Dalton Transactions

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Single-site bismuth alkoxide catalysts for the ring-opening polymerization of lactide†

Cite this: *Dalton Trans.*, 2013, **42**, 11234

Vagulejan Balasanthiran, Malcolm H. Chisholm,* Christopher B. Durr and Judith C. Gallucci

Received 6th March 2013,
Accepted 15th June 2013

DOI: 10.1039/c3dt50629k

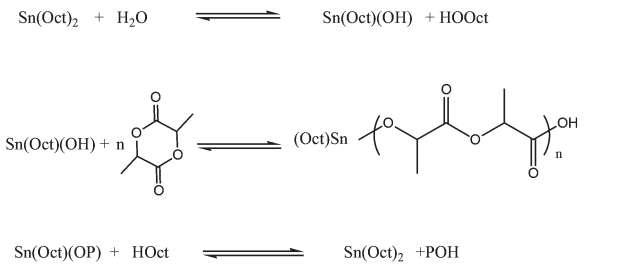
www.rsc.org/dalton

Salen bismuth alkoxides, where the salen ligand contains 2,4-di-*tert*-butylphenoxy groups and one of ethylene, cyclohexane or *ortho*-phenyl as a backbone have been prepared from reactions involving $Bi[N(SiMe_3)_2]_3$ and the free salen ligand followed by alcoholysis (Bu^tOH, Pr^iOH and 2,6-$Bu^t{}_2C_6H_3OH$). The molecular structures of the salen ligand with the cyclohexyl back-bone have been determined for the complexes salenBiCl and salenBiOC_6H_3-2,6-$Bu^t{}_2$. The chloro compound is a dimer with chloride bridges while the phenoxide is monomeric with an unusually distorted five-coordinate geometry. The phenoxide and *tert*-butoxide complexes have been employed in the ring-opening polymerization of lactides (L- and *rac*-) to give polylactides, PLAs. With *rac*-LA heterotactic PLA is formed preferentially, P_r = ~0.9, in dichloromethane or toluene at room temperature. The reaction is first order in [Bi] and is notably faster than most aluminum and zinc initiators as well as tin(II) octanoate. These results are discussed in terms of a recent report on the polymerization of LA by Peptobismol® and bismuth subsalicylate.

Introduction

The ring-opening polymerization (ROP) of lactides to produce the biodegradable and biocompatible polymers polylactides, PLAs, has been shown to be accomplished by both organic[1] and coordinate catalysis[2] with the latter involving metal complexes having nucleophilic initiator ligands such as alkoxides, amides, and hydroxides. Commercially, $Sn(Oct)_2$, where Oct = 2-ethyl hexanoate, is employed in a melt polymerization process. The alkanoate ligand is not the initiator but rather a Sn–OH bond that is formed reversibly in the presence of water and the chain propagation can be understood in terms of the reactions shown in Scheme 1.

This living or immortal system has an essential requirement that the M–OH bond be chemically persistent during the reaction conditions. It should not react to form an inert oxo metal derivative nor react with other species present such as CO_2 to form an inert carbonate. This led us to question whether alternative M–OH bonds (but not those of alkali metals that effect epimerization) might be similarly active in melt polymerizations. We subsequently investigated the reactivity of a number of biocompatible metal containing oral relief aids and dietary supplements that contain hydroxyl groups, and found that the most active of the bismuth containing species was bismuth subsalicylate (BSS) which is the active ingredient in Peptobismol®.[3] Both Bi(III) and Sn(II) has can support M–OH bonds that will reversibly react to form an oxo species as shown in eqn (1).



Scheme 1 Mechanism of ROP of LA by tin(II) octanoate [where POH = hydroxyl terminated oligomer].

$$2[M]OH \rightleftharpoons [M]_2O + H_2O \quad (1)$$

As a melt polymerization catalyst bismuth subsalicylate was just slightly less active than $Sn(Oct)_2$ based on its empirical formula. Since bismuth subsalicylate is a polymeric material of unknown structure,[4] we reasoned that the activity of bismuth should be higher than that of tin based on the fact that only a few active sites were present when the BSS powder was employed. Interestingly, no well defined bismuth alkoxide

Department of Chemistry and Biochemistry, The Ohio State University, 100W. 18th Avenue, Columbus, Ohio 43210-1185, USA.
E-mail: Chisholm@chemistry.ohio-state.edu

†Electronic supplementary information (ESI) available: M_n values with times and plots of M_n and PDI with % conversion. CCDC 928067–928069. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50629k

has been employed in the ROP of LAs, though Kricheldorf[5] has reported that bismuth alkanoates $Bi(O_2CR)_3$ may be used as initiators. Here presumably the reactions proceed similarly to $Sn(Oct)_2$ due to adventitious water (see Scheme 1). We report now on the preparation of single-site Bi(III) alkoxide complexes supported by the Schiff base salen class of ligands and show that these are indeed active in the ROP of LA and more active than $Sn(Oct)_2$ under comparable conditions.

Results and discussion

Synthesis

The salen ligands employed in this study are depicted in Chart 1. Each of these Schiff bases employs the 2,4-di-*tert*-butylphenoxy groups and they differ only in the back-bone of the ligand which is employed in the condensation reaction for their synthesis, namely ethylene diamine, 1,2-cyclohexyldiamine or *ortho*-phenyl diamine. For abbreviation we refer hereafter to each of these as en-salen, cy-salen and ph-salen, respectively.

Two synthetic procedures toward the synthesis of the salenBi(OR) compounds have been employed. The first involves the synthesis of $Bi[N(SiMe_3)_2]_3$ and its reaction with the free salen-H_2 ligands shown in Chart 1 leading to the preparation of salenBi$N(SiMe_3)_2$ which was then allowed to react with the appropriate alcohol or phenol. The second was the synthesis of salenBiCl followed by a metathetic reaction involving $KOBu^t$. The salenBiCl compound can be readily prepared by the direct reaction between $BiCl_3$ and Na_2salen or *via* the reaction between $Bi[N(SiMe_3)_2]_2Cl$ and the free salen-H_2 ligand.

The specific syntheses are reported in the Experimental section. In general the alkoxide and phenoxide complexes were soluble in toluene, hexane, pentane, THF and dichloromethane. However, chloroform was often found to be reactive, not surprisingly as it is well known to react with bases *via* elimination of HCl. The synthesis of several of these alkoxides in common organic solvents often presented a problem in obtaining crystals suitable for single crystal X-ray diffraction because of their high solubility.

