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Interaction between $TiCl_4$ and *o*-, *m*- and *p*-diesters. The crystal structures of $[o\text{-}C_6H_4(COO\text{-}i\text{-}Bu)_2TiCl_4] \cdot CH_2Cl_2$ and $[p\text{-}C_6H_4(COOMe)_2TiCl_4]$

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Abstract

The crystal structures of $[o\text{-}C_6H_4(COO\text{-}i\text{-}Bu)_2TiCl_4] \cdot CH_2Cl_2$, I, and $[(\mu\text{-}Cl)_2\{\mu\text{-}p\text{-}C_6H_4(COOMe)_2\}Cl_6Ti_2]_\infty$, II, which in the presence of activators are good catalysts for olefin polymerization, have been determined by X-ray diffraction methods and the data refined by full-matrix least-squares techniques to $R = 0.049$ and $R = 0.028$ for 1511 and 1549 independent non-zero reflections for I and II, respectively. Crystals of I are orthorhombic, space group $P2_12_12_1$ with 4 molecules in a unit cell of dimensions $a = 14.408(6)$, $b = 13.717(7)$, $c = 12.486(5)$ Å. Crystals of II are monoclinic, space group $P2_1/n$, with four molecules in cell with $a = 8.474(5)$, $b = 13.130(7)$, $c = 9.362(7)$ Å and $\beta = 109.12(5)°$. The Ti atoms in I are octahedrally coordinated by four chlorine atoms and two carbonyl oxygen atoms of di-iso-butyl *o*-phthalate. The chelating ligand atoms and the titanium atom together form a seven-membered ring. Compound II in crystalline state is a linear polymer formed by the dimeric units $Cl_3Ti(\mu\text{-}Cl)_2TiCl_3$ connected together by two carbonyl oxygen atoms of $p\text{-}C_6H_4(COOMe)_2$.

Introduction

Polymerization studies have revealed that the interaction of aromatic esters with the Ziegler–Natta catalyst ensures high isotacticity. The enhancement of isospecific activity is strongly dependent on the nature of the esters although the initial activity of the catalyst with *o*-, *m*- or $p\text{-}C_6H_4(COOMe)_2$ is similar. However, after about 20–30 min, the activity of the catalyst with *m*- or $p\text{-}C_6H_4(COOR)_2$ declines steadily [1]. However, the activity of the catalyst with diethyl *o*-phthalate is constant and its productivity is about twice as high [2–8]. To elucidate the differing behaviors of *o*-, *m*- or $p\text{-}C_6H_4(COOR)_2$ and the aromatic or aliphatic monoesters during the catalytic propylene polymerization process, the reaction between di-iso-butyl *o*-phthalate (DIBP) and dimethyl *p*-phthalate (DMPP) with $TiCl_4$ in the present

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paper was studied. Here we describe the crystal structure of $[o\text{-}C_6H_4(COO\text{-}i\text{-}Bu)_2TiCl_4] \cdot CH_2Cl_2$, I, and $[(\mu\text{-}Cl)_2\{\mu\text{-}p\text{-}C_6H_4(COOMe)_2\}Cl_6Ti_2]_\infty$, II.

Experimental

All reactions were carried out under N_2 in dried solvents with Schlenk-tube techniques. Anhydrous $TiCl_4$ was commercial material. The DIBP and DMPP were prepared by standard procedures by the reactions of *o*-phthalic acid with isobutanol and terephthalic acid with methanol, respectively, in the presence of *p*-toluenesulfonic acid [9].

Tetrachloro(di-iso-butyl o*-phthalate)titanium(IV) dichloromethane (I)*

To 5 cm^3 of $TiCl_4$ (8.63 g; 45 mmol) was added dropwise 23.9 cm^3 (25.05 g; 90 mmol) of di-iso-butyl *o*-phthalate into 150 cm^3 n-hexane and stirred under N_2. After 1 h the yellow precipitate was filtered off and washed with n-hexane (3×15 cm^3), (95% yield).

Crystals suitable for the structure determination were grown by slow diffusion of n-hexane into a solution of the $[o\text{-}C_6H_4(COO\text{-}i\text{-}Bu)_2TiCl_4]$ in dichloromethane.

