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TITANIUM ORGANOMETALLIC COMPOUNDS: ANALYSIS AND CLASSIFICATION OF CRYSTALLOGRAPHIC DATA

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ABBREVIATIONS

bme	bis(2-methoxyethyl)ether
C_7H_7	cycloheptatrienyl
C_8H_8	cyclooctatetraenyl
C_9H_7	indenyl
C_9H_{11}	tetrahydroindenyl
$C_{10}H_8$	fulvalenide
C_6H_5COO	benzoate
$(CH_2)_2(\eta^5\text{-Cp*})_2$	1,1′-dimethylene-bis(tetramethylcyclopentadienyl)
$(CH_2)_3(\eta^5\text{-Cp})_2$	1,1′-trimethylene-bis(cyclopentadienyl)
CH_2Ph	benzyl
ClPhO	2-chlorophenoxy
CNT	centroid of a ring

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C_2O_4	oxalate
Cp	cyclopentadienyl
Cp′	$1\text{-}CH_3\text{-}3\text{-}CH(CH_3)_2C_5H_3$
Cp*	pentamethylcyclopentadienyl
CpBu	t-butylcyclopentadienyl
CpMe	methylcyclopentadienyl
CpPr	isopropylcyclopentadienyl
COMe	methyl acyl
C_2Ph_2	diphenylacetylene
C_4Ph_2	1,4-diphenylbutadiene
C_4Ph_4	tetraphenylbutadiene
dea	diethylamine
dedm	diethyldiazomalonate
dme	dimethoxyethane
dmp	*o*-(*N*,*N*-dimethylaminomethyl)phenyl
dmpe	1,2-bis(dimethylphosphino)ethane
DPhCp	1,3-diphenylcyclopentadienyl
dppae	1-diphenylphosphino-2-diphenylarsinoethane
dppet	(diphenylphosphino)ethanethiol
Et	ethyl
$Et_2C_2B_4H_4$	*C*,*C*′-diethyldicarbatetraborate(2 −)
hmb	hexamethylbenzene
hx	hexagonal
m	monoclinic
MAPh	2-(dimethylaminomethyl)phenyl
Me_3BCp	methyl-3-α,α-dimethylbenzyl-1-cyclopentadienyl
MCp	methylcyclopentadienyl
Me	methyl
Me_2al	1,2-dimethylallyl
$MeC_2B_{10}H_{10}$	decahydro-1,6-dimethyl-1,6-dicarba-tridecaborane(2 −)
Me_3CCOO	trimethylacetate
MeC_6H_4	*p*-tolyl
Me_2CO	acetone
Me_4N	tetramethylammonium
Me_2Ph	2,6-dimethylphenyl
Me_2PhO	2,6-dimethylphenoxy
Me_3SiCp	trimethylsilylcyclopentadienyl
MIPh	$C_6H_5CN\text{-}2,6\text{-}(CH_3)_2C_6H_3$
mnt	maleonitriledithiolate
NC_4H_4	pyrrolyl
NC_6H_5	azobenzene
N_2CPh_2	diphenylhydrazonide

NH_2NPh	phenylhydrazine
N_2Ph	phenyldiazenide
p-$NO_2C_6H_4COO$	*p*-nitrobenzoate
NPh	phenylimide
$O_2CC_4H_6CO_2$	*trans*-cyclobutane-1,2-dicarboxylate
$O_2C_2Me_4$	pinacolate
$OC(NPh)_2$	diphenylureylene
O_2CPhCO_2	1,2-benzene-dicarboxylate
OEt	ethoxy
OEt_2	ethyl ether
OPh	phenoxy
or	orthorhombic
PEt_3	triethylphosphine
pfpb	2,3-bis(pentafluorophenyl)benzene
Ph	phenyl
$Ph_2CN_2C(O)N_2CPh_2$	diphenyldiazomethane carbohydrazide(2 −)
Ph_2C_2O	diphenylketene
PMe_3	trimethylphosphine
Pu	purinate
pz	pyrazole
quin	quinoline
rh	rhombic
Rphen	4-methylene-3,7,8-trimethyl-1,10-phenanthroline
S_5	pentasulfide
S_6	hexasulfide
$S_2(CH)_2$	ethylene-1,2-dithiolate
$S_2C_6H_4$	benzol-1,2-dithiolate
S_4CH_2	1-mercapto-1-methanosulfeno(dithioperoxoate)(2 −)
S_2CNMe_2	*N*, *N*-dimethyldithiocarbamate
SMe	methyl sulfide
$SiMe_3$	trimethylsilyl
$S_2N_2C_4H_2$	2,4-dithiopyrimidinate
S_3N_4	trisulfurtetranitride
SPh	phenylsulfide
p-tcd	*N*, *N′*-di-*p*-tolylcarbodiimide
tg	tetragonal
theo	theophyllinate
thf	tetrahydrofuran
tmen	tetramethylethylenediamine
tol	toluene
tr	triclinic
tSipb	2-trimethylsilyl-3-phenylbenzene

