

Note

Facile synthesis and X-ray structures of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OAr}^{\text{F}})_3$
($\text{OAr}^{\text{F}} = \text{OC}_6\text{F}_5$, $\text{OCH}_2\text{C}_6\text{F}_5$, and $\text{OCH}_2\text{C}_6\text{F}_2\text{H}_3$)Junseong Lee^a, Youngkyu Do^{a,*}, Youngjo Kim^{b,*}^a Department of Chemistry, School of Molecular Science BK21, Center for Molecular Design and Synthesis, KAIST, Daejeon 305-701, Republic of Korea^b Department of Chemistry, Chungbuk National University, Cheongju, Chungbuk 361-763, Republic of Korea

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Abstract

New half-sandwich titanocene complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OC}_6\text{F}_5)_3$ (**1**), $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OCH}_2\text{C}_6\text{F}_5)_3$ (**2**), and $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OCH}_2\text{C}_6\text{F}_2\text{H}_3)_3$ (**3**) were synthesized via the displacement of methoxide ligands in $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OMe})_3$ by the corresponding aryloxy or benzyloxy ligands. These compounds have been fully characterized by various spectroscopic methods including X-ray crystallography. Compound **1** has a distorted three-legged piano stool structure. However, complexes **2** and **3** have the chariot-like structure, where chariot means a two-wheeled horse-drawn vehicle. The π electron donation of oxygen atom to Ti center in complexes **1–3** is considerable.

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Keywords: Titanium; Half-sandwich metallocene; X-ray structure; Pentafluorophenol; Pentafluorobenzylalcohol; 2,5-Difluorobenzylalcohol; Pentamethylcyclopentadienyl; π - π Interaction

1. Introduction

Since the discovery of the Ziegler–Natta catalyst systems in early 1950s [1], tremendous advances in the design and application of organometallic complexes as α -olefin polymerization catalysts have been achieved [2]. Of the extensive previous work, most has focused on the development of catalytic systems based on cyclopentadienyl group 4 compounds suitable for the polymerization of monomers such as ethylene, propylene, and styrene. However, there are only few reports for the polymerization catalysis using non-bridged $\text{Cp}'\text{TiX}_3$ complexes, which contain both one pentahapto ligand and three monodentate ligands, though the syntheses of these complexes have been known for several decades [3]. The examples include $(\eta^5\text{-C}_5\text{R}_5)\text{TiCl}_3$ [4] and $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$ ($\text{R} = \text{H}$ and Me ; $\text{R}' = \text{Me}$, Et ,

Bu , and so on) [5,6]. Several types of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$ have been synthesized by a two-step reaction in which LiOR' is made from $\text{R}'\text{OH}$ and $n\text{-BuLi}$, followed by reaction with a third equivalent of $(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3$ [5,6]. However, yields were somewhat low and some by-product could be obtained. Other synthetic route to $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$ is an amine or methane displacement with alkoxide ligand using $(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3$ or $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{NR}'_2)_3$ [7], which is commercially unavailable and difficult to purify. In addition, complexes of the type $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$ complexes can be prepared by reacting $\text{Cp}'\text{TiCl}_3$ with $\text{R}'\text{OH}$ in the presence of NEt_3 [8] in spite of the high dependence of yield on R' group. In this regard, we are interested in the facile one-pot and quantitative synthetic route to $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OR}')_3$ using commercially available starting materials. Herein we report the simple one-pot and quantitative synthesis, characterization, and X-ray structures of complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OC}_6\text{F}_5)_3$ (**1**), $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OCH}_2\text{C}_6\text{F}_5)_3$ (**2**), and $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OCH}_2\text{C}_6\text{F}_2\text{H}_3)_3$ (**3**) from the reaction between commercially available $(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OMe})_3$ and corresponding aryloxy or benzyloxy ligand.