The IR spectrum of I shows the characteristic ν(C=O) bands at 1648 cm^{-1} (vs) and 1615 cm^{-1} (s) of a coordinated carbonyl group and ν(Ti–Cl) at 365 cm^{-1} (vs) and 400 cm^{-1} (s). The ^1H NMR and X-ray data reveal that the crystal is composed of $[o\text{-}C_6H_4(COO\text{-}i\text{-}Bu)_2TiCl_4]$ and uncoordinated CH_2Cl_2 molecules in a 1 : 1 ratio.

catena-*[{di-μ-chloro-μ-(dimethyl* p*-phthalate)hexachloro}titanium(IV)] (II)*

To 0.58 g of $p\text{-}C_6H_4(COOMe)_2$ (3 mmol) in 100 cm^3 1,2-dichloroethane was added dropwise 1.14 g (6 mmol) of $TiCl_4$ with stirring under N_2. The post-reaction mixture was heated under reflux up to complete dissolution of the precipitate. Then the solution was placed in a Dewar vessel for slow cooling. After 24 h the crystalline compound was filtered off and washed with n-hexane (3×5 cm^3). Yield 1.6 g; 93%.

The IR spectrum of II shows the stretching ν(C=O) at 1600 cm^{-1} (vs,br).

X-Ray crystal structure determination

Crystal data. $C_{16}H_{22}Cl_4O_4Ti \cdot CH_2Cl_2$, I, $M = 553.0$, $a = 14.408(6)$, $b = 13.717(7)$, $c = 12.486(5)$ Å, $U = 2468(2)$ Å^3, $D_m = 1.49$ g cm^{-3} $Z = 4$, $D_c = 1.488(2)$ g cm^{-3}, $F(000) = 1128$, space group $P2_12_12_1$, Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 10.24$ cm^{-1}, $T = 304(1)$ K. $C_{10}H_{10}Cl_8O_4Ti_2$, II, $M = 573.6$, $a = 8.474(5)$, $b = 13.130(7)$, $c = 9.362(7)$ Å, $\beta = 109.12(5)°$, $U = 984.2(12)$ Å^3, $D_m = 1.919$ g cm^{-3} $Z = 2$, $D_c = 1.935(3)$ g cm^{-3}, $F(000) = 564$, space group $P2_1/c$, Mo-K_α radiation, $\mu = 19.28$ cm^{-1}, $T = 303$ K.

The space groups for both crystals were uniquely determined from systematic absences in Weissenberg photographs. Suitable portions of dimensions $0.5 \times 0.5 \times 0.6$ mm for I, and $0.5 \times 0.5 \times 0.5$ mm for II were cut from large crystals and sealed in capillaries. The intensity data for both crystals were recorded on a Syntex $P2_1$ automated diffractometer with graphite-monochromatized Mo-K_α radiation. The intensities of two standard reflections, monitored after every 50 scans, showed ± 5 and ± 4% variation for I and II, respectively. 2895 reflections up to $2\theta = 50°$ for I and 1874 up to $2\theta = 52°$ for II were measured by $2\theta/\theta$ scan technique from which

