The hydrolysis of pentamethylcyclopentadienyltitanium trihalides and the formation of di-, tri-, and tetra-nuclear μ-oxo complexes. Crystal structure of $[(C_5Me_5)TiBr(\mu\text{-O})]_4CHCl_3$, which contains a Ti_4O_4 ring

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Abstract

Controlled hydrolysis of pentamethylcyclopentadienyltitanium trihalides $Cp^\star TiX_3$ in toluene in the presence of $NHEt_2$ leads to the isolation of compounds of the types $[Cp^\star TiX_2]_2(\mu\text{-O})$ (X = Cl, Br, I), $[Cp^\star TiX(\mu\text{-O})]_n$ (X = Cl, $n = 3$; X = Br, $n = 4$] and finally $[Cp^\star Ti]_4(\mu\text{-O})_6$ depending upon the Ti/H$_2$O stoichiometry. The crystal structure of $[Cp^\star TiBr(\mu\text{-O})]_4$ has been determined: the compound crystallizes with one molecule of CHCl$_3$ in the orthorhombic space group *Pnca* and contains a Ti_4O_4 ring of alternating Ti and O atoms. The four oxygen atoms lie in a plane, with the titanium atoms situated alternately $\pm 0.191(2)$ Å above and below this plane.

Introduction

Studies of the organometallic chemistry of titanium have revealed the existence of a large number of oxo derivatives containing Ti_nO_m cores of different types, which is not surprising in view of the strongly oxophilic character of the metal. If we restrict ourselves to the monocyclopentadienyl series in which oxygen acts as a double bridging ligand, the following types have been so far characterized by X-ray studies:

(i) Dinuclear compounds containing $Ti_2(\mu\text{-}O)$ units, like $[CpTiCl_2]_2(\mu\text{-}O)$ [1], $[Cp^{\star}Ti(CH_2SiMe_3)_2]_2(\mu\text{-}O)$ [2] and $[Cp^{\star}TiMe_2][Cp^{\star}TiMe(MeN_2CPh_2)](\mu\text{-}O)$ [3] $(Cp = C_5H_5$ and $Cp^{\star} = C_5Me_5)$; the first of these has a perfectly linear Ti–O–Ti arrangement and the other two have crowded structures with very unusual departure from this linearity.

(ii) Dinuclear $Ti_2(\mu\text{-}O)_2$ derivatives, of which $[Cp^{\star}Ti]_2$ $(\mu\text{-}\eta^5 : \eta^1\text{-}C_5Me_4CH_2)(\mu\text{-}O)$ [4] is the sole example.

(iii) Trinuclear $Ti_3(\mu\text{-}O)_2$ derivatives, of which $[Cp_2ClTi]_2[CpClTi](\mu\text{-}O)_2$ [5] is the sole example.

(iv) The trinuclear $Ti_3(\mu\text{-}O)_3$ cyclic compound $[Cp^{\star}TiMe(\mu\text{-}O)]_3$ [6]; this was made by the following hydrolytic sequence:

$$Cp^{\star}TiMe_3 \rightarrow [Cp^{\star}TiMe_2]_2(\mu\text{-}O) \rightarrow [Cp^{\star}TiMe(\mu\text{-}O)]_3 \qquad (1)$$
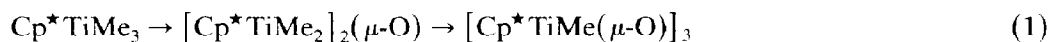
(v) Tetranuclear $Ti_4(\mu\text{-}O)_4$ cyclic derivatives obtained by hydrolysis in sequences similar to 2 [7]:

$$CpTiCl_3 \rightarrow [CpTiCl_2]_2(\mu\text{-}O) \rightarrow [CpTiCl(\mu\text{-}O)]_4 \qquad (2)$$
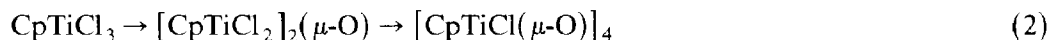
(vi) Tetranuclear $Ti_4(\mu\text{-}O)_6$ cage compounds such as $[Cp^{\star}Ti]_4(\mu\text{-}O)_6$ [8,10].
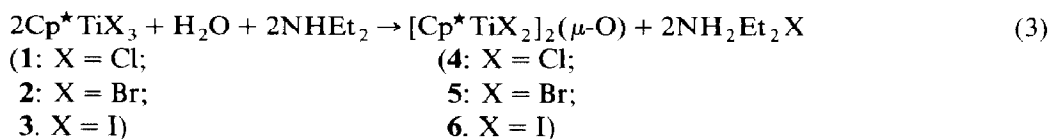
References to other Ti compounds, such as dicyclopentadienyl derivatives, structures containing $\mu_3\text{-}O$ groups, and polyoxometalates can be found in a recent review [9].