A. INTRODUCTION

The rapid growth of transition metal organometallic chemistry since the 1950s has been remarkable, and is partly because many of these compounds are effective catalysts, and because they can themselves be precursors for a wide range of derivatives. This has also led to the development of new methods in organic synthesis, and to a better understanding of catalytic processes. During the past few years there have been several developments in the theoretical aspects of structure and bonding which have prompted a better understanding of the nature of the organometallic molecules.

The chemistry of titanium is characterized by its multiple oxidation states and has long been an active field of study. The relationship between structure, reactivity, and catalytic activity has been of major importance. There have been many structural studies of titanium compounds which have been summarized in annual reports [1–3] and several reviews [4,5], but there has not been a comprehensive review and classification of the crystallographic data. This review presents the structural data for titanium organometallics. The material has been obtained from published literature up to at least volume 102 (1985) of Chemical Abstracts. The activity and interest in the area is evident from the appearance of several new structures during the few months that this manuscript was in preparation, many of which have been included.

The available structural information for titanium coordination compounds (excluding organometallics) has also been compiled and will be presented elsewhere [6]. The aim of this review is to provide the first overview of organometallic compounds for which structures have been determined by X-ray crystallography, and to make comparisons between the organometallic and other complexes of titanium. Whenever possible the estimated standard deviations and the maximum deviation from the mean value quoted, are given in parentheses.

With over three hundred coordination and organometallic structures, the chemistry of titanium is the richest of the Group IVB elements. The systems to be discussed here can be largely regrouped into two classes, those containing one aromatic multidentate ligand, and those containing at least two such aromatic ligands.

B. HOMOLEPTIC TITANIUM COMPOUNDS AND DERIVATIVES WITH ONE MULTIDENTATE RING LIGAND

(i) Monometallic compounds

The crystal and structural data for titanium monometallic compounds in which the organic moiety is bonded by a unidentate carbon σ-donor atom or multidentate ligand are given in Table 1. The data have been arranged so that the structures are in increasing order of coordination number. The titanium atom in (η^5-Cp)TiCl$_3$ [7], (η^7-C$_7$H$_7$)Ti(dmpe)Et [8], and in Ti(CH$_2$Ph)$_4$ [9,10], has approximately tetrahedral coordination. The environment about the titanium in the first compound consists of three chlorine ligands with Ti–Cl bond distances ranging from 2.201(5) to 2.248(5) Å, and a Cp ligand. The Cl–Ti–Cl and Cl–Ti–CNT angles vary from 102.2 to 115.0(2)° which demonstrates the deviation from an ideal tetrahedron. One bidentate dmpe ligand (Ti–P=2.636(1) and 2.673(1) Å), one ethyl group (Ti–C=2.211(5) Å) and one cycloheptatrienyl in the second complex, and four unidentate CH$_2$Ph ligands in the third, build up four-coordination about the titanium atom (Table 1). The Ti–CNT distance of 2.01 Å in the former is smaller than the centroid distance in the latter (2.243 Å), as was expected.

The titanium(II) atom in (η^6-hmb)Ti(Cl$_2$AlCl$_2$)$_2$ [11] possesses a square-pyramidal coordination. The four chlorine atoms (Ti–Cl=2.600–2.624(4) Å) form the corners of a square and the π-bonded hexamethylbenzene takes the axial position (Ti–CNT=2.055 Å). Other examples of five-coordination around titanium have been found also in (η^5-Cp)TiCl$_2$(NH$_2$NPh), (η^5-Cp)TiCl$_2$(N$_2$Ph) [13], and (η^5-Cp)Ti(dmp)$_2$ [14].