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2. Experimental

2.1. General procedures

All reactions were carried out under dinitrogen atmosphere using standard Schlenk and glove box techniques [9]. Dinitrogen was deoxygenated with activated Cu catalyst and dried with drierite. All chemicals were purchased from Aldrich and were used as supplied unless otherwise indicated. Cp*Ti(OMe)₃ were purchased from Strem Co. All solvents (Aldrich anhydrous grade) were dried by distilling from sodium–potassium alloy (*n*-hexane) or CaH₂ (dichloromethane) under a dinitrogen atmosphere and stored over the activated molecular sieves 3A [10]. CDCl₃ was dried over activated molecular sieves (4A) and were used after vacuum transfer to a Schlenk tube equipped with J. Young valve. ¹H, ¹³C{¹H} and ¹⁹F NMR spectra were recorded at ambient temperature on a Bruker AM300 spectrometer using standard parameters. The chemical shifts are referenced to the peaks of residual CDCl₃ (δ 7.24 in ¹H NMR). Elemental analyses were performed by EA 1110-FISONS(CE).

2.2. Synthesis of (η⁵-C₅Me₅)Ti(OC₆F₅)₃ (1)

To a dichloromethane solution of (η⁵-C₅Me₅)Ti(OMe)₃ (0.55 g, 2 mmol) was added dropwise at –78 °C a solution of pentafluorophenol (1.14 g, 6.2 mmol) in 30 mL of dichloromethane. The reaction mixture was warmed to room temperature and stirred for 12 h. The residue, obtained by removing the solvent under vacuum, was washed with 20 ml of *n*-hexane several times. The desired product **1** was isolated as orange crystals after recrystallization from the dichloromethane/*n*-hexane solution at –20 °C in a refrigerator for overnight (1.43 g, 98%).

¹H NMR (CDCl₃, 300.133 MHz): δ = 2.18 (s, 15H, C₅-Me₅).

¹⁹F NMR (CDCl₃, 282.376 MHz): δ = –168.74 (t, 3H, *J* = 22.0 Hz), –165.47 (dd, 6H, *J* = 21.5 and 18.6 Hz), –160.60 (m, 6H).

Anal. Calc. for C₂₈H₁₅F₁₅O₃Ti: C, 45.93; H, 2.06. Found: C, 46.04; H, 2.20%.

2.3. Synthesis of (η⁵-C₅Me₅)Ti(OCH₂C₆F₅)₃ (2)

The desired product **2** as yellow crystals was prepared in an isolated yield of 95 % (1.49 g) in a manner analogous to the procedure for **1** using pentafluorobenzylalcohol (1.23 g, 6.2 mmol) and (η⁵-C₅Me₅)Ti(OMe)₃ (0.55 g, 2 mmol).

¹H NMR (CDCl₃, 300.133 MHz): δ = 5.17 (s, 6H, OCH₂PhF₅), 1.96 (s, 15H, C₅Me₅).

¹⁹F NMR (CDCl₃, 282.376 MHz): δ = –163.13 (m, 6H), –155.95 (t, 3H, *J* = 20.3 Hz), –145.50 (dd, 6H, *J* = 13.3 and 8.75 Hz).

Anal. Calc. for C₃₁H₂₁F₁₅O₃Ti: C, 48.08; H, 2.73. Found: C, 48.43; H, 2.62%.

2.4. Synthesis of (η⁵-C₅Me₅)Ti(OCH₂C₆F₂H₃)₃ (3)

The desired product **3** as yellow crystals was prepared in an isolated yield of 96% (1.18 g) in a manner analogous to the procedure for **1** using 2,5-difluorobenzylalcohol (0.89 g, 6.2 mmol) and (η⁵-C₅Me₅)Ti(OMe)₃ (0.55 g, 2 mmol).

¹H NMR (CDCl₃, 300.133 MHz): δ = 7.1–6.6 (m, 9H, OCH₂C₆F₂H₃), 5.25 (s, 6H, OCH₂C₆F₂H₃), 2.02 (s, 15H, C₅Me₅).

¹⁹F NMR (CDCl₃, 282.376 MHz): δ = –119.73 (d, 3H, *J* = 18.4 Hz), –126.74 (d, 3H, *J* = 18.4 Hz).

Anal. Calc. for C₃₁H₃₀F₆O₃Ti: C, 60.80; H, 4.94. Found: C, 60.80; H, 5.03%.