Table 1

Final atomic parameters with esd's in parentheses for $[o\text{-}C_6H_4(COO\text{-}i\text{-}Bu)_2TiCl_4]\cdot CH_2Cl_2$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.84735(12)	0.71460(12)	0.03357(14)	0.0660(11)	0.0609(11)	0.0596(10)	0.0049(11)	−0.0019(11)	0.0004(10)
Cl(1)	0.85306(20)	0.70661(20)	0.21603(19)	0.0849(19)	0.0783(17)	0.0601(15)	0.0015(15)	0.0052(15)	−0.0061(18)
Cl(2)	0.84929(22)	0.69712(20)	−0.15001(20)	0.1043(22)	0.0816(19)	0.0563(15)	0.0059(15)	0.0003(17)	−0.0098(20)
Cl(3)	0.70312(18)	0.77518(21)	0.03534(26)	0.0731(17)	0.0980(21)	0.0976(20)	0.0131(21)	0.0024(18)	0.0174(16)
Cl(4)	0.93107(19)	0.85173(18)	0.02409(24)	0.0937(20)	0.0673(15)	0.0802(17)	0.0065(17)	0.0003(19)	−0.0138(15)
Cl(5)	0.11749(26)	0.95662(23)	0.23067(31)	0.1220(30)	0.0844(21)	0.1361(31)	0.0001(23)	0.0152(25)	−0.0113(21)
Cl(6)	0.09862(36)	0.78999(29)	0.36459(30)	0.2225(47)	0.1292(31)	0.1027(25)	0.0118(27)	−0.0060(31)	−0.0256(33)
O(1)	0.9719(5)	0.6339(5)	0.0448(6)	0.0569(40)	0.0704(44)	0.0706(45)	0.0002(45)	−0.0048(40)	0.0021(36)
O(2)	0.7949(5)	0.5723(5)	0.0360(6)	0.0701(42)	0.0599(42)	0.0624(40)	−0.0036(42)	0.0013(40)	−0.0086(37)
O(3)	1.0710(5)	0.5133(5)	0.0703(6)	0.0687(47)	0.0721(45)	0.0709(48)	−0.0078(40)	−0.0141(40)	0.0104(41)
O(4)	0.7357(5)	0.4297(5)	−0.0157(6)	0.0710(45)	0.0716(46)	0.0780(49)	−0.0103(43)	0.0043(44)	−0.0059(41)
C(11)	1.0033(7)	0.5543(8)	0.0186(9)	0.0515(66)	0.0663(71)	0.0739(79)	0.0157(75)	0.0172(64)	−0.0009(60)
C(12)	0.9715(8)	0.4946(7)	−0.0744(8)	0.0775(81)	0.0568(63)	0.0523(67)	−0.0064(56)	−0.0027(63)	−0.0008(60)
C(13)	1.0386(8)	0.4624(9)	−0.1420(9)	0.0701(78)	0.0843(81)	0.0628(73)	−0.0017(70)	−0.0015(67)	0.0132(67)
C(14)	1.0163(10)	0.4051(9)	−0.2300(10)	0.098(11)	0.0837(83)	0.0706(85)	−0.0103(75)	0.0055(78)	0.0152(76)
C(15)	0.9252(10)	0.3773(8)	−0.2476(10)	0.107(11)	0.0709(77)	0.0718(78)	−0.0075(70)	−0.0122(85)	0.0118(79)
C(16)	0.8561(8)	0.4051(8)	−0.1767(9)	0.0668(75)	0.0717(73)	0.0741(74)	−0.0091(65)	−0.0056(70)	−0.0059(67)
C(17)	0.8766(8)	0.4681(8)	−0.0925(8)	0.0791(85)	0.0595(63)	0.0467(59)	0.0005(56)	−0.0054(58)	0.0035(59)
C(18)	0.8008(8)	0.4962(9)	−0.0174(9)	0.0658(68)	0.0798(74)	0.0600(71)	0.0166(73)	−0.0165(67)	−0.0102(71)
C(1)	1.1069(8)	0.5633(8)	0.1660(8)	0.0802(73)	0.0790(75)	0.0530(62)	−0.0083(64)	−0.0171(63)	0.0012(68)
C(2)	1.1660(8)	0.4913(9)	0.2255(9)	0.0622(69)	0.0838(72)	0.0808(76)	0.0119(68)	−0.0043(70)	−0.0025(63)
C(3)	1.2468(8)	0.4539(11)	0.1562(11)	0.0686(81)	0.126(11)	0.098(10)	−0.0106(97)	−0.0067(80)	0.0069(93)
C(4)	1.1971(9)	0.5367(10)	0.3285(9)	0.0825(87)	0.113(11)	0.0785(85)	−0.0098(84)	−0.0146(77)	0.0013(90)
C(5)	0.6536(7)	0.4466(8)	0.0522(9)	0.0763(70)	0.0849(77)	0.0679(76)	−0.0054(63)	0.0189(68)	−0.0096(68)
C(6)	0.5851(7)	0.3655(8)	0.0200(10)	0.0794(73)	0.0774(74)	0.0843(73)	0.0044(71)	0.0108(71)	−0.0236(63)
C(7)	0.6267(10)	0.2665(8)	0.0307(12)	0.1162(99)	0.0658(72)	0.111(11)	0.0009(86)	0.0018(99)	−0.0160(72)
C(8)	0.4958(9)	0.3778(9)	0.0887(10)	0.0764(86)	0.104(11)	0.0920(92)	−0.0087(80)	0.0153(75)	0.0015(75)
C(9)	0.0978(12)	0.8284(8)	0.2360(10)	0.150(13)	0.0611(71)	0.0879(82)	−0.0027(69)	−0.0015(95)	−0.0122(81)

