Dinuclear dialkoxo-bridged cyclopentadienylsiloxo titanium complexes†

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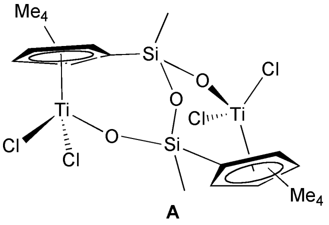
The dinuclear dialkoxo-bridged complexes [(TiCl)$_2$(μ-O$_2$L)(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (O$_2$L = 1,2-O$_2$C$_2$H$_4$ **1a**, 1,2-O$_2$C$_6$H$_4$ **1b**, 1,2-(OCH$_2$)$_2$C$_6$H$_4$ **1c**, O$_2$SiPh$_2$ **1d**) were obtained by reaction of [(TiCl$_2$)$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (**A**) with the corresponding dilithium salt (**1a**) or diol (**1b**, **1c**, **1d**). Alkylation of **1a** and **1b** with ClRMg afforded [(TiR)$_2$(μ-O$_2$L)(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (O$_2$L = 1,2-O$_2$C$_2$H$_4$, R = Me **2a**, Bz **3a**; O$_2$L = 1,2-O$_2$C$_6$H$_4$, R = Me **2b**, Bz **3b**). Addition of four equiv. of LiO*i*Pr to **A** afforded [{Ti(O*i*Pr)$_2$}$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (**4**). Reaction of **1a** with Al(C$_6$F$_5$)$_3$ produced the elimination of the dialkoxo ligand to give [{TiCl(C$_6$F$_5$)}$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (**5**), whereas the same reaction of **1b** with Al(C$_6$F$_5$)$_3$ produced the oxo-alane adduct [(TiCl)$_2$(μ-O$_2$L)(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O·Al{C$_6$F$_5$}$_3$)})] (O$_2$L = 1,2-O$_2$C$_6$H$_4$ **6**) which was further transformed to give a mixture of **5** and [(TiCl){Ti(C$_6$F$_5$)}(μ-O$_2$L)(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (O$_2$L = 1,2-O$_2$C$_6$H$_4$ **7**). One benzyl group of complexes **3** was abstracted with E(C$_6$F$_5$)$_3$ (E = B, Al) to give the monoionic compounds [Ti(TiBz)(μ-O$_2$L)(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})][BzE(C$_6$F$_5$)$_3$] (O$_2$L = 1,2-O$_2$C$_2$H$_4$, E = B **8B**, Al **8Al**; O$_2$L = 1,2-O$_2$C$_6$H$_4$, E = B **9B**), although **8Al** was unstable in CD$_2$Cl$_2$ evolving to a mixture of compounds where [(TiBz)$_2$(μ-Cl)(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})][BzAl(C$_6$F$_5$)$_3$] (**10**) was identified, and compound **9B** was also unstable at ambient temperature. Polymerization of ε-caprolactone was only achieved with the tetraalkoxo compound **4**. All of these complexes were characterized by NMR spectroscopy and **1a**, **1b** and **7** by X-ray diffraction studies.

Introduction

The design of ligands to generate bimetallic systems has been developed with the aim of finding reactivity patterns different from those observed for similar monometallic complexes.[1] In this regard, olefin polymerization and copolymerization processes with group 4 dinuclear complexes have provided modified final products with respect to those obtained using mononuclear derivatives.[2–14]

Alkoxo, aryloxo and related ligands stabilize high oxidation metal complexes and chelating diol derivatives are adequate ligands for generating bimetallic systems. Furthermore, modifications of the oxygen substituents may also affect the M–O interaction.[1,15] However, the alkoxo group is not only an ancillary ligand, but also plays an important role in the activation of cyclic esters such as caprolactone and lactide.[16–23]

Our interest in studying functionalized cyclopentadienyl compounds with SiClMe$_2$ moieties,[24–32] moved our research group to synthesize bimetallic cyclopentadienyl disiloxane derivatives with Si–O–Si bridges for Nb,[25,31,33] Mo[30] and W[30] and with Si–O–M bridges for group 4 metals[26,32,34] and Nb[25,33] by hydrolysis of the Si–Cl bonds or CO$_2$ insertion into Si–N bonds. Conversely, hydrolysis of the functionalized cyclopentadienyl titanium compound [Ti{η^5-C$_5$Me$_{4(}$SiMeCl$_2$)}Cl$_3$][35] with a SiCl$_2$Me moiety gave the dititanium derivative [(TiCl$_2$)$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (**A**, Fig. 1) with both Si–O–Si and Si–O–Ti bridges.[36] Complex **A** presented two stereogenic Si atoms although formation of the Si–O–Si bridge required the reaction to be regioselective and only one diastereoisomer of C$_2$ symmetry was obtained.



A

Fig. 1 Compound **A**.

Whereas these types of dinuclear complexes have two potentially active metal centres for olefin polymerization, reactions of the titanium complexes [(TiBz$_2$)$_2$(μ-{η^5-C$_5$Me$_4$SiMe$_2$O}$_2$)] and [(TiBz$_2$)$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] with Lewis acids formed benzyl bridges between the Ti atoms, which react further in halogenated solvents providing halogen bridges.[36,37] The ease of formation of bridges caused complex **A** to be inactive in ethylene polymerization, although the methyl derivative [(TiMe$_2$)$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] was active in MMA polymerization.[36] Abstraction of two alkyl groups was only possible in the reaction of complex [(TiBz$_2$)$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] with excess B(C$_6$F$_5$)$_3$ for several days, although the transformation was not complete.

In view of these results and with the aim of generating dicationic dititanium compounds, we report in this paper the synthesis of dialkoxo-bridged dinuclear titanium compounds from complex **A**. Alkylation reactions of the new complexes, their reactivity toward Lewis acids and finally their activity for polymerization of ε-caprolactone are also presented.

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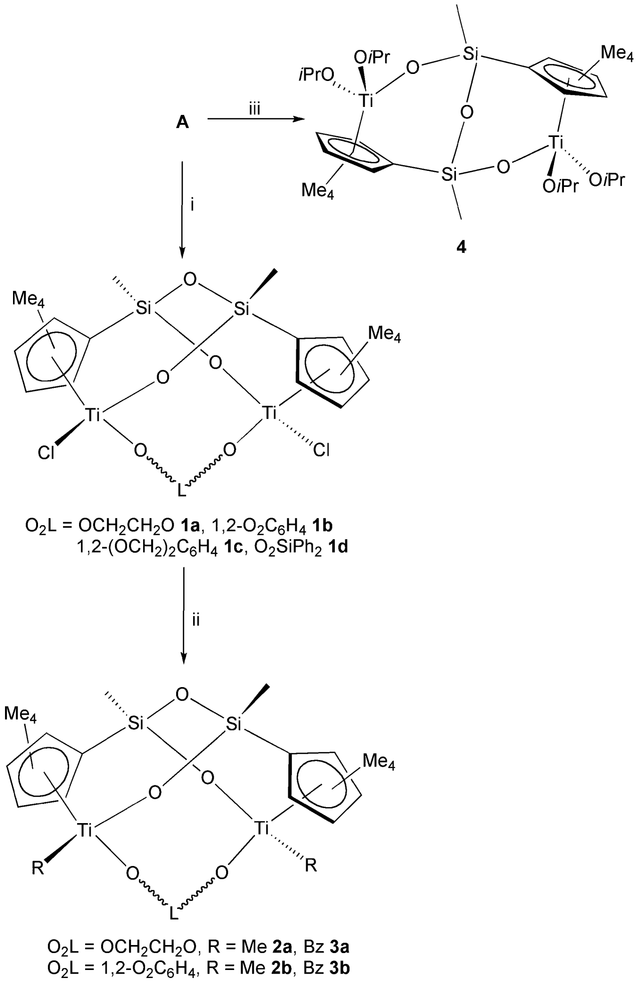
‡ X-Ray diffraction studies.

Results and discussion

Synthesis of dialkoxo-bridged compounds

The dinuclear disiloxane complex [$(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})$] (**A**) reacted with the lithium salt $Li_2(OCH_2)_2$ and the free diol compounds $(HO)_2L$ [$(HO)_2L$ = 1,2-$(HO)_2C_6H_4$, 1,2-$(HOCH_2)_2C_6H_4$, $(HO)_2SiPh_2$], in the presence of NEt_3, in toluene to give the dialkoxo-bridged compounds [$(TiCl)_2(\mu\text{-}O_2L)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})$] ($O_2L$ = OCH_2CH_2O **1a**, 1,2-$O_2C_6H_4$ **1b**, 1,2-$(OCH_2)_2C_6H_4$ **1c**, O_2SiPh_2 **1d**) (Scheme 1). The resulting yields of these reactions and the stability of these compounds were dependent on the bridge length. Thus, the four-atom bridged compounds **1a** and **1b** were obtained in good yield and were stable at room temperature, whereas the six-atom and three-atom bridged derivatives **1c** and **1d** were respectively obtained in low and rather poor yield, and were also more air sensitive.