Single crystal X-ray studies

Several attempts were made to obtain a full structural determination of various *tert*-butoxides but with no success. In all cases we observed sample decomposition in the X-ray beam or upon placing the sample within the oil employed for air-sensitive work. Decomposition in the oil may be due to either solvent of crystallization loss or fast sample decomposition. We were, however, able to obtain crystals of a phenoxide derivative and note that the molecular structure of the homoleptic phenoxides $Bi(OC_6H_3\text{-}2,6\text{-}R_2)_3$ where R = Ph, Pr^i [6] or Me[7] are known to be monomeric while that of the pentafluorophenoxide complex is dimeric.[8] Other alkoxides of the form $Bi(OR)_3$ are polymeric and the ethoxide has been shown to be have a cyclic octameric structure $[Bi(OEt)_3]_8\cdot(7 + x)EtOH$.[9] As a structural model for a salenBi(OR) compound, where R = Me or Et, we have examined the molecular structure of a salenBiCl. For a bulky alkoxide or aryloxide we might anticipate a monomeric salenBi(OR) structure but for a lesser steric demanding group we anticipate a higher degree of aggregation.

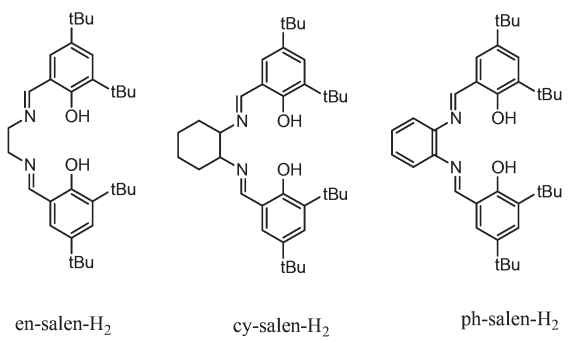


Chart 1 Free salen ligands with different backbones employed in this work.

SalenBiCl structure

Two crystalline samples were examined en-salenBiCl (**3**) and cy-salenBiCl (**2**). The former complex was determined from a twinned data set and it also suffered from disorder of various types of solvent molecules. As a result, it was necessary to use many restraints in the refinement of the model, and the final results are less than optimal. However, the structure clearly indicates an arrangement of tetranuclear $[BiCl]_4$ units, which indicate the ability of the Bi(III) ions to establish six-coordination by formation of a tetranuclear aggregate as opposed to a more simple dimeric structure.

The central $[BiCl]_4$ core is shown in Fig. 1 where the κ^4-en-salen ligands have been omitted. This 8 membered ring contains a non-crystallographic two-fold rotation axis through its center and a boat conformation.

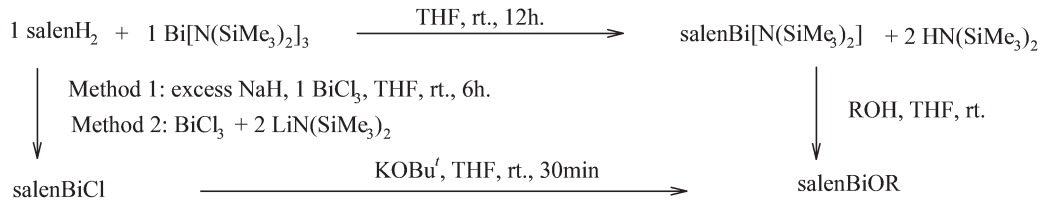
The molecular structure of the cy-salenBiCl was more successfully determined and its dimeric chloride bridged structure is shown in Fig. 2. There is a planar $[BiCl]_2$ unit supported by κ^4-cy-salen ligands. Also we see that the N_2O_2 unit of the cy-salen ligand is planar or near planar and as such the central $N_2O_2BiCl_2$ core can simply be described as being derived from an octahedral geometry. The view in Fig. 2 which is almost parallel to the Bi_2Cl_2 plane emphasizes the tilt of the two cy-salen ligands which allows one to speculate that this distortion arises from what can be termed a stereochemically active lone-pair. The present structure is seemingly most closely related to that of t*p*ClppBiCl (t*p*Clpp = 5,10,15,20-tetra-*p*-chlorophenylporphyrin)[10] except that the latter structure does not clearly implicate a stereochemically active lone pair.

In the view shown in Fig. 2, the two "lone pairs" would be mutually anti as indicated in the simple representation shown below in Fig. 3.

Selected bond distances and angles for [cy-salenBiCl]$_2$ are given in Table 1.

SalenBi-phenoxide structure

The molecular structure of cy-salenBiOC_6H_3-2,6-Bu^t_2 (**1**) is shown in Fig. 4. This structure can easily be described as that of a distorted square based pyramid. The view shown in Fig. 4



Scheme 2 Reaction scheme for the general synthesis of salenBiOR.

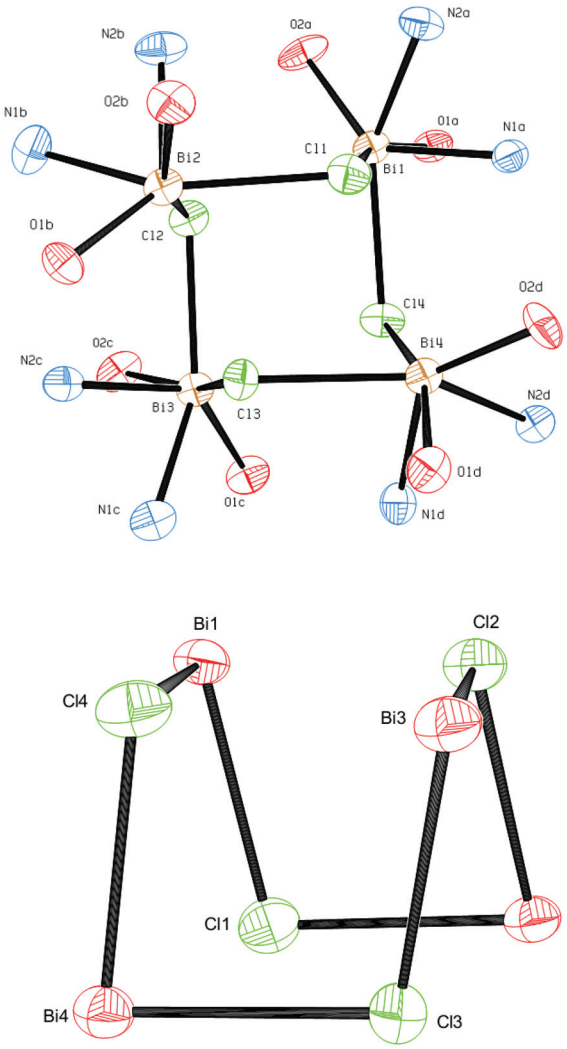


Fig. 1 The central core of the tetranuclear en-salenBiCl molecule (top) and its central $[BiCl]_4$ core (bottom).

