

Interaction of titanium(III) zwitterionic complex $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}$ with organic halides: Synthesis and X-ray crystal structure determination of zwitterionic titanocene monohalides $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiX}$ ($\text{X} = \text{Cl}, \text{Br}$) and their catalytic activity in the ring-opening polymerization of ϵ -caprolactone

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Abstract

The reaction of the titanium(III) zwitterionic complex $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}$ (**1**) with CCl_4 at 20 °C under Ar results in the formation of hexachloroethane and the zwitterionic titanocene monochloride $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiCl}$ (**3**) containing a $\text{B}(\text{C}_6\text{F}_5)_3$ moiety in the η^5 -cyclopentadienyl ring. Under similar conditions, the reaction of **1** with 1,2-dibromoethane affords ethylene and the corresponding zwitterionic monobromide $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiBr}$ (**4**). An X-ray diffraction study of **3** and **4** revealed the presence of a coordinative bond between the *ortho*-fluorine atom of one of the C_6F_5 substituents and the positively charged titanium centre. In the interaction of **1** with *n*-propyl iodide at 20 °C, titanocene diiodide, $\text{B}(\text{C}_6\text{F}_5)_3$ and propylene are produced. The mechanism of this interesting reaction is discussed. The synthesized zwitterions **3** and **4** are able to catalyze the ring-opening polymerization of ϵ -caprolactone in a toluene solution and in bulk. The highest activity in this process is exhibited by **3**. The first X-ray diffraction study of Cp_2TiI_2 has been carried out.

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1. Introduction

Zwitterionic metallocenes of the Group IVB metals are of great interest as potential single-component catalysts for Ziegler-type olefin polymerization and other processes (see, e.g., reviews [1–4] and papers [5–14]). They represent uncharged analogues of the well-known cationic Group IVB metallocenes whose coordination and catalytic chem-

istry has received extensive development in the last decades (for reviews, see e.g., [15–17]). Recently, we reported the first examples of the successful application of zwitterionic metallocenes of the Group IVB metals in catalysis of cationic ring-opening polymerization [18]. It has been shown that the oxidation of the zwitterionic paramagnetic titanium(III) complex $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}$ (**1**) [19] by air oxygen affords the zwitterionic titanoxane $\{\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}\}_2\text{O}$ (**2**) [20] containing two positively charged titanium(IV) atoms and being capable of catalyzing the THF and ϵ -caprolactone (ϵ -CL) polymerization even at room temperature. This result evidences for a high electrophilicity of the cationic centres in the molecule of

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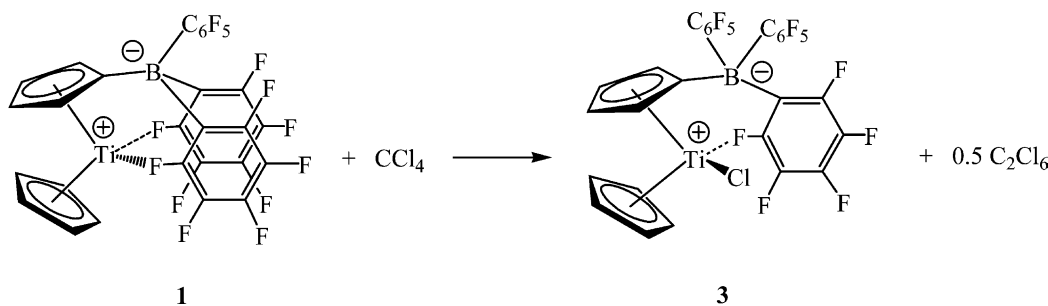
2 which can be used for the accomplishment of other reactions catalyzed or promoted by Lewis acids.

In the present paper, the synthesis and structures of chloride and bromide analogues of the above titanoxane **2**, viz. $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiCl}$ (**3**) and $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiBr}$ (**4**), are described in detail. The complexes are readily formed in the interaction of the Ti(III) zwitterion **1** with CCl_4 and 1,2-dibromomethane, respectively. The reactions proceed at room temperature with high rates. However, attempts to prepare the corresponding iodide analogue of titanoxane **2** by the interaction of **1** with *n*-propyl iodide have led to an unexpected formation of titanocene diiodide, $\text{B}(\text{C}_6\text{F}_5)_3$ and propylene. The mechanism of this interesting reaction has been proposed. The synthesized zwitterions **3** and **4** were tested as catalysts for the cationic ring-opening ϵ -CL polymerization and the results obtained are presented below. The first X-ray diffraction study of Cp_2TiI_2 is also reported.

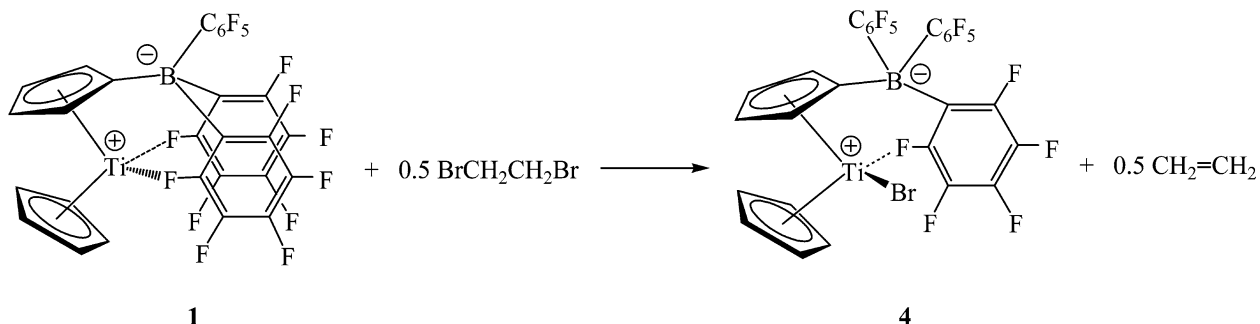
For a short preliminary account of a small part of this work, see [21]. The first examples of metallocenes containing a $\text{B}(\text{C}_6\text{F}_5)_3$ group in the C_5 ring have been described in [22,23].