Table 1 (continued)

Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(13)	1.110	0.482	−0.127	0.132(48)	H(15)	0.908	0.334	−0.317	0.097(37)
H(14)	1.070	0.382	−0.285	0.133(48)	H(16)	0.786	0.378	−0.187	0.063(27)
H(1)	1.148	0.626	0.143	0.104(37)	H(5)	0.671	0.441	0.136	0.051(24)
H(11)	1.050	0.587	0.216	0.076(31)	H(51)	0.624	0.518	0.037	0.067(27)
H(2)	1.126	0.427	0.244	0.097(7)	H(6)	0.568	0.372	−0.064	0.118(8)
H(3)	1.287(6)	0.405(5)	0.206(6)	0.122(46)	H(7)	0.652(5)	0.252(5)	0.111(3)	0.046(22)
H(31)	1.289(6)	0.517(4)	0.137(6)	0.161(61)	H(71)	0.677(5)	0.231(16)	−0.030(5)	0.36(14)
H(32)	1.228(6)	0.417(5)	0.083(4)	0.113(44)	H(72)	0.554(11)	0.233(11)	0.024(9)	0.67(13)
H(4)	1.137(3)	0.554(4)	0.377(5)	0.061(27)	H(8)	0.478(6)	0.454(2)	0.081(6)	0.101(41)
H(41)	1.242(3)	0.488(4)	0.372(5)	0.100(38)	H(81)	0.520(5)	0.364(5)	0.169(3)	0.072(31)
H(42)	1.234(4)	0.603(3)	0.311(5)	0.072(32)	H(82)	0.434(5)	0.334(6)	0.075(7)	0.68(13)
H(9)	0.152	0.791	0.192	0.29(12)	H(91)	0.031	0.812	0.200	0.238(89)

Table 2

Final atomic parameters with esd's in parentheses for [p-$C_6H_4(COOMe)_2TiCl_4$]

Atom	x	y	z	U_{11}/U_{iso}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.37902(6)	0.04866(4)	0.12828(6)	0.0220(3)	0.0321(3)	0.0287(3)	−0.0020(2)	0.0048(2)	0.0013(2)
Cl(1)	0.62607(9)	0.09299(6)	0.05128(9)	0.0288(4)	0.0309(4)	0.0391(4)	−0.0061(3)	0.0097(3)	−0.0074(3)
Cl(2)	0.22396(10)	0.14302(7)	−0.06360(9)	0.0378(4)	0.0461(5)	0.0399(4)	0.0056(4)	0.0064(3)	0.0142(4)
Cl(3)	0.17266(10)	−0.02713(8)	0.18147(11)	0.0313(4)	0.0728(6)	0.0528(5)	0.0059(5)	0.0164(4)	−0.0078(4)
Cl(4)	0.42734(12)	0.17572(7)	0.29389(10)	0.0473(5)	0.0524(5)	0.0498(5)	−0.0233(4)	0.0068(4)	0.0030(4)
O(1)	0.55252(25)	−0.03814(16)	0.28691(24)	0.0282(11)	0.0360(12)	0.0336(11)	0.0035(10)	0.0023(9)	−0.0011(9)
O(2)	0.66919(26)	−0.18499(16)	0.38322(24)	0.0311(12)	0.0315(12)	0.0424(13)	0.0063(10)	0.0050(10)	−0.0053(9)
C(1)	0.67728(37)	−0.08840(23)	0.35969(31)	0.0295(16)	0.0322(16)	0.0229(14)	0.0013(12)	0.0063(12)	−0.0019(12)
C(2)	0.84402(36)	−0.04260(23)	0.43080(31)	0.0281(15)	0.0321(16)	0.0217(13)	0.0021(12)	0.0042(11)	−0.0027(12)
C(3)	0.85928(37)	0.06231(25)	0.44936(35)	0.0268(16)	0.0325(17)	0.0363(17)	0.0016(13)	0.0017(13)	0.0036(12)
C(4)	0.98477(39)	−0.10508(23)	0.48128(34)	0.0317(16)	0.0285(16)	0.0320(16)	0.0018(13)	0.0028(13)	−0.0004(12)
C(5)	0.50755(43)	−0.23617(27)	0.32100(42)	0.0375(19)	0.0401(19)	0.0514(21)	0.0009(17)	0.0049(16)	−0.0151(15)
H(51)	0.417(3)	−0.212(3)	0.372(3)	0.085(16)					
H(52)	0.454(4)	−0.230(3)	0.200(1)	0.075(14)					
H(53)	0.540(5)	−0.315(2)	0.351(4)	0.118(20)					
H(3)	0.748(3)	0.108(3)	0.427(4)	0.051(11)					
H(4)	0.969(4)	−0.187(2)	0.469(4)	0.036(9)					

