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Synthesis and crystal structure of a pentacoordinate 1,2-oxagermetanide ☆

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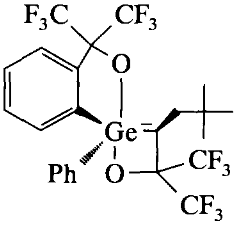
Abstract

A pentacoordinate 1,2-oxagermetanide **1**, K^+ 18-crown-6 $\{[-C_6H_4C(CF_3)_2O-]GePh[-CH(CH^t_2Bu)C(CF_3)_2O-]\}^-$, was quantitatively synthesized as a colourless block (m.p. 217–218°C (decomp.)) by deprotonation of the corresponding β-hydroxygermane **2**, $[-C_6H_4C(CF_3)_2O-]GePhCH(CH^t_2Bu)C(CF_3)_2OH$, which can be prepared by unique cycloelimination of benzene from *o*-$HO(CF_3)_2CC_6H_4GePh_2[CH(CH^t_2Bu)C(CF_3)_2OH]$ (**3**). On heating in CD_3CN at 150°C for 30 days, **1** equilibrates with another diastereomer **4** and then undergoes the Peterson-type reaction to give the corresponding olefin **5**, $(F_3C)_2C{=}CHCH^t_2Bu$ (13%), and its double-bond migrated isomer **6**, $(F_3C)_2CHCH{=}CH^tBu$ (33%). The yields of the olefins **5** and **6** are not very high, because their polymerization takes place under the reaction conditions. X-ray crystallographic analysis of **1** shows that it has a distorted trigonal bipyramidal structure with two oxygen atoms at apical positions.

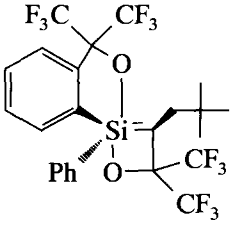
Keywords: Alkene; Germanium; Crystal structure; Crown ether; Potassium; X-ray diffraction

1. Introduction

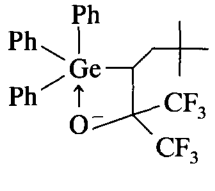
Peterson-type reactions, using β-hydroxysilanes, -germanes, -stannanes and -plumbanes, stereospecifically produce the corresponding olefins under acidic and neutral (or basic) conditions [1]. Recently, we achieved the synthesis of intermediates **7**, **8** and **9** of the Peterson [2], the germanium–Peterson [3] and tin–Peterson [4] reactions, respectively. These are pentacoordinate anionic species with an oxetane ring except for the germanium derivative **8** [3].



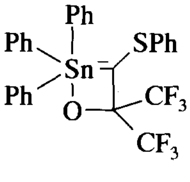
K^+, 18-c-6
1



K^+, 18-c-6
7



K^+, 18-c-6
8



K^+, 18-c-6
9

We now report the first synthesis and crystal structure of a pentacoordinate 1,2-oxagermetanide **1** via unique intramolecular cycloelimination reaction of benzene from a phenylgermane derivative having a hydroxyl group.

2. Results and discussion

Ring opening reaction of $[-C_6H_4C(CF_3)_2O-]GePh_2$ (**10**) (37%), which was prepared from *o*-LiC_6H_4-$C(CF_3)_2OLi$ [5] and dibromodiphenylgermane [6], with vinylmagnesium bromide gave diphenylvinylgermane **11** (85%). Sequential treatment of **11** with 6 equiv. of ^{t}BuLi (THF, −72°C, 1 h), excess hexafluoroacetone (THF, −72°C, 15 min) and aqueous NH_4Cl afforded crude β-hydroxygermane **3** (Scheme 1). Even upon standing overnight in solution (CH_3CN or $CHCl_3$) at

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☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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room temperature, **3** readily underwent cycloelimination reaction of benzene [7] to give cyclic β-hydroxygermane **2**, which was purified by HPLC and subsequent recrystallization from hexane (25%).