2. Results and discussion

On vigorous shaking of solid **1** with a large excess of dry CCl_4 at room temperature under Ar, a rapid disappearance of dark blue colour of the starting Ti(III) zwitterion occurs and a dark reddish-brown solution is produced from which complex **3** can be isolated in a yield of 71%. Hexachloroethane was found in organic products of the reaction by GLC–MS (Scheme 1).



Scheme 1.



Scheme 2.

Under similar conditions, the interaction of solid **1** with a large excess of dry 1,2-dibromoethane at 20 °C results in the rapid formation of complex **4** which was isolated from the solution in an analytically pure state in a 65% yield. The reaction is accompanied by liberation of ethylene (Scheme 2).

Complexes **3** and **4** are dark brown crystalline solids moderately stable in air. According to elemental analysis and ^1H NMR spectra, they contain (after drying in vacuum at 20 °C) half a mole of CCl_4 and, correspondingly, half a mole of 1,2-dibromoethane per mole of the complex. For carrying out the X-ray diffraction studies, the crystals of **3** and **4** were not dried in vacuum. Under such conditions, the content of CCl_4 and 1,2-dibromoethane in **3** and **4**, respectively, increased to one mole. The mass spectra of **3** and **4** exhibit the corresponding parent ion peak (at m/z 724 for **3** and at m/z 768 for **4**) and characteristic peaks of fragmental ions (see Section 4).

The molecular structure of **3** is shown in Fig. 1. Complex **4** has a similar structure. The selected bond distances and angles for **3** and **4** are listed in Table 1. The numbering of atoms for **4** is the same as for **3**. The complexes are isomorphous and represent titanocene monohalide derivatives in which one of the hydrogen atoms of the $\eta^5\text{-C}_5\text{H}_5$ ring is substituted by a $\text{B}(\text{C}_6\text{F}_5)_3$ moiety. A characteristic feature of the complexes is the presence of a coordinative bond between the *ortho*-fluorine atom (F(28)) of one of the C_6F_5 groups and the positively charged titanium(IV) centre. The $\text{Ti}(1)\cdots\text{F}(28)$ distance in **3** (2.168(2) Å) is close to that in **4** (2.171(2) Å). However, both these distances are significantly shorter than the corresponding $\text{Ti}\cdots\text{F}$ distances in titanoxane **2** (2.181(2)–2.241(2) Å, av. 2.20 Å for two independent

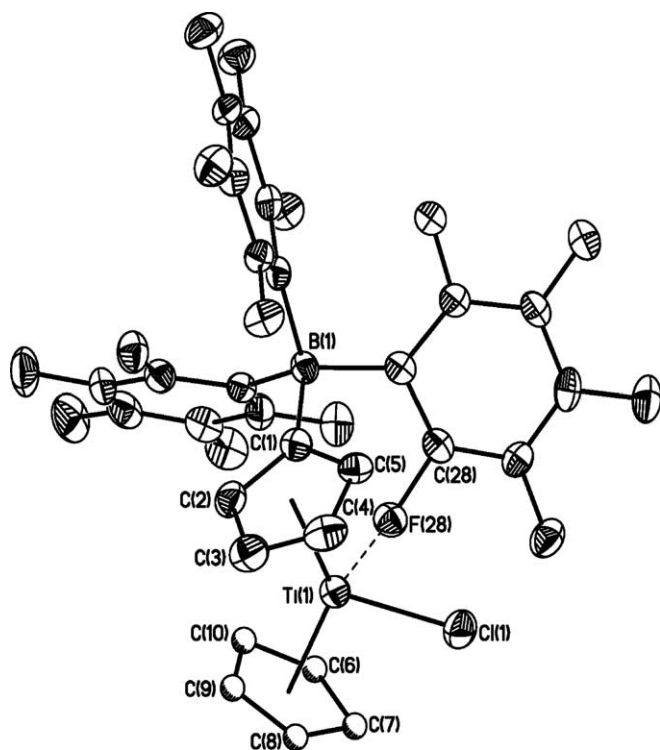


Fig. 1. ORTEP representation of the molecular structure of complex **3** with thermal ellipsoids drawn at the 50% probability level. Thermal ellipsoids for the carbon atoms of the η^5 -C₅H₅ ring are not shown due to its disorder.

molecules of **2**) and in other known zwitterionic titanocene complexes containing a B(C₆F₅)₃ group in the η^5 -cyclopentadienyl ligand (2.219–2.264 Å [19,20]). As a result of the coordination of the F(28) atom to titanium, the C(28)–F(28) bond in **3** and **4** becomes noticeably longer (1.406(3) and 1.413(4) Å, respectively) in comparison with other C–F bonds in these molecules (1.337(3)–1.363(3) Å, av. 1.351(3) Å in **3**; 1.333(4)–1.352(4) Å; av. 1.344(4) Å in **4**). The elongation of the C(28)–F(28) bond is accompanied by an increase in the endocyclic C(23)–C(28)–C(27) bond angle of the coordinated C₆F₅ substituent (to 127.9(2)° in **3** and to 128.3(3)° in **4**). In the non-coordinated C₆F₅ rings, the endocyclic C–C–C angles range from 117.8(3)° to 124.6(3)° in **3** (av. 121.1(3)°) and from 117.7(3)° to 124.7(4)° in **4** (av. 120.9(4)°).

An interesting structural peculiarity of complexes **3** and **4** is also a considerable shortening of the Ti(1)–Cl(1) (2.302(1) Å) and Ti(1)–Br(1) (2.460(1) Å) bonds as compared to the corresponding Ti–Hal distances in Cp₂TiCl₂ (Ti–Cl 2.364(3) Å [24]) and Cp₂TiBr₂ (Ti–Br 2.534(2) Å [25]). This result can be explained by an increase in the positive charge on the Ti atom on going from Cp₂TiCl₂ and Cp₂TiBr₂ to **3** and **4**, respectively, and, as a consequence, by an increase in the efficiency of donation of the lone electron pair of the halogen atom to the vacant orbital of the titanium.