The most common synthetic route to the group 4 oxo derivatives involves hydrolysis of various parent compounds. We have investigated the hydrolysis of pentamethylcyclopentadienyltitanium trihalides and in this paper we show that it leads to μ-oxo derivatives of types i, iv, v and vi mentioned above, and describe the crystal structure of one of them, $[Cp^{\star}TiBr(\mu\text{-}O)]_4$.

Results and discussion

Pentamethylcyclopentadienyltitanium trihalides can be exposed to the air for short periods without change, but if their solutions in organic solvents are kept in the open air for a few days some decomposition occurs, and the ^1H NMR spectra of the remaining substances show the presence of several $Cp^{\star}$ peaks in relative ratios which depend on the particular solvent, its purity, and the exposure time. Boiling of such solutions open to the air, or keeping of solutions made in wet solvents, similarly lead to mixtures.
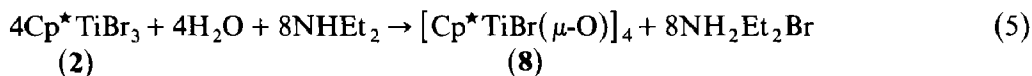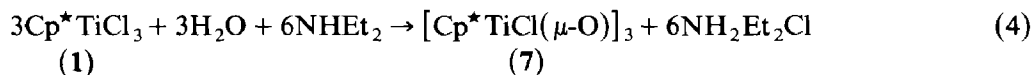
Because in all these experiences the amount of water present is variable and unknown, a controlled hydrolysis seemed much more appropriate. The reactions require the presence of a base to drive then to completion. In this way, use of a molar ratio $Cp^{\star}TiX_3/H_2O$ 2/1 leads to the formation of the dimers 4–6, according to eq. 3:

$$2Cp^{\star}TiX_3 + H_2O + 2NHEt_2 \rightarrow [Cp^{\star}TiX_2]_2(\mu\text{-}O) + 2NH_2Et_2X \qquad (3)$$

(1: X = Cl;   (4: X = Cl;
 2: X = Br;   5: X = Br;
 3. X = I)   6. X = I)

The rates of the reactions increase in the order $3 < 2 < 1$, which is the opposite of what one would expect in terms of the bond strengths and degree of covalent
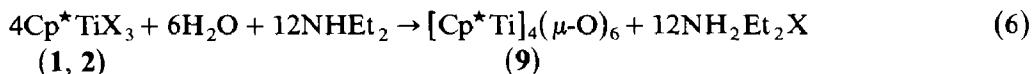
character of the Ti–X bonds. Thus it seems likely that steric effects are dominant, and the bulkier the halogen the slower the hydrolysis because of hindrance to attack of the water molecule on the metal center. Compounds **4–6** show only one peak in the ^{1}H NMR spectra and must be structural analogues of $[CpTiCl_2]_2(\mu\text{-}O)$ [1]. They are useful precursors of the μ-oxoalkyls $[Cp^{\star}TiR_2]_2(\mu\text{-}O)$, into which they can be converted by simple alkylation reactions [2].

When the Ti/H_2O molar ratio is lowered to $1:1$, **7** and **8** (eq. 4 and 5) can be isolated:

$$3Cp^{\star}TiCl_3 + 3H_2O + 6NHEt_2 \rightarrow [Cp^{\star}TiCl(\mu\text{-}O)]_3 + 6NH_2Et_2Cl \tag{4}$$
$$\quad\text{(1)} \qquad\qquad\qquad\qquad\qquad\text{(7)}$$

$$4Cp^{\star}TiBr_3 + 4H_2O + 8NHEt_2 \rightarrow [Cp^{\star}TiBr(\mu\text{-}O)]_4 + 8NH_2Et_2Br \tag{5}$$
$$\quad\text{(2)} \qquad\qquad\qquad\qquad\qquad\text{(8)}$$