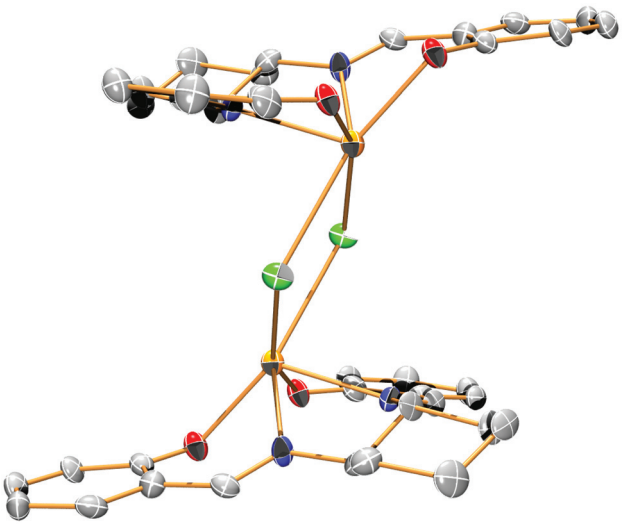


Fig. 2 ORTEP representations of $[cy\text{-}salenBiCl]_2$ (orange = bismuth, green = chlorine, scarlet = oxygen, blue = nitrogen, gray = carbon) drawn at 50% probability. Hydrogen atoms, solent molecules and *tert*-butyl groups are excluded for clarity.

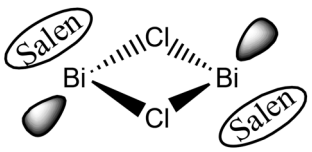


Fig. 3 Sketch of the locations and influence of the stereochemically active lone-pairs in $[cy\text{-}salenBiCl]_2$.

Table 1 Selected bond distances (Å) and bond angles (°) for cy-salenBiCl

Compound **2**			
Bi(1)–O(2)	2.154(7)	Bi(1)–Cl(1)	2.932(3)
Bi(1)–O(1)	2.233(7)	Bi(1)–N(2)	2.404(8)
Bi(1)–N(1)	2.325(8)		
O(2)–Bi(1)–O(1)	74.6(3)	O(2)–Bi(1)–N(1)	79.3(3)
O(1)–Bi(1)–N(1)	115.9(3)	O(2)–Bi(1)–N(2)	118.6(3)
O(1)–Bi(1)–N(2)	74.7(3)	N(1)–Bi(1)–N(2)	68.7(3)
O(2)–Bi(1)–Cl(1)	82.50(19)	O(1)–Bi(1)–Cl(1)	147.7(2)
N(1)–Bi(1)–Cl(1)	80.9(2)	N(2)–Bi(1)–Cl(1)	137.3(2)
C(22)–N(1)–Bi(1)	125.7(7)	C(21)–N(1)–Bi(1)	110.4(6)
C(15)–N(2)–Bi(1)	121.7(7)	C(16)–N(2)–Bi(1)	116.3(6)

emphasizes again the presence of the "stereochemically active lone pair". Not only does this influence the N_2O_2BiO geometry but it also influences the Bi–O–C angle which is 130.7°. Typically in terminal metal–phenoxide bonds we see linear M–O–C angles. This is favored by the oxygen lone pair interaction with the π-system of the aryl ring and often in transition metal complexes by Md_π–Op_π bonding. In the present case if we assume a linear M–O–C moiety one of the oxygen pπ orbitals would be forced into a filled–filled orbital interaction with the Bi lone-pair. By rehybridization toward sp^2 this interaction is minimized as schematically represented below in Fig. 5.

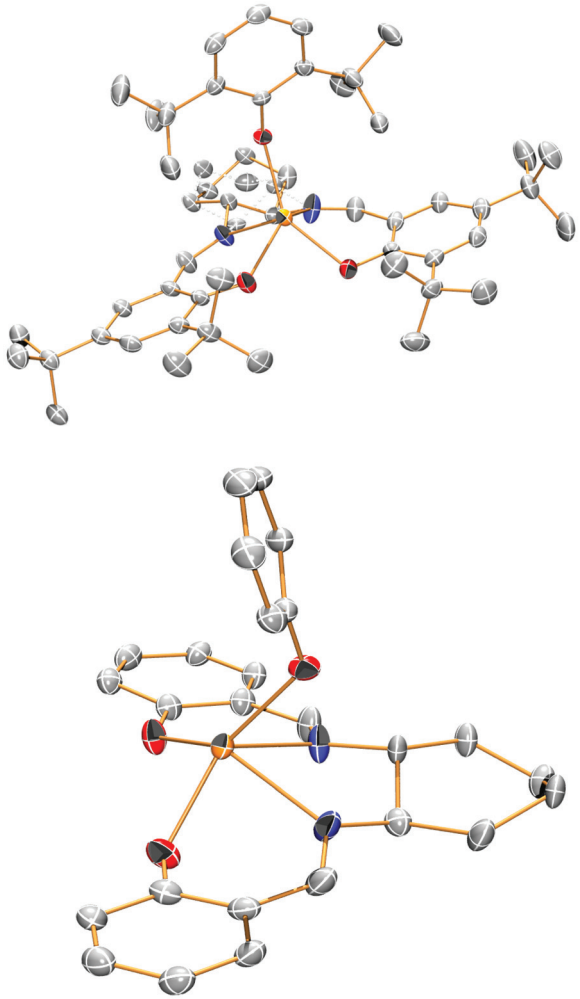


Fig. 4 (Top) ORTEP representation of cy-salenBiOC$_6$H$_3$-2,6-^{t}Bu (orange = bismuth, scarlet = oxygen, blue = nitrogen, gray = carbon) drawn at 50% probability. Hydrogen atoms excluded for clarity. (Bottom) ORTEP representation of cy-salenBiOC$_6$H$_3$-2,6-Bu^t (with *tert*-butyl groups removed for clarity) and emphasizing the nature of the BiO_3N_2 core.