Scheme 1 (i) $Li_2(OCH_2)_2$ or $(HO)_2L/NEt_3$ ($(HO)_2L$ = 1,2-$(HO)_2C_6H_4$, 1,2-$(HOCH_2)_2C_6H_4$, $(HO)_2SiPh_2$), toluene; (ii) ClRMg (R = Me, Bz), Et_2O; (iii) LiO*i*Pr, toluene.

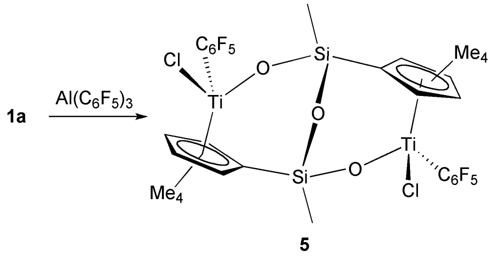
These new dialkoxo-bridged compounds present two new stereogenic Ti atoms in addition to the two stereogenic Si atoms. However, formation of the dialkoxo bridge, which was located opposite to the Si–O–Si bridge, was regioselective due to the presence of the disiloxane moiety; therefore signals for only one diastereoisomer were observed in the NMR spectra. Hence, the C_2 symmetry complexes **1a–d** presented an ABCD spin system for the equivalent C_5Me_4Si substituents, one resonance for the equivalent Si–Me groups and the resonances corresponding for the symmetric bridge. In the particular case of the ethylene bridge of **1a** and the methylene groups of the dialkoxo bridge of **1c**, the ^1H NMR spectra showed two doublets for the diastereotopic protons of both CH_2 groups.

Complexes **1a** and **1b** reacted with two equiv. of ClRMg (R = Me, Bz) to afford the alkyl derivatives [$(TiR)_2(\mu\text{-}O_2L)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})$] ($O_2L$ = 1,2-$O_2C_2H_4$, R = Me **2a**, Bz **3a**; O_2L = 1,2-$O_2C_6H_4$, R = Me **2b**, Bz **3b**) (Scheme 1). Addition of excess Grignard reagent afforded the tetraalkyl derivatives [$(TiR_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})$]. The NMR spectra of complexes **2** and **3** showed similar patterns to those observed for compounds **1a** and **1b**, with new resonances for the equivalent Ti–Me and Ti–Bz groups, respectively, consistent with C_2-symmetric compounds. Furthermore, the ^1H NMR spectrum of the benzyl complexes showed two doublets for the diastereotopic CH_2 protons of the benzyl ligands.

The tetraalkoxo derivative [$\{Ti(O\textit{i}Pr)_2\}_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})$] (**4**) was obtained in good yield upon addition of four equiv. of LiO*i*Pr to compound **A**. Compound **4** was also air sensitive but thermally stable; its ^1H and ^{13}C NMR spectra corresponded to a C_2 symmetry complex with resonance patterns similar to those discussed for complexes **1–3**. Furthermore, in the ^1H and ^{13}C NMR spectra two sets of resonances were observed for the two diastereotopic O*i*Pr groups of each Ti atom.

Reactions with the Lewis acids $E(C_6F_5)_3$ (E = B, Al)

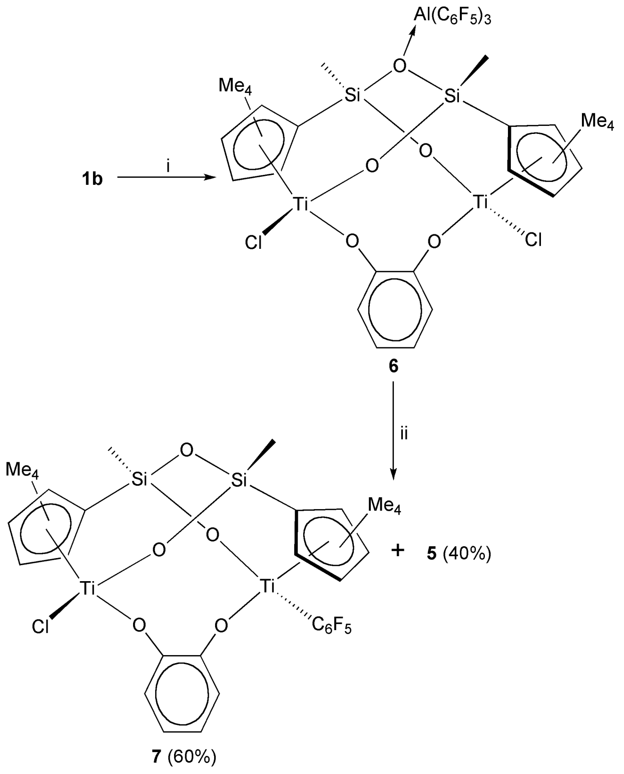
Neither of the chloro derivatives **1a** and **1b** reacted with $B(C_6F_5)_3$. However, the ethyleneglycolate derivative **1a** reacted with $Al(C_6F_5)_3$ with substitution of the dialkoxo ligand by two pentafluorophenyl groups to give [$\{TiCl(C_6F_5)\}_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})$] (**5**) as the unique titanium product (Scheme 2). Transfer of one C_6F_5 group from the Al atom to each Ti atom with exchange of the dialkoxo ligand is consistent with the higher oxophilicity of the Al atom, although we could not identify the aluminium species formed in this reaction. Compound **5** retained the C_2 symmetry of the starting product **1a**, as evidenced by its NMR spectra, with the two C_6F_5 groups located opposite to the Si–O–Si bridge, in the position previously occupied by the alkoxo bridge, consistent with the concerted mechanism of this metathesis reaction. Hence, the ^1H and ^{13}C NMR spectra also presented an ABCD spin system for the equivalent C_5Me_4Si substituents, one resonance for the equivalent Si–Me groups, and



Scheme 2

three resonances for the three types of F nuclei were observed in the ^{19}F NMR spectrum for the C_6F_5 groups.

Conversely, the reaction of $Al(C_6F_5)_3$ with the catecholate-bridged complex **1b** gave the oxo-alane adduct $[(TiCl)_2(\mu\text{-}O_2L)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O{\cdot}Al\{C_6F_5\}_3)\})]$ (O_2L = 1,2-$O_2C_6H_4$ **6**) (Scheme 3), which was identified by NMR spectroscopy. Formation of the oxo-alane adduct **6** at ambient temperature can be attributed to the lower accessibility of the oxygen atom in the phenylenedialkoxo-bridged complex **1b** with respect to the ethyleneglycolate complex **1a**, due to the higher steric requirement of the phenylene moiety and also to its π acceptor capability. The ^{1}H and ^{13}C NMR spectra of **6** showed resonances very close to those of **1b**, although the most remarkable feature that confirmed the formation of an oxo-alane adduct was the ^{19}F NMR spectrum which showed the three expected resonances characteristic of these type of complex.



Scheme 3 (i) $Al(C_6F_5)_3$, 5 min; (ii) 3 days.

Compound **6** was unstable and further transformation occurred at ambient temperature to give a mixture of **5** and $[(TiCl)\{Ti(C_6F_5)\}(\mu\text{-}O_2L)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (O_2L = 1,2-$O_2C_6H_4$ **7**) in a 2 : 3 molar ratio after three days (Scheme 3). The resulting aluminium by-product could not be identified. This process required de-coordination of the $Al(C_6F_5)_3$ moiety from the oxygen atom in compound **6**, recovering the initial reaction products as a consequence of the weak O–Al interaction. Formation of compound **7** as the major reaction product can also be justified by the different steric and electronic characteristic of the phenylenedialkoxo bridge, with regard to the ethylenedialkoxo bridge, which would make the approach of $Al(C_6F_5)_3$ to the bridging oxygen atoms difficult, rather favouring exchange of the chloro ligand with the C_6F_5 group. However, it is important to note that formation of **7** should be independent of the formation of adduct **6**, de-coordination of $Al(C_6F_5)_3$ from the oxygen atom of **6** is required to obtain **7**. Compound **7** is an asymmetric molecule and thus, its ^{1}H and ^{13}C NMR spectra showed resonances for two C_5Me_4Si ABCD spin systems, two resonances for both SiMe groups and four multiplets for the four protons of the catecholate bridge in the ^{1}H NMR spectrum. Furthermore, three resonances for the $Ti(C_6F_5)$ moiety were observed in the ^{19}F NMR spectrum.