The corresponding hydrolysis of **3** is even slower, and it is not easily reproducible, and thus it was not studied further. The ^{1}H NMR spectrum of compound **7** shows two $Cp^{\star}$ signals in a 2/1 ratio; the same effect was previously noticed with complex $[Cp^{\star}TiMe(\mu\text{-}O)]_3$ which was characterysed by X-ray diffraction [6], and which can be prepared from **7** and three moles of LiMe. Similar structures are thus expected. Compound **8**, however, is a tetramer, not a trimer, as was previously thought [10], and shows only one $Cp^{\star}$ ^{1}H-NMR peak. Its crystal structure is discussed below.

All the three halogens can be removed from the starting trihalides by using a 3/2 Ti/H_2O molar ratio (eq. 6):

$$4Cp^{\star}TiX_3 + 6H_2O + 12NHEt_2 \rightarrow [Cp^{\star}Ti]_4(\mu\text{-}O)_6 + 12NH_2Et_2X \tag{6}$$
$$\quad\text{(1, 2)} \qquad\qquad\qquad\qquad\quad\text{(9)}$$

Compound **9** can also be obtained by hydrolysis of $Cp^{\star}Ti(CH_2SiMe_3)_3$ in organic solvents [10] or hydrolysis of **1** with $1.5\ M\ NH_4OH$ [8].

Some important spectroscopic and analytical data for the new compounds are listed in Table 1.

Table 1

Spectroscopic and analytical data of the compounds

Compound	$\nu(TiOTi)$ [a]	$\delta(^1H)$ [b]	Analysis (Found (calcd.) (%))	
			C	H
4	765	2.25	45.5	5.6
			(45.8)	(5.8)
5	760	2.36	35.2	4.6
			(35.0)	(4.4)
6	735	2.50	26.6	3.4
			(27.0)	(3.4)
7	780	2.09(30H)	51.9	6.6
		2.07(15H)	(51.2)	(6.5)
8	780	2.15	43.1	5.9
			(43.0)	(5.4)

[a] Very intense and broad bands centered approximately at this wavenumber (cm^{-1}). [b] ppm relative to TMS in $CDCl_3$.

Table 2

Coordinates for **8**, and with thermal parameters as $U_{eq} = \frac{1}{3}\Sigma[U_{ij}a_i a_j \times a_i a_j \cos(a_i a_j)] \times 10^3$

Atom	x	y	z	U_{eq}
Br1	0.5429(1)	0.0368(1)	0.3399(1)	60(0)
Br2	0.7573(1)	−0.2043(1)	0.1236(1)	57(0)
Ti2	0.6736(1)	−0.0803(1)	0.1411(1)	33(1)
Ti1	0.6577(1)	−0.0627(1)	0.3255(1)	36(1)
O5	0.6538(4)	−0.0816(4)	0.2328(4)	36(2)
O2	0.7500(0)	0.0000(0)	0.1271(5)	35(3)
O1	0.7500(0)	0.0000(0)	0.3408(5)	43(4)
C11	0.6248(8)	−0.2032(7)	0.3396(7)	51(4)
C12	0.5716(8)	−0.1612(8)	0.3842(7)	52(5)
C13	0.6227(9)	−0.1219(8)	0.4354(7)	59(5)
C14	0.7080(8)	−0.1416(8)	0.4204(7)	53(5)
C15	0.7084(8)	−0.1892(7)	0.3594(6)	48(4)
C111	0.5989(9)	−0.2585(9)	0.2810(8)	69(6)
C121	0.4765(9)	−0.1632(11)	0.3849(10)	90(7)
C131	0.5924(11)	−0.0740(9)	0.4967(7)	82(6)
C141	0.7824(10)	−0.1200(9)	0.4644(7)	71(6)
C151	0.7878(8)	−0.2248(8)	0.3277(7)	58(5)
C21	0.5536(8)	−0.0099(8)	0.1051(6)	47(4)
C22	0.6024(7)	−0.0215(8)	0.0434(6)	46(4)
C23	0.6056(9)	−0.1070(9)	0.0296(7)	57(5)
C24	0.5560(8)	−0.1453(8)	0.0835(7)	58(5)
C25	0.5250(8)	−0.0870(9)	0.1282(7)	57(5)
C212	0.5354(8)	0.0698(9)	0.1383(7)	61(5)
C222	0.6379(8)	0.0444(8)	0.0009(6)	56(5)
C232	0.6476(10)	−0.1483(10)	−0.0299(8)	78(6)
C242	0.5389(10)	−0.2364(9)	0.0846(10)	86(7)
C252	0.4648(7)	−0.1021(9)	0.1874(8)	62(5)
CL2	0.7470(5)	0.0866(4)	0.6765(4)	163(3)
CL1	0.7500(0)	0.0000(0)	0.8022(4)	174(5)
C26	0.7077(21)	−0.0082(20)	0.7119(16)	100(16)

