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Pentamethylcyclopentadienylselenium derivatives VI: Synthesis and characterisation of ferrocenyl(pentamethylcyclopentadienyl)selenium

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Abstract

The novel mono(cyclopentadienyl)selenium derivatives, $Se(C_5Me_4R)Fc$ (Fc = ferrocenyl, $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4)]$; R = H or Me) have been prepared by treatment of diferrocenyl diselenide with LiC_5Me_4R, and characterised by NMR spectroscopy and mass spectrometry. The structure of $Se(C_5Me_5)Fc$ has been confirmed by X-ray crystallography, and its redox properties have been examined by cyclic voltammetry. It reacts with $[W(CO)_5(THF)]$ to form $[W_2(\mu\text{-}SeFc)_2(CO)_8]$ via C–Se bond cleavage.
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1. Introduction

We have previously described the synthesis and structure of a number of pentamethylcyclopentadienylselenium compounds. Bis(pentamethylcyclopentadienyl)-selenium, $Se(C_5Me_5)_2$ (**1**) shows unusual reactivity towards low-valent transition metal fragments, as a result of the steric crowding at the selenium atom [1]. We used the reaction of $LiSe_xC_5Me_5$ [2] with methyl iodide to prepare methyl(pentamethylcyclopentadienyl)selenium, $Se(C_5Me_5)Me$ (**2**) in order to compare its behaviour with that of **1** [3]. As expected, the smaller alkyl group results in the formation of a "normal" complex with the $W(CO)_5$ fragment. Compound **2** is, however, an oil, so that no quantitative structural information could be obtained. Phenyl(pentamethylcyclopentadienyl)selenium has been studied by Mikhailov et al. [4], but is also an "oily substance". We now report the preparation of a crystalline mono(pentamethylcyclopentadienyl)selenium derivative, its characterisation by X-ray crystallography, and reactivity towards $[W(CO)_5(THF)]$. The tetramethylcyclopentadienyl analogue has also been prepared.

2. Results and discussion

Shu et al. [5] showed in 1976 that ferrocenyl butyl selenide can be prepared by treatment of diferrocenyl diselenide with butyllithium. In the same way, addition of one equivalent of tetramethylcyclopentadienyllithium or pentamethylcyclopentadienyllithium to a tetrahydrofuran solution of diferrocenyl diselenide, followed by an aerobic work-up, led cleanly to the mono(cyclopentadienyl)selenium derivatives $Se(C_5Me_4R)Fc$ (**3**: R = H; **4**: R = Me; Fc = $[Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4)]$) (Eq. (1)). The reaction involves addition of the organolithium reagent to the selenium–selenium bond, and, as well as the desired product, results initially in the formation of a

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ferrocenyl selenolate, which reverts to the diselenide on aerial oxidation. The two products are easily separated by column chromatography.

(1)
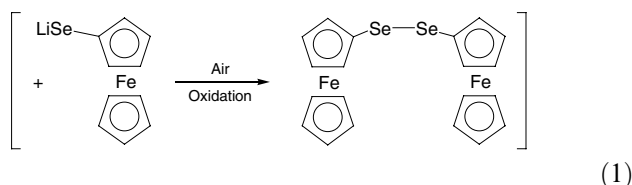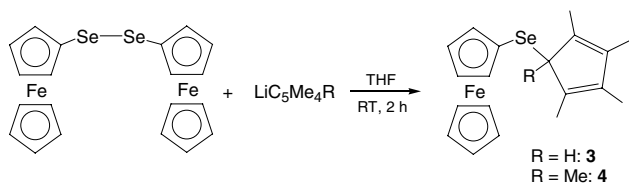
Three other possible methods may be envisaged for the synthesis of ferrocenyl(pentamethylcyclopentadienyl)selenium compounds: (i) by analogy with the preparation of **2**, the reaction of $LiSe_xC_5Me_5$ with iodoferrocene; (ii) reduction of diferrocenyl diselenide with sodium borohydride, followed by addition of 5-iodopentamethylcyclopentadiene [6], employing the procedure we have used previously for a large number of ferrocenyl alkyl selenides [7]; (iii) treatment of bis(pentamethylcyclopentadienyl) diselenide [2] with ferrocenyllithium, followed by an aerobic work-up, a route developed by Honeychuck et al. [8] for $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SeMe)]$. These methods were all rejected because of the extra difficulties involved in preparing and handling the required starting materials.