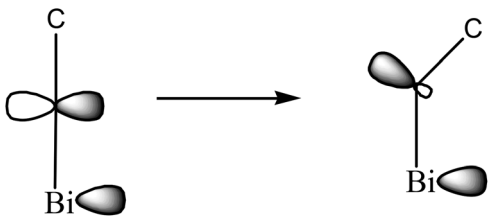


Fig. 5 Minimization of lone pair–lone pair interactions.

A summary of crystallographic data for the three molecules described above is given in Table 3 and selected bond distances for cy-salenBiOC$_6$H$_3$-2,6-Bu$^t_2$ and bond angles are given in Table 2.

Ring-opening polymerization of lactide

Both the *tert*-butoxide and the phenoxide complexes with the cy-salen supporting ligands are active in the ring opening polymerizations of L- and *rac*-lactide in either toluene or dichloromethane solutions at room temperature. Interestingly, the polymerization of *rac*-LA proceeds to give predominantly heterotactic PLA with *isi* and *sis* tetrads. The preference for the alternating ring-opening of L and D lactides is given by $P_r \sim 0.9$ when reactions are carried out to 80% completion. The spectrum of a sample of heterotactic PLA is given in Fig. 6.

Table 2 Selected bond distances (Å) and bond angles (°) for cy-salenBiOC$_6$H$_3$-2,6-Bu$^t_2$

Compound **1**			
N(1)–Bi	2.335(3)	N(2)–Bi	2.343(3)
O(1)–Bi	2.237(3)	O(2)–Bi	2.260(2)
O(3)–Bi	2.324(2)	N(1)–C(16B)	1.478(9)
N(1)–C(16A)	1.569(7)	N(2)–C(21A)	1.506(6)
N(2)–C(21B)	1.554(9)		
C(37)–O(3)–Bi	130.7(2)	C(24)–O(2)–Bi	117.5(2)
C(1)–O(1)–Bi	132.7(2)	O(1)–Bi–O(2)	83.54(9)
O(1)–Bi–O(3)	133.96(9)	O(2)–Bi–O(3)	142.05(9)
O(1)–Bi–N(1)	77.66(10)	O(2)–Bi–N(1)	111.38(11)
O(3)–Bi–N(1)	6.72(10)	O(1)–Bi–N(2)	128.87(12)
O(2)–Bi–N(2)	74.73(11)	O(3)–Bi–N(2)	82.11(11)
N(1)–Bi–N(2)	68.72(11)	C(22)–N(2)–Bi	123.8(3)

We have also studied the kinetics of these polymerizations involving the initiator cy-salenBiOC$_6$H$_3$-2,6-Bu$^t_2$ at room temperature in dichloromethane. Plots of $\ln\{[LA]_0/[LA]_t\}$ *versus* time are shown in Fig. 7 and reveal the living polymerization by the catalyst system and moreover, that the order of polymerization is first order in [Bi]. The plot of $-\ln k_{app}$ *versus* $-\ln$[cat] is shown in Fig. 8. The k_p value of 5×10^{-2} M^{-1} s^{-1} is notably faster than any salenAl(OR) system and just a little slower than the most active Zn based catalyst systems.[12,13] The k_p value for the polymerization of *rac*-LA by cy-salenBiOBu^t is 9.2×10^{-2} M^{-1} s^{-1} in toluene at room temperature. For a direct comparison with cy-salenAlOPr^i which has $k_p = 9.02 \times 10^{-3}$ M^{-1} s^{-1} at 70 °C in toluene,[14] we note that the bismuth complex is ~10 times faster at room temperature.

Concluding remarks

This work describes the first single-site alkoxide catalyst for the ROP of lactide by a bismuth complex. The reactivity of the Bi–OR bond is greater than that of aluminum alkoxides of related formula and notably much more active than Sn(Oct)$_2$ at room temperature. The compounds of formula salenBiOR are, however, regrettably not tolerant to water which is clearly a limiting feature when compared to Sn(Oct)$_2$ or bismuth subsalicylate. The reaction with water is believed to lead to ligand scrambling and crystals of a bismuth salen complex of formula (en-salen)Bi-(en-salenH) have been obtained and will be reported elsewhere.

Experimental

General considerations

All the experiments were carried out under a rigorously dried nitrogen atmosphere either using Schlenk techniques or a

Table 3 Selected crystallographic information for cy-salenBiOC$_6$H$_3$-2,6-Bu^t (**1**), [cy-salenBiCl]$_2$ (**2**) and en-salenBiCl (**3**)

Compound	1	2	3
Chemical formula	$C_{50}H_{73}BiN_2O_3$	$C_{76}H_{112}Bi_2Cl_{10}N_4O_4$	$C_{128}H_{184}Bi_4Cl_4N_8O_8$, 0.598 ($C_6H_{19}NSi_2$), C_4H_8O, 0.2 ($C_4H_{10}O$),
Formula weight	959.08	1918.16	3124.01
Temperature (K)	150(2)	150(2)	150(2)
Space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$
a (Å)	12.4091(1)	15.2904(5)	17.4471(3)
b (Å)	14.7848(2)	10.4994(3)	17.4510(3)
c (Å)	14.9983(1)	27.3011(8)	58.3860(11)
α (°)	110.801(1)		
β (°)	102.945(1)	103.756(1)	
γ (°)	100.046(1)		
V (Å^3)	2407.55(4)	4257.2(2)	17 776.7(5)
Z	2	2	4
D_{calcd} (Mg m^{-3})	1.323	1.496	1.167
Crystal size (mm)	0.19 × 0.12 × 0.12	0.12 × 0.10 × 0.08	0.19 × 0.19 × 0.35
Theta range for data collection	1.66 to 27.48°	1.72 to 25.03°	1.05 to 25.19°
μ (Mo, Kα) (mm^{-1})	3.701	4.488	4.06
F(000)	988	1928	6297
Reflections collected	51 970	63 237	214 449
Unique reflections	11 011 [R(int) = 0.040]	7490 [R(int) = 0.112]	31 482 [R(int) = 0.083]
Completeness to θ_{max}	99.9%	99.6%	98.7%
Data/restraints/parameters	11 011/0/542	7490/0/433	31 482/206/1426
R_1[a] (%) (all data)	2.40 (6.08)	6.92 (9.95)	5.43 (7.86)
wR_2[b] (%) (all data)	3.31 (8.33)	18.44 (20.20)	13.25 (14.39)
Goodness-of-fit on F^2	1.198	1.046	1.047
Largest diff. peak and hole (e Å^{-3})	2.154 and −0.941	5.126 and −2.851	1.748 and −0.851

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} \times 100$.