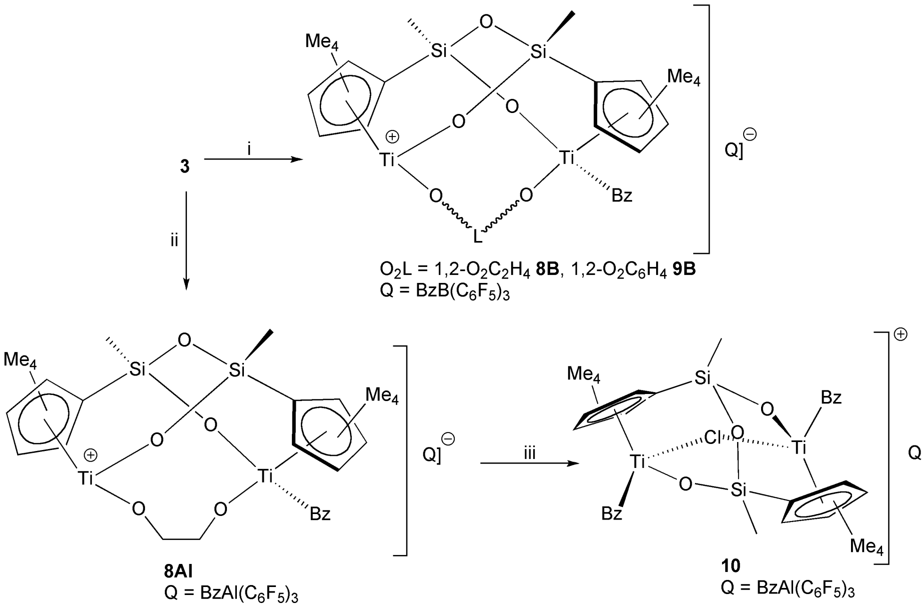
The methyl derivatives **2**, when treated with any of the Lewis acids $E(C_6F_5)_3$ (E = B, Al), decomposed even at low temperatures. In contrast, the benzyl compounds **3** reacted with one equiv. of $B(C_6F_5)_3$ to give the asymmetric monoionic complexes $[Ti(TiBz)(\mu\text{-}O_2L)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})][BzB(C_6F_5)_3]$ (O_2L = 1,2-$O_2C_2H_4$ **8B**, O_2L = 1,2-$O_2C_6H_4$ **9B**) (Scheme 4). However, **9B** was unstable at ambient temperature. The same reaction employing $Al(C_6F_5)_3$ as Lewis acid afforded the analogous compound $[Ti(TiBz)(\mu\text{-}O_2L)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})][BzAl(C_6F_5)_3]$ (O_2L = 1,2-$O_2C_2H_4$ **8Al**) for **3a**, while only decomposition was observed for the catecholate derivative **3b**. The cation of **8Al** was also unstable at room temperature and was further transformed into a mixture of compounds in which the chloro-bridged compound $[(TiBz)_2(\mu\text{-}Cl)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})][BzAl(C_6F_5)_3]$ (**10**) was identified.[36] The same reaction employing $[Ph_3C][B(C_6F_5)_4]$ resulted in decomposition of the starting materials.

These Ti complexes are asymmetric cations presenting eight resonances for two ABCD C_5Me_4Si spin systems and two resonances for both SiMe groups in their ^{1}H and ^{13}C NMR spectra. Four multiplets for the four protons of the dialkoxo bridge and two doublets for both protons of the Ti-CH_2 groups were also observed in the ^{1}H NMR spectra. The ^{19}F NMR spectra of the borate anions of derivatives **8B** and **9B** showed an important difference regarding the type of anion–cation interactions.[38] For **8B**, with the ethylenedialkoxo bridge, the $\Delta\delta(F_p\text{–}F_m)$ of 2.8 indicated unpaired ions, whereas for **9B**, with the phenylenedialkoxo bridge, the $\Delta\delta(F_p\text{–}F_m)$ of 5.4 was indicative of an ion-pair interaction. This difference is consistent with the donor ability of each dialkoxo bridge, which is related to the π acceptor contribution of the phenylene ring.

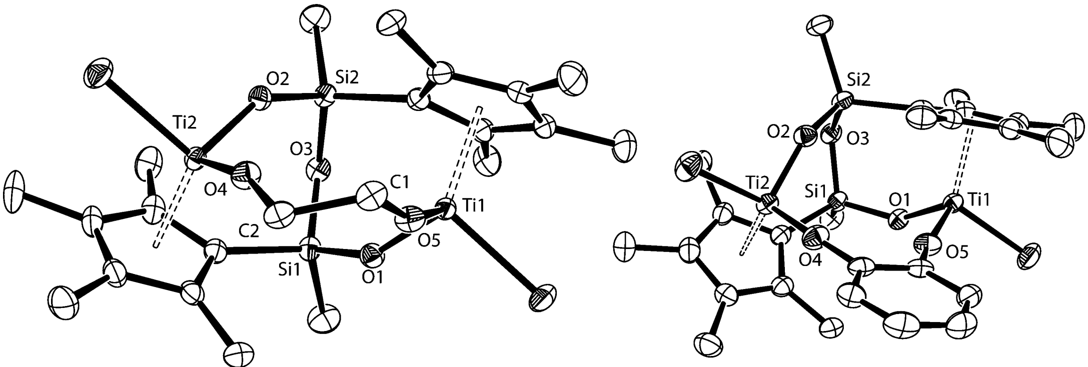
Addition of excess $E(C_6F_5)_3$ (E = B, Al) did not result in abstraction of the second benzyl group in these monocationic derivatives, where no reaction was observed even after heating. In addition, the abstraction did not occur in the presence of donor ligands such as THF or pyridine or by addition of one equiv. of $[Ph_3C][B(C_6F_5)_4]$. It would seem that generation of a cationic titanium atom hinders the abstraction of the remaining benzyl ligand bounded to the other metal centre, although both titanium atoms are separated by bridges and also are bound to electronegative and π donor oxygen atoms, which should help to stabilize the metal's electron deficiency.

X-Ray diffraction studies

The molecular structures of **1a**, **1b** and **7** are illustrated in Fig. 2 and 3. Selected bond lengths and angles for these structures are listed in Table 1. The molecular structures of these three complexes consist of a dinuclear molecule formed by two Ti atoms connected by two bridging $[\mu\text{-}(\eta^5\text{-}C_5R_4SiMe_2O)]$ fragments, each of these Ti



Scheme 4 (i) $B(C_6F_5)_3$, CD_2Cl_2; (ii) $Al(C_6F_5)_3$, CD_2Cl_2; (iii) CD_2Cl_2.



1a **1b**

Fig. 2 ORTEP diagrams of $[(TiCl)_2(\mu\text{-}O_2L)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ ($O_2L = 1,2\text{-}O_2C_2H_4$ **1a**, $1,2\text{-}O_2C_6H_4$ **1b**). Hydrogen atoms have been omitted and thermal ellipsoids are shown at the 30% level.

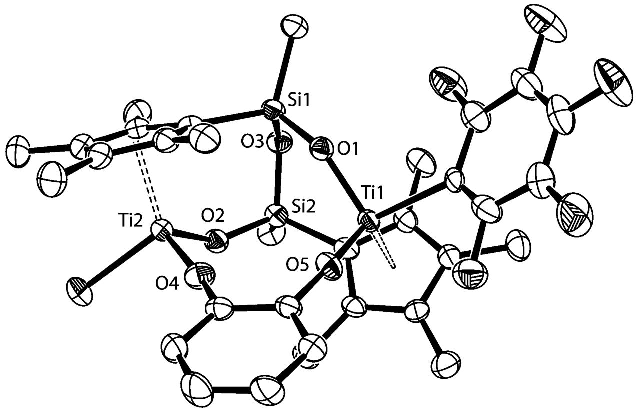


Fig. 3 ORTEP diagrams of $[(TiCl)\{Ti(C_6F_5)\}(\mu\text{-}O_2L)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (**7**). Hydrogen atoms have been omitted and thermal ellipsoids are shown at the 30% level.

atoms is bound to one η^5-C_5R_4Si ring and to one oxygen atom κ-*O* of the different bridges. One additional oxygen atom also links both bridges through a Si–O–Si system, retaining the initial geometry of compound **A**. Furthermore, both Ti atoms are also bridged by a chelating ethyleneglycolate (**1a**) or catecholate (**1b**, **7**) ligands, located opposite to the Si–O–Si bridge. The environment about each Ti atom corresponds to the typical pseudo-tetrahedral geometry found in such compounds and the coordination sphere of each Ti atom is completed by one Cl ligand (**1a**, **1b**) or one Cl and one C_6F_5 group (**7**).