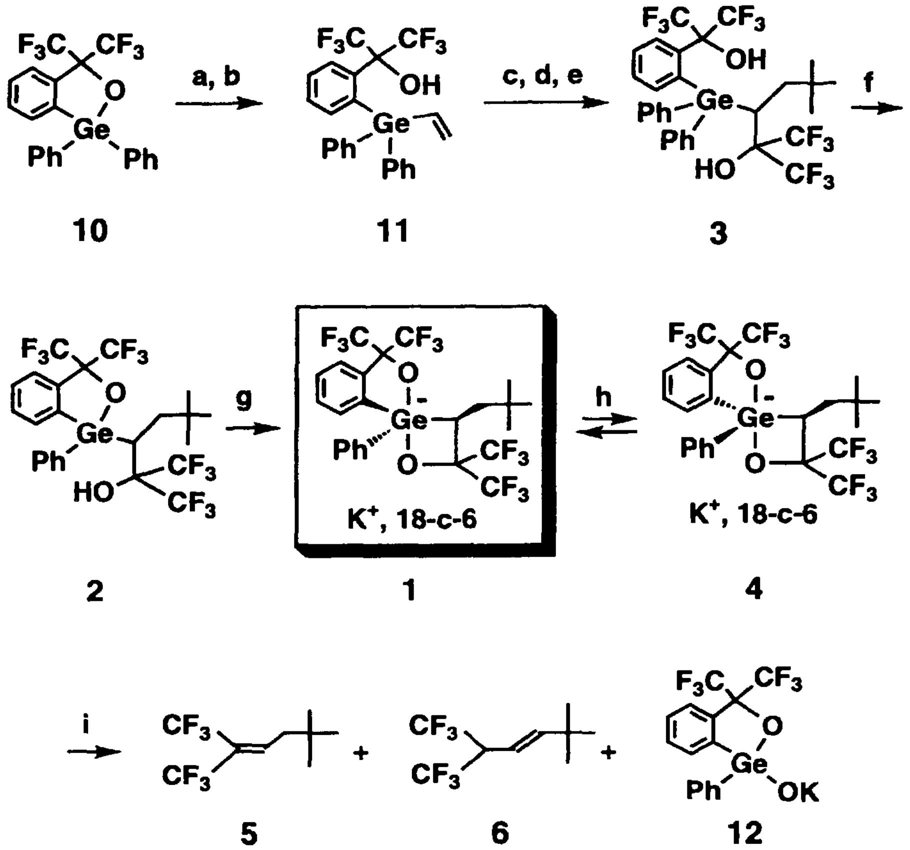
Deprotonation of **2** with KH in the presence of 18-crown-6 in THF gave quantitatively a pentacoordinate 1,2-oxagermetanide **1**. The ^{1}H, ^{19}F and ^{13}C NMR spectra of **1** were very similar to those of a silicon analogue **7** [2], suggesting that **1** exists as a pentacoordinate 1,2-oxagermetanide.

Monitoring of the thermolysis of **1** by ^{19}F NMR spectroscopy showed that first two sets of a new double quartet, assignable to another diastereomer **4** of **1**, appeared and increased until the **1** : **4** ratio became constant (ca. 2 : 1), and then decreased accompanied by the appearance of signals due to the olefin **5** (13%), its double-bond migrated olefin **6** (33%) and potassium germyloxide **12**. The yields of **5** and **6** are not very high, because their polymerization took place under the reaction conditions. Recently, a similar equilibration between diastereomers was observed in the system of the tetracoordinate 1,2-oxathietane [8]. Although there is no evidence, pseudorotation or elimination–recombination is considered as a possible mechanism for this interesting stereomutation.

The product **1** was recrystallized from dichloromethane–hexane to afford colourless blocks that melted at 217–218°C with decomposition. The X-ray crystallographic analysis of **1** indicated that it is a pentacoordinate 1,2-oxagermetanide similar to that of the silicon analogue **7** [2] (Fig. 1) [9]. This is the first example of a pentacoordinate 1,2-oxagermetanide.