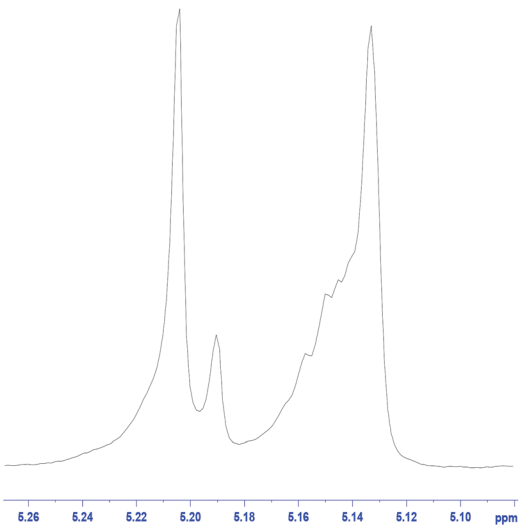


Fig. 6 ^{1}H NMR spectra (CDCl$_3$, 400 MHz) of the homodecoupled *CH* resonance of poly(*rac*-lactide) obtained by cy-salenBiOBu^t as initiator. For details of assignments see ref. 11.

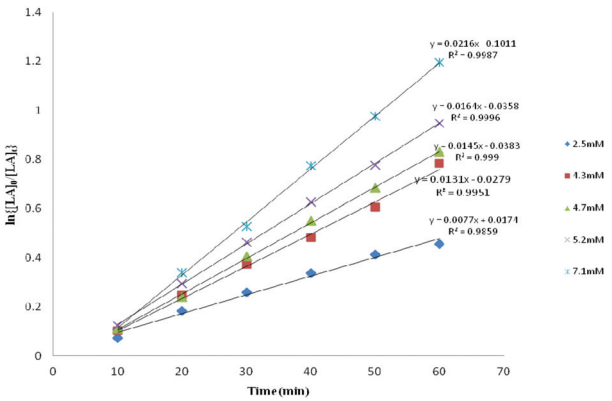


Fig. 7 Linear plots of ln{[LA]$_0$/[LA]$_t$} *versus* time (min) for the polymerization of *rac*-LA initiated by cy-salenBiOC$_6$H$_3$-2,6-Bu$^t_2$ in CH$_2$Cl$_2$ at room temperature.

glove box. Pentane, hexane, THF, toluene, and dichloromethane were distilled under nitrogen over CaH$_2$. Methanol, ethanol, BiCl$_3$, LiN(SiMe$_3$)$_2$, 1,2-cyclohexanediamine, ethylenediamine, *ortho*-aminoaniline, anhydrous Bu^{t}OH, anhydrous Pr^{i}OH and 2,6-di-Bu^{t}C$_6$H$_3$OH were purchased from Sigma Aldrich. 3,5-Di-*tert*-butylsalicylaldehyde was purchased from Alfa Aesar. All of the above chemicals were used without further purification. L-Lactide (L-LA), and *rac*-lactide (*rac*-LA) were purchased from Sigma Aldrich, and purified by sublimation, followed by recrystallization in dry toluene. Then the lactides were dried under reduced pressure at room temperature overnight. Chloroform-d and benzene-d$_6$ were purchased from Cambridge Isotopes and distilled under nitrogen over CaH$_2$. Bi[N(SiMe$_3$)$_2$]$_3$ was prepared according to the literature procedure.[15]

Measurements

^{1}H and ^{13}C spectra were recorded in CDCl$_3$ (δ: 7.24) or C$_6$D$_6$ (δ: 7. 15) and ^{13}C$_6$D$_6$ (δ: 128.06) on Bruker DPX-400 NMR or DRX-500 NMR spectrometers and referenced against the ^{1}H or ^{13}C signal quoted. Gel permeation chromatography (GPC) measurements were carried out using a Waters 1525 binary

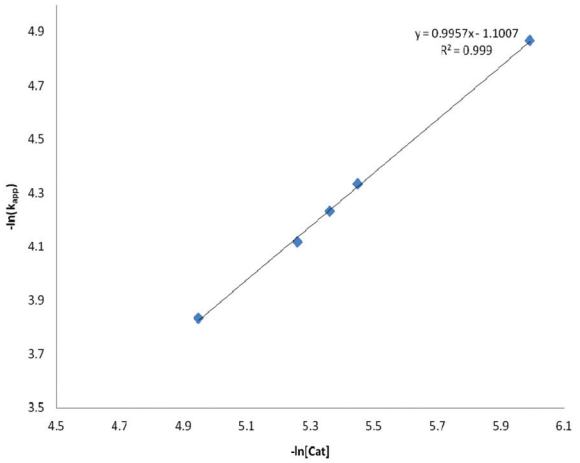


Fig. 8 Plot of $-\ln(k_{app})$ *versus* $-\ln[Cat]$ for the *rac*-LA initiated by cy-salen-BiOC$_6$H$_3$-2,6-Bu$^t_2$ in CH_2Cl_2 at room temperature.

HPLC pump and Waters 1525 differential refractometer equipped with styragel HR 2 and 4 columns (100 to 1000 Å). THF was used as an eluent at 1 mL min^{-1} at 40 °C and the calibration was done with polystyrene standards. MALDI-TOF mass spectra were collected on a Bruker Microflex mass spectrometer.