The bond distances and angles within the $[Ti_2(\mu\text{-}\{\eta^5\text{-}C_5Me_4SiMeO\}_2)]$ moiety are very similar to **1a**, **1b**, **7** and **A** and are also close to those found for related Si–O–Ti bridged dinuclear compounds $[(TiCl_2)_2(\mu\text{-}\{\eta^5\text{-}C_5R_4SiMe_2O\}_2)]$ (R = H[32] **B**, Me[39] **C**) and $[(TiMe_2)_2(\mu\text{-}CH_2)(\mu\text{-}\{\eta^5\text{-}C_5Me_4SiMe_2O\}_2)]$[40] (**D**), with the exception of the Ti(1)–O–Si(1) angle which is clearly smaller for **1a**, **1b**, **7**, **A**, due to the bridging Si–O–Si system. The tightening of this angle is also observed in the methylidene-bridged derivative **D**. The presence of the dialkoxo bridge in complexes **1a**, **1b** and **7** causes both Ti atoms to be closer compared with **A**, **B** and **C**, although it was smaller than that observed for compound **D** with a shorter one-atom methylidene bridge.

A striking structural feature for all of these complexes is the disposition of the cyclopentadienyl rings. While for complexes

Table 1 Selected bond distances (Å) and angles (°) of compounds **1a·0.5C$_6$H$_{14}$**, **1b**, **7**, [(TiCl$_2$)$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (**A**), [(TiCl$_2$)$_2$(μ-{η^5-C$_5$R$_4$SiMe$_2$O}$_2$)] (R = H **B**,[32] Me **C**[39]) and [(TiMe$_2$)$_2$(μ-CH$_2$)(μ-{η^5-C$_5$Me$_4$SiMe$_2$O}$_2$)][40] (**D**)

Complex	1a·0.5C$_6$H$_{14}$	1b	7	A	B	C	D
Ti(1)–O(1)	1.857(3)	1.837(2)	1.843(3)	1.803(1)	1.767(2)	1.771(4)	1.827(1)
Si(1)–O(1)	1.640(3)	1.644(2)	1.645(3)	1.643(1)	1.653(1)	1.650(4)	1.640(1)
Si(1)–O(3)	1.655(3)	1.660(2)	1.658(3)	1.640(1)			
Ti···Cp	2.061	2.056	2.049	2.038	2.026	2.031	2.058
Ti···Ti	4.467	4.479	4.434	5.193	5.255	5.099	3.371
Si···Si	2.864	2.891	2.889	2.845	4.700	4.829	4.535
Ti(1)–O(1)–Si(1)	148.98(18)	149.03(12)	147.47(17)	147.96(9)	160.2(1)	159.8(2)	150.09(7)
Ti(2)–O(2)–Si(2)	146.65(17)	143.59(12)	147.56(16)				
PCp···O[a]	1.005	0.828	0.931	0.463	0.631	1.047	1.625
Si(1)–O(3)–Si(2)	119.06(16)	121.12(11)	120.83(16)	120.2(1)			
C–Si(1)–O(1)	109.02(16)	108.04(11)	100.96(19)	108.63	106.40	108.29	107.21
Ti(2)–O(4)	1.778(3)	1.810(2)	1.813(3)				
Ti(1)–O(5)	1.794(3)	1.818(2)	1.815(3)				
Ti(1)–O(5)–C	158.0(3)	166.61(19)	169.6(3)				
Ti(2)–O(4)–C	162.1(3)	163.73(19)	165.8(3)				
O(5)–C(1)–C(2)	110.5(3)	119.8(12)	119.7(3)				
PCp–PCp[a]	50.60	43.11	44.70	29.06	0.000	0.000	28.78

[a] PCp stands for the plane containing the cyclopentadienyl ring and PCp–PCp corresponds to the angle formed by planes containing both cyclopentadienyl ligands.

B and **C** the planes containing the cyclopentadienyl ligands are parallel, for **A** and **D**, with one additional bridge between the Si and Ti atoms respectively, they form an angle of about 30°. Furthermore, the presence of the dialkoxo bridge between the Ti atoms in complexes **1a**, **1b** and **7** forces this angle to open, also noting an increasing value from **1b** and **7**, with the planar phenylenedialkoxo bridge, with respect to the ethylenedialkoxo-bridged compound **1a**.

The molecular structures of all of these complexes (**1a**, **1b**, **7**, **A–D**) resembles that of the dinuclear derivative [(TiCl$_2$)$_2$(μ-{(η^5-C$_5$H$_4$B{NHMe$_2$}O)$_2$(μ-O)})].[41] In this last case, the smaller size of the boron atom favours the approximation of both Ti atoms to a value (4.647 Å) similar to those observed in the alkoxo-bridged compounds **1a**, **1b** and **7**, although the angle between the cyclopentadienyl rings of 27.60° is comparable with that of **A**, without dialkoxo bridges.

Polymerization of ε-caprolactone (ε-CL)

The dinuclear dialkoxo-bridged **1a** and **1b** and tetraalkoxo **4** and the mononuclear trialkoxo [TiCp*(O*i*Pr)$_3$] (**E**) complexes were tested as catalysts for the polymerization of ε-CL (Table 2). Whereas no activity was observed for the chloro derivatives **1a** and **1b**, the alkoxo complexes **4** and **E** displayed parallel behaviour in the polymerization conditions, the yield obtained at 100 °C was lower (*ca.* 13%) than that at 140 °C (*ca.* 75%). The results observed with compound **E** were also are very similar to those reported for [TiCp(O*i*Pr)$_3$].[42]

These polymers showed a striking difference among themselves with respect to their molecular weight, which for the dinuclear compound **4** was close to twice the molecular weight of PCL obtained with the mononuclear derivative **E**. Probably, in the dinuclear compound **4** the proximity of both titanium atoms allows polymerization at only one of them, with the other titanium atom blocked by the growing chain. Similar behaviour was described for a titanium–aluminium dinuclear compound.[43]

Activation of ε-CL with complexes **4** and **E** proceeded in both cases by cleavage of the acyl–oxygen bond, confirmed by ^{1}H NMR spectroscopy with the resonances at about δ 5.0 and δ 1.3 ascribed to an ester isopropoxy group.[16–23]

Conclusions

The dinuclear compound with Ti–O–Si and Si–O–Si bridges [(TiCl$_2$)$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] reacts with dilithium salts or diols to give the new dinuclear complexes with bridging dialkoxo ligands [(TiCl)$_2$(μ-O$_2$L)(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (O$_2$L = OCH$_2$CH$_2$O **1a**, 1,2-O$_2$C$_6$H$_4$ **1b**, 1,2-(OCH$_2$)$_2$C$_6$H$_4$ **1c**, O$_2$SiPh$_2$ **1d**). These complexes are stable and are also obtained in good yield for the four-membered bridged derivatives **1a** and **1b**.

Table 2 ε-CL polymerization with complexes [{Ti(O*i*Pr)$_2$}$_2$(μ-{(η^5-C$_5$Me$_4$SiMeO)$_2$(μ-O)})] (**4**) and [TiCp*(O*i*Pr)$_3$] (**E**)[a]

Run	Complex	*T*/°C	PCL/g	Yield (%)	Mw[b]/10^4	Mw/Mn[b]
1	**E**	100	0.14	14	—	—
2	**4**	100	0.12	12	—	—
3	**E**	140	0.76	76	1.63	1.11
4	**4**	140	0.75	75	2.95	1.24

[a] Polymerization conditions: dinuclear complexes [**4**] = 0.04 mmol and mononuclear complex [E] = 0.08 mmol, toluene (5 mL), 1 g ε-caprolactone, [ε-caprolactone]/[*n*Ti] = 110 (*n* = number of titanium atoms per molecule). [b] Determined by GPC in THF *vs.* polystyrene standard.

The reactivity of the chloro derivatives **1a** and **1b** toward $Al(C_6F_5)_3$ depends on the type of bridging dialkoxo ligand, the ethyleneglycolate bridge is totally transferred to aluminium whereas substitution of one chloro ligand is preferred for the catecholate-bridged compound **1b**. This difference is attributed to the lesser accessibility of the π electrons of the oxygen atoms in this last type of bridging group, due to higher arene ring acidity, which should hinder the interaction with the Lewis acid.