2.5. X-ray structural determination

The crystals were coated with paraton oil. The diffraction data for **1** were collected on a Bruker 1K SMART CCD-based diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The hemisphere of reflection data were collected as ω scan frames with 0.3°/frame and an exposure time of 5 s/frame. Cell parameters were determined and refined by the SMART program [11]. Data reduction were performed using SAINT software [12]. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [13]. The diffraction data of complexes **2** and **3** were measured at 193 K with synchrotron radiation (λ = 0.75000 Å) on a 4AMXW ADSC Quantum-210 detector with a silicon double crystal monochromator at the Pohang Accelerator Laboratory, Korea. The HKL2000 (Ver.0.98.689) [14] was used for data collection, cell refinement, reduction, and absorption correction. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms [15]. Further details are listed in Tables 1 and 2.

3. Results and discussion

Complexes **1–3** could be prepared via the displacement of methoxide ligands in (η⁵-C₅Me₅)Ti(OMe)₃ by the corresponding fluorine-substituted aryloxy or benzyloxy ligands. The treatment of commercially available (η⁵-C₅Me₅)Ti(OMe)₃ with three equivalents of pentafluorophenol, pentafluorobenzylalcohol, or 2,5-difluorobenzylalcohol ligand in dichloromethane gave, after workup, the new half-sandwich titanocene **1–3** as orange or yellow crystals in more than 95% isolated yield. Unlike the previous reported literature [4–8], attempted reaction between (η⁵-C₅Me₅)TiCl₃ and corresponding lithiated aryloxy or benzyloxy species in toluene or THF was not successful and a mixture of the desired product with non-separable impurities was obtained. In addition, the same result was observed in the reaction between (η⁵-C₅Me₅)TiCl₃ and corresponding species in the presence of NEt₃. These suggest that the reaction

Table 1
Crystallographic data and parameters for 1–3

Compound	1	2	3
Empirical formula	(C ₂₈ H ₁₅ F ₁₅ O ₃ Ti) _{1/2}	C ₃₁ H ₂₁ F ₁₅ O ₃ Ti	C ₃₁ H ₃₀ F ₆ O ₃ Ti
Formula weight	366.15	774.38	612.45
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 21/ <i>m</i>	<i>P</i> 21/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.532(3)	12.433(3)	11.081(2)
<i>b</i> (Å)	16.188(6)	8.7550(18)	11.671(2)
<i>c</i> (Å)	10.283(4)	28.694(6)	13.257(3)
α (°)	90	90	96.32(3)
β (°)	90.603(7)	94.81(3)	105.81(3)
γ (°)	90	90	117.60(3)
<i>V</i> (Å ³)	1420.1(9)	3112.4(11)	1404.5(5)
<i>Z</i>	4	4	2
<i>d</i> _{calcd} (g/cm ³)	1.713	1.653	1.448
<i>F</i> (000)	728	1552	632
Crystal size (mm)	0.5 × 0.4 × 0.2	0.3 × 0.3 × 0.2	0.4 × 0.3 × 0.2
<i>T</i> (K)	193(2)	193(2)	193(2)
μ (Mo K α) (mm ⁻¹)	0.71073	0.75000	0.75000
θ Range (°)	1.98 ≤ θ ≤ 27.92	1.64 ≤ θ ≤ 28.67	1.66 ≤ θ ≤ 20.84
Number of unique reflections	8290	13210	2792
Number of observed reflections (<i>I</i> > 2 σ (<i>I</i>))	3245	7709	2792
Number of parameters refined	278	456	457
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0475	0.0475	0.0776
<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^b	0.1269	0.1323	0.2184
Goodness-of-fit (<i>I</i> > 2 σ (<i>I</i>))	1.011	1.072	1.056

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = [\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2]^{1/2}.$$

condition of methoxide-elimination is essential and required for the synthesis of 1–3.

