scheme 1).

In the present paper, we report the synthesis, redox properties and solid state structures of hexacoordinated germanium ($7^{+}TFPB^{-}$) and silicon ($8^{+}TFPB^{-}$) cations containing three phenalenyl (PLY) units; such octahedral silicon and germanium complexes with 9-oxophenalenone ligands are not well known.

2. Results and discussion

2.1. Synthesis

The synthetic procedure for the preparation of $7^{+}TFPB^{-}$ and $8^{+}TFPB^{-}$ are shown in Scheme 2. A toluene solution of 9-hydroxyphenalenone was treated with GeCl₄ and SiCl₄ to obtain the corresponding chlo-



Fig. 1. Cyclic voltammetry of: (a) $7^{+}TFPB^{-}$ and (b) $8^{+}TFPB^{-}$ in acetonitrile, reference to SCE via internal ferrocene (not shown).

ride salts which were used as such for the next reaction without further purification. The chloride salts are quite insoluble in most common organic solvent but are sparingly soluble in dichloromethane. The anion exchange reactions were performed in dry dichloromethane at



room temperature. Addition of solid sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) leads to dissolution of the cations due to the formation of the TFPB salt. The excess chloride salt and the NaCl formed during the reaction were separated by filtration. Compound 7^+TFPB^- and 8^+TFPB^- were found to be stable in the solid state and in solution at room temperature.

2.2. Electrochemistry

The cyclic voltammetry of $7^{+}TFPB^{-}$ and $8^{+}TFPB^{-}$ exhibit three reversible redox waves at $E_1^{1/2} = -0.56$ V, $E_2^{1/2} = -0.78$ V, $E_3^{1/2} = -1.06$ V and $E_1^{1/2} = -0.57$ V, $E_2^{1/2} = -0.81$ V and $E_3^{1/2} = -1.13$ V versus SCE (Fig. 1) corresponding to the successive reduction to radical, anion and dianion of the phenalenyl moiety (Scheme 3). The relative ease of reduction of these com-





plexes follows the electronegativities of the central atoms: Ge, 2.02; Si, 1.74. The potentials may be compared to the reduction potentials observed for 9^+ : $E_1^{1/2} = -0.34$ V and $E_2^{1/2} = -0.62$ V (Scheme 4), and 10^+ : $E_1^{1/2} = -0.29$ V versus SCE (Scheme 5). The ease of the first reduction of these compounds follows the order: $10^+ > 9^+ > 7^+$ and 8^+ , which is in the sequence of 1,



Scheme 3.



Scheme 4.

2 and 3 phenalenyl units per molecule. This sequence may be understood by considering the degree of charge that is localized in a single phenalenyl ring in the complexes – clearly one PLY ring bears most of the charge density in the salt 10^+ , and along this series it is apparent that any given PLY unit will bear a lower positive charge in the salt as the number of the PLY units increases and, therefore, the first electron transfer will become progressively more difficult. This is in agreement with the bond length data for the salts 7^+ , 8^+ and the beryllium compound, [8] shown in Table 3 where it may be seen that the C1-O1 and C9-O2 bond lengths are 1.302, 1.296, 1.287 and 1.300, 1.308, 1.290 Å, respectively. The bond length should be a sensitive indicator of the degree of charge separation in the complexes with longer bond lengths associated with a greater degree of charge separation. A six-coordinated silicon (IV) complex with a tripodal phenalenyl-based hexadentate ligand was recently shown to undergo three reductions at potentials of -0.97, -1.19 and -1.43 V versus SCE [9], due to reduction to the radical, anion and dianion. This compound is more difficult to reduce than 7⁺TFPB⁻ and 8⁺TFPB⁻, because of the presence of nitrogen in the coordination sphere of silicon.

The disproportionation potential of 7^+ and 8^+ , $\Delta E_{2-1} = E_2^{1/2} - E_1^{1/2} = -0.22$ and -0.24 V versus SCE, are considerably lower in magnitude than the values found for the boron compounds previously reported [3–5]. Table 1 lists the results of the cyclic voltammetry experiments carried out on salts 1^+ , 2^+ , 3^+ , 4^+ , 5^+ , 6^+ (with BPh₄⁻ as the counterion) together with the new compounds. The small ΔE_{2-1} value seen in 7^+ and 8^+ can be explained in terms of the reduction in the electron repulsion by the delocalization of the charge over the three PLY sites. The ΔE_{2-1} value largely determines the on-site Coulomb correlation energy (U) in the solid