The bis(cyclopentadienyl)titanium fragment in **3** and **4** has a typically bent sandwich geometry. The dihedral angle

Table 1
Selected bond lengths (Å) and angles (°) in complexes **3**·0.5CCl₄ and **4**·0.5C₂H₄Br₂

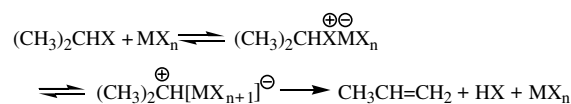
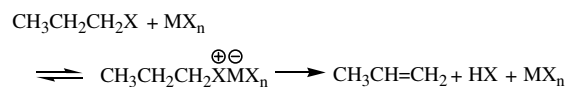
	3 ·0.5CCl ₄	4 ·0.5C ₂ H ₄ Br ₂
Ti(1)–F(28)	2.168(2)	2.171(2)
Ti(1)–Cl(1)	2.302(1)	–
Ti(1)–Br(1)	–	2.460(1)
Ti(1)–C(1)	2.394(3)	2.396(4)
Ti(1)–C(2)	2.338(3)	2.335(4)
Ti(1)–C(3)	2.320(3)	2.319(4)
Ti(1)–C(4)	2.334(3)	2.310(4)
Ti(1)–C(5)	2.337(3)	2.312(4)
Ti(1)–C(6)	2.28(3)	2.337(6)
Ti(1)–C(7)	2.32(2)	2.362(7)
Ti(1)–C(8)	2.31(2)	2.321(7)
Ti(1)–C(9)	2.31(1)	2.344(6)
Ti(1)–C(10)	2.30(2)	2.357(6)
C(28)–F(28)	1.406(3)	1.413(4)
C(1)–B(1)	1.647(4)	1.636(6)
C(11)–B(1)	1.653(4)	1.660(5)
C(17)–B(1)	1.659(4)	1.661(6)
C(23)–B(1)	1.662(4)	1.656(5)
Ti(1)–Cp(1)	2.013(4)	2.002(4)
Ti(1)–Cp(2)	2.041(9)	2.025(6)
F(28)–Ti(1)–Cl(1)	88.99(5)	–
F(28)–Ti(1)–Br(1)	–	88.58(6)
Cp(1)–Ti(1)–Cp(2)	136.1(5)	133.9(3)
Ti(1)–F(28)–C(28)	127.9(1)	127.4(2)
C(1)–B(1)–C(11)	110.3(2)	110.0(3)
C(1)–B(1)–C(17)	109.1(2)	109.1(3)
C(1)–B(1)–C(23)	104.8(2)	105.3(3)
C(11)–B(1)–C(17)	106.6(2)	107.0(3)
C(11)–B(1)–C(23)	111.3(2)	112.1(3)
C(17)–B(1)–C(23)	114.8(2)	113.4(3)
C(23)–C(28)–C(27)	127.9(2)	128.3(3)

between the planes of the C₅ rings in both complexes is 67.2° (72.1° in Cp₂TiCl₂ [24], 71.1° in Cp₂TiBr₂ [25]). The Ti atom as well as the halogen and the coordinated fluorine atoms in **3** and **4** are arranged practically in the bisector plane of this dihedral angle. The coordination environment at titanium can be described as pseudotetrahedral, with the large Cp(1)–Ti(1)–Cp(2) angle (136.1(5)° in **3**, 133.9(3)° in **4**) and small F(28)–Ti(1)–Hal(1) angle (88.99(5)° for Hal = Cl in **3**, 88.58(8)° for Hal = Br in **4**) due to the size difference between the Cp ligand and halogen atoms (Cp(1) and Cp(2) are the centroids of Cp rings C(1)–C(5) and C(6)–C(10), respectively). In both complexes, the Ti(1)–Cp(1) distance (2.013(4) Å in **3**, 2.002(4) Å in **4**) is somewhat shorter than Ti(1)–Cp(2) (2.041(9) Å in **3**, 2.025(6) Å in **4**), which can be due to the bonding of the Cp ring C(1)–C(5) to titanium via the C–B–C–C–F bridge. On going from **3** to **4**, the Ti(1)–Cp(1) and Ti(1)–Cp(2) distances decrease. The Ti(1)–F(28)–C(28) angles are 127.9(1)° and 127.4(2)° for **3** and **4**, respectively. The Cp ligands in **3** and **4** are in staggered conformation. The Ti–C distances span the range 2.28(3)–2.394(3) Å in **3** and 2.310(4)–2.396(4) Å in **4**. The boron atom deviates from the corresponding C₅ ring plane (in the direction away from the Ti atom) by 0.077(5) Å in **3** and by 0.081(7) Å in **4**. Coordination at the boron is essentially tetrahedral.

In a benzene solution, complexes **3** and **4** are coordinatively flexible: their NMR spectra exhibit broadened signals at room temperature. This is most prominent for the fluorine atoms in *ortho*-position and for the CH groups of the borylated η^5 -cyclopentadienyl ligand. For the latter it was shown by ^1H NMR exchange spectroscopy that there is a pairwise exchange between the two hydrogen atoms in α positions as well as between those in β positions. This is most likely to explain by a “flip-flop” coordination of the two perfluorophenyl groups to titanium, which would virtually make the hydrogen atoms of the C_5H_4 ring change their positions from the “left” to the “right” side of the boron substituent, and vice versa (see Scheme 3; ^1H NOE is observed between the H atoms of the C_5H_5 ligand and 2-H (α position) as well as 3-H (β position) atoms of the $\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3$ moiety). The proposed interpretation is supported by the observation of the temperature-dependent lineshapes of the proton signals and the failure to observe the coordinated C_6F_5 group in the ^{13}C NMR spectra. The signals for the α protons of the $\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3$ ligand in complex **3** coalesce at about 69°C but no such a coalescence was observed for complex **4** up to 80°C . As the chemical shifts proved to be extraordinarily dependent not only on temperature but also on concentration and co-solutes, no attempt was made to determine activation barriers for the “flip-flop” process.