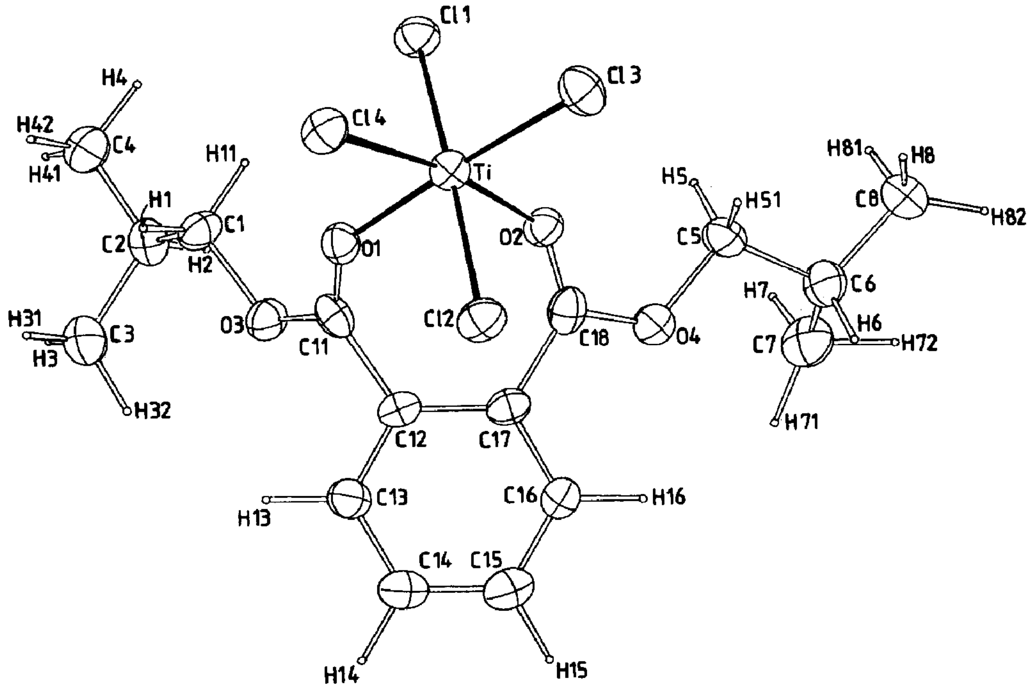

Fig. 1. The molecular structure and numbering scheme of [o-$C_6H_4(COO\text{-i-}Bu)_2TiCl_4$] molecule in tetrachloro(di-iso-butyl o-phthalate)titanium(IV) dichloromethane crystal, I.

1511 for I and 1549 for II with $I > 3\sigma(I)$ were used for structure determination. Neutral atom scattering factors from ref. 10; real and imaginary components of anomalous dispersion were included for all non-H atoms. Both structures were solved by direct methods and refined by full-matrix least-squares methods [11]. The H atoms were located from difference maps and refined with constraint that $d(\text{C–H}) = 1.08$ Å. In the case of I the non-methyl H-atoms were included in geometrically calculated positions. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The absorption corrections were applied (DIFABS [12]). The minimum and maximum absorption corrections were 0.897 and 1.630 and 0.946 and 1.069 for I and II, respectively. The final R and R_w were (0.0274 and 0.0283) and (0.0482 and 0.0440) for I and II, respectively. (The refinement of the inverted structure for I gave $R = 0.0498$ and $R_w = 0.0458$). For the last cycle of the refinement the maximal value of the Δ/σ ratio was 0.4 for I and 0.08 for II and the final difference maps showed a general background within -0.33 and 0.26 and -0.26 and 0.031 e Å^{-3} for I and II, respectively. The final atom parameters for I are listed in Table 1 and for II in Table 2.