Table 2 Crystal data for **7⁺TFPB⁻** and **8⁺TFPB⁻**

Table 1

Half-wave potentials^a and the disproportionation potentials of various tetraphenylborate and TFPB salts

Cation	$E_1^{1/2}$	$E_2^{1/2}$	$E_{3}^{1/2}$	ΔE_{2-1}	References
7 ⁺ TFPB ⁻	-0.56	-0.78	-1.06	-0.22	this work
8 ⁺ TFPB ⁻	-0.57	-0.81	-1.13	-0.24	this work
1+	-0.75	-1.10		-0.35	[5]
2 ⁺	-0.75	-1.10		-0.35	[6]
3 ⁺	-0.73	-1.09		-0.36	[5]
4 ⁺	-0.74	-1.11		-0.37	[7]
5 ⁺	-0.74	-1.11		-0.37	[3]
6 ⁺	-0.68	-1.02		-0.34	[4]

^a In acetonitrile, referenced to SCE (saturated calomel electrode) via internal reference ferrocene.

state and is well established as an important discriminator for organic metals [10,11]. The three reduction waves in the cyclic voltammogram indicate that it is possible to introduce one electron into each of the PLY ring (Scheme 3).

2.3. Crystallography

Single crystals of $7^{+}TFPB^{-}$ and $8^{+}TFPB^{-}$ were grown from diethyl ether and hexane solution at room temperature and studied by single crystal X-ray diffraction. Crystallization of $7^{+}TFPB^{-}$ and $8^{+}TFPB^{-}$ gave needle like crystals of diethyl ether solvates, which belong to the triclinic space group $P\bar{1}$, with two molecules per unit cell. Table 2 provides crystal data of compound $7^{+}TFPB^{-}$ and $8^{+}TFPB^{-}$. An ORTEP plot of the molecular structure of $7^{+}TFPB^{-}$ and $8^{+}TFPB^{-}$ are shown in Fig. 2.

The molecular geometry around germanium and silicon are approximately octahedral, consisting of three bidentate chelating PLY ligands. The plane of the three PLY rings in $7^{+}TFPB^{-}$ reveal some distortion from the ideal octahedral symmetry; their dihedral angles are 84°

Compound	7 ⁺ TFPB ⁻	8 ⁺ TFPB ⁻
Formula	$C_{71}H_{33}BF_{24}GeO_6 \cdot [C_4H_{10}O]_{2.5}$	C ₇₁ H ₃₃ BF ₂₄ SiO ₆ [C ₄ H ₁₀ O] _{2.5}
Crystal system	triclinic	triclinic
Formula weight	1706.67	1662.17
Unit cell dimensions		
a (Å)	12.2965(16)	12.297(2)
$b(\mathbf{A})$	17.104(2)	17.124(3)
c (Å)	18.536(2)	17.124(3)
α (°)	75.645(3)	75.762(3)
β (°)	82.109(3)	82.337(4)
γ (°)	74.879(2)	74.869(3)
$V(\dot{A})$	3635.0(8)	3636.0(11)
Space group	$P\bar{1}$	$P\overline{1}$
Z	2	2
Temperature (K)	223(2)	233(2)
$\mu (\mathrm{mm}^{-1})$	0.543	0.154
Data/restrain/parameter	14 870/1082/1227	14 864/631/1323
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0543, wR_2 = 0.1489$	$R_1 = 0.0589, wR_2 = 0.1557$
R indices (all data)	$R_1 = 0.0758, wR_2 = 0.1676$	$R_1 = 0.0949, wR_2 = 0.1873$



Fig. 2. ORTEP diagram of the molecular structure of: (a) 7⁺TFPB⁻ and (b) 8⁺TFPB⁻.



Fig. 3. ORTEP diagram of the molecular structure of: (a) 7⁺TFPB⁻ and (b) 8⁺TFPB⁻ (only the cation part) and the numbering of the atoms.

 $(C_1-C_{9b}, C_{11}-C_{19b})$, 80.5° $(C_{11}-C_{19b}, C_{21}-C_{29b})$ and 102.9° (C₂₁-C_{29b}, C₁-C_{9b}) (see Fig. 3), rather than 90° as expected in ideal octahedral symmetry. The corresponding dihedral angles for the silicon compound are 83.8°, 80.1° and 102.8°. The dihedral angles are different from that observed in the cis-hexacoordinate (tropolonato)₂ SiPh₂ (an α -diketonate compound) in which the angle of the two tropolonate chelating planes is 81.1° [12]. The structure distorts so that the metal atom deviates from the chelate-ring plane, and this has been noted in studies of several acetylacetonato complexes and is ascribed to the packing forces in the crystals [13]. The comparison of the bond lengths in Table 3 indicates that there is a considerable amount of charge separation in the cationic complexes of germanium and silicon as reflected by the C–O bond lengths in these compounds.