Compounds 1–3 in the solid state were slightly moisture and air sensitive. According to ¹H NMR spectroscopy, they decomposed slightly after a few days at room temperature in CDCl₃ solutions contained in capped NMR tubes. As expected, they are freely soluble in toluene, THF, and dichloromethane. Interestingly, they are slightly soluble even in hydrocarbon solvents such as *n*-hexane and *n*-pentane.

The ¹H and ¹⁹F NMR spectra of complexes 1–3 display well-defined resonances with their expected integrations. However, their ¹³C{¹H} NMR spectra were not informative due to the complicated peaks arising from *J*_{C–F} coupling. In comparison to the starting precursor (η^5 -C₅Me₅)Ti(OMe)₃, methyl signals of η^5 -C₅Me₅ in complex 1 are shifted to downfield (0.17 ppm) in ¹H NMR, which is a consequence of the electron-withdrawing effect from OC₆F₅. Unusually, methyl signals of η^5 -C₅Me₅ in com-

Table 2
Selected bond lengths (Å) and angles (°) for 1–3

	1	2	3
Ti–O1	1.840(2)	1.8544(13)	1.803(4)
Ti–O2	1.848(6)	1.8108(14)	1.860(5)
Ti–O3	1.840(2)	1.8237(24)	1.808(5)
Ti–(η^5 -C ₅ Me ₅ centroid)	2.034(3)	2.0444(10)	2.035(4)
O1–C11	1.325(3)	1.416(2)	1.404(7)
O2–C18	1.324(7)	1.390(3)	1.422(8)
O3–C25	1.325(3)	1.397(3)	1.571(12)
(η^5 -C ₅ Me ₅ centroid)–Ti–O1	115.77(1)	109.31(6)	121.1(2)
(η^5 -C ₅ Me ₅ centroid)–Ti–O2	118.37(1)	119.66(6)	110.9(2)
(η^5 -C ₅ Me ₅ centroid)–Ti–O3	115.77(1)	118.42(6)	115.5(3)
O1–Ti–O2	101.69(6)	102.74(6)	101.46(21)
O1–Ti–O3	101.47(9)	102.57(6)	101.5(2)
O2–Ti–O3	101.69(6)	101.84(6)	104.3(3)
Ti–O1–C11	162.53(19)	122.51(10)	166.7(4)
Ti–O2–C18	158.55(25)	155.69(12)	119.9(4)
Ti–O3–C25	162.53(19)	145.58(12)	134.2(6)

plexes in 2 and 3 did not show any chemical shift owing to the existence of methylene group as a buffer between O and electron-withdrawing phenyl group.

In order to confirm the molecular structure and to elucidate the metal–ligand bonding in these complexes, the single-crystal X-ray diffraction studies for 1–3 were performed. Single-crystal X-ray structure for 1–3 are shown in Figs. 1–3, respectively. The selected bond distances and selected bond angles are given in Table 2.

Like other half-sandwich titanocene complexes [8], compound 1 has a distorted “three-legged piano stool” structure as shown in Fig. 1. Compound 1 has a crystallographic mirror plane embracing Ti, O2, and C18 in Fig. 1. Actually, C11¹ and O1¹, which stand for atoms generated by mirror plane, in CIF file are replaced by C25 and O3 in Fig. 1, respectively, for comparison with compounds 2 and 3. However, complex 2 and 3 have the chariot-like structure, where chariot means a two-wheeled horse-drawn vehicle (see Figs. 2 and 3). The average Ti–O bond distances for all three oxygens in each of 1 [1.843(3) Å], 2 [1.8296(17) Å], and 3 [1.824(5) Å] are similar to the average of this distance

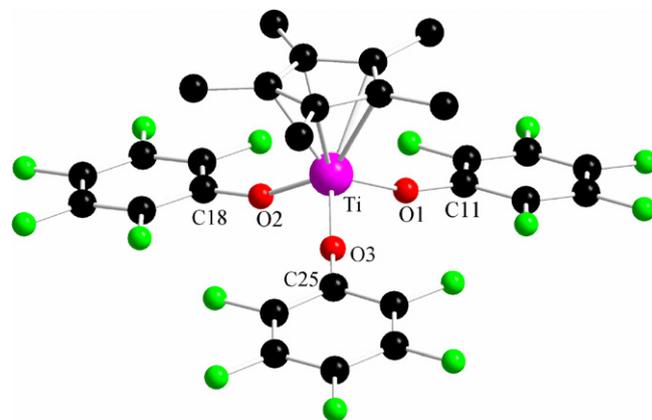


Fig. 1. X-ray structure for compound 1 and atom labeling. (H atoms were omitted for clarity.)