General procedure for lactide polymerization

0.500 g (3.47 mmol) of L-LA/*rac*-LA was loaded into a Schlenk flask containing a magnetic bar and dissolved in 10 mL CH_2Cl_2 in the glove box. An appropriate amount of initiator (0.0347 mmol initiator for [LA]/[initiator] = 100 and 3.47×10^{-3} mmol initiator for [LA]/[initiator] = 1000) was loaded into another flask and dissolved in 10 mL CH_2Cl_2 in the glove box. Both flasks were taken out from the glove box and attached to the Schlenk line. The initiator solution was quickly added to the LA containing flask using a cannula and stirred at room temperature. The polymerization was quenched in 5 N acidic methanol. The polymer was precipitated in excess methanol and dried under high vacuum. The conversion of LA was estimated by ^{1}H NMR spectroscopy and the molecular weights and PDI were determined by GPC.

General procedures for kinetics studies of *rac*-lactide polymerization

0.500 g (3.47 mmol) of *rac*-LA was loaded in the Schlenk flask containing a magnetic bar and dissolved in 10 mL CH_2Cl_2 in the glove box. 33.0 mg of cy-salenBiOC$_6$H$_3$-2,6-OBu$^t_2$ initiator (0.0347 mmol initiator for [*rac*-LA]/[initiator] = 100) was loaded in another Schlenk flask and dissolved in 10 mL CH_2Cl_2 in the glove box. Both flasks were taken out from the glove box and attached to the Schlenk line. The initiator solution was quickly transferred by cannula into the lactide solution and stirred at room temperature. Then ~0.5 mL aliquots were removed at appropriate time intervals and quenched with 5 N acidic MeOH. The aliquots were dried under vacuum and the % conversions were obtained by ^{1}H NMR spectroscopy. Similar procedures were followed for the kinetics studies of cy-salen-BiOBu^t in toluene at room temperature.

General procedure for the synthesis of salen ligands

All the salen ligands were prepared by the condensation reaction of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde with the appropriate diamine (2 : 1 ratio) in ethanol under reflux for 3 h.[16] The desired product was precipitated in ice bath and collected by filtration. Then the ligands were dried under vacuum at 60 °C overnight.

Synthesis of cy-salenBiN(SiMe$_3$)$_2$

The solution of cy-salenH$_2$ (1.0 g, 1.8 mmol) in 15 mL of THF and the solution of Bi[N(SiMe$_3$)$_2$]$_3$ (1.2 g, 1.8 mmol) in 15 mL of THF were prepared in a glove box. Then the cy-salenH$_2$ solution was transferred to the Bi[N(SiMe$_3$)$_2$]$_3$ solution *via* cannula and the solution was stirred at room temperature for 12 h in a Schlenk flask under a N_2 atmosphere. All the volatile components were removed under vacuum. The completion of the reaction was monitored by ^{1}H NMR. Orange microcrystalline product was obtained with 95% yield. The resulting product was employed in the synthesis below without further purification.

Synthesis of cy-salenBiOBu^t

1.0 g (1.1 mmol) of cy-salenBiN(SiMe$_3$)$_2$ was dissolved in THF and 0.15 mL (1.6 mmol) of Bu^{t}OH was added and stirred for 6 h at room temperature. The volatile components were removed under vacuum and the crude product was dissolved in pentane and placed in a freezer at −25 °C for 2 days. An orange precipitate (product) was obtained in 70% yield by filtration. ^{1}H NMR (C_6D_6, δ, ppm, 500 MHz) 1.41 (s, 18 H, C(C**H**$_3$)$_3$), 1.76 (s, 18 H, C(C**H**$_3$)$_3$), 0.60–0.90, 1.42, 1.44, 2.52, 3.59 (cyclohexyl), 1.46 (s, 9H, OC(C**H**$_3$)$_3$), 7.03 (s, 1H, Ar**H**), 7.07 (s, 1H, Ar**H**), 7.80 (s, 2H, Ar**H**), 7.82 (s, 1H, N=C**H**), 7.88 (s, 1H, N=C**H**). ^{13}C NMR (C_6D_6, δ, ppm, 500 MHz) 24.84, 25.05, 30.15, 30.24, 30.63, 31.48, 31.77, 31.79 (^{t}Bu), 33.96, 34.25, 34.39, 35.73 (^{t}Bu), 66.27, 69.77 (HC–N), 121.93, 122.02, 129.19, 129.43, 130.57, 130.85, 135.16, 135.26, 142.01, 142.08, 164.93, 166.23 (phenyl), 166.83, 167.23 (HC=N). MS(MALDI-TOF): *m*/*z* M^+ calculated 826.45; found 826.14.

Synthesis of cy-salenBiOC$_6$H$_3$-2,6Bu$^t_2$

1.0 g (1.1 mmol) of cy-salenBiN(SiMe$_3$)$_2$ was dissolved in THF and 0.25 mL (1.1 mmol) of OH-C$_6$H$_3$-2,6Bu$^t_2$ was added and stirred for 6 h at room temperature. The volatile components were removed under vacuum and the crude product was dissolved in pentane and placed in a freezer at 0 °C for 2 days. A yellow precipitate (product) was obtained in 75% yield. Crystals suitable for single-crystal X-ray crystallography were obtained by placing a concentrated hexane solution in freezer at −25 °C for a week. ^{1}H NMR (C_6D_6, δ, ppm, 500 MHz) 1.32, 1.34 (s, s, 18 H, C(C**H**$_3$)$_3$), 1.43 (s, 18 H, C(C**H**$_3$)$_3$), 1.61, 1.64 (s, s, 18 H, C(C**H**$_3$)$_3$), 0.87, 1.23, 1.47, 1.71, 2.39, 5.51 (cyclohexyl), 6.69 (t, 1H, Ar**H**), 6.98 (d, 1H, Ar**H**), 7.24 (d, 1H, Ar**H**), 7.39 (d, 2H, Ar**H**), 7.83 (d, 1H, Ar**H**), 7.87 (d, 1H, Ar**H**), 8.21 (s, 1H, N=C**H**), 8.26 (s, 1H, N=C**H**). ^{13}C NMR (C_6D_6, δ, ppm,

500 MHz) 24.52, 25.65, 25.83, 27.78, (CH_2 in cyclohexyl) 30.10, 30.43, 31.59, 31.70 ($C(CH_3)_3$), 32.18, 32.25, 34.05, 34.08 ($C(CH_3)_3$), 34.40, 34.98, 35.63, 35.76 ($C(CH_3)_3$), 65.28, 69.93 (CH–N), 115.70, 121.69, 122.61, 124.95, 125.41, 128.56, 128.86, 130.89, 132.29, 137.93, 138.29, 140.63, 142.57, 142.91, 162.12, 165.29 (phenyl), 164.71, 169.94 (HC═N). MS(MALDI-TOF): *m*/*z* M^+ calculated 958.54; found 958.42.