The structure of the counter anion (TFPB) also deviates from the ideal tetrahedral geometry and this is probably due to the presence of bulky substituents (CF₃) on the phenyl ring. In the crystal structure of $7^{+}TFPB^{-}$ four out of eight CF₃ groups in the counter anion show disorder. In compound $8^{+}TFPB^{-}$ all the CF₃ groups were refined as disordered CF₃. In the molecular structure of the salt (7^+TFPB^-) , each cation is involved in $\pi-\pi$ interactions with two neighbouring molecules and thus these cations form chains in the solid state (Fig. 4). The chain formation

Table 3							
Comparison	of bond	length ((in Å)	among	Re	Ge and Si	complexes

Bond type	[PLY(O,O)]2Be	7 ⁺ TFPB ⁻	8 ⁺ TFPB ⁻
O1–C1	1.287(2)	1.302(4)	1.296(4)
O2–C9	1.290(2)	1.300(4)	1.308(4)
C1-C2	1.427(3)	1.419(4)	1.428(4)
C1–C9a	1.421(2)	1.412(4)	1.417(4)
C2–C3	1.345(3)	1.349(5)	1.351(5)
C3–C3a	1.422(3)	1.424(5)	1.430(5)
C3a–C9b	1.422(2)	1.408(4)	1.421(4)
C3a–C4	1.397(2)	1.402(5)	1.396(5)
C4–C5	1.375(3)	1.383(6)	1.372(6)
C5-C6	1.384(3)	1.370(6)	1.380(6)
C6–C6a	1.400(2)	1.404(5)	1.406(5)
C6a–C9b	1.408(2)	1.414(4)	1.421(4)
C6a–C7	1.423(2)	1.415(5)	1.421(5)
C7–C8	1.349(2)	1.356(5)	1.351(5)
C8–C9	1.430(2)	1.423(4)	1.426(4)
C9–C9a	1.426(2)	1.418(4)	1.414(4)
C9a–C9b	1.424(2)	1.430(4)	1.418(4)



Fig. 4. Packing diagram of the cations (7^+) in the lattice, showing the overlap between four of the neighbouring cations: (a) and (b) are perpendicular views of each of the two sets of phenalenyl units.



Fig. 5. Overlap between a pair of cations 7^+ .

occurs along the Z-direction of the unit cell. Out of the three two PLY are involved in π -dimer chain formation. But the C–C distances of the PLY carbon with the nearest neighbour are not identical. There are two sets of C-C distances are shown in the Fig. 6. The shortest C-C distance observed is 3.274 Å for compound 7^+TFPB^- and 3.297 Å for compound 8⁺TFPB⁻. The projection of cation 7^+ (Fig. 5) demonstrates the almost perfect superposition of some of the carbon atoms in the π -dimers. A similar packing pattern was observed for cation 8^+ which are not shown in the figure.

3. Experimental

3.1. Materials and methods

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were dried and distilled according to the standard procedures. Toluene was distilled from sodium benzophenone ketyl immediately before use. Dichloro-



Fig. 6. The closest distances between a pair of cations 7^+ .

methane was distilled from anhydrous CaH₂ before use. Germanium tetrachloride and silicon tetrachloride (Aldrich) were all commercial products and were used as received. 9-Hydroxyphenalenone and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) were synthesized according to literature procedures [14,15]. Melting points are uncorrected. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer (at 2 cm⁻¹ resolution). ¹H NMR spectra were run on a Varian Inova 300 MHz NMR spectrometer. Elemental analysis were performed by Microanalysis Laboratory (School of Chemical Science, University of Illinois, Urbana, IL).

3.2. Preparation of 7^+Cl^-

9-Hydroxyphenalenone (1.96 g, 10 mmol) in anhydrous toluene (50 mL) was treated with germanium tetrachloride (0.71 g, 3.3 mmol) under argon and the mixture was refluxed for 12 h. The yellow solid was isolated by filtration (1.5 g, 32%). Melting point: Compound does not melt till 380 °C. ¹H NMR (CD₃OD); δ 8.28 (d, 6H), 8.18 (d, 6H), 7.69 (t, 3H), 7.18 (d, 6H). IR (ATR, 4000–600 cm⁻¹): 3002 (w), 2986 (w), 1622 (m), 1570 (s), 1496 (s), 1467 (w), 1429 (w), 1353 (w), 1335 (w), 1322 (w), 1273 (s), 1238 (m), 1181 (w), 1142 (w), 1129 (w), 982 (w), 851 (s), 763 (s), 750 (s), 701 (w), 682 (w).