Results and discussion

The structure of tetrachloro(di-iso-butyl o-phthalate)titanium(IV) molecule is depicted in Fig. 1. Selected bond lengths are listed in Table 3. Four Cl atoms and two O atoms of the ligands carbonyl group form the distorted octahedron around titanium atom. The molecules of di-iso-butyl o-phthalate are coordinated to titanium atoms via the carbonyl oxygen atoms. The chelate ligand and titanium atom form a seven-membered ring. The general structure of the complex molecule is similar to that of [o-$C_6H_4(COOEt)_2OMoCl_3$] [13] but somewhat different from that of [o-$C_6H_4(COOEt)_2TiCl_4$] [14], which has $m(C_s)$ point symmetry. This is demonstrated by the fact, that the Cl(2) atom is in 3.290(12), 3.247(11), 3.422(11) and 3.632(11) Å distances from C(18), C(17), C(12), C(11) and corresponding Cl atom in [o-$C_6H_4(COOEt)_2TiCl_4$] [14], is in 3.295(5) and 3.217(5) Å distances from the similar four carbon atoms. In the titanium complex with iso-butyl o-phthalate the angles of torsion Ti–O(1)–C(11)–C(12), Ti–O(2)–C(18)–C(17) [27.0(16)° and 21.8(15)°] are

Table 3

Principal interatomic distances (Å), bond angles (°), and torsion angles (°) for tetrachloro(di-iso-butyl o-phthalate)titanium(IV) molecule

Ti–Cl(1)	2.282(3)	Ti–Cl(2)	2.305(3)
Ti–Cl(3)	2.238(3)	Ti–Cl(4)	2.238(3)
Ti–O(1)	2.113(7)	Ti–O(2)	2.093(7)
O(1)–C(11)	1.226(12)	O(2)–C(18)	1.242(13)
O(3)–C(11)	1.298(12)	O(4)–C(18)	1.308(13)
O(3)–C(1)	1.472(12)	O(4)–C(5)	1.474(12)
C(11)–C(12)	1.493(15)	C(18)–C(17)	1.489(15)
C(12)–C(17)	1.433(16)	C(14)–C(15)	1.384(19)
C(12)–C(13)	1.356(15)	C(16)–C(17)	1.393(14)
C(13)–C(14)	1.388(16)	C(15)–C(16)	1.386(17)
C(1)–C(2)	1.501(15)	C(5)–C(6)	1.540(14)
C(2)–C(3)	1.539(16)	C(6)–C(7)	1.491(15)
C(2)–C(4)	1.497(16)	C(6)–C(8)	1.555(16)
Cl(1)–Ti–Cl(2)	170.8(2)	Cl(1)–Ti–Cl(3)	92.4(2)
Cl(1)–Ti–Cl(4)	94.2(2)	Cl(2)–Ti–Cl(3)	93.4(2)
Cl(2)–Ti–Cl(4)	91.6(2)	Cl(3)–Ti–Cl(4)	100.9(2)
O(1)–Ti–Cl(1)	83.0(3)	O(1)–Ti–Cl(2)	90.1(3)
O(1)–Ti–Cl(3)	169.2(3)	O(1)–Ti–Cl(4)	89.2(3)
O(2)–Ti–Cl(1)	87.4(3)	O(2)–Ti–Cl(2)	85.5(3)
O(2)–Ti–Cl(3)	90.6(3)	O(2)–Ti–Cl(4)	168.3(3)
O(1)–Ti–O(2)	79.5(3)		
Ti–O(1)–C(11)	139.6(7)	Ti–O(2)–C(18)	138.7(7)
C(11)–O(3)–C(1)	117.8(8)	C(18)–O(4)–C(5)	118.4(8)
O(1)–C(11)–O(3)	122.0(10)	O(2)–C(18)–O(4)	121.8(10)
O(1)–C(11)–C(12)	125.7(10)	O(2)–C(18)–C(17)	127.3(10)
O(3)–C(11)–C(12)	112.3(9)	O(4)–C(18)–C(17)	110.9(9)
C(11)–C(12)–C(17)	123.6(10)	C(18)–C(17)–C(12)	122.4(10)
C(11)–C(12)–C(13)	116.4(10)	C(18)–C(17)–C(16)	118.7(10)
C(13)–C(12)–C(17)	120.0(10)	C(12)–C(17)–C(16)	118.6(10)
C(12)–C(13)–C(14)	120.8(11)	C(17)–C(16)–C(15)	120.0(10)
C(13)–C(14)–C(15)	120.1(12)	C(16)–C(15)–C(14)	120.3(11)
O(3)–C(1)–C(2)	107.1(8)	O(4)–C(5)–C(6)	104.5(8)
C(1)–C(2)–C(3)	111.7(9)	C(5)–C(6)–C(7)	112.2(10)
C(1)–C(2)–C(4)	108.7(9)	C(5)–C(6)–C(8)	107.9(9)
C(3)–C(2)–C(4)	113.2(10)	C(7)–C(6)–C(8)	112.4(10)
C(4)–C(2)–C(1)–O(3)	–175.2(11)	C(7)–C(6)–C(5)–O(4)	55.4(11)
C(3)–C(2)–C(1)–O(3)	59.1(12)	C(8)–C(6)–C(5)–O(4)	179.8(10)
C(2)–C(1)–O(3)–C(11)	166.0(12)	C(6)–C(5)–O(4)–C(18)	170.2(10)
C(1)–O(3)–C(11)–O(1)	3.0(14)	C(5)–O(4)–C(18)–O(2)	–0.2(13)
O(3)–C(11)–O(1)–Ti	–154.2(15)	O(4)–C(18)–O(2)–Ti	–156.0(13)
Ti–O(1)–C(11)–C(12)	27.0(16)	Ti–O(2)–C(18)–C(17)	21.8(15)