Reactions of the corresponding benzyl derivatives $[(TiBz)_2(\mu\text{-}O_2L)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ ($O_2L = OCH_2CH_2O$ **3a**, 1,2-$O_2C_6H_4$ **3b**) with the Lewis acids $E(C_6F_5)_3$ (E = B, Al) showed behaviour that was also dependent on the dialkoxo bridge. In both cases, abstraction of one benzyl group occurred, although ^{19}F NMR spectroscopic measurements indicated the absence of ion-pairing for the ethyleneglycolate derivative whereas an ion-pairing interaction was observed for the catecholate compound. Again, this difference is attributed to the diverse donor ability of the bridging dialkoxo ligands.

Polymerization of ε-CL with the tetraalkoxo dinuclear compound $[\{Ti(O\textit{i}Pr)_2\}_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (**4**) and with the mononuclear derivative $[TiCp^*(O\textit{i}Pr)_3]$ (**E**) gave polycaprolactone in good yield at high temperature, while the chloro derivatives were inactive. The ε-CL was activated by the nucleophilic attack of an isopropoxo ligand on the acyl carbon atom, as was shown by ^1H NMR of the PCL.

Experimental section

General considerations

All manipulations were carried out under an argon atmosphere and solvents were purified from appropriate drying agents. NMR spectra were recorded at 400.13 (^1H), 376.70 (^{19}F) and 100.60 (^{13}C) MHz on a Bruker AV400. Chemical shifts (δ) are given in ppm. ^1H and ^{13}C resonances were measured relative to solvent peaks considering TMS = 0 ppm, meanwhile ^{19}F resonance were measured relative to external $CFCl_3$. Assignment of resonances was made from HMQC and HMBC NMR experiments. Elemental analyses were performed on a Perkin-Elmer 240C. $(HO)_2L$ ($(HO)_2L = HOCH_2CH_2OH$, 1,2-$(HO)_2C_6H_4$, 1,2-$(HOCH_2)_2C_6H_4$, $(HO)_2SiPh_2$) and LiO*i*Pr were purchased from Aldrich, degassed and stored under argon with molecular sieves ($HOCH_2CH_2OH$) or sublimed ($(HO)_2L$ = 1,2-$(HO)_2C_6H_4$, 1,2-$(HOCH_2)_2C_6H_4$, $(HO)_2SiPh_2$). $Li_2(OCH_2)_2$ was prepared by addition of 2 equiv. of LiBu to $HOCH_2CH_2OH$ in hexane. Compounds $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$,[36] $B(C_6F_5)_3$,[44] 0.5(toluene)·$Al(C_6F_5)_3$[45] and $[Ph_3C][B(C_6F_5)_4]$[46] were prepared by literature methods and $[TiCp^*(O\textit{i}Pr)_3]$[47] was prepared from $[TiCp^*Cl_3]$[48] and Li(O*i*Pr) in toluene.

$[(TiCl)_2(\mu\text{-}1,2\text{-}O_2C_2H_4)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (1a). A suspension of $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (0.60 g, 0.98 mmol) and $Li_2(OCH_2)_2$ (0.11 g, 1.47 mmol) was stirred in toluene (30 mL) for 5 h at ambient temperature. Afterwards, hexane (10 mL) was added and the solution was filtered. The yellow residue was extracted again into a mixture of solvents toluene–hexane (20 mL/10 mL). The volatiles were removed under vacuum, leaving a yellow solid (0.35 g, 60%). Data for **1a**: ^1H-NMR (C_6D_6): 0.39 (s, 6 H, Si*Me*), 1.72 (s, 6 H, $C_5\textit{Me}_4$), 2.17 (s, 6 H, $C_5\textit{Me}_4$), 2.25 (s, 6 H, $C_5\textit{Me}_4$), 2.30 (s, 6 H, $C_5\textit{Me}_4$), 3.54 (dd, 2 H, $^2J = 8$ Hz, $^3J = 2$ Hz, $O_2C_2\textit{H}_4$), 4.63 (dd, 2 H, $^2J = 8$ Hz, $^3J = 2$ Hz, $O_2C_2\textit{H}_4$); ^{13}C-NMR (C_6D_6): −0.6 (Si*Me*), 10.7, 13.4, 14.0 and 14.1 ($C_5\textit{Me}_4$), 75.8 ($O_2\textit{C}_2H_4$), 122.3, 129.3, 134.2, 134.9 and 136.3 ($\textit{C}_5Me_4$). Anal. Calcd for $C_{22}H_{34}O_5Si_2Ti_2Cl_2$ (600.57): C, 43.94; H, 5.66%. Found: C, 44.75; H, 5.36%.

$[(TiCl)_2(\mu\text{-}1,2\text{-}O_2C_6H_4)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (1b). A solution of $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (1.00 g, 1.63 mmol) in toluene (50 mL) was treated with two equivalents of NEt_3 (0.33 g, 3.26 mmol) and one equivalent of catechol (1,2-$(OH)_2C_6H_4$, 0.18 g, 1.63 mmol). The mixture was stirred overnight at ambient temperature. Hexane (30 mL) was then added and the solution was filtered. The red residue was extracted again into a mixture of solvents toluene–hexane (30 mL/20 mL). The volatiles were pumped off yielding **1b** as a red solid (0.90 g, 85%). Data for **1b**: ^1H-NMR (C_6D_6): 0.35 (s, 6 H, Si*Me*), 1.72 (s, 6 H, $C_5\textit{Me}_4$), 2.01 (s, 6 H, $C_5\textit{Me}_4$), 2.20 (s, 6 H, $C_5\textit{Me}_4$), 2.25 (s, 6 H, $C_5\textit{Me}_4$), 6.67 (m, 2 H, $O_2C_6\textit{H}_4$), 6.93 (m, 2 H, $O_2C_6\textit{H}_4$); ^{13}C-NMR (C_6D_6): −0.8 (Si*Me*), 11.0, 12.9, 13.4 and 14.2 ($C_5\textit{Me}_4$), 120.2, 122.9 and 155.6 (*Ci*) ($O_2\textit{C}_6H_4$), 123.4, 132.4, 134.5, 136.7 and 138.5 ($\textit{C}_5Me_4$). Anal. Calcd for $C_{26}H_{34}O_5Si_2Ti_2Cl_2$ (648.62): C, 48.10; H, 5.24%. Found: C, 49.06; H, 5.28%.

$[(TiCl)_2\{\mu\text{-}1,2\text{-}(OCH_2)_2C_6H_4\}(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (1c). A solution of $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (0.70 g, 1.14 mmol) in toluene (50 mL) was treated with two equivalents of NEt_3 (0.23 g, 2.28 mmol) and one equivalent of 1,2-benzenedimethanol (0.15 g, 1.14 mmol). The mixture was stirred overnight at ambient temperature. Hexane (30 mL) was added and the solution was filtered. The yellow residue was extracted again into a mixture of solvents toluene–hexane (30 mL/20 mL). The volatiles were pumped off yielding a yellow solid (0.20 g). The isolated solid consisted mainly of **1c**, but it contained some irremovable decomposition products, which prevented us from obtaining a correct elemental analysis, though satisfactory spectroscopy data were obtained. Data for **1c**: ^1H-NMR ($CDCl_3$): 0.33 (s, 6 H, Si*Me*), 1.96 (s, 6 H, $C_5\textit{Me}_4$), 2.06 (s, 6 H, $C_5\textit{Me}_4$), 2.22 (s, 6 H, $C_5\textit{Me}_4$), 2.26 (s, 6 H, $C_5\textit{Me}_4$), 5.50 (d, 2 H, ^2J = 12 Hz, $(OC\textit{H}_2)_2C_6H_4$), 5.33 (d, 2 H, ^2J = 12 Hz, $(OC\textit{H}_2)_2C_6H_4$), 7.32 (bs, 4 H, $(OCH_2)_2C_6\textit{H}_4$); ^{13}C-NMR ($CDCl_3$): −1.0 (Si*Me*), 11.2, 13.3, 13.7 and 13.9 ($C_5\textit{Me}_4$), 64.2 ($(O\textit{C}H_2)_2C_6H_4$), 123.4, 132.4, 134.5 and 136.1 ($\textit{C}_5Me_4$), 129.0, 131.3 and 139.3 (C_i) ($(OCH_2)_2\textit{C}_6H_4$).