3.3. Preparation of 7⁺TFPB⁻

A mixture of 7^+ Cl⁻ (1.02 g, 1.47 mmol) and NaTFPB (1.15 g, 1.30 mmol) was added to 100 mL of dry CH₂Cl₂. The mixture was stirred for 3 h until all yellow solids went into the solution and a white solid had precipitated. The yellow solution was filtered and the solvent was evaporated to give a brownish-yellow solid. Crystallization from ether–hexane (10:1) gave yellow needles. Yield: 1.85 g (93%); m.p. 98 °C. ¹H NMR (CDCl₃): δ 8.36 (d, 6H), 8.28 (d, 6H), 7.79 (t, 3H), 7.72 (br, 8H), 7.48 (br, 4H), 7.28 (d, 6H). IR (ATR, 4000–600 cm⁻¹): 3050 (w), 3028 (w), 1627 (w), 1618 (w), 1568 (m), 1496 (m), 1470 (w), 1434 (w), 1354 (w), 1336 (w), 1273 (s), 1241 (m), 1122 (s), 987 (w), 854 (w), 759 (w), 712 (w). *Anal.* Calc. for C₇₁H₃₃BO₆GeF₂₄: C, 56.05; H, 2.19; B, 0.71; Ge, 4.77. Found: C, 57.80; H, 2.71; B, 0.69; Ge, 4.39%.

3.4. Preparation of 8^+Cl^-

9-Hydroxyphenalenone (2.4 g, 12.2 mmol) was dissolved in 50 mL of dry toluene followed by addition of SiCl₄ (4 mL, 4 mmol) in dichloromethane. The reaction mixture was refluxed for 8 h. The yellow solid was isolated by filtration (3.0 g, 86%). When a melting point determination was attempted, the salt turned brown (~290 °C). ¹H NMR (CD₃OD): δ 8.60 (d, 6H), 8.48 (d, 6H), 7.91 (t, 3H), 7.26 (d, 6H). IR (ATR, 4000–600 cm⁻¹): 3004 (w), 2987 (w), 1621 (w), 1571 (w), 1501 (w), 1343 (w), 1274 (m), 1256 (m), 1144 (w), 1125 (w), 993 (w), 852 (w), 764 (s), 749 (s), 652 (m), 641 (s).

3.5. Preparation of 8⁺TFPB⁻

Synthesis of **8**⁺**TFPB**⁻ is exactly the same as the preparation of **7**⁺**TFPB**⁻. Yield: 1.8 g (88%); m.p. 84 °C. ¹H NMR (CDCl₃); δ 8.37 (d, 6H), 8.26 (d, 6H), 7.78 (t, 3H), 7.70 (br, 8H), 7.45 (br, 4H), 7.24 (d, 6H). IR (ATR, 4000–600 cm⁻¹): 3004 (w), 2987 (w), 1621 (w), 1576 (m), 1504 (m), 1349 (m), 1275 (s), 1240 (w), 1119 (s), 993 (w), 851 (m), 764 (m), 751 (m). *Anal.* Calc. for C₇₁H₃₃BO₆SiF₂₄: C, 57.74; H, 2.24. Found: C, 57.95; H, 2.11%.

3.6. X-ray crystallography

Data were collected on a Bruker SMART 1000 platform-CCD X-ray diffractometer system (Mo radiation, $\lambda = 0.71073$ Å, 50 kV/40 mA power) at 223 K. The orange crystal gave a triclinic unit cell (space group $P\bar{1}$, z = 2), with unit cell parameters a = 12.2965(16) Å, b = 17.104(2) Å, c = 18.536(2) Å, $\alpha = 75.645(3)^{\circ}$, $\beta = 82.109(3)^{\circ}$, $\gamma = 74.879(2)^{\circ}$ and V = 3635.0(8) Å³ for compound 7⁺TFPB⁻ and a = 12.297(2) Å, b =17.124(3) Å, c = 18.505(3) Å, $\alpha = 75.762(3)^{\circ}$, $\beta =$ 82.337(4)°, $\gamma = 74.869(3)^{\circ}$ and V = 3636.0(11) Å³ for compound 8⁺TFPB⁻. The structure (7⁺TFPB⁻) was refined with 14870 reflections, yielding $R[I > 2\sigma(I)]$, $R_1 = 0.0543$, $wR_2 = 0.1489$, and R indices for all data $R_1 = 0.0758$ and $wR_2 = 0.1676$ (Table 2). The structure of **8**⁺**TFPB**⁻ was refined with 14864 reflections, yielding $R[I > 2\sigma(I)]$, $R_1 = 0.0589$, $wR_2 = 0.1557$, and R indices for all data $R_1 = 0.0949$, and $wR_2 = 0.1873$ (Table 2). Full details, including bond lengths and bond angles, are given in the supporting Information.