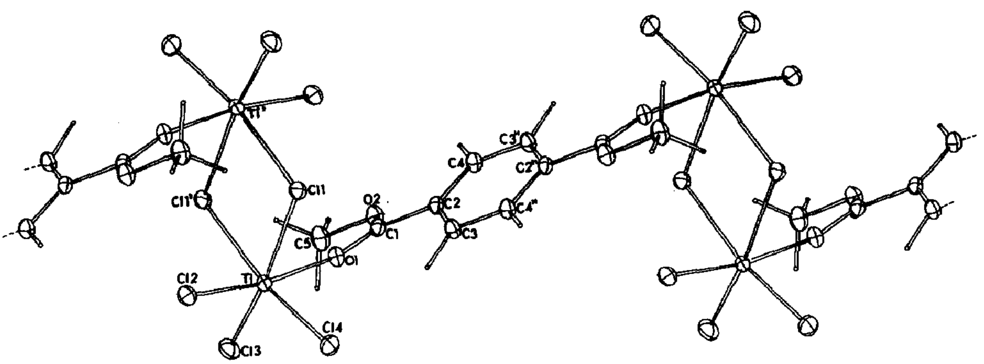

Fig. 2. View of the polymeric structure and numbering scheme of [p-$C_6H_4(COOMe)_2 \cdot TiCl_4$] adduct in crystal II.

different but the bond angles Ti–O(1)–C(11) [139.6(7)°] and Ti–O(2)–C(18) [138.7(7)°], and the bond lengths Ti–O(1) and Ti–O(2) [2.113(7) and 2.093(7) Å] are similar. The benzene ring is planar and Cl(1) chlorine atom is the remotest atom from the ring. The Ti–Cl(1) and Ti–Cl(2) distances of 2.282(3) and 2.305(3) Å are longer than the Ti–Cl(3) and Ti–Cl(4) distances of 2.238(3) Å, (Table 3).

The spatial structure of complexes with the o-diester suggest that the addition of $AlEt_3$ as co-catalyst to [o-C_6H_4(COO-i-Bu)$_2TiCl_4$] or [o-$C_6H_4(COOEt)_2TiCl_4$]

Table 4

Principal interatomic distances (Å), bond angles (°) and torsion angles for crystalline [p-$C_6H_4(COOMe)_2TiCl_4$] [a]