Coexistence of the two monomers in [(η^5-Cp)TiCl$_2$(thf)][(η^5-Cp)TiCl$_2$(thf)$_2$] has been found [12]. While the coordination about titanium

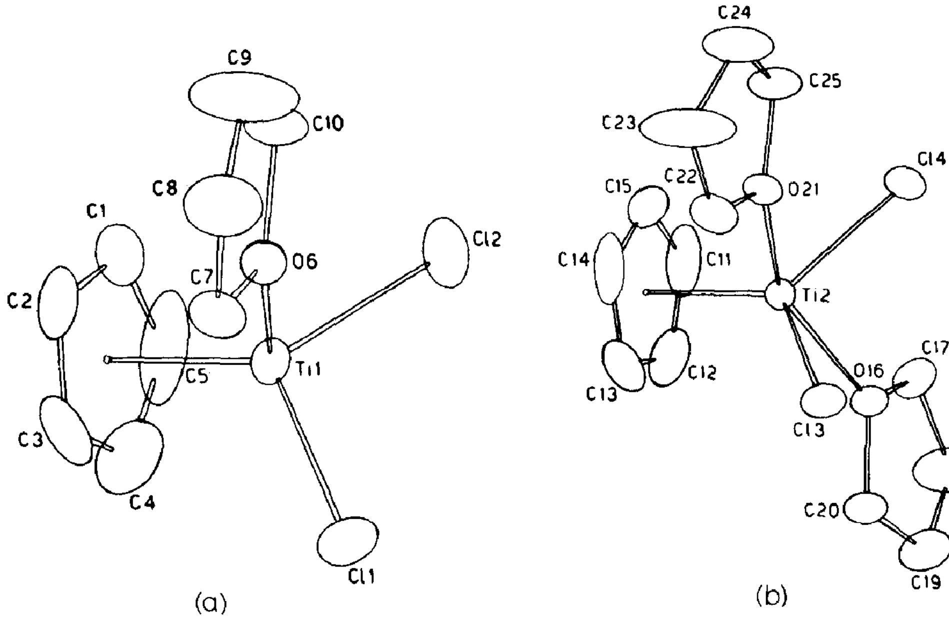

Fig. 1. Structure of (η^5-Cp)TiCl$_2$(thf) (a), and (η^5-Cp)TiCl$_2$(thf)$_2$ (b). Reproduced with permission from ref. 12.

TABLE 1

Structural data for mononuclear titanium compounds with unidentate multidentate/ligands [a]

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–CNT (Å) L–Ti–CNT [b,c] (°)	L–Ti–L (°)	Ref.
(η^5-Cp)Ti^{IV}Cl$_3$	m	$P2_1$	2	6.588 (2) 10.419 (3) 6.680 (2)	115.86 (2)	Cl 2.223 (4, 22) (Cp)C 2.31 (2, 5)	2.01 Cl 115.5(–, 1.7)	103.2 (2, 1.0) (86.2–144.7 (6)) [c]	7
(η^7-C$_7$H$_7$)Ti^{II}(dmpe)Et	m	$P2_1/c$	4	8.138 (1) 25.657 (4) 8.791 (5)	109.65 (3)	(Et)C 2.211 (5) P 2.655 (1, 19) (C$_7$H$_7$)C [d]	2.243	[d]	8
Ti^{IV}(CH$_2$Ph)$_4$	or	$P2_12_12_1$	4	19.28 (10) 13.03 (7) 9.26 (5)		C 2.14 (3.1)		109 (1, 14)	9
Ti^{IV}(CH$_2$Ph)$_4$ [f]	or	$P2_12_12_1$	4	9.204 (12) 13.026 (14) 19.120 (17)		C 2.13 (4, 9)		109 (–, 10)	10
(η^6-hmb)Ti^{II}(Cl$_2$AlCl$_2$)$_2$ (C$_6$H$_6$)	or	$P2_12_12_1$	4	18.339 (6) 14.129 (5) 11.318 (10)		Cl 2.615 (4, 15) (hmb)C 2.498 (14, 56)	2.055 Cl 117.3 (–, 2.3)	78.1 (1, 1.9)	11
(η^5-Cp)Ti^{III}Cl$_2$(thf) [g]	tr	$P\bar{1}$	2	11.139 (4) 13.641 (5) 9.398 (4)	95.31 (3) 106.94 (2) 98.51 (3)	(thf)O 2.065 (4) Cl 2.325 (3, 15) (Cp)C [d]	2.014 (13) O 113.6 (4) Cl 121.5 (4, 0)	94.0 (1, 4) [h] 105.6 (1)	12
(η^5-Cp)Ti^{III}Cl$_2$(thf)$_2$ [g]						(thf)O 2.258 (4, 17) Cl 2.369 (2, 1) (Cp)C [d]	2.059 (8) O 104.5 (3, 5) Cl 123.5 (3, 3.0)	82.3 (1, 1.9) [h] 114.5 (1) 151.0 (2)	
(η^5-Cp)Ti^{IV}Cl$_2$(NH$_2$NPh)	tr	$P\bar{1}$	2	7.664 (8) 9.322 (8)	95.27 (8) 105.8 (8)	Cl [d] N 2.011 (10, 134)		40.4 (4) [i]	13