3.7. Cyclic voltammetry

Cyclic Voltammetry was performed using a PINE Bipotentiostat, model AFCC1BP1, with scan rates 50– 100 mV s⁻¹ on solutions (<10⁻³ M) of 7⁺TFPB⁻ and 8⁺TFPB⁻ in CH₃CN (dried by distillation from P₂O₅ and CaH₂) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Potentials were scanned with respect to the quasi-reference electrode in a single compartment cell fitted with Pt electrodes and referenced to the Fc/Fc⁺ couple of ferrocene at 0.38 V versus SCE [16]. The $E_{pa} - E_{pc}$ separation of the reversible couples was within 10% of that of the Fc/Fc⁺ couple.

4. Summary and conclusions

In summary, two new cationic tris-(9-oxophenalenone) germanium (IV) and silicon (IV) of 7^+ and 8^+ have been synthesized in high yield and high purity. Cyclic voltammetry indicated these complexes could be easily reduced to its corresponding radical. The hexacoordinated geometry was determined by single crystal X-ray diffraction analysis in the solid state. Molecular structure also shows a π - π interaction between the two neighboring PLY plane and a one-dimensional chain like structure in the solid state.

5. Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center, CCDC Reference Nos. 265567 (**7**⁺**TFPB**⁻) and 265568 (**8**⁺**TFPB**⁻). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44 1223 336033; e-mail: deposit@ ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk).

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References

- [1] R.C. Haddon, Aust. J. Chem. 28 (1975) 2343.
- [2] R.T. Oakley, Can. J. Chem. 71 (1993) 1775.

- [3] X. Chi, M.E. Itkis, B.O. Patrick, T.M. Barclay, R.W. Reed, R.T. Oakley, A.W. Cordes, R.C. Haddon, J. Am. Chem. Soc. 121 (1999) 10395.
- [4] S.K. Pal, M.E. Itkis, R.W. Reed, R.T. Oakley, A.W. Cordes, F.S. Tham, T. Siegrist, R.C. Haddon, J. Am. Chem. Soc. 126 (2004) 1478.
- [5] X. Chi, M.E. Itkis, K. Kirschbaum, A.A. Pinkerton, R.T. Oakley, A.W. Cordes, R.C. Haddon, J. Am. Chem. Soc. 123 (2001) 4041.
- [6] X. Chi, M.E. Itkis, R.W. Reed, R.T. Oakley, A.W. Cordes, R.C. Haddon, J. Phys. Chem. B 106 (2002) 8278.
- [7] X. Chi, M.E. Itkis, F.S. Tham, R.T. Oakley, A.W. Cordes, R.C. Haddon, Int. J. Quantum Chem. 95 (2003) 853.
- [8] R.C. Haddon, S.V. Chichester, J.H. Marshall, Tetrahedron 42 (1986) 6293.

- [9] S. Samanta, M.E. Itkis, R.W. Reed, R.T. Oakley, F.S. Tham, R.C. Haddon, Synthetic Met. (2004), submitted.
- [10] A.F. Garito, A.J. Heeger, Acc. Chem. Res. 7 (1974) 232.
- [11] J.B. Torrance, Acc. Chem. Res. 12 (1979) 79.
- [12] M. Kira, L. Zhang, C. Kabuto, H. Sakurai, Chem. Lett. 8 (1995) 659.
- [13] T. Ito, K. Toriumi, F.B. Ueno, K. Saito, Acta Cryst. B 36 (1980) 2998.
- [14] R.C. Haddon, F. Wudl, M.L. Kaplan, J.H. Marshall, R.E. Cais, F.B. Bramwell, J. Am. Chem. Soc. 100 (1978) 7629.
- [15] R.S. Bahr, P. Boudjouk, J. Org. Chem. 57 (1992) 5545.
- [16] R.T. Boere, K.H. Moock, M. Parvez, Z. Anorg. Allg. Chem. 620 (1994) 1589.