The apical bond length Ge1–O1 (2.150(5) Å) is much shorter than that (2.832(8) Å) of **8**, and slightly longer than another bond, Ge1–O2 (1.928(6) Å), a reasonable value compared with a typical pentacoordinate germate [10]. The Ge atom is almost in the equatorial plane, as observed also in the silicon analogue **7**. The torsion angle Ge1–C16–C17–O1 is 16.9(6)°, indicating that the four-membered ring is slightly puckered. The potassium atom is located in the plane of the crown ether and interacts with O1 and one fluorine atom of one trifluoromethyl group in addition to six oxygen atoms of the crown ether. It is interesting that in the major isomer the neopentyl and phenyl groups are *trans* to each other, as observed in **7**, since the stereochemistry must be determined at the different stages in the cases of **1** and **7**, that is, cycloelimination for **1** and carbonyl condensation for **7**.

Taking into consideration the structures of **1**, **7**, **8** and **9**, the following conclusions can be drawn. First, all of them have a Peterson-type reactivity in spite of their different structures. Second, a substituent on the central atom plays an important role in determining what crys-



Scheme 1. (a) $CH_2=CHMgBr$ (2 equiv.), THF, −72°C, 30 min; (b) aqueous NH_4Cl; (c) $^{t}BuLi$ (6 equiv.), THF, −72°C; −30°C, 1 h; (d) excess $(CF_3)_2C=O$, −72°C, 1.5 h; (e) aqueous NH_4Cl; (f) CH_3CN or $CHCl_3$, 25°C, overnight; (g) KH, 18-crown-6, THF, −72°C, 20 min; 25°C, 20 min; (h) CD_3CN, 80–150°C; (i) CD_3CN, 150°C, 30 days.

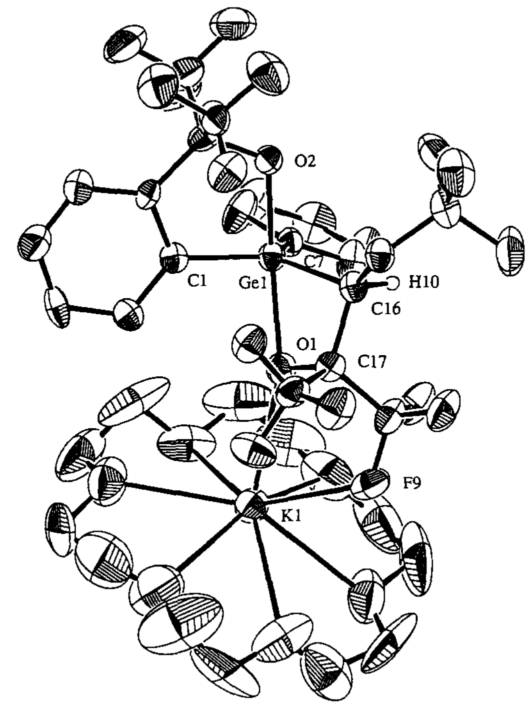


Fig. 1. ORTEP drawing of **1** (omitting CH_2Cl_2 for clarity). Selected bond lengths (Å) and angles (°): Ge1–O1, 2.150(5); Ge1–O2, 1.928(6); Ge1–C1, 1.941(8); Ge1–C7, 1.960(9); Ge1–C16, 1.972(8); C16–C17, 1.57(1); C17–O1, 1.393(9); K1–O1, 2.881(6); K1–F9, 2.895(6); O1–Ge1–O2, 165.5(2); C1–Ge1–C7, 115.0(3); C1–Ge1–C16, 129.3(3); C7–Ge1–C16, 114.3(3); O1–Ge1–C16, 69.1(3); Ge1–C16–C17, 92.6(5); C16–C17–O1, 104.2(7); Ge1–O1–C17, 90.7(5).

tal structure the compound has, and in the present case the Martin ligand could change the structure from β-germylalkoxide to a pentacoordinate germate having a distorted trigonal bipyramid.