Synthesis of cy-salenBiOPr^i

1.0 g (1.1 mmol) of cy-salenBiN$(SiMe_3)_2$ was dissolved in THF and 0.15 mL, (2.0 mmol) of Pr^{i}OH was added and stirred for 6 h at room temperature. The volatile components were removed under vacuum and the crude product was dissolved in pentane and placed in a freezer at −25 °C for 2 days. An orange precipitate (product) was obtained in 65% yield. ^{1}H NMR (C_6D_6, δ, ppm, 500 MHz) 1.03 (bs(broad)6H, $^iCH(CH_3)_2$), 1.39 (s, 18 H, $C(CH_3)_3$), 1.77 (s, 18 H, $C(CH_3)_3$), 0.68, 0.74, 1.15, 1.45, 2.59, 3.17 (cyclohexyl), 4.0–4.4 (m, 1H, $^iCH(CH_3)_2$), 7.06 (s, 1H, ArH), 7.09 (s, 1H, ArH), 7.82 (2, 2H, ArH), 7.82 (s, 1H, N═CH), 8.04 (s, 1H, N═CH). ^{13}C NMR (C_6D_6, δ, ppm, 500 MHz) 24.90, 24.99, 25.97, 27.15, 29.66, 30.05, 30.13, 31.77, 31.90, 34.00, 35.76, 35.82, 68.11, 68.23, 122.21, 129.40, 129.54, 130.85, 130.88, 135.40, 135.64, 141.89, 142.02, 164.22, 166.89, 166.99. MS(MALDI-TOF): *m*/*z* M^+ calculated 812.43; found 812.81.

Synthesis of ph-salenBiOBu^t

A solution of ph-salenH_2 (1.0 g, 1.8 mmol) in 15 mL of THF and a solution of Bi$[N(SiMe_3)_2]_3$ (1.2 g, 1.8 mmol) in 15 mL of THF were prepared in a glove box. Then the cy-salenH_2 solution was transferred to the Bi$[N(SiMe_3)_2]_3$ solution *via* cannula and the solution was stirred at room temperature for 12 h. The volatile components were removed under vacuum. The completion of the reaction was monitored by ^{1}H NMR. The resultant product was redissolved in THF and 0.20 mL (2.1 mmol) Bu^{t}OH was added and stirred for another 6 h. All the volatile components were removed under vacuum. The residue was redissolved in pentane and placed in a freezer at −25 °C for two days. A deep orange precipitate was obtained in 80% yield. ^{1}H NMR (C_6D_6, δ, ppm, 500 MHz) 1.05 (bs, 9 H, $C(CH_3)_3$), 1.34 (bs, 18 H, $C(CH_3)_3$), 1.75 (bs, 18 H, $C(CH_3)_3$), 6.51 (s, 2H, ArH), 6.90 (s, 2H, ArH), 7.04 (s, 2H, ArH), 7.84 (s, 2H, ArH), 8.18 (s, 2H, N═CH). ^{13}C NMR (C_6D_6, δ, ppm, 500 MHz) 30.30, 31.44, 33.89, 35.69 ($C(CH_3)_3$), 120.17, 122.78, 127.34, 129.64, 131.91, 136.19, 141.95, 144.0, 162.77 (phenyl), 170.50 (HC═N). MS (MALDI-TOF): *m*/*z* M^+ calculated 820.40; found 820.94.

Synthesis of en-salenBiCl

Method 1. 1.0 g of en-salenH_2 (2.0 mmol) dissolved in THF and 0.12 g (5.0 mmol) of NaH were charged in Schlenk flasks in the glove box. The flasks were taken out from the glove box and attached to the Schlenk line. The en-salenH_2 solution was cooled in an ice bath and transferred to the NaH containing Schlenk flask *via* cannula and stirred overnight. The conversion was monitored by the disappearance of the OH peak by ^{1}H NMR. To the resultant mixture 0.64 g (2.0 mmol) of $BiCl_3$ was added and stirred for overnight. All the volatile components were removed under vacuum and the crude product was dissolved in pentane and centrifuged. The resulting solution was transferred to another flask and placed in a freezer at −25 °C for three months. Yellow colored crystals were obtained with a yield of 85%.

Method 2. Bi$[N(SiMe_3)_2]_2$Cl was prepared by adding 2 equivalents of Li$N(SiMe_3)_2$ to 1 equivalent of $BiCl_3$ in THF at 0 °C. 1.0 g (2.0 mmol); en-salenH_2 dissolved in THF was then added to the solution of 1.1 g (2.0 mmol) Bi$[N(SiMe_3)_2]_2$Cl in THF. The resulting solution was stirred overnight and all volatile components were removed under vacuum. The crude product was dissolved in pentane and placed in a freezer at −25 °C for one month. Yellow colored crystals were obtained in 70% yield.

^{1}H NMR (C_6D_6, δ, ppm, 500 MHz) 1.33 (bs, 18 H, $C(CH_3)_3$), 1.71 (bs, 18 H, $C(CH_3)_3$), 3.00 (bs, 2H, CH_2), 4.16 (bs, 2H, CH_2), 6.89 (bs, 2H, ArH), 7.28 (bs, 2H, N═CH), 7.82 (bs, 2H, ArH). MS(MALDI-TOF): *m*/*z* M^+ calculated 734.30; found 734.94.

Synthesis of cy-salenBiCl

1.0 g of cy-salenH_2 (1.8 mmol) dissolved in THF and 0.12 g (5.0 mmol) of NaH were charged separately in Schlenk flasks in the glove box. The cy-salenH_2 solution was cooled in an ice bath and transferred to the NaH containing Schlenk flask *via* cannula and stirred overnight. The conversion was monitored by the disappearance of OH the peak by ^{1}H NMR. To the resultant mixture 0.58 g (1.8 mmol) of $BiCl_3$ was added and stirred overnight. All the volatile components were removed under vacuum and the crude product was dissolved in pentane and centrifuged. The resulting solution was transferred to another flask and placed in a freezer at −25 °C for one month. Yellow colored crystals were obtained in 65% yield.