Table 3

Important bond distances (Å) and angles (°) in the structure of **8** [a]

Bond distances

Br1–Ti1	2.460(3)	Br2–Ti2	2.452(3)
Ti1–O1	1.813(3)	Ti2–O2	1.810(2)
Ti1–O5	1.815(7)	Ti2–O5	1.797(7)
Ti1–C11	2.380(12)	Ti2–C21	2.329(12)
Ti1–C12	2.398(13)	Ti2–C22	2.397(12)
Ti1–C13	2.395(14)	Ti2–C23	2.442(14)
Ti1–C14	2.379(13)	Ti2–C24	2.417(14)
Ti1–C15	2.319(12)	Ti2–C25	2.369(13)
Ti1–Cp1 [b]	2.05	Ti2–Cp2	2.06

Bond angles

Cp1–Ti1–O1	114.8	Cp2–Ti2–O2	114.7
Cp1–Ti1–O5	115.7	Cp2–Ti2–O5	116.8
Cp1–Ti1–Br1	114.8	Cp2–Ti2–Br2	113.3
Br1–TI1–O1	101.6(1)	Br2–TI2–O2	102.8(1)
Br1–TI1–O5	101.5(2)	Br2–TI2–O5	102.7(3)
O5–TI1–O1	106.5(2)	O5–Ti2–O2	105.7(3)
TI2–O5–TI1	164.1(4)	Ti2–O2–Ti2 [c]	164.0(3)
Ti1–O1–Ti1 [a]	162.6(3)		

[a] e.s.d. values in parentheses. [b] Cp1 and Cp2 are the centroids of the C11...C5 and C21...C25 rings respectively. [c] The corresponding symmetry is: $\frac{3}{2} - x$, $-y$, z.

X-Ray structure of 8

The atomic coordinates are listed in Table 2 and the most important bond distances and angles in Table 3. Fig. 1 depicts the structure. The single crystals grown from $CHCl_3$ solution have one solvent molecule per tetramer molecule; the latter has a two-fold rotation axis, which passes through O1 and O2, thereby reducing the number of molecules in the orthorhombic unit cell to four. The structure can be described as assembled from four Cp^*TiBrO_2 fragments that share both O atoms in such a way that a Ti_4O_4 eight-membered ring of alternating Ti and O atoms is formed. The ring is not strictly planar: the four oxygen atoms lie in a plane, but the four titanium atoms are alternately separated up and down that plane by 0.191(2) Å in both cases. Compound 8 nevertheless has the most planar of all the five Ti_4O_4 rings so far described [7]. Two Cp^* rings and two bromine atoms lie alternately at one side of the Ti_4O_4 best plane and the other two Cp^* and Br on the opposite side. The size of the eight-membered ring reduces steric interactions between the Cp^* groups, and they have regular and similar geometries. The dihedral angles between the O_4 plane and the Cp^* best planes are 54.6(4) and 52.5(4)°.