With the aim of the synthesis of the iodide analogue of **3** and **4**, viz. $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiI}$ (**5**), the interaction of solid **1** with a large excess of dry *n*-propyl iodide at room temperature has been studied. However, it turned out unexpectedly that under such conditions a mixture of titanocene diiodide, $\text{B}(\text{C}_6\text{F}_5)_3$ and propylene is produced instead of **5**. As is known, a treatment of alkyl halides RX with Lewis acids MX_n (AlX_3 , BX_3 , GaX_3 , Ag^+ , etc.) gives the appropriate olefin and hydrogen halide due to proton elimination from the β -position of the alkyl group in an intermediate dipolar complex $\text{R}^+\text{X}^-\text{MX}_n$ or a tight ion pair $\text{R}^+[\text{MX}_{n+1}]^-$ of the corresponding alkyl cation

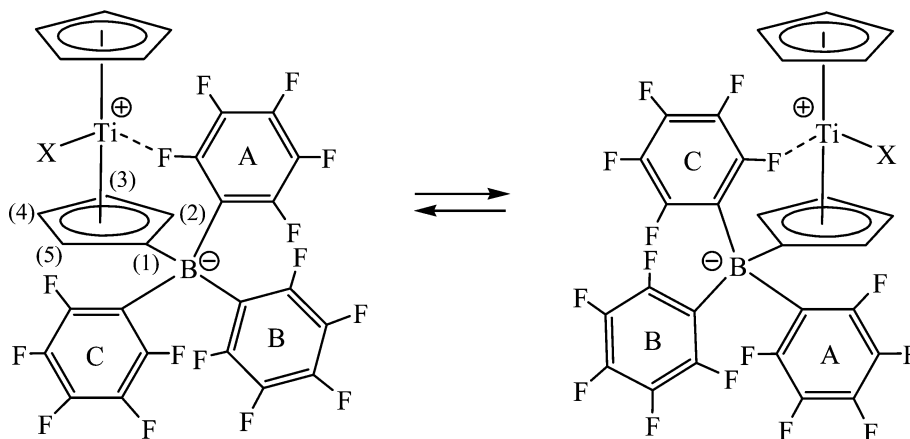
with its counteranion [26–31]. It is usually assumed that in the interaction of primary alkyl halides with Lewis acids the formation of a dipolar complex is more preferable while in the case of secondary and tertiary alkyl halides further polarization of the R-X bond may occur to afford the alkyl cation, e.g.:



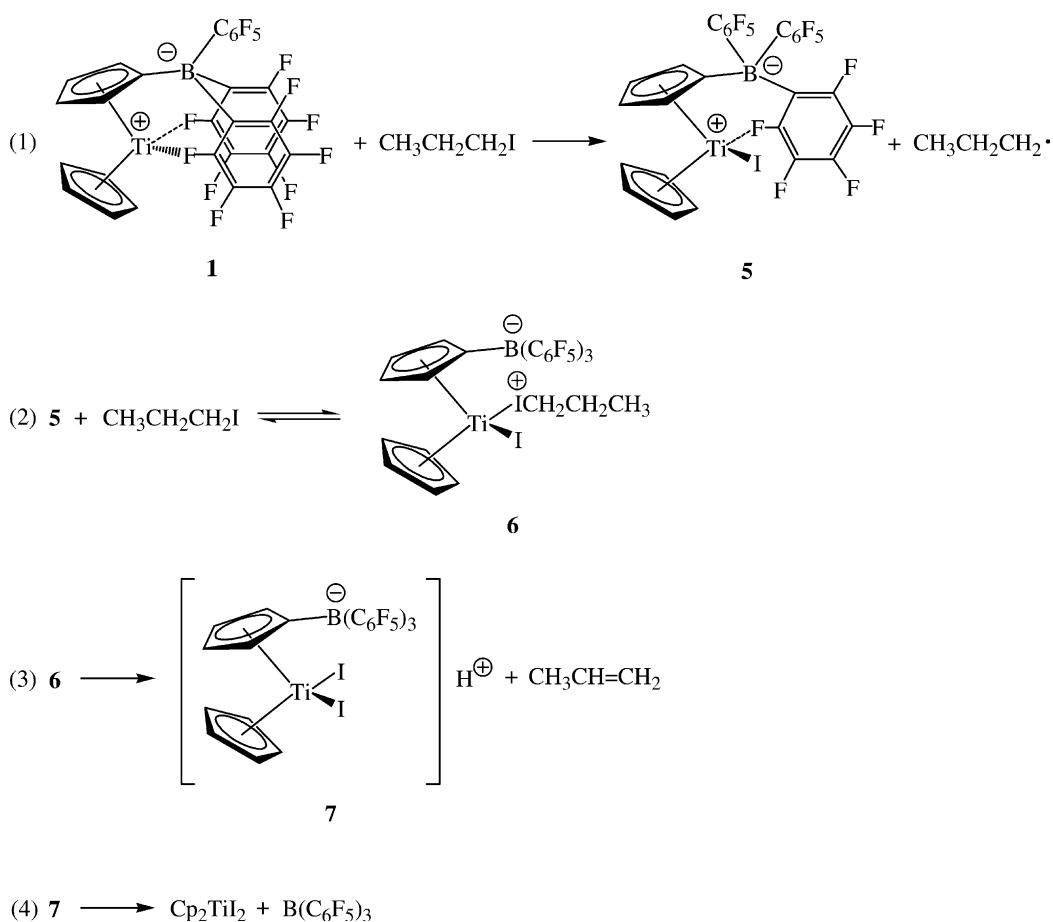
On the basis of these literature data, the following hypothetical mechanism of the reaction of **1** with *n*-propyl iodide can be proposed (see Scheme 4).

One may suggest that in the first stage, the starting Ti(III) zwitterion **1**, having one unpaired electron, abstracts iodine atom from *n*-propyl iodide to give *n*-propyl radical and the desired monoiodide zwitterionic complex **5**. As the positively charged Ti(IV) centre in this complex possesses, apparently, a sufficiently high Lewis acidity, it could react further with other molecule of *n*-propyl iodide yielding dipolar complex **6** (stage 2). Then the resulting **6** seems to decompose with the formation of propylene and the anionic diiodide complex $\{\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiI}_2\}^-$ (**7**) with H^+ as the counteranion (stage 3), and the subsequent attack of H^+ on the $\text{C}_5\text{H}_4\text{-B}$ bond in $\{\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiI}_2\}^-$ gives rise to the final Cp_2TiI_2 and $\text{B}(\text{C}_6\text{F}_5)_3$ (stage 4). Thus, according to the scheme, the intermediate zwitterion **5** behaves as a typical strong Lewis acid in the reaction with *n*-propyl iodide.