NMR spectroscopic data for **3** and **4** are summarised in Table 1. These confirm that the C_5Me_4R ring in **3** and **4** is σ-bonded to the selenium atom, as it is in **1** and **2**. The ^1H NMR spectra of **3** and **4** are generally as expected, although it is notable that the resonances for H(6)–H(9) occur upfield of those for H(1)–H(5). In all the known alkyl derivatives $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SeR)]$ the opposite ordering is observed [7]. The chemical shifts of the corresponding carbon atoms are, however, "normal" (**4**: $\delta = 69.3$, 76.1 ppm; cf. $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SePr)]$: $\delta = 69.5$, 75.2 ppm). As was the case for some other compounds of this type [7], no ^{13}C resonance for C(10) (the ferrocenyl carbon bound to selenium) was observed.

The ^{77}Se NMR chemical shifts of unsymmetrical dialkyl selenides may generally be predicted by halving the sum of the chemical shifts of the symmetrical derivatives [9]. In the case of **3** this procedure gives good agreement with the experimental value ($Se(C_5Me_4H)_2$: $\delta = 292$ [10]; $SeFc_2$: $\delta = 275$ [11]; **3**: $\delta = 280$). The observed resonance for **4** is, however, significantly downfield of the expected region (**1**: $\delta = 324$; $SeFc_2$: $\delta = 275$; **4**: $\delta = 378$). The extra steric effect of the allylic methyl group in pentamethylcyclopentadienylselenium derivatives, which we believe is

Table 1
NMR spectroscopic data for **3** and **4**

Nucleus (frequency)	Assignment[a]	Chemical shift (ppm)	
		3	**4**
^1H (400 MHz)	H(16)	–	1.20[b]
	H(17), H(20)	1.53	1.56
	H(18), H(19)	1.82	1.82
	H(11)	3.60	–
	H(6), H(9)	4.02 (m)	4.02 (m)
	H(7), H(8)	4.04 (m)	4.09 (m)
	H(1)–H(5)	4.08	4.11
^{13}C (100 MHz)	C(17), C(20)	11.1	10.3
	C(18), C(19)	12.4	10.9
	C(16)	–	18.2
	C(11)	57.6	63.7
	C(10)	–*	–*
	C(1)–C(5)	69.1	69.0
	C(7), C(8)	69.3	69.3
	C(6), C(9)	75.8	76.1
	C(12), C(15)	134.2	133.7
	C(13), C(14)	136.5	138.0
^{77}Se (47.7 MHz)		280	378

[a] For labelling schemes, see Fig. 1.
[b] $^3J(^1H\text{–}^{77}Se) = 14$ Hz.
* Not observed.

partly responsible for the unusual reactivity of these compounds, may also be the cause of their anomalous behaviour in terms of $\delta(^{77}Se)$.

The mass spectra of **3** and **4** have intense clusters of ions around $m/e = 386$ and 400, respectively, corresponding to the molecular ion in each case, with isotope patterns that match that expected for a compound containing one selenium atom. The molecular structure of **4** was confirmed by X-ray crystallography and is shown in Fig. 2. Selected bond lengths and angles are listed in Table 2. The Se–C(11) distance of 2.017(8) Å is comparable with the equivalent values in **1** (1.995(4) Å [12]) and the diselenide complexes $[M(CO)_5\{Se_2(C_5Me_5)_2\}]$ (M = Cr: 2.033(7), 2.023(8) Å; M = W: 2.038(9), 2.034(10) Å [13]). The Se–C(10) distance is considerably shorter (1.868(10) Å), as would be expected for a bond to an sp^2 hybridised carbon atom, and indeed appears to be one of the shortest carbon–selenium single bonds
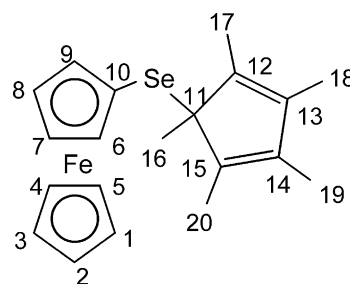