$[(TiCl)_2(\mu\text{-}O_2SiPh_2)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (1d). A solution of $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (0.20 g, 0.32 mmol) in dichloromethane (20 mL) was treated with two equivalents of NEt_3 (0.06 g, 0.64 mmol) and one equivalent of $(HO)_2SiPh_2$ (0.08 g, 0.32 mmol). The mixture was stirred for three days at ambient temperature. The volatiles were then pumped off and the remaining solid was extracted into a mixture of solvents toluene–hexane (20 mL/10 mL). The volatiles were pumped off yielding a yellow solid (0.10 g). The isolated solid consisted mainly of **1d**, but it contained some irremovable decomposition products, which prevent us from obtaining correct elemental analysis, though satisfactory spectroscopy data were obtained. Data for **1d**: ^1H-NMR ($CDCl_3$): 0.43 (s, 6 H, Si*Me*), 1.81 (s, 6 H, $C_5\textit{Me}_4$), 1.95 (s, 6 H, $C_5\textit{Me}_4$), 2.32 (s, 6 H, $C_5\textit{Me}_4$), 2.36 (s, 6 H,

C_5Me_4), 7.30 (m, 6 H, C_6H_5), 7.63 (m, 4 H, C_6H_5); ^{13}C-NMR ($CDCl_3$): −0.8 (Si*Me*), 11.4, 13.3, 14.3 and 15.7 (C_5Me_4), 122.2, 135.2, 137.1, 138.3 and 138.6 (C_5Me$_4$), 127.7, 129.84, 134.3 and 133.1 (C_i) (C_6H$_5$).

[(TiMe)$_2$(μ-1,2-$O_2C_2H_4$)(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (2a). A solution of **1a** (0.56 g, 0.93 mmol) in diethyl ether (40 mL) at −78 °C was treated with two equivalents of a solution of LiMe (1,5 M, 1.24 mL, 1.86 mmol). The reaction mixture was warmed to room temperature and stirred overnight. 10 mL of hexane was then added and the solution was filtered. The yellow residue was extracted again into a mixture of solvents diethyl ether–hexane (20 mL/10 mL). The volatiles were pumped off to give a mixture of compounds **2a** and [(TiMe$_2$)$_2$(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (0.36 g) in 3 : 1 molar ratio. Data for **2a**: ^{1}H-NMR (C_6D_6): 0.45 (s, 6 H, Si*Me*), 0.82 (s, 6 H, *Me*-Ti), 1.67 (s, 6 H, C_5Me_4), 1.98 (s, 6 H, C_5Me_4), 2.20 (s, 6 H, C_5Me_4), 2.47 (s, 6 H, C_5Me_4), 3.70 (dd, 2 H, ^2J = 8 Hz, ^3J = 2 Hz, $O_2C_2H_4$), 4.67 (dd, 2 H, ^2J = 8 Hz, ^3J = 2 Hz, $O_2C_2H_4$); ^{13}C-NMR (C_6D_6): 0.1 (Si*Me*), 10.7, 11.9, 13.7 and 13.9 (C_5Me_4), 44.7 (*Me*-Ti), 74.3 ($O_2C_2H_4$), 116.6, 126.0, 127.4, 128.8 and 130.8 (C_5Me$_4$).

[(TiMe)$_2$(μ-1,2-$O_2C_6H_4$)(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (2b). The same procedure described aboved for **2a** was applied by using **1b** (0.30 g, 0.46 mmol) and LiMe (1.5 M, 0.60 mL, 0.92 mmol) to give **2b** as a yellow solid (0.22 g, 80%). Data for **2b**: ^{1}H-NMR (C_6D_6): 0.43 (s, 6 H, Si*Me*), 1.03 (s, 6 H, *Me*-Ti), 1.64 (s, 6 H, C_5Me_4), 2.02 (s, 6 H, C_5Me_4), 2.16 (s, 12 H, C_5Me_4), 6.74 (m, 2 H, $O_2C_6H_4$), 6.82 (m, 2 H, $O_2C_6H_4$); ^{13}C-NMR (C_6D_6): −0.1 (Si*Me*), 10.7, 11.9, 12.6 and 14.0 (C_5Me_4), 48.7 (*Me*-Ti), 117.3, 129.1, 129.5, 130.2 and 131.0 (C_5Me$_4$), 120.2, 121.5 and 155.3 (C_i) (O_2C_6H$_4$). Anal. Calcd for $C_{28}H_{40}O_5Si_2Ti_2$ (607.72): C, 55.28; H, 6.58%. Found: C, 54.67; H, 5.84%.

[(TiBz)$_2$(μ-1,2-$O_2C_2H_4$)(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (3a). BzMgCl (2 M, 1.66 mL, 3.32 mmol) was injected to a solution of **1a** (1.00 g, 1.66 mmol) in diethyl ether (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. 10 mL of hexane were added and the solution was filtered. The red residue was extracted again into a mixture of solvents diethyl ether–hexane (30 mL/20 mL). The volatiles were pumped off and the remaining solid was washed with 10 mL of hexane to isolate **1c** as a red solid (0.71 g, 60%). Data for **3a**: ^{1}H-NMR (C_6D_6): 0.45 (s, 6 H, Si*Me*), 1.62 (s, 6 H, C_5Me_4), 1.79 (s, 6 H, C_5Me_4), 1.84 (s, 6 H, C_5Me_4), 1.97 (d, 2 H, ^2J = 10 Hz, PhC*H*$_2$-Ti), 2.10 (d, 2 H, ^2J = 10 Hz, PhC*H*$_2$-Ti), 2.18 (s, 6 H, C_5Me_4), 3.51 (dd, 2 H, ^2J = 8 Hz, ^3J = 2 Hz, $O_2C_2H_4$), 4.05 (dd, 2 H, ^2J = 8 Hz, ^3J = 2 Hz, $O_2C_2H_4$), 6.82–7.23 (m, 10 H, *Ph*CH$_2$Ti); ^{13}C-NMR (C_6D_6): −0.2 (Si*Me*), 10.5, 11.4, 13.2 and 14.1 (C_5Me_4), 73.8 (Ph*C*H$_2$–Ti), 74.0 (O_2C_2H$_4$), 121.8, 127.5, 128.9, 152.0 (C_i) (*Ph*CH$_2$Ti) 117.3, 126.1, 127.2, 130.1 and 130.9 (C_5Me$_4$). Anal. Calcd for $C_{36}H_{48}O_5Si_2Ti_2$ (711.67): C, 60.70; H, 6.74%. Found: C, 60.94; H, 6.62%.

[(TiBz)$_2$(μ-1,2-$O_2C_6H_4$)(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (3b). The same procedure described above for **3a** was applied by using **1b** (0.40 g, 0.61 mmol) and MgClBz (2 M, 0.62 mL, 1.22 mmol) to give **3b** as an orange solid (0.28 g, 60%). Data for **3b**: ^{1}H-NMR (C_6D_6): 0.42 (s, 6 H, Si*Me*), 1.49 (s, 6 H, C_5Me_4), 1.59 (s, 6 H, C_5Me_4), 1.88 (s, 6 H, C_5Me_4), 2.17 (s, 6 H, C_5Me_4), 2.20 (d, 2 H, ^2J = 10 Hz, PhC*H*$_2$-Ti), 2.26 (d, 2 H, ^2J = 10 Hz, PhC*H*$_2$-Ti), 6.79 (bs, 4 H, $O_2C_6H_4$), 7.01–7.22 (m, 10 H, C_6H_5); ^{13}C-NMR (C_6D_6): −0.5 (Si*Me*), 10.6, 11.5, 11.9 and 14.0 (C_5Me_4), 77.5 (Ph*C*H$_2$Ti), 120.0, 121.3, 122.5, 127.0, 129.2, 149.9 (C_i, *Ph*CH$_2$Ti) and 154.8 (C_i, O_2C_6H$_4$) (C_6H$_5$, O_2C_6H$_4$), 120.0, 126.1, 128.8, 130.8 and 131.8 (C_5Me$_4$). Anal. Calcd for $C_{40}H_{48}O_5Si_2Ti_2$ (759.72): C, 63.18; H, 6.31%. Found: C, 62.69; H, 5.83%.