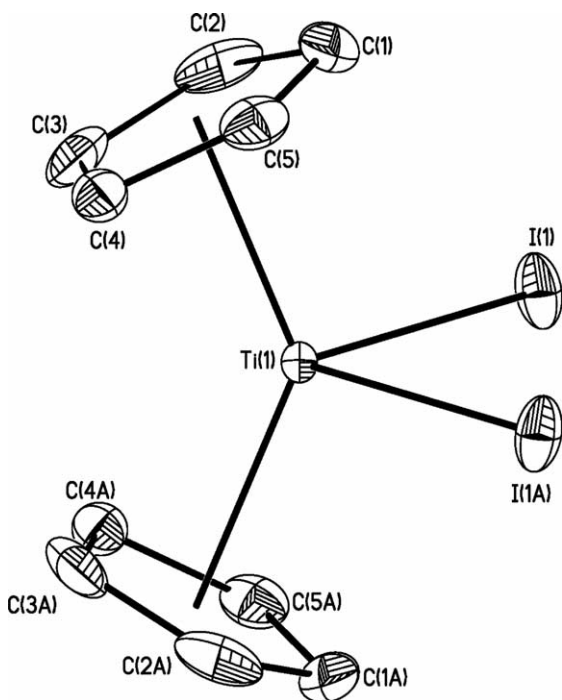
Although titanocene diiodide has been known for many years its exact structure has not been determined until now. So we decided to use crystals of Cp_2TiI_2 formed in the course of the reaction of **1** with *n*-propyl iodide for carrying out the X-ray diffraction study of this titanocene sandwich.



Scheme 3.



Scheme 4.

Fig. 2. ORTEP representation of the molecular structure of Cp_2TiI_2 with thermal ellipsoids drawn at the 50% probability level.

This study was also necessary to confirm the formation of Cp_2TiI_2 in the above reaction. Fig. 2 shows the structure of Cp_2TiI_2 . The selected bond distances and angles are presented in Table 2.

In its geometry, the molecule of Cp_2TiI_2 is very close to the previously studied Cp_2TiCl_2 [24] and Cp_2TiBr_2 [25]. The complex occupies in the crystal a special position on the twofold axis which bisects the $\text{I}(1)\text{--Ti}(1)\text{--I}(1\text{A})$ bond angle. The planes of the η^5 -cyclopentadienyl rings in the bent Cp_2Ti sandwich fragment of Cp_2TiI_2 form a dihedral angle of 70.9° . The titanium atom and the two iodine atoms are disposed in the bisector plane of this angle. The $\text{Ti}(1)\text{--I}(1)$ and $\text{Ti}(1)\text{--I}(1\text{A})$ bond lengths are 2.7690(7) Å. On going from Cp_2TiCl_2 and Cp_2TiBr_2 to Cp_2TiI_2 , the $\text{Ti}(1)\text{--Cp}(1)$ and $\text{Ti}(1)\text{--Cp}(2)$ distances slightly decrease (2.056 and 2.060 Å in Cp_2TiCl_2 [24], 2.054 and

Table 2
Selected bond lengths (Å) and angles ($^\circ$) in Cp_2TiI_2

Ti(1)–I(1)	2.7690(7)	Ti(1)–C(4)	2.339(3)
Ti(1)–C(1)	2.382(3)	Ti(1)–C(5)	2.393(2)
Ti(1)–C(2)	2.366(3)	Ti(1)–Cp(1)	2.045(3)
Ti(1)–C(3)	2.342(3)		
I(1)–Ti(1)–I(1A) ^a	92.78(3)	Cp(1)–Ti(1)–Cp(1A) ^a	132.3(1)

^a Atom is obtained from the base one by the symmetry transformation: $-x + 1, y, -z + 1/2$.

Table 3
Ring-opening polymerization of ϵ -CL under the action of complexes **3** and **4** as catalysts^a

Catalyst	Solvent	ϵ -CL: catalyst (mol/mol)	t (°C)	Polymer yield (%)	M_w	M_w/M_n
3	Toluene	1000:1	75	45	69 000	1.47
	Toluene	5000:1	75	36	168 000	1.54
		1000:1	75	61	65 000	1.63
		1000:1	60	24	65 000	1.51
		6000:1	60	11	69 000	1.41
4	Toluene	5000:1	75	22	152 000	1.52
		1000:1	60	14	88 000	1.49
		6000:1	60	6	70 000	1.27

^a Reaction time is 8 days. In all experiments carried out in toluene, the initial concentration of ϵ -CL is $2 \text{ mol} \cdot \text{l}^{-1}$.

2.059 Å in Cp_2TiBr_2 [25], 2.045 Å in Cp_2TiI_2 ; Cp(1) and Cp(2) are the centroids of Cp rings), thus suggesting somewhat greater strength of the Ti–Cp bonds in Cp_2TiI_2 than in its chloride and bromide analogues. The Ti–C distances range from 2.327(4) to 2.394(4) Å in Cp_2TiCl_2 (av. 2.365(4) Å), from 2.336(4) to 2.397(4) Å in Cp_2TiBr_2 (av. 2.373(4) Å) and from 2.339(3) to 2.393(2) Å in Cp_2TiI_2 (av. 2.364(3) Å). The Ti atom in Cp_2TiI_2 as in Cp_2TiCl_2 and Cp_2TiBr_2 has again a pseudotetrahedral coordination environment, with the Cp(1)–Ti(1)–Cp(1A) angle of $132.3(1)^\circ$ (131.0° in Cp_2TiCl_2 , 131.2° in Cp_2TiBr_2) and the I(1)–Ti(1)–I(1A) angle of $92.78(3)^\circ$ (the corresponding Hal–Ti–Hal angles in Cp_2TiCl_2 and Cp_2TiBr_2 are $94.6(1)^\circ$ and $94.1(1)^\circ$, respectively). The C–C bond lengths in the Cp rings of Cp_2TiI_2 span the range 1.388(4)–1.402(5) Å (1.344(7)–1.420(7) Å in the case of Cp_2TiCl_2 , 1.359(7)–1.422(7) Å in the case of Cp_2TiBr_2).