Ti···Ti^i	3.851(4)	Ti–Cl(1)	2.496(3)
Ti–Cl(1^i)	2.498(3)	Ti–Cl(2)	2.223(3)
Ti–Cl(3)	2.206(3)	Ti–Cl(4)	2.222(3)
Ti–O(1)	2.058(3)	O(1)–C(1)	1.243(4)
O(2)–C(1)	1.293(4)	O(2)–C(5)	1.464(4)
C(1)–C(2)	1.478(4)	C(2)–C(3)	1.389(4)
C(2)–C(4)	1.396(5)	C(3)–C(4^{ii})	1.386(5)
Cl(1)–Ti–Cl(1^i)	79.1(1)	Cl(1)–Ti–Cl(2)	88.1(1)
Cl(1)–Ti–Cl(3)	166.5(1)	Cl(1)–Ti–Cl(4)	92.6(1)
Cl(1^i)–Ti–Cl(2)	89.8(1)	Cl(1^i)–Ti–Cl(3)	88.6(1)
Cl(1^i)–Ti–Cl(4)	170.8(1)	Cl(2)–Ti–Cl(3)	97.5(1)
Cl(2)–Ti–Cl(4)	94.0(1)	Cl(3)–Ti–Cl(4)	99.2(1)
O(1)–Ti–Cl(1)	82.5(1)	O(1)–Ti–Cl(1^i)	85.6(1)
O(1)–Ti–Cl(2)	170.1(1)	O(1)–Ti–Cl(3)	91.1(1)
O(1)–Ti–Cl(4)	89.3(1)	Ti–Cl(1)–Ti^i	100.9(1)
Ti–O(1)–C(1)	165.4(3)	O(1)–C(1)–O(2)	122.1(3)
O(1)–C(1)–C(2)	123.1(3)	C(2)–C(1)–O(2)	114.7(3)
C(1)–O(2)–C(5)	118.5(3)	C(1)–C(2)–C(3)	119.7(3)
C(1)–C(2)–C(4)	119.9(3)	C(3)–C(2)–C(4)	120.4(3)
C(2)–C(3)–C(4^{ii})	119.7(3)	C(2)–C(4)–C(3^{ii})	119.9(3)
C(5)–O(2)–C(1)–O(1)	0.3(7)	Ti–O(1)–C(1)–O(2)	−114.0(13)

[a] Symmetry codes: (i) $1-x, -y, -z$; (ii) $2-x, -y, 1-z$.

should be followed by replacement of the most distant Cl(1) by ethyl group. However, the reduction of Ti^{4+} to Ti^{3+} in [o-$C_6H_4(COOEt)_2TiCl_4$] should also result in abstraction of Cl(1), as indicated by the structure of Ti^{3+} compound [$(\mu$-$Cl)_2Cl_4\{o$-$C_6H_4(COOEt)_2\}_2Ti_2$], which was obtained by the reduction of [o-$C_6H_4(COOEt)_2TiCl_4$] with aluminium in CH_2Cl_2 [15].

Compound II in crystalline state is polymeric. This structure is depicted in Fig. 2. The dimeric unit $Cl_3Ti(\mu$-$Cl)_2TiCl_3$ occupies the center of symmetry at ($\frac{1}{2}$,0,0) and the p-$C_6H_4(COOMe)_2$ ligand occupies the center of symmetry at (1,0,$\frac{1}{2}$). The $Cl_3Ti(\mu$-$Cl)_2TiCl_3$ units are connected by carbonyl oxygens of p-$C_6H_4(COOMe)_2$ to form a polymer in the [101] direction. The Ti–Cl and Ti–O bond lengths and Cl–Ti–Cl and Cl–Ti–O bond angles (see Table 4) are consistent with other Ti^{4+} chloro-complexes containing organic esters [14,16,17].

A comparison of the structure of the polymeric [$(\mu$-$Cl)_2(\mu$-p-$C_6H_4(COOMe)_2Cl_6Ti_2$] and the dimeric [$\{\mu$-m-$C_6H_4(COOEt)_2\}_2Cl_8Ti_2$] [17] with the monomeric [o-C_6H_4(COO-i-Bu)$_2TiCl_4$] and [o-$C_6H_4(COOEt)_2TiCl_4$] compounds permitted a partial elucidation of the fall in the catalytic activity of the catalysts containing m- and p-$C_6H_4(COOR)_2$. In all these compounds the terminal chlorine atoms are chemically similar. We conclude from this that after addition of co-catalyst the replacement of the chlorine atoms by ethyl group should proceed in a similar fashion. For that reason at the initial catalytic activities of the compounds discussed are similar. After some time, however, the compounds in which the titanium atoms form either a linear polymer or the dimer with p- and m-$C_6H_4(COOR)_2$, respectively, decompose to form new compounds of lower catalytic activity.

Supplementary material available: The tables of observed and calculated structure factors for crystals I and II are available from the authors.

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