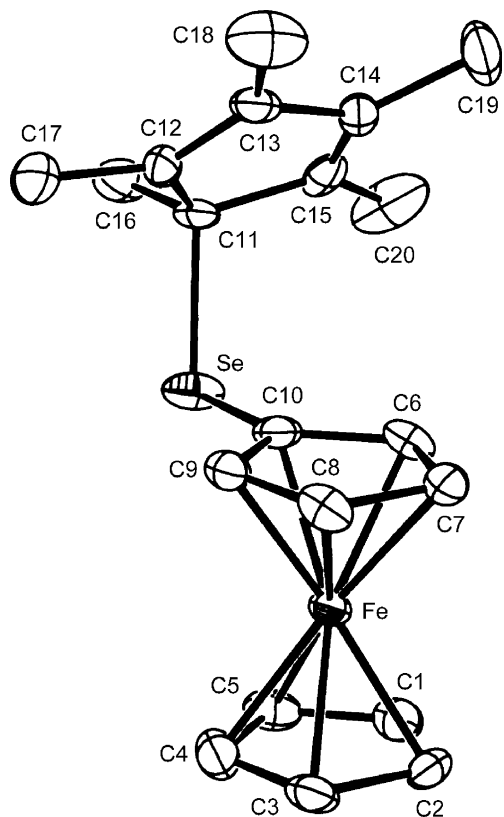Fig. 1. Numbering scheme for assignment of NMR spectra.

Fig. 2. Molecular structure of **4**. Hydrogen atoms are not shown for clarity and displacement ellipsoids are traced at the 20% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Se–C(10)	1.868(10)	Se–C(11)	2.017(8)
Fe–C(10)	2.028(8)	Fe–C(5)	2.055(9)
Fe–C(9)	2.020(7)	Fe–C(4)	2.032(9)
Fe–C(8)	2.042(9)	Fe–C(3)	2.039(9)
Fe–C(7)	2.058(9)	Fe–C(2)	2.037(9)
Fe–C(6)	2.032(8)	Fe–C(1)	2.036(8)
C(10)–C(9)	1.402(11)	C(5)–C(4)	1.432(14)
C(9)–C(8)	1.403(14)	C(4)–C(3)	1.394(17)
C(8)–C(7)	1.485(13)	C(3)–C(2)	1.445(12)
C(7)–C(6)	1.392(15)	C(2)–C(1)	1.388(14)
C(6)–C(10)	1.437(12)	C(1)–C(5)	1.414(13)
C(11)–C(12)	1.483(12)	C(11)–C(16)	1.508(15)
C(12)–C(13)	1.309(11)	C(12)–C(17)	1.473(10)
C(13)–C(14)	1.465(11)	C(13)–C(18)	1.506(13)
C(14)–C(15)	1.326(13)	C(14)–C(19)	1.519(13)
C(15)–C(11)	1.533(13)	C(15)–C(20)	1.517(13)
C(10)–Se–C(11)	101.8(4)	C(9)–C(10)–C(6)	105.8(9)
Se–C(10)–C(9)	127.2(7)	Se–C(10)–C(6)	127.0(7)
Se–C(11)–C(12)	109.2(6)	Se–C(11)–C(15)	108.2(6)
Se–C(11)–C(16)	105.3(6)	C(12)–C(11)–C(15)	103.0(8)
C(15)–C(11)–C(16)	113.8(9)	C(16)–C(11)–C(12)	117.2(9)
C(11)–C(12)–C(13)	109.8(8)	C(12)–C(13)–C(14)	109.8(8)
C(13)–C(14)–C(15)	109.9(8)	C(14)–C(15)–C(11)	107.5(8)