3. Experimental

The ^{1}H and ^{13}C NMR spectra were measured with a Bruker AM-500 spectrometer using tetramethylsilane (TMS) as internal standard. ^{19}F NMR spectra were taken with a JEOL EX-270 spectrometer using Freon as external standard. Mass spectra were recorded with a JEOL JMX-SX102 mass spectrometer operating in the electron impact (EI) ionization mode. Melting points were determined on a Yanaco micro melting point apparatus. Dry column chromatography (dry CC) was carried out with ICN silica DCC 60A. Elemental analyses were carried out at the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo, and determined on a Perkin-Elmer Micro Analyzer.

3.1. Preparation of diphenyl{2-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]phenyl}vinylgermane (11)

To a solution of cyclic diphenylgermane **10** (422 mg, 0.90 mmol), which was prepared in 37% yield from dibromodiphenylgermane [6], in dry THF (6 ml) was added a THF solution (0.94 M) of vinylmagnesium bromide (1.9 ml, 1.8 mmol) at −72°C under an argon atmosphere. The resulting solution was stirred at −72°C for 0.5 h and then quenched with aqueous NH_4Cl. After the usual work-up, the residue was subjected to dry CC (hexane–CH_2Cl_2 (1 : 1)) to give diphenylvinylgermane **11** (380 mg, 85%): colourless crystals, m.p. 132–135°C (decomp.) (hexane). Anal. Calc. for $C_{23}H_{18}F_6GeO$: C, 55.58; H, 3.65. Found: C, 55.40; H, 3.81%. ^{1}H NMR (500 MHz, $CDCl_3$), δ 3.86 (s, 1H, OH), 5.68 (dd, $J = 3$ Hz, $J = 20$ Hz, 1 H), 6.21 (dd, $J = 3$ Hz, $J = 13$ Hz, 1H), 6.78 (dd, $J = 13$ Hz, $J = 20$, 1H), 7.31–7.38 (m, 7H), 7.40–7.42 (m, 4H), 7.44–7.48 (m, 1H), 7.53–7.55 (m, 1H), 7.73–7.74 (m, 1H); $^{13}C\{^{1}H\}$ NMR (68 MHz, $CDCl_3$), δ 79.1 (sept, $J_{CF} = 29$ Hz), 122.7 (q, $J_{CF} = 289$ Hz), 127.3 (m), 128.0, 128.6, 129.1, 129.4, 133.2, 134.2, 135.0, 135.9, 137.6, 138.8, 139.1; ^{19}F NMR (253.8 MHz, $CDCl_3$), δ −74.97.

3.2. Preparation of 1-{3,3-dimethyl-1-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]butyl}-1-phenyl-3,3-bis(trifluoromethyl)-1,3-dihydro-2,1-benzoxagermole (2)

To a solution of **11** (151 mg, 0.30 mmol) in dry THF (6 ml) was added a 1.78 M pentane solution of ^{t}BuLi (1.0 ml, 1.8 mmol) at −72°C under an argon atmosphere. The temperature was allowed to warm to −30°C for 1 h, and then cooled to −72°C again. To the resulting orange solution was added excess hexafluoroacetone, which was freshly prepared by adding its trihydrate (0.5 ml, 3.6 mmol) to concentrated H_2SO_4 (30 ml) at 120°C. The solution turned colourless and stirring was continued at −72°C for an additional 1.5 h. After the usual work-up, dry CC (hexane–ether (3 : 1)) of the residue gave crude {3,3-dimethyl-1-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]butyl}diphenyl{2-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]-yl)ethyl]phenyl}germane (**3**), (3,3-dimethylbutyl)diphenyl{2-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]phenyl}germane (**13**) (20%) and (*E*)-(3,3-dimethyl-1-butenyl)diphenyl{2-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]phenyl}germane (**14**) (28%). Even on standing in solution at room temperature, **3** readily underwent cycloelimination of benzene to give 1-{3,3-dimethyl-1-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]butyl}-1-phenyl-3,3-bis(trifluoromethyl)-1,3-dihydro-2,1-benzoxagermole (**2**), which was purified by HPLC (column: JAIGEL H-1, H-2, Japan Analytical Industry) and then by recrystallization from hexane (25%).