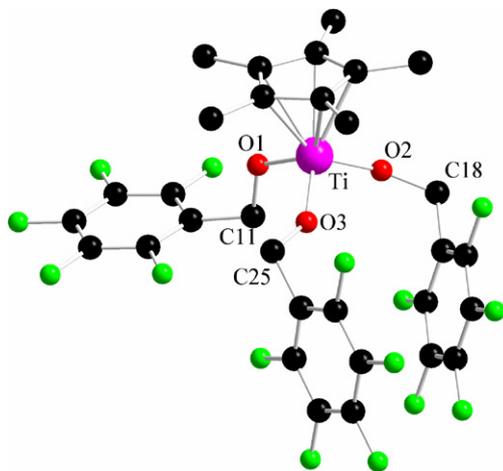


Fig. 2. X-ray structure for compound **2** and atom labeling. (H atoms were omitted for clarity.)

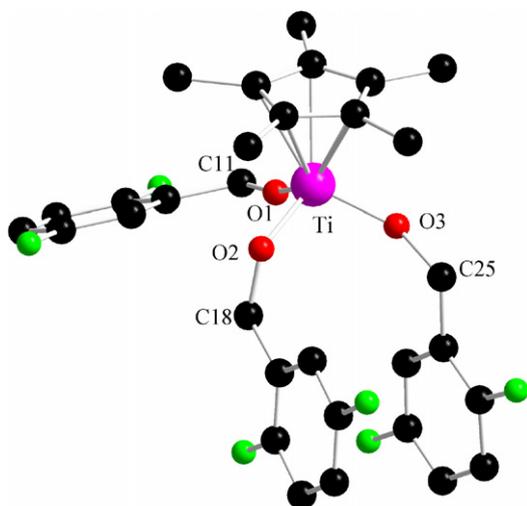


Fig. 3. X-ray structure for compound **3** and atom labeling. (H atoms were omitted for clarity.)

observed for titanium complexes having Ti–O bonds [8,16]. The Ti to η^5 -C₅Me₅ centroid distance [2.034(3) Å for **1**, 2.0444(10) Å for **2**, and 2.035(4) Å for **3**] is in a reasonable range [8,16]. The (η^5 -C₅Me₅ centroid)–Ti–O angles range from 115.77(1)° to 118.37(1)° for **1**, from 109.31(6)° to 119.66(6)° for **2**, and from 110.9(2)° to 121.1(2)° for **3**, similar to those [from 111.14° to 118.4°] found for structurally related compounds [8,16]. The average O–Ti–O angles in each of **1** [101.62(7)°], **2** [102.38(6)°], and **3** [102.42(24)°] are in the normal range [8g,16]. The bond angles among Ti, oxygen and the *ipso* carbon of the aryl rings in **1** are somewhat regular [Ti–O1–C11 = 162.53(19)°, Ti–O2–C18 = 158.55(25)°, Ti–O3–C25 = 162.53(19)°]. However, the bond angles among Ti, oxygen and methylene carbon of phenyl ring in **2** and **3** fluctuate very widely [Ti–O1–C11 = 122.51(10)°, Ti–O2–C18 = 155.69(11)°, Ti–O3–C25 = 145.56(11)° for **2** and Ti–O1–C11 = 166.67(41)°,

Ti–O2–C18 = 119.96(41)°, Ti–O3–C25 = 134.23(61)° for **3**]. Large Ti–O–C angles and short Ti–O distances, which affect stability of metal center and enhancement of catalytic behavior, would be indicative of double bond character for the Ti–O bond due to π -electron donation from the aryloxy or benzyloxy ligands [17].