The synthesized complexes **3** and **4** were tested as catalysts for cationic ring-opening polymerization of ϵ -CL. The experiments were conducted in a toluene solution and in bulk. On carrying out the reactions in bulk, a rapid dissolution of **3** and **4** in ϵ -CL even at room temperature occurred and thus the process of the polymerization proceeded here also under homogeneous conditions. In all experiments performed in toluene, the initial concentration of ϵ -CL was kept constant (5 mol l^{-1}) while the catalyst concentration was varied.

The results obtained are presented in Table 3 from which it is seen that the both zwitterions are able to catalyze the ϵ -CL polymerization at 60–75 °C but they differ markedly from each other in their efficiency in this process. The highest polymerization rates are observed on the use of zwitterion **3** which gives a 61% yield of poly- ϵ -CL with the molecular mass (M_w) of 65 000 when the reaction is carried out in bulk for 8 d at 75 °C and the ϵ -CL:**3** molar ratio of 1000:1. A decrease in the reaction temperature to 60 °C decreases the polymer yield but its molecular mass remains practically unchanged. A similar effect on the efficiency of the polymerization is exerted by an enhancement in the ϵ -CL:**3** ratio from 1000:1 to 6000:1. On carrying out the reaction in a toluene solution at 75 °C and the ϵ -CL:**3** molar ratio of 5000:1, the molecular mass of the polymer increases to 168 000 (the poly- ϵ -CL yield is 36%). The replacement of **3** by **4** lowers the efficiency of the process. Under the same

conditions, the ϵ -CL polymerization in bulk, catalyzed by **3**, proceeds with a noticeably higher rate than that in a toluene solution. The polydispersity of the resulting polymers is in the range 1.27–1.63 (Table 3), thus indicating that the process of the ϵ -CL polymerization is not living. In the absence of **3** or **4**, poly- ϵ -CL is not formed.

3. Conclusion

The paramagnetic Ti(III) zwitterion **1** behaves as an organometallic free radical in the interaction with organic halides. Like unstable organic free radicals, it readily abstracts chlorine atom from CCl_4 to afford the final Ti(IV) zwitterion **3** and CCl_3 radical, the subsequent dimerization of which gives hexachloroethane. Similarly, the interaction of **1** with 1,2-dibromoethane results in the formation of Ti(IV) zwitterion **4** and ethylene. A more complicated picture is observed when **1** reacts with *n*-propyl iodide. We believe that in this case the intermediately arising Ti(IV) zwitterion **5** rapidly coordinates the iodine atom of the starting alkyl iodide, yielding dipolar complex **6**. The subsequent decomposition of **6** could lead to Cp_2TiI_2 , $\text{B}(\text{C}_6\text{F}_5)_3$ and propylene as the final products. The supposed ability of zwitterion **5** to generate propylene from *n*-propyl iodide is reminiscent of the behaviour of anhydrous aluminum halides and related compounds in their reactions with alkyl halides, thus suggesting a high Lewis acidity of the positively charged Ti(IV) atom in this zwitterionic metallocene. The Ti(IV) centre in zwitterionic complexes **3** and **4** is also characterized by a sufficiently high Lewis acidity which is evidenced by their capacity to catalyze the cationic ring-opening polymerization of ϵ -CL. The highest activity in this process is exhibited by complex **3**.

4. Experimental

Experiments were carried out under Ar with careful exclusion of air and moisture using standard Schlenk techniques. Starting **1** was prepared by the method described in [19]. Commercial CCl_4 , 1,2-dibromoethane and *n*-propyl iodide were stored under Ar over molecular sieves (4 Å) after drying over P_2O_5 and distillation in an Ar atmosphere. ϵ -CL was dried over molecular sieves (4 Å) and CaH_2 and then was distilled under Ar. $[\text{D}_6]$ Benzene was

dried over sodium tetraethylaluminate, distilled and stored under Ar. GLC–MS analyses were performed on a VG 7070E instrument (ionization energy 70 eV, temperature of ion source 150 °C) using the capillary SE-54 column. Ethylene and propylene were determined by GLC on a Chromatograph 3700-00 instrument with a flame ionization detector and the capillary OV-101 column (30 °C). The mass spectra of **3** and **4** were measured on a AMD 402 instrument (70 eV). The ^1H , ^{13}C and ^{11}B NMR spectra were recorded on a Bruker ARX-400 spectrometer, the ^{19}F NMR spectra were registered on a AC-250 spectrometer. ^1H and ^{13}C chemical shifts are given relative to TMS and are referenced to signals of the $[\text{D}_6]\text{benzene}$ used ($\delta_{\text{H}} = 7.16$ ppm, $\delta_{\text{C}} = 128.0$ ppm); ^{19}F chemical shifts are given relative to CFCl_3 ; ^{11}B chemical shifts are given relative to $\text{BF}_3 \cdot \text{OEt}_2$ in CDCl_3 ($\mathcal{E}(^{11}\text{B}) = 32.083971$ MHz). The assignment of the NMR signals was conducted with the help of DEPT and shift correlation experiments. The molecular masses of poly- ϵ -CL were measured by the GPC method on a Hewlett–Packard liquid chromatograph 1090 HP (SDV column $10^4 \text{ \AA} + 10^3 \text{ \AA} + 100 \text{ \AA}$ (Polymer Standard Service), eluent THF) and were corrected by the universal calibration relative to polystyrene standards.