The metal atom exhibit a fairly undistorted three-legged piano stool arrangement: the angles between the legs vary from 101.5(2) to 106.5(2)°, with the O–Ti–O angles the more obtuse, and the Cp^* centroid–Ti–substituent angles lie between 113.3 and 116.8°, the larger values corresponding to Cp–Ti–O angles. The Ti–C distances are normal for monopentamethylcyclopentadienyltitanium compounds [10], and the Ti–O distances are of the same order as in the other cyclic tetramers [7] and the related $[Cp^*TiMe(\mu\text{-}O)]_3$ [6] and 9 [8,10]. Compared with these in the last two species, the angles at oxygen in 8 are substantially larger, in keeping with the

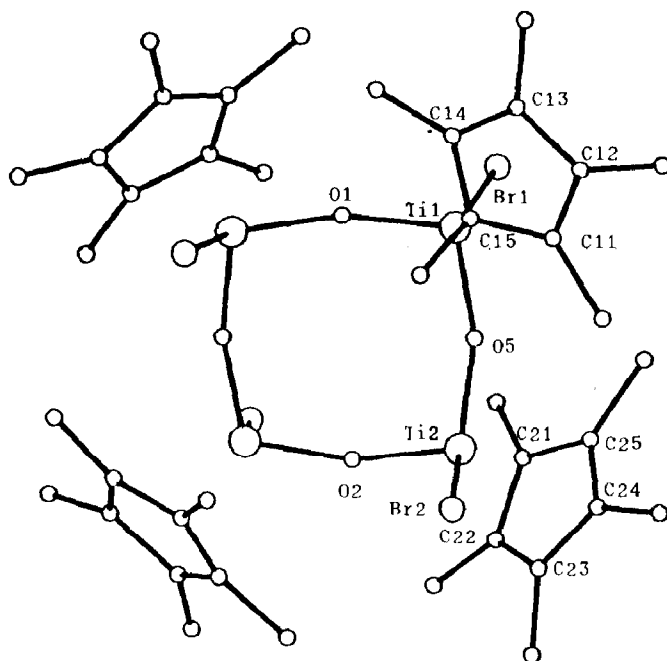Fig. 1. View of the structure of 8 with the atom numbering scheme (co-crystallized $CHCl_3$ ommited).
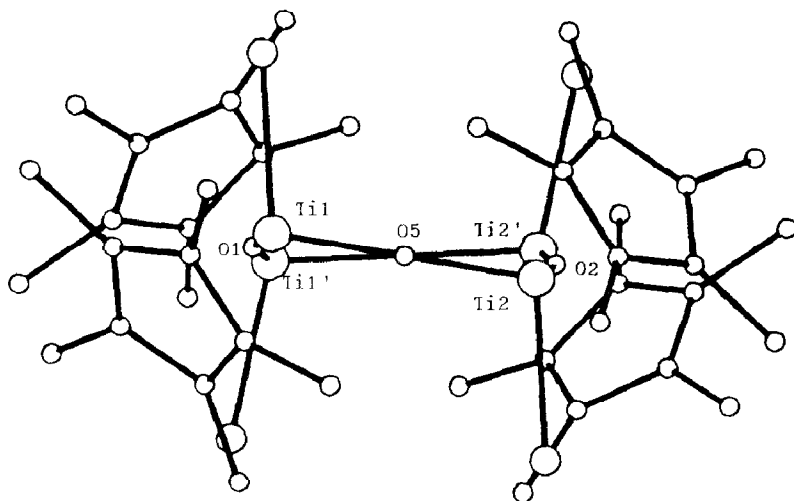
Fig. 2. Perspective of the structure of **8** parallel to the (μ-O)$_4$ plane.

larger size of the four- vs. the three-membered rings; the mean values are 163.6° in **8**, 132.9(3)° in the trimer and 122.9 (2)° in the cage tetramer **9**.

Experimental

All manipulations were carried out under dry N$_2$ by conventional Schlenk techniques. The starting pentamethylcyclopentadienyltitanium trihalides were prepared by a published procedure [11]. Diethylamine was distilled over KOH, and diethyl ether over Na/benzophenone, and toluene over Na, all under N$_2$. A Varian FT-80A spectrometer was used to record the ^{1}H NMR spectra; the IR spectra were recorded on a Perkin–Elmer 599 apparatus as Nujol mulls. C, H analyses were performed with a Perkin–Elmer 240B microanalyzer.

[Cp*TiCl$_2$]$_2$(μ-O) (4). To a solution of 0.31 g (1.07 mmol) of Cp*TiCl$_3$ in 40 ml of toluene at 5°C, 9.63 μl (0.53 mmol) of H$_2$O and 0.11ml (1.07 mmol) of NHEt$_2$ were added from a syringe. The solution was allowed to warm to room temperature, stirred for 24 h, filtered, and taken to dryness. The residue was crystallized from diethyl ether to yield 0.25 g of red **4** (92%).