Three phenyl rings in compound **1** are almost parallel to η^5 -C₅Me₅ ring, where the dihedral angles between phenyl ring and η^5 -C₅Me₅ ring are 9.1°, 6.5°, and 9.1° (see Fig. 1). However, **2** and **3** have the totally different structure from **1**. They exhibit interesting intra- and intermolecular π – π stackings. Although packing effect cannot be excluded, those probably relate to the flexibility of benzyl group. One phenyl ring is parallel to η^5 -C₅Me₅ ring but other phenyl rings, which have strong internal π – π interaction, are perpendicular to η^5 -C₅Me₅ ring (see Figs. 2 and 3). Dihedral angles between two parallel phenyl rings are 20.78° for **2** and 11.3(10)° for **3** and their distances between centroids are 3.9720(16) Å for **2** and 3.655(12) Å for **3**. In addition, average dihedral angles between one of parallel phenyl rings and η^5 -C₅Me₅ ring are 75.04(10)° for **2** and 86.0(9)° for **3**. Furthermore, the phenyl ring unrelated to the internal π – π interaction in complex **2** is almost parallel to the η^5 -C₅Me₅ ring in the adjacent molecule with the dihedral angle at 3.82(10)° and the distance between their centroids is 3.5985(14) Å, which supports the existence of external π – π interaction. Interestingly, complex **3** has internal fluorine–fluorine interaction. Even in disordered structure, this interaction is preserved. (The distances between F5 and F3 or between F5 and F3a are 3.396(16) Å and 3.311(18) Å, respectively.) (see Fig. 4) Cone angle of benzyloxy ligands was measured to estimate the steric hindrance around titanium center. As expected, the decrease of cone angle in the order of **1** (72.52–72.36°) > **2** (57.31–64.48°) > **3** (55.20–60.97°) means that steric hindrance of phenyl ring is greater than that of benzyl group.

In conclusion, novel half-sandwich titanocene complexes (η^5 -C₅Me₅)Ti(OC₆F₅)₃ (**1**), (η^5 -C₅Me₅)Ti(OCH₂C₆F₅)₃ (**2**), and (η^5 -C₅Me₅)Ti(OCH₂C₆F₂H₃)₃ (**3**) were synthesized via methoxide displacement in (η^5 -C₅Me₅)Ti(OMe)₃ with pentafluorophenol, pentafluorobenzylalcohol or 2,5-difluorobenzylalcohol ligand, respectively, and characterized by X-ray crystallography. Compounds **2** and **3** have internal π – π interaction and also compound **2** has external π – π interaction. The π electron donations of oxygen to titanium center in these complexes are considerable. Detail studies for olefin polymerization behaviors using **1–3** are in progress.

4. Supplementary material

CCDC 641403, 641404 and 641405 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk.

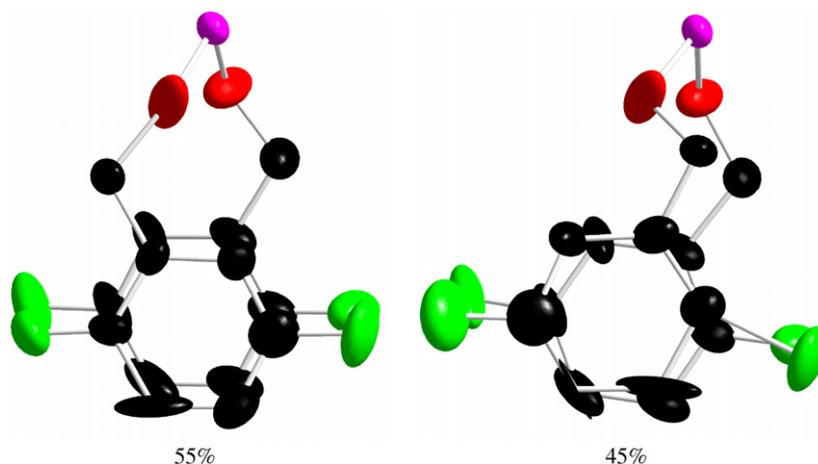


Fig. 4. X-ray structure for disordered pair of compound 3. (H atoms were omitted for clarity.)

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