so far reported. Comparable distances are present in those cyclopentadienylselenium compounds in which, as a consequence of the nature of the substituents, the selenium atom is able to adopt a vinylic position (e.g., $Se\{C_5H_2(SiMe_3)_3\}_2$: 1.902(10), 1.904(11) Å [14]), and in related ferrocene derivatives (e.g., $[Fe\{\eta^5,\eta^5\text{-}(C_5H_4)_2Se_3\}]$: 1.909(9), 1.897(9) Å [15]). The C(10)–Se–C(11) angle of 101.8(4)° is considerably smaller than its equivalent in **1** (109.6(2)° [12]), where the steric requirements of the two allylic methyl groups appear to be dominant in determining the observed geometry, and resembles that in $Se(C_5Bu^t_2H_3)Ph$ (100.3(3)° [14]) and $Se(C_5Me_4H)_2$ (99.7(1)° [10]), where these methyl groups are absent.

The electrochemical behaviour of **4** was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The cyclic voltammogram is shown in Fig. 3. The reversible oxidation of the ferrocenyl moiety has $E_{1/2}$ (CV) and E_p (DPV) = +0.080 V vs. $[Fe(\eta^5\text{-}C_5H_5)_2]/[Fe(\eta^5\text{-}C_5H_5)_2]^+$. These values are almost the same as those for $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SePr)]$ [7], and provide further indication that the selenium substituent has little influence on the electron density at the iron centre in compounds of this type. The voltammograms of **4** reveal the occurrence of two further, essentially irreversible, processes, having E_p = +0.565, +0.695 V. These are believed to be associated with oxidation of the cyclopentadienyl ring. No features are present in this region in the voltammograms of the ferrocenyl alkyl selenides, where the oxidation of the selenium atom does not occur below ca. 1.3 V. On the other hand, the oxidation of **1** occurs at +0.400 V, and the orbital from which the electron is lost has been identified as part of the ring π-system [1].