[{Ti(O*i*Pr)$_2$}$_2$(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (4). Toluene (25 mL) was added to a mixture of [(TiCl$_2$)$_2$(μ-{(η^5-C_5Me_4-SiMeO)$_2$(μ-O)})] (0.33 g, 0.53 mmol) and LiO*i*Pr (0.18 g, 2.65 mmol) at −78 °C. The cooling bath was removed and the reaction mixture was allowed to warm to ambient temperature and further stirred overnight. 10 mL of hexane was then added and the solution was filtered. The volatiles were pumped off to yield **4** as a yellow solid (0.29 g, 80%). Data for **4**: ^{1}H-NMR ($CDCl_3$): 0.26 (s, 6 H, Si*Me*), 1.12 (m, 24 H, *Me*$_2$CH), 2.03 (s, 6 H, C_5Me_4), 2.05 (s, 6 H, C_5Me_4), 2.21 (s, 6 H, C_5Me_4), 2.22 (s, 6 H, C_5Me_4), 4.68 (m, 4 H, Me$_2$C*H*); ^{13}C-NMR ($CDCl_3$): −0.7 (Si*Me*), 11.9, 12.0, 13.7 and 14.0 (C_5Me_4), 25.7 (Me$_2$*C*H), 26.1, 26.4, 26.5 and 26.7 (*Me*$_2$CH), 118.8, 127.6, 127.7, 129.4 and 129.7 (C_5Me$_4$). Anal. Calcd for $C_{32}H_{58}O_7Si_2Ti_2$ (705.72): C, 54.41; H, 8.21%. Found: C, 53.86; H, 7.95%.

[{TiCl(C_6F_5)}$_2$(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (5). Compounds **1a** (0.040 g, 0.06 mmol) and (0.5toluene)·Al(C_6F_5)$_3$ (0.038 g, 0.06 mmol) were stirred in toluene (2 mL) for 12 h. The solution was filtered and the volatiles were removed under vacuum leaving an oil that was washed with hexane (2 × 2 mL) to give **5** as a yellow solid (0.031 g, 60%). Data for **5**: ^{1}H-NMR (C_6D_6) 0.33 (s, 6 H, Si*Me*), 1.98 (s, 6 H, C_5Me_4), 2.04 (s, 6 H, C_5Me_4), 2.15 (s, 6 H, C_5Me_4), 2.39 (s, 6 H, C_5Me_4); ^{13}C-NMR (C_6D_6): −2.0 (Si*Me*), 12.8, 13.3, 15.1 and 15.9 (C_5Me_4), 119.3, 138.7, 139.1, 141.3 and 144.7 (C_5Me$_4$), 139.2, 145.4 and 150.1 (m, C_6F$_5$); ^{19}F-NMR (C_6D_6): −120.1 (o-C_6F_5), −153.4 (p-C_6F_5), −162.3 (m-C_6F_5). Anal. Calcd for $C_{32}H_{30}O_3Si_2Ti_2Cl_2F_{10}$ (874.50): C, 43.91; H, 3.43%. Found: C, 43.99; H, 4.11%.

Reaction of 1b with Al(C_6F_5)$_3$. Formation of [(TiCl)$_2$(μ-1,2-$O_2C_6H_4$){μ-({η^5-C_5Me_4SiMeO}$_2${μ-O·Al(C_6F_5)$_3$})}] (6) and [(TiCl){Ti(C_6F_5)}(μ-1,2-$O_2C_6H_4$)(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (7). A solution of [(TiCl)$_2$(μ-1,2-$O_2C_6H_4$)(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (**1b**) (0.020 g, 0.03 mmol) in C_6D_6 in a NMR tube was treated with one equivalent of 0.5(toluene)·Al(C_6F_5)$_3$ (0.017 g, 0.03 mmol). The reaction was immediately monitored by NMR spectroscopy, showing a complete transformation into **6** after 5 min. The solution of **6** evolved to a mixture of **7** and **5** in *ca.* 2 : 1 after two days at ambient temperature. Data for **6**: ^{1}H-NMR (C_6D_6): 0.31 (s, 6 H, Si*Me*), 1.64 (s, 6 H, C_5Me_4), 1.84 (s, 6 H, C_5Me_4), 2.03 (s, 6 H, C_5Me_4), 2.19 (s, 6 H, C_5Me_4), 6.65 (m, 2 H, $O_2C_6H_4$), 6.78 (m, 2 H, $O_2C_6H_4$); ^{13}C-NMR (C_6D_6): −1.7 (Si*Me*), 10.9, 12.6, 13.1 and 14.1 (C_5Me_4), 119.9, 123.9 and 154.9 (C_i) (O_2C_6H$_4$), 122.3, 132.4, 135.2, 137.8, 141.1 (C_5Me$_4$), 137.2, 141.3 and 150.9 (m, C_6F$_5$); ^{19}F-NMR (C_6D_6): −121.1 (o-C_6F_5), −151.2 (p-C_6F_5), −160.7 (m-C_6F_5). Data for **7**: ^{1}H-NMR (C_6D_6): 0.40 (s, 3 H, Si*Me*), 0.48 (s, 3 H, Si*Me*), 1.40 (s, 3 H, C_5Me_4), 1.69 (s, 3 H, C_5Me_4), 1.71 (s, 3 H, C_5Me_4), 1.93 (s, 3 H, C_5Me_4), 2.03 (s, 3 H, C_5Me_4), 2.19 (s, 3 H, C_5Me_4), 2.25 (s, 3 H, C_5Me_4), 2.26 (s, 3 H, C_5Me_4), 6.95–7.23 (m, 4 H, $O_2C_6H_4$);

Table 3 Crystal data and structure refinement details for **$1a\cdot0.5C_6H_{14}$**, **1b** and **7**

	$1a\cdot0.5C_6H_{14}$	**1b**	**7**
Formula	$C_{25}H_{41}Cl_2O_5Si_2Ti_2$	$C_{26}H_{34}Cl_2O_5Si_2Ti_2$	$C_{32}H_{34}ClF_5O_5Si_2Ti_2$
FW	644.46	649.41	781.02
Color/habit	Yellow/block	Red/prism	Orange/prism
Cryst. dimensions/mm	0.48 × 0.43 × 0.36	0.49 × 0.35 × 0.31	0.45 × 0.20 × 0.10
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	17.207(5)	14.112(3)	11.597(4)
b/Å	11.438(3)	10.4098(7)	17.888(3)
c/Å	17.691(3)	21.228(3)	16.826(5)
β/°	116.591(10)	104.083(14)	95.61(2)
V/Å^3	3113.5(14)	3024.7(8)	3473.8(15)
Z	4	4	4
T/K	200	200	200
ρ_c/g cm^{-3}	1.375	1.426	1.493
μ/mm^{-1}	0.793	0.817	0.671
F(000)	1348	1344	1600
θ range/°	3.56–27.51	3.15–27.50	3.53–27.50
no. of rflns collected	67211	21976	70795
no. of indep. rflns/R_{int}	7118/0.0667	6948/0.0674	7957/0.1090
no. of obsd rflns ($I > 2\sigma(I)$)	5599	4787	4936
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0646/0.1616	0.0441/0.1067	0.0583/0.1427
R_1, wR_2 (all data)[a]	0.0799/0.1711	0.0808/0.1184	0.1132/0.1613
Extinction coefficient	0.058(3)		0.0080(9)
GOF (on F^2)[a]	1.089	1.039	1.046
Largest diff. peak/hole/e Å^{-3}	+0.664/−0.617	0.549/−0.437	+0.495/−0.539

^{19}F-NMR (C_6D_6): −114.7 (o-C_6F_5), −154.3 (p-C_6F_5), −162.1 (m-C_6F_5).