[Cp*TiBr$_2$]$_2$(μ-O) (5). This is prepared similarly from 0.21 g (0.50 mmol) of Cp*TiBr$_3$, 4.46 μl (0.25 mmol) of H$_2$O and 51 μl (0.50 mmol) of NHEt$_2$, with 5 days, stirring. The yield of red **5** was ca. 85%.

[Cp*TiI$_2$]$_2$(μ-O) (6). It can also be prepared as above from 0.1 g (0.18 mmol) of Cp*TiI$_3$, 1.59 μl (0.09 mmol) of H$_2$O and 18 μl (0.18 mmol) of NHEt$_2$ in 60 ml toluene, with the mixture stirred for one week at 45°C. The yield of brown **6** is ca. 80%.

*[Cp*TiCl(μ-O)]₃ (7).* This is prepared similarly from 1 g (1.83 mmol) of Cp*TiCl₃, 32 μl (1.83 mmol) of H_2O and 0.37 ml (3.66 mmol) of NHEt₂ in 80 ml toluene, with stirring for three days. Yield ca. 85% of yellow trimer.

*[Cp*TiBr(μ-O)]₄ (8).* This was made similarly from 0.6 g (1.41 mmol) of Cp*TiBr₃, 25 μl (1.41 mmol) of H_2O and 0.294 ml (2.83 mmol) of NHEt₂ in 65 ml toluene, with stirring for one week. The yield of orange **8** was ca. 80%.

*[Cp*Ti]₄(μ-O)₆ (9).* This was made similarly from 1.02 g (3.52 mmol) of Cp*TiCl₃, 95 μl (5.28 mmol) of H_2O and 1.09 ml (10 mmol) of NHEt₂ in 80 ml toluene, with stirring for 5 days. The yield of the yellow compound was ca. 80%.

Crystal structure of 8. $[Ti_2Br_2O_2C_{20}H_{30}]_2CHCl_3$, $M = 1235.505$; orthorhombic, *Pnca*, a 15.839(4), b 16.414(6) and c 19.282(5) Å, V 5012.9(26) Å³; $Z = 4$; D_c 1.6270 g/cm⁻³; $\lambda(Mo-K_\alpha)$ 0.7107 Å; graphite monochromator, μ 39.649 cm⁻¹; $F(000) = 2472$.

Single crystals were grown by slow evaporation (some weeks) of a chloroform solution. A crystal of about $0.2 \times 0.2 \times 0.3$ mm was mounted along the main axis. The cell dimensions were refined from 42 general reflections with the Bragg angle θ max 20° on a CAD-4 diffractometer. 7100 independent reflections were measured in the range $2 < \theta < 30°$, 2354 of which were considered as observed on the criterion $I > 3\sigma(I)$. Two standard reflections were monitored after every 100 reflections and no decomposition was detected. Intensities were corrected for Lorentz and polarization effects in the usual way. The structure was solved by direct and Fourier methods; this revealed the complete organometallic framework and two other peaks, one of them in a special position, belonging to the chlorine atoms of a co-crystallized CHCl₃ molecule; the C atom of the CHCl₃ is disordered and oscillates between two symmetric positions with an occupational factor of 0.5. The structure was refined by full-matrix least-squares procedures, with minimization of $\Sigma(F)^2$, with isotropic temperature factors. An absorption corection following the DIFABS procedure [12] was applied to isotropically refined data; max. and min. absorption factors 1.107 and 0.653, respectively. The refinement was continued by full-matrix least-squares methods with anisotropic temperature factors. The H atoms were located from the difference synthesis and included with isotropic temperature factors. Final refinement led to $R = 0.057$ and $R_w = 0.061$, with ω from an empirical weighting scheme such as to give no trends in $\langle w\Delta^2 F \rangle$ vs. F_0 and $\sin \theta / \lambda$ [13]. (Δ/θ) max. 0.005. The chloroform molecule is markedly disordered, as can be seen from the high temperature factors of its Cl, C and H atoms. The atomic scattering factors were taken from ref. 14. The computation was made on a VAX 11/750 with MULTAN 80 [15], DIRDIF [16], XRAY [17] and PARST [18].

Acknowledgement

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