4.1. Reaction of complex **1** with CCl_4

An amount of 11.4 ml of dry CCl_4 was added to 0.39 g (0.53 mmol) of $\mathbf{1} \cdot 0.5\text{PhCH}_3$ and the resulting mixture was vigorously shaken for several minutes at room temperature in an Ar atmosphere. In the course of the reaction, dark blue colour of starting $\mathbf{1} \cdot 0.5\text{PhCH}_3$ rapidly disappeared and a dark reddish-brown solution was formed. After 1 day, the solution was concentrated to ca. 8 ml and allowed to stand at 20 °C under Ar. After 18 h, the precipitated dark brown crystals of complex **3** were separated from the mother liquor by decanting, washed with dry CCl_4 and dried at 20 °C in vacuum. Despite drying, the obtained complex contained half a mole of CCl_4 per one mole of **3**. The yield of $\mathbf{3} \cdot 0.5\text{CCl}_4$ is 0.3 g (71%), m.p. 186–187 °C (dec.) under Ar. Anal. Calc. for $\text{C}_{28}\text{H}_9\text{TiBClF}_{15} \cdot 0.5\text{CCl}_4$: C, 42.71; H, 1.13. Found: C, 42.10; H, 1.10%. ^1H NMR (C_6D_6 , 297 K, δ , ppm): 5.58 (m, 1H, $\text{C}_5\text{H}_4(3)$), 5.60 (m, 1H, $\text{C}_5\text{H}_4(4)$), 5.62 (s, 5H, C_5H_5), 6.69 (br, 1H, $\text{C}_5\text{H}_4(5)$), 7.02 (br, 1H, $\text{C}_5\text{H}_4(2)$). ^{13}C NMR (C_6D_6 , 297 K, δ , ppm): 117.9 ($\text{C}_5\text{H}_4(3)$), 122.6 (C_5H_5), 125.5 ($\text{C}_5\text{H}_4(2)$), 133.4 ($\text{C}_5\text{H}_4(4)$), 136.6 ($\text{C}_5\text{H}_4(5)$), 137.5 (*meta*- C_6F_5 , $^1J_{\text{C,F}} = 251$ Hz), 139.5 (*para*- C_6F_5 , $^1J_{\text{C,F}} = 251$ Hz), 149.0 (*ortho*- C_6F_5 , $^1J_{\text{C,F}} = 234$ Hz); signals of the $\text{C}_5\text{H}_4(1)$ and *ipso*- C_6F_5 carbon atoms were not observed. ^{11}B NMR (C_6D_6 , 297 K, δ , ppm): –16.5 (half width 21 Hz). ^{19}F NMR (C_6D_6 , 297 K, δ , ppm): –160.6 (t, 23 Hz, *meta*- C_6F_5), –155.8 (t, 21 Hz, *para*- C_6F_5), –136.8 (br, *ortho*- C_6F_5). MS (m/z): 724 [M^+], 689 [$(\text{M} - \text{Cl})^+$], 658 [$(\text{M} - \text{CpH})^+$], 576 [$(\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)^+$], 512 [$(\text{B}(\text{C}_6\text{F}_5)_3)^+$]. For identification of organic products of the reaction, the solution obtained after separation of crystals of **3** was analyzed by

the GLC–MS method. The analysis revealed the presence of hexachloroethane in the solution.

4.2. Reaction of complex **1** with 1,2-dibromoethane

A mixture of 0.34 g (0.46 mmol) of $\mathbf{1} \cdot 0.5\text{PhCH}_3$ and 12 ml of dry 1,2-dibromoethane was vigorously shaken for several minutes at 20 °C under Ar and the resulting dark reddish-brown solution was allowed to stand at the same temperature in an Ar atmosphere. After 20 h, the solution was concentrated to ca. 8 ml and kept overnight. In the next day, the precipitated dark brown crystals of complex **4** were separated by decanting and dried at 20 °C for 2 h in vacuum. After drying, the complex contained half a mole of 1,2-dibromoethane per one mole of **4**. The yield of $\mathbf{4} \cdot 0.5\text{C}_2\text{H}_4\text{Br}_2$ is 0.26 g (65%), m.p. 192–194 °C (dec.) under Ar. Anal. Calc. for $\text{C}_{28}\text{H}_9\text{TiBBrF}_{15} \cdot 0.5\text{C}_2\text{H}_4\text{Br}_2$: C, 40.37; H, 1.28. Found: C, 40.39; H, 1.11%. ^1H NMR (C_6D_6 , 297 K, δ , ppm): 5.42 (dt, 1H, $\text{C}_5\text{H}_4(3)$), 5.67 (s, 5H, C_5H_5), 5.80 (dt, $^3J = 2.8$ Hz, $^4J = 2.2$ Hz, 1H, $\text{C}_5\text{H}_4(4)$), 6.91 (br, 1H, $\text{C}_5\text{H}_4(5)$), 7.08 (br, 1H, $\text{C}_5\text{H}_4(2)$). ^{13}C NMR (C_6D_6 , 297 K, δ , ppm): 117.2 ($\text{C}_5\text{H}_4(3)$), 122.4 (C_5H_5), 125.8 ($\text{C}_5\text{H}_4(2)$), 132.9 ($\text{C}_5\text{H}_4(4)$), 136.1 ($\text{C}_5\text{H}_4(5)$), 137.5 (*meta*- C_6F_5 , $^1J_{\text{C,F}} = 252$ Hz), 139.5 (*para*- C_6F_5 , $^1J_{\text{C,F}} = 251$ Hz), 149.0 (*ortho*- C_6F_5 , $^1J_{\text{C,F}} = 234$ Hz); signals of the $\text{C}_5\text{H}_4(1)$ and *ipso*- C_6F_5 carbon atoms were not observed. ^{11}B NMR (C_6D_6 , 297 K, δ , ppm): –16.7 (half width 21 Hz). ^{19}F NMR (C_6D_6 , 297 K, δ , ppm): –160.5 (t, 20 Hz, *meta*- C_6F_5), –155.7 (t, 21 Hz, *para*- C_6F_5), –136.7 (br, *ortho*- C_6F_5). MS (m/z): 768 [M^+], 689 [$(\text{M} - \text{Br})^+$], 703 [$(\text{M} - \text{Cp})^+$], 576 [$(\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)^+$], 512 [$(\text{B}(\text{C}_6\text{F}_5)_3)^+$]. The analysis of organic products of the reaction by GLC showed the presence of ethylene in the gaseous phase and in the reaction solution.