The reactivity of **4** towards the complex $[W(CO)_5(THF)]$ was investigated. The metal carbonyl derivative was stirred overnight at room temperature with an equimolar quantity of **4** (Eq. (2)). A gradual colour change was observed. The solution was concentrated and the products passed through a short silica column using hexane as the eluting solvent. Two bands were collected. The first of these contained $C_{10}Me_{10}$ [16]. The second green band yielded $[W_2(\mu\text{-}SeFc)_2(CO)_8]$ (**5**) in approximately 60% yield. It can be seen therefore that the reactivity of **4** is different from that of both the related mono(cyclopentadienyl) derivative **2**, and the bis(cyclopentadienyl) compound **1**. Carbon–selenium bond cleavage occurs as for **1**, but the resultant diselenide does not coordinate intact to the metal centre; instead it undergoes oxidative addition to yield a diselenolate complex. We have previously prepared **5** by the reaction of diferrocenyl diselenide with $[W(CO)_5(THF)]$; details of the spectroscopic characterisation of **5**, and its structure as determined by X-ray diffraction, will be reported separately [17].
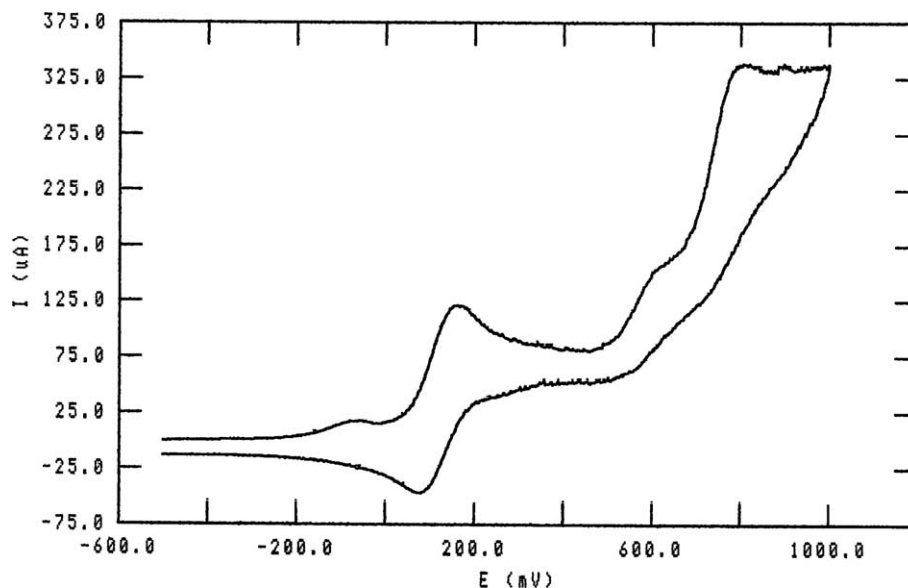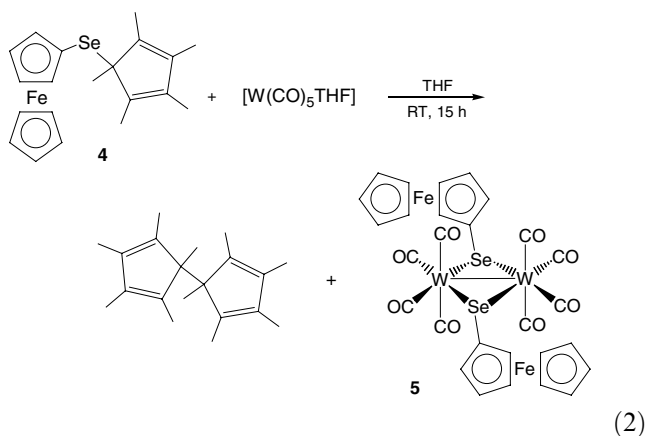
Fig. 3. Cyclic voltammogram of **4**.

$$(2)$$

Attempts to prepare the tellurium analogues of **3** and **4** were unsuccessful, and the only cyclopentadienyltellurium compounds known remain those in which the substitution pattern of the cyclopentadienyl ring allows tellurium to occupy a vinylic position [18].

3. Experimental

All reactions were performed using standard Schlenk techniques and pre-dried solvents under an atmosphere of dinitrogen. ^{1}H and ^{13}C NMR spectra: CDCl$_3$ solutions; Bruker AC400; tetramethylsilane as internal standard. ^{77}Se NMR spectra: CDCl$_3$ solutions (ca. 0.4 mol dm^{-3}); Bruker WM250; dimethyl selenide as external standard. IR spectra: Perkin–Elmer 1725X. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre, using Electron Impact (EI) or Fast Atom Bombardment (FAB). Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV): EG&G

model 273 scanning potentiostat; Pt working and auxiliary electrodes; Ag/Ag$^+$ (0.1 M AgNO$_3$ in CH$_3$CN) as reference electrode; 0.1 M [NBu$_4$][ClO$_4$] in CH$_3$CN as supporting electrolyte; scan rates 100 mV s^{-1} (CV), 36 mV s^{-1} (DPV); under these conditions [Fe(η^5-C$_5$H$_5$)$_2$]/[Fe(η^5-C$_5$H$_5$)$_2$]$^+$ has $E_{1/2}$ = +0.035 V, E_p = +0.025 V vs. Ag/Ag$^+$. LiC$_5$Me$_5$ was prepared from equimolar amounts of pentamethylcyclopentadiene [19] and butyllithium in hexane. [Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Se)]$_2$ was prepared from [Fe(η^5-C$_5$H$_5$)$_2$] via lithiation in THF with 0.9 equivalents of LiBu^t, treatment with excess selenium, and air oxidation, in a minor modification of the literature procedure [20,21]. [W(CO)$_5$(THF)] was prepared as described in the literature [22].