2: Colorless crystals; m.p. 111.5–114.0°C. Anal. Calc. for $C_{24}H_{22}F_{12}GeO_2$: C, 44.83; H, 3.45. Found: C, 45.00; H, 3.63%. ^{1}H NMR (270 MHz, $CDCl_3$), δ 0.94 (s, 9H, $C(CH_3)_3$), 1.60 (d, $J = 17$ Hz, 1H), 2.10 (dd, $J = 17$ Hz, $J = 9$ Hz, 1H), 2.95 (d, $J = 9$ Hz, 1H), 4.55 (br s, 1H, OH), 7.37–7.41 (m, 3H), 7.49–7.53 (m, 2H), 7.60–7.67 (m, 3H), 7.72–7.73 (m, 1H); $^{13}C\{^{1}H\}$ NMR

(125 MHz, $CDCl_3$), δ 28.97 (s, CH_3), 30.98 (s, $C(CH_3)_3$), 33.99 (s, CH_2), 34.45 (s, CH), 79.50 (sept, $J_{CF} = 29$ Hz), 84.40 (sept, $J_{CF} = 30$ Hz), 122.61 (q, $J_{CF} = 288$ Hz), 123.26 (q, $J_{CF} = 287$ Hz), 123.32 (q, $J_{CF} = 289$ Hz), 123.48 (q, $J_{CF} = 288$ Hz), 125.49 (m), 128.52, 130.23 (2 × s), 130.31, 132.10, 132.72, 136.82, 137.22, 138.94; ^{19}F NMR (253.8 MHz, $CDCl_3$), δ −76.51 (q, $J_{FF} = 9$ Hz), −75.38 (q, $J_{FF} = 9$ Hz), −75.15 (m), −70.55 (m). HRMS (70 eV), *m/z* calc. for $C_{24}H_{22}F_{12}{}^{74}GeO_2$: 644.0640. Found: 644.0634. IR (KBr), ν_{OH} 3558 cm^{-1}.

3: ^1H NMR (270 MHz, $CDCl_3$), δ 0.65 (s, 9H, $C(CH_3)_3$), 1.65 (d, $J = 14$ Hz, 1H), 2.14 (dd, $J = 14$ Hz, $J = 8$ Hz, 1H), 3.09 (m, 1H), 3.93 (s, 1H, OH), 4.25 (s, 1H, OH), 7.24–7.78 (m, 13H), 8.00–8.03 (m, 1H); ^{19}F NMR (253.8 MHz, $CDCl_3$), δ −74.60 (q, $J_{FF} = 8$ Hz), −74.02 (q, $J_{FF} = 8$ Hz), −73.91 (q, $J_{FF} = 8$ Hz), −68.43 (q, $J_{FF} = 8$ Hz).

13: colourless crystals; m.p. 82–85°C. Anal. Calc. for $C_{27}H_{28}F_6GeO$: C, 58.42; H, 5.08. Found: C, 58.27; H, 5.12%. ^1H NMR (500 MHz, $CDCl_3$), δ 0.87 (s, 9H, $C(CH_3)_3$), 1.38–1.41 (m, 2H), 1.61–1.65 (m, 2H), 3.49 (s, 1H, OH), 7.31–7.35 (m, 7H), 7.40–7.46 (m, 5H), 7.52–7.54 (m, 1H), 7.71–7.73 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ 12.1 (s, CH_2), 28.8 (s, CH_3), 31.6 (s, $C(CH_3)_3$), 39.2 (s, CH_2), 79.3 (sept, $J_{CF} = 30$ Hz), 122.7 (q, $J_{CF} = 289$ Hz), 127.3 (m), 128.0, 128.4, 128.8, 129.3, 134.3, 134.8, 137.0, 139.0, 140.4; ^{19}F NMR (253.8 MHz, $CDCl_3$), δ −74.84.