4.3. Reaction of complex **1** with *n*-propyl iodide

A mixture of 0.24 g (0.33 mmol) of $\mathbf{1} \cdot 0.5\text{PhCH}_3$ and 5 ml of *n*-propyl iodide was vigorously shaken for several minutes at room temperature under Ar. During the course of the reaction, the rapid formation of a dark brown solution was observed, and small amounts of fine dark crystals of Cp_2TiI_2 appeared on the walls and the bottom of the Schlenk tube. After 24 h, the solution was concentrated to 2–3 ml and allowed to stand at 20 °C in an Ar atmosphere. After 3 days, the resulting dark red crystals of Cp_2TiI_2 were separated by decanting and dried at 20 °C in vacuum. The yield of Cp_2TiI_2 is 0.1 g (70%), m.p. 317–319 °C (dec.) under Ar (lit. m.p. 317–319 °C [32]). Anal. Calc. for $\text{C}_{10}\text{H}_{10}\text{TiI}_2$: C, 27.81; H, 2.33. Found: C, 28.08; H, 2.15%. The decanted solution was then evaporated in vacuum to dryness at 20 °C and the residue was carefully extracted with dry *n*-hexane (3×20 ml). The subsequent evaporation of the resulting *n*-hexane extract and drying in vacuum at 20 °C gave a white powder of crude $\text{B}(\text{C}_6\text{F}_5)_3$ with m.p. 129–135 °C (dec.) under Ar (lit. m.p.

132–134 °C [33]). The analysis of organic products of the reaction by GLC showed the presence of propylene in the gaseous phase and in the reaction solution.

4.4. Polymerization of ϵ -CL in bulk

To 0.032 g (0.04 mmol) of complex $3 \cdot 0.5\text{CCl}_4$ was added 4.641 g (40.7 mmol) of ϵ -CL and the resulting yellow-brown solution was heated at 75 °C under Ar. During the course of heating, the reaction mixture gradually thickened and after 4 days it was transformed into a yellow resin-like material. After 8 days, the resulting yellow viscous product was dissolved in 8–10 ml of toluene and then treated with an excess of methanol. The precipitated white solid poly- ϵ -CL was separated by decanting, washed with methanol and dried in vacuum. The yield of poly- ϵ -CL is 2.83 g (61%), $M_w = 65000$, $M_n = 40000$.

4.5. Polymerization of ϵ -CL in toluene

To 0.032 g (0.04 mmol) of complex $3 \cdot 0.5\text{CCl}_4$ was added under Ar 4.571 g (40.0 mmol) of ϵ -CL and 3.76 ml of toluene and the resulting yellow-brown solution was heated at 75 °C in an Ar atmosphere. After 8 days, the yellow resin-like mixture formed was diluted with 5 ml of toluene and then (after stirring) was treated with an excess of methanol. The precipitated white solid poly- ϵ -CL was separated by decanting, washed with methanol and dried at 20 °C in vacuum. The yield of poly- ϵ -CL is 2.05 g (45%), $M_w = 69000$, $M_n = 47000$.

4.6. X-ray crystallographic study

X-ray diffraction experiments were carried out on a Bruker SMART 1000 CCD diffractometer with area detector, using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å, ω -scans with a 0.3° step in ω and 10 s per frame exposure) at 110 K. Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N₂ gas cryostat. Reflection intensities were integrated with the use of SAINT software [34] and absorption correction was carried out semi-empirically using SADABS program [35]. The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically. The analysis of Fourier density synthesis revealed that in **3** and **4** one of the Cp-rings is disordered by two positions. The refinement of occupancies for two positions showed that in **3** they are equal (0.5) while in **4** they are 0.2 and 0.8. Crystal data and structure refinement parameters for **3**, **4** and Cp₂TiI₂ are given in Table 4. All calculations were performed using the SHELXTL software [36].

5. Supplementary material

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 274701 for **3**, 274702 for **4** and 274703 for Cp₂TiI₂. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2

Table 4
Crystal data and structure refinement parameters for **3**, **4** and Cp₂TiI₂

Compound	3	4	Cp ₂ TiI ₂
Formula	C ₂₈ H ₉ BClF ₁₅ Ti · 0.5CCl ₄	C ₂₈ H ₉ BBrF ₁₅ Ti · 0.5C ₂ H ₄ Br ₂	C ₁₀ H ₁₀ I ₂ Ti
Molecular weight	801.42	862.92	431.88
Dimension (mm ³)	0.41 × 0.31 × 0.15	0.43 × 0.32 × 0.30	0.38 × 0.35 × 0.29
Diffractometer	SMART CCD	SMART CCD	SMART CCD
<i>T</i> (K)	120(2)	120(2)	120(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	10.762(3)	10.714(1)	13.426(4)
<i>b</i> (Å)	14.617(4)	14.254(2)	7.173(2)
<i>c</i> (Å)	18.356(4)	18.547(2)	13.096(4)
β (°)	94.713(6)	94.037(3)	116.686(5)
<i>V</i> (Å ³)	2877.7(12)	2825.7(5)	1126.9(6)
<i>Z</i> (<i>Z'</i>)	4(1)	4(1)	4(1)
<i>F</i> (0 0 0)	1572	1668	792
ρ_{calc} (g cm ⁻³)	1.850	2.028	2.546
Linear absorption, μ (cm ⁻¹)	6.96	32.53	61.91
Scan type	ω	ω	ω
θ range (°)	3.57–29.00	2.22–30.00	3.31–30.00
Measured	18085	19998	6227
Unique (<i>R</i> _{int})	7463 (0.0430)	6763 (0.0497)	1586 (0.0399)
With [<i>I</i> > 2 σ (<i>I</i>)]	3773	3995	1545
Parameters	505	449	81
Final <i>R</i> (<i>F</i> _{hkl}): <i>R</i> ₁	0.0501	0.0483	0.0228
<i>wR</i> ₂	0.1036	0.1070	0.0524
Goodness-of-fit	1.016	0.978	1.074
$\rho_{\text{max}}/\rho_{\text{min}}$ (e Å ⁻³)	0.612/–0.416	0.931/–0.525	0.990/–1.246

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