3.1. Preparation of ferrocenyl(tetramethylcyclopentadienyl)selenium (3), and ferrocenyl(pentamethylcyclopenta dienyl)selenium (4)

Solutions of [Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Se)]$_2$ (200 mg, 0.38 mmol) and LiC$_5$Me$_4$R (R = H: 49 mg, 0.38 mmol; R = Me: 54 mg, 0.38 mmol) in THF (total volume 50 cm^3) were mixed, and stirred at room temperature for 2 h. The mixture was exposed to air and the solvent then removed without heating by evaporation under reduced pressure. The residue was chromatographed on an alumina column using hexane/diethyl ether (99:1) as eluent. The first band to be collected contained C$_5$Me$_4$RH; the second band was reduced in volume to give **3** (R = H) or **4** (R = Me) as an orange solid. A further band yielded regenerated [Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$Se)]$_2$. Compounds **3** and **4** were recrystallised from hexane.

3: Yield: 35 mg (24%, based on LiC_5Me_4H); m.p.: 70–72 °C. NMR: see Table 1. MS (FAB, ^{80}Se): m/e = 386 ($M + H^+$, 36%), 265 ($FcSe^+$, 96%), 186 (FcH^+, 100%).

4: Yield: 65 mg (43%, based on LiC_5Me_5); m.p.: 75–77 °C. NMR: see Table 1. MS (EI, ^{80}Se): m/e = 400 ($M + H^+$, 13%), 265 ($FcSe^+$, 100%), 186 (FcH^+, 38%).

3.2. Preparation of $[W_2(SeFc)_2(CO)_8]$ (5)

Stirring a mixture of **3** (100 mg, 0.25 mmol) and $[W(CO)_5(THF)]$ (100 mg, 0.28 mmol) in THF solution (50 cm^3) at room temperature led overnight to a gradual deepening of the colour from orange to green. The solution was reduced to dryness by evaporation of the solvent in vacuo, and the residue then dissolved in the minimum volume of hexane. The products were passed through a short silica column using this solvent as eluent under an inert atmosphere. A yellow solution containing C_5Me_{10} [16] was obtained first; a subsequent green band afforded **5**, identified by comparison of its NMR, IR and mass spectra with those of an authentic sample [17]. Yield: 85 mg (61%).

3.3. X-ray crystallography

Details of the data collection and refinement are summarised in Table 3. Data collection: Enraf–Nonius CAD4, graphite-monochromated Mo Kα radiation, T = 295 K, $\omega - 2\theta$ scans. Absorption correction by psi scans (min/max transmission factors 0.489/0.985). Structure solution by direct methods, with SIR [23], and heavy atom procedures with SHELXL-97 [24]. Final refinement cycles performed against F^2 with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions. Absolute configuration assigned, with Flack parameter's value −0.02(3) [25]. ORTEP3 used for graphics [26].

Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structure of **4** have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), and are available on request quoting the deposition number CCDC 265181. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.03.035.

Table 3
Crystal data and details of data collection and refinement for **4**

Empirical formula	$C_{20}H_{24}$ FeSe
Formula weight	399.20
T (K)	295(2)
Wavelength (Å)	0.71069
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	7.792(6)
b (Å)	8.568(2)
c (Å)	27.314(7)
Volume (Å^3)	1824(2)
Z	4
D_c (Mg m^{-3})	1.454
Absorption coefficient (mm^{-1})	2.82
F (0 0 0)	816
Crystal size (mm)	$0.10 \times 0.30 \times 0.60$
Θ Range for data collection (°)	2.72–24.96
Index ranges	$-9 \leqslant h \leqslant 9$, $-10 \leqslant k10$, $0 \leqslant l \leqslant 31$
Reflections collected	6057
Independent reflections	3009 [R_{int} = 0.128]
Data/restraints/parameters	3009/0/204
Goodness-of-fit on F^2	1.009
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0533, wR_2 = 0.115
R indices (all data)	R_1 = 0.104, wR_2 = 0.137
Largest difference peak and hole (e Å^{-3})	0.61 and −0.54

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