[Ti(TiBz)(μ-1,2-$O_2C_2H_4$)(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})][BzB-(C_6F_5)$_3$] (8B). A solution of **3a** (0.100 g, 0.14 mmol) and B(C_6F_5)$_3$ (0.071 g, 0.14 mmol) in CH_2Cl_2 (2 mL) were stirred for 5 min. The volatiles were removed under vacuum leaving an oil that was washed with hexane (2 × 2 mL) to give **8B** as an orange solid (0.146 g, 85%). Data for **8B**: ^{1}H-NMR (CD_2Cl_2): 0.47 (s, 3 H, Si*Me*), 0.54 (s, 3 H, Si*Me*), 1.77 (s, 3 H, C_5*Me$_4$*), 1.84 (s, 3 H, C_5*Me$_4$*), 2.05 (s, 3 H, C_5*Me$_4$*), 2.09 (s, 3 H, C_5*Me$_4$*), 2.26 (s, 3 H, C_5*Me$_4$*), 2.27 (s, 3 H, C_5*Me$_4$*), 2.34 (s, 6 H, C_5*Me$_4$*), 2.71 (d, 1 H, ^2J = 12 Hz, PhC*H$_2$*-Ti), 2.77 (bs, 2 H, PhC*H$_2$*-B), 3.15 (d, 1 H, ^2J = 12 Hz, PhC*H$_2$*-Ti), 3.40 (m, 1 H, O_2C_2*H$_4$*), 3.70 (m, 2 H, O_2C_2*H$_4$*), 4.25 (m, 1 H, O_2C_2*H$_4$*), 6.70–7.26 (m, 10 H, C_6*H$_5$*); ^{13}C-NMR (CD_2Cl_2): −1.5 (Si*Me*), −0.8 (Si*Me*), 12.1, 12.4, 13.2, 13.5, 15.1, 15.9, 16.3 and 17.0 (C_5*Me$_4$*), 31.9 (Ph*C*H$_2$–B), 68.8 and 77.4 (O_2*C$_2$*H$_4$), 95.0 (Ph*C*H$_2$–Ti), 121.9 (*C$_i$*), 122.7, 126.2 (*C$_i$*), 126.4 (*C$_i$*), 126.5, 126.8, 127.0, 128.7 (*C$_i$*), 128.9, 129.3, 129.9, 131.7 (*C$_i$*), 135.8 (*C$_i$*), 137.4 (*C$_i$*), 138.3 (*C$_i$*), 141.3 (*C$_i$*), 141.40 (*C$_i$*), 149.24 (*C$_i$*), 151.03 (*C$_i$*) (*Ph*CH$_2$–B, *C$_5$*Me$_4$, *Ph*CH$_2$–Ti); ^{19}F-NMR (CD_2Cl_2): −127.9 (o-C_6F_5), −161.5 (p-C_6F_5), −164.4 (m-C_6F_5). Anal. Calcd for $C_{54}H_{48}O_5Si_2Ti_2BF_{15}$ (1223.20): C, 52.96; H, 3.92%. Found: C, 53.50; H, 4.21%.

[Ti(TiBz)(μ-1,2-$O_2C_2H_4$)(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})]-[BzAl(C_6F_5)$_3$] (8Al). Compounds **3a** (0.020 g, 0.02 mmol) and 0.5(toluene)·Al(C_6F_5)$_3$ (0.032 g, 0.04 mmol) were loaded into a NMR tube and 0.5 mL of CD_2Cl_2 was added. The tube was then shaken vigorously and the reaction was monitored by NMR spectroscopy at 25 °C, formation of **8Al** occurred immediately. Data for **8Al**: ^{1}H-NMR (CD_2Cl_2): 0.62 (s, 3 H, Si*Me*), 0.69 (s, 3 H, Si*Me*), 1.36 (s, 3 H, C_5*Me$_4$*), 1.71 (s, 3 H, C_5*Me$_4$*), 2.00 (s, 3 H, C_5*Me$_4$*), 2.06 (s, 3 H, C_5*Me$_4$*), 2.24 (s, 3 H, C_5*Me$_4$*), 2.32 (s, 3 H, C_5*Me$_4$*), 2.36 (s, 3 H, C_5*Me$_4$*), PhC*H$_2$*-Al was not observed, 2.47 (d, 1 H, ^2J = 12 Hz, PhC*H$_2$*-Ti), 2.89 (s, 3 H, C_5*Me$_4$*), 3.36 (d, 1 H, ^2J = 12 Hz, PhC*H$_2$*-Ti), 3.79 (m, 1 H, O_2C_2*H$_4$*), 3.91 (m, 1 H, O_2C_2*H$_4$*), 4.62 (m, 2 H, O_2C_2*H$_4$*), 6.81–7.42 (m, 10 H, C_6*H$_5$*); ^{13}C-NMR (CD_2Cl_2): −2.0 (Si*Me*), −1.9 (Si*Me*), 11.5, 12.3, 12.6, 12.9, 13.8, 15.9, 16.4 and 16.6 (C_5*Me$_4$*), PhCH$_2$–Al was not observed, 67.2 and 75.2 (O_2*C$_2$*H$_4$), 99.4 (Ph*C*H$_2$–Ti), 120.6 (*C$_i$*), 121.7 (*C$_i$*), 126.8, 126.9 (*C$_i$*), 127.4, 127.5 (*C$_i$*), 127.8 (*C$_i$*), 129.8, 129.8 (*C$_i$*), 130.2, 130.2 (*C$_i$*) and 133.3 (*Ph*CH$_2$–Al, *C$_5$*Me$_4$, *Ph*CH$_2$–Ti); ^{19}F-NMR (CD_2Cl_2): −120.1 (o-C_6F_5), −155.8 (p-C_6F_5), −161.7 (m-C_6F_5).

[Ti(TiBz)(μ-1,2-$O_2C_6H_4$)(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})][BzB-(C_6F_5)$_3$] (9B). 0.5 mL of CD_2Cl_2 previously cooled at −78 °C were added to a mixture of **3b** (0.030 g, 0.03 mmol) and B(C_6F_5)$_3$ (0.025 g, 0.03 mmol) in a NMR tube cooled at −78 °C. The NMR spectra, run at −20 °C, showed formation of **9B** as the only product. Data for **9B**: ^{1}H-NMR (CD_2Cl_2): 0.26 (s, 3 H, Si*Me*), 0.37 (s, 3 H, Si*Me*), 1.42 (s, 3 H, C_5*Me$_4$*), 1.47 (s, 3 H, C_5*Me$_4$*), 1.91 (s, 3 H, C_5*Me$_4$*), 1.93 (s, 3 H, C_5*Me$_4$*), 2.12 (s, 3 H, C_5*Me$_4$*), 2.17 (bs, 1 H, PhC*H$_2$*-Ti), 2.24 (s, 3 H, C_5*Me$_4$*), 2.29 (s, 3 H, C_5*Me$_4$*), 2.41 (bs, 2 H, PhC*H$_2$*-Ti), 2.46 (s, 3 H, C_5*Me$_4$*), 2.71 (bs, 1 H, Ph*CH$_2$*-B), 6.70–7.20 (m, 10 H, C_6*H$_5$*, O_2C_6*H$_4$*); ^{13}C-NMR (CD_2Cl_2): −2.1 (Si*Me*), −2.0 (Si*Me*), 11.2, 12.4, 13.1, 13.8, 14.7, 15.2, 15.8 and 16.6 (C_5*Me$_4$*), 38.4 (Ph*C*H$_2$–B), 80.2 (Ph*C*H$_2$–Ti), 120.1–140.3 (*C$_6$*H$_5$, *C$_6$*F$_5$, O_2*C$_6$*H$_4$, *C$_5$*Me$_4$); ^{19}F-NMR (CD_2Cl_2): −133.1 (o-C_6F_5), −158.4 (p-C_6F_5), −163.8 (m-C_6F_5).

Polymerization of ε-caprolactone with dinuclear complex 4. ε-Caprolactone (1 g) was added *via* syringe to a stirred solution of complex **4** (0.04 mmol) in toluene (5 mL), in a glove box. The polymerization mixture was stirred at the desired temperature. After the measured time interval, the flask was quenched by adding 5 mL of MeOH–HCl diluted. The quenched mixture was precipitated into 150 mL of methanol, stirred overnight, filtered, and washed with methanol. The polymer collected was dissolved in acetone, precipitated in methanol at 0 °C, filtered, and dried in a vacuum oven at 80 °C. A ^{1}H NMR ($CDCl_3$) spectrum of the polymer was obtained for an end group analysis. Gel permeation chromatography (GPC) analyses of polymer samples were carried out in THF as solvent at 25 °C (Varian HPLC) in Alcalá University.

Polymerization of ε-caprolactone with mononuclear complex [TiCp*(O*i*Pr)$_3$] (E). Polymerization was carried out as described above except a toluene solution of **E** (0.08 mmol) was used with the aim of introducing an equal number of metal centers into the solution in each experiment.

X-Ray structure determination of 1a·0.5C_6H_{14}, 1b and 7

Suitable single crystals of **1a·0.5C_6H_{14}**, **1b** and **7** for the X-ray diffraction study were selected. Data collection for was performed at 200(2) K, with the crystals covered in perfluorinated ether. The crystals were mounted on a Bruker-Nonius Kappa CCD single crystal diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Multiscan[49] absorption correction procedures were applied to the data. The structures were solved, using the WINGX package,[50] by direct methods (SHELXS-97) and refined by using full-matrix least-squares against F^2 (SHELXL-97).[51] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. Also in **1a** a molecule of hexane crystallized with every two molecules of the compound. This solvent molecule was found in the difference Fourier map but was very disordered and it was not possible to get a chemical sensible model for it, so Squeeze procedure[52] was used to remove its contribution to the structure factors. Relevant crystallographic data and details of the refinements for the three structures are given in Table 3. CCDC 708809 (**1a·0.5C_6H_{14}**), CCDC 708810 (**1b**) and CCDC 708811 (**7**) contain the supplementary crystallographic data for this paper. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b820092k

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