^{1}H NMR (C_6D_6, δ, ppm, 400 MHz) 0.70, 1.13, 1.35, 1.45, 2.14, 5.15 (cyclohexyl), 1.30, 1.34, 1.68, 1.75 ($C(CH_3)_3$), 6.89 (s, 1H, ArH), 7.08 (bs, 1H, ArH), 7.46 (bs, 1H, ArH), 7.77 (s, 1H, N═CH), 7.79 (s, 1H, N═CH), 7.88 (s, 1H, ArH). MS(MALDI-TOF): *m*/*z* M^+ calculated 788.35; found 788.24.

Crystallographic studies

Single crystals of **1–3** were isolated under a pool of fluorinated oil and were found to be quite reactive. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with Mo Kα radiation. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. Data integration was done with Denzo, and scaling and merging of the data was done with SADABS[17] for **3** and Scalepack[18] for **1** and **2**. The structures were solved by the direct methods program in SHELXS-97. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-97,[19] as incorporated in the WinGX package.[20] For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with $U(H) = 1.5U_{eq}$ (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with $U(H) = 1.2U_{eq}$ (bonded atom).

Neutral atom scattering factors were used and include terms for anomalous dispersion.[21]

Structure **1** contains a disordered cyclohexane backbone which crystallized in two conformations. The two orientations were found in the difference map and their occupancy was allowed to refine to 0.55/0.45. The pivot carbon atoms C17A/C17B and C20A/C20B were restrained with EXYZ and EADP commands.

Structure **3** consists of an en-salen[Bi-Cl] tetramer plus three different solvent molecules: fully occupied THF, $(CH_3)_3Si–NH–Si(CH_3)_3$ with a refined occupancy factor of 0.598(9), and diethyl ether with an occupancy factor set to 0.2. There are other regions of lower electron density, which are most likely very disordered solvent molecules, and these were not modeled. Pseudo-merohedral twinning is present and the following twin law was applied to the data (0–1 0 −1 0 0/0 0 1) with a twin fraction of 0.3633(8).

It was necessary to use many restraints (SADI, DFIX, and FLAT) during the refinement for both the Bi tetramer and the solvent molecules.

Acknowledgements

We thank the Department of Energy, Office of Basic Sciences, Chemistry Division for support of this work.

References

1 F. Nederberg, E. F. Connor, M. Moller, T. Glauser and J. L. Hedrick, *Angew. Chem., Int. Ed.*, 2001, **40**, 2712.
2 H. R. Kricheldorf and R. Dunsing, *Makromol. Chem.*, 1986, **187**, 1611.
3 V. Balasanthiran, T. L. Beilke and M. H. Chisholm, *Dalton Trans.*, 2013, **42**, 9274.
4 P. C. Andrews, G. B. Deacon, C. M. Forsyth, P. C. Junk, I. Kumar and M. Maguire, *Angew. Chem., Int. Ed.*, 2006, **45**, 5638.
5 (*a*) H. R. Kricheldorf, H. Hachmann-Thiessen and G. J. Schwarz, *J. Biomater. Sci., Polym. Ed.*, 2006, **17**, 721; (*b*) H. R. Kricheldorf, K. Bornhorst and H. Hachmann-Thiessen, *Macromolecules*, 2005, **38**, 5017; (*c*) H. R. Kricheldorf, H. Hachmann-Thiessen and G. Schwarz, *Biomacromolecules*, 2004, **5**, 492.
6 X. Kou, X. Wang, D. Mendoza-Espinosa, L. N. Zakharov, A. L. Rheingdd, W. H. Watson, K. A. Brien, L. K. Jayarathna and T. A. Hanna, *Inorg. Chem.*, 2009, **48**, 11002.
7 W. J. Evans, J. H. Hain and J. W. Ziller, *J. Chem. Soc., Chem. Commun.*, 1989, 1628.
8 C. M. Jones, M. D. Burkart, R. E. Bachman, D. L. Serra, S. Hwu and K. H. Whitmore, *Inorg. Chem.*, 1993, **32**, 5136; K. H. Whitmore, S. Hoppe, O. Sydora, J. L. Jolas and C. M. Jones, *Inorg. Chem.*, 2000, **39**, 85.
9 V. G. Kessler, N. Ya. Turova and E. P. Turevskaya, *Inorg. Chem. Commun.*, 2002, **5**, 549; T. Hatanpaa, M. Vehkamaki, M. Ritala and M. Leskela, *Dalton Trans.*, 2010, **39**, 3219.
10 B. Boitrel, M. Breede, P. J. Brothers, M. Hodgson, L. Michaudet, C. E. F. Rickard and N. A. Salim, *Dalton Trans.*, 2003, 1803.
11 M. T. Zell, B. E. Padden, A. J. Patrick, K. A. M. Thakur, R. T. Kean, M. A. Hillmyer and E. J. Munson, *Macromolecules*, 2002, **35**, 7700.
12 L. E. Breyfogle, C. K. Williams, V. G. Young Jr, M. A. Hillmyer and W. B. Tolman, *Dalton Trans.*, 2006, 928.
13 C. A. Wheaton and P. G. Hayes, *Chem. Commun.*, 2010, **46**, 8404.
14 Z. Zhong, P. J. Dijkstra and J. Feijen, *J. Am. Chem. Soc.*, 2003, **125**, 11291.
15 C. J. Carmalt, N. A. Compton, R. J. Errington, G. A. Fisher, I. Moenandar, N. C. Norman and K. H. Whitmire, *Inorg. Synth.*, 1997, **31**, 98.
16 P. Hormnirun, E. L. Marshall, V. C. Gibson, R. I. Pugh and A. J. P. White, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15343.
17 G. M. Sheldrick, *SADABS*, University of Göttingen, Germany.
18 Z. Otwinowski and W. Minor, *Methods in Enzymology, Vol. 276: Macromolecular Crystallography, Part A*, Academic Press, 1997.
19 G. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
20 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
21 *International Tables for Crystallography*, Kluwer Academic Publishers, Dordrecht, 1992, vol. C.