14: ^1H NMR (500 MHz, $CDCl_3$), δ 1.04 (s, 9H, $C(CH_3)_3$), 3.65 (s, 1H, OH), 6.14 (d, $J = 19$ Hz, 1H), 6.20 (d, $J = 19$ Hz, 1H), 7.31–7.44 (m, 13H), 7.74 (d, 1H, $J = 8$ Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ 29.0 (s, CH_3), 35.7 (s, $C(CH_3)_3$), 79.5 (sept, $J_{CF} = 30$ Hz), 120.1 (s, GeCH), 122.7 (q, $J_{CF} = 289$ Hz), 127.4 (m), 128.0, 128.6, 129.0, 129.4, 134.4, 135.1, 136.5, 139.2, 139.4, 160.1 (s, GeCH = CH); ^{19}F NMR (253.8 MHz, $CDCl_3$), δ −74.83. HRMS (70 eV), *m/z* found: 554.1075. Calc. for $C_{27}H_{26}F_6{}^{74}GeO$: 554.1099.

3.3. Synthesis of potassium 18-crown-6 [α,α-bis(trifluoromethyl)benzenemethanolato(2 −)-C^2,O]phenyl[1,1,1-trifluoro-5,5-dimethyl-2-(trifluoromethyl)-2-hexanolato-(2 −)-C^3,O]germate(1 −) (1)

To a solution of **2** (35.2 mg, 0.055 mmol) and 18-crown-6 (15.4 mg, 0.056 mmol) in dry THF (1.8 ml) was added a THF suspension of excess of KH at −72°C. The mixture was stirred at −72°C for 20 min and 25°C for 20 min, and the solvent was evaporated to give a tarry oil. The oil was recrystallized from hexane–CH_2Cl_2 to give potassium 18-crown-6 [α,α-bis(trifluoromethyl)benzenemethanolato(2 −)-C^2,*O*]phenyl-[1,1,1-trifluoro-5,5-dimethyl-2-(trifluoromethyl)-2-hexanolato(2 −)-C^3,*O*]germate(1 −) (**1**) as colourless crystals: m.p. 217–218°C (decomp). Anal. Calc. for $C_{36}H_{45}F_{12}GeKO_8$: C, 45.74; H, 4.80. Found: C, 45.48; H, 4.71%. ^1H NMR (500 MHz, $CDCl_3$), δ 0.92 (s, 9 H), 1.48 (d, $J = 15$ Hz, 1 H), 2.08 (dd, $J = 15$ Hz, $J = 8$ Hz, 1 H), 3.35 (d, $J = 8$ Hz, 1 H), 3.55 (s, 24 H), 7.21–7.22 (m, 3H), 7.28–7.31 (m, 1H), 7.35–7.38 (m, 1H), 7.66–7.68 (m, 1H), 7.80–7.81 (m, 2H), 8.06–8.07 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ 29.16 (s, CH_3), 30.94 (s, $C(CH_3)_3$), 35.70 (s, CH_2), 46.66 (s, CH), 69.82 (s, OCH_2CH_2O), 80.36 (sept, $J_{CF} = 26$ Hz), 82.66 (sept, $J_{CF} = 28$ Hz), 124.52 (m), 124.62 (q, $J_{CF} = 289$ Hz), 126.03 (q, $J_{CF} = 291$ Hz), 126.90, 127.41, 128.08, 128.14, 134.16, 134.47, 139.96, 142.39, 145.43; ^{19}F NMR (253.8 MHz, $CDCl_3$), δ −75.91 (q, $^4J_{FF} = 8.9$ Hz), −74.90 (q, $^4J_{FF} = 8.7$ Hz), −74.61 (q, $^4J_{FF} = 8.9$ Hz), −71.63 (q, $^4J_{FF} = 8.7$ Hz).

Acknowledgements

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[9] $C_{36}H_{45}GeF_{12}O_8K \cdot CH_2Cl_2$, FW = 1030.35, crystal dimensions (mm) 0.50 × 0.50 × 0.40, monoclinic, space group $P2_1/n$, $a = 11.183(3)$ Å, $b = 12.455(4)$ Å, $c = 12.455(4)$ Å, $\beta = 89.80(1)°$, $V = 4714(1)$ Å^3, $Z = 4$, $D_{Calc.} = 1.452$ g cm^{-3}, $R = 0.069$ ($R_w = 0.051$). A single crystal for X-ray analysis was grown in CH_2Cl_2–pentane. Atomic coordinates, bond length and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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