				9.851 (1)	112.59 (7)	(Cp)C ^{d}			
(η^5-Cp)Ti^{IV}Cl$_2$(N$_2$Ph)	m	$P2_1/c$	8	13.73 (1)		Cl ^{d}		34.8 (2) ^{i}	13
				12.854 (5)	109.85 (5)	N 2.029 (5, 25)			
				14.567 (7)		(Cp)C ^{d}			
(η^5-Cp)Ti^{III}(dmp)$_2$	m	$C2/c$	4	16.143 (5)		(dmp)C 2.197 (6)	2.05 (1)	78.6 (2, 5.2) ^{j}	14
				7.889 (3)	100.63 (6)	(dmp)N 2.389 (4)	N 118.1 (2)	123.9 (2)	
				16.347 (4)		(Cp)C 2.38 (1)	C 114.8 (2)	130.5 (2)	
(η^5-Cp)Ti^{IV}Cl(quin)$_2$	m	$P2_1/c$	4	8.82 (2)		Cl 2.372 (5)	2.101	73.8 (3) ^{k}	15
				13.85 (2)	111.7 (2)	O 1.971 (7, 17)		78.2 (3, 5.2)	
				16.80 (2)		N 2.247 (10, 23)		77.8, 150.4 (2)	
						(Cp)C 2.416 (14, 44)		93.9 (2, 3.1)	
								150.0 (3)	
[C$_4$Ph$_4$TiCl$_3$] [Mg$_2$Cl$_3$(thf)$_6$]	m	$C2$	4	17.74 (1)		Cl 2.24 (1, 1)	2.0	43.3 (9) ^{l}	16
				14.45 (1)	92.94 (6)	C 2.24 (2, 3)		101.6 (7, 3.3)	
				22.03 (1)				92.6–141.9 (7)	
				17.58 (1) ^{m}					
				14.20 (1) ^{m}	95.2 (1) ^{l}				
				21.72 (1) ^{m}					
(η^5-Cp)Ti^{IV}(S$_2$CNMe$_2$)$_3$	m	$P2_1/c$	4	10.154 (1)		S 2.611 (2, 55)	2.103 (6)	73.44 (5, 8.82) ^{n}	17
				11.444 (2)	97.11 (6)	(Cp)C 2.422 (6, 3)	S 100.6–171.4 (2)	79.1 (2, 4.4)	
				22.411 (2)				33.9 (2, 4)	

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[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the estimated standard deviation, and the second is the maximum deviation from the mean value. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] The centroid of the ring. [d] Value not given. [e] The values of the Cl–Ti–C(Cp) bond angles. [f] At 233 K. [g] Both mono- and bis-thf coordinated molecules are found in the crystal in a 1 : 1 ratio. Empirical formula: CpTiCl$_2$(thf)$_{1.5}$. [h] The values of the Cl–Ti–O (first number in the column), Cl–Ti–Cl (second), and O–Ti–O (third) angles. [i] The value of the N–Ti–N angle. [j] The values of the C–Ti–N, N–Ti–N, and C–Ti–C angles, respectively. [k] The values (from top to bottom in the column) of N–Ti–N, N–Ti–O, N–Ti–Cl, O–Ti–Cl, and O–Ti–O angles. [l] The values (from top to bottom in the column) of C–Ti–C, Cl–Ti–Cl, and Cl–Ti–C angles. [m] At 100 K. [n] The values (from top to bottom in the column) of S–Ti–S, S–Ti–C, and C–Ti–C angles.

TABLE 2

Structural data for bi- and oligo-nuclear compounds [a]

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–Ti (Å) Ti–CNT (Å) [c] Ti–L–Ti (°)	L–Ti–L L–Ti–CNT [c] (°)	Ref.
$[(\eta^8\text{-}C_8H_8)TiMeC_2Ph]_2$	m	*Cc*		16.30		C 2.24 (10, 26)	2.94 (4)		18
				9.65	100.20	$(C_8H_8)C$ [d]	[d]		
				17.11					
$\{(Ti^{IV}(CH_2Ph)_3]_2(\mu\text{-}O)\}$	rh	$R\bar{3}$	1	9.58 (2)	83.6 (2)	C 2.076 (9)		109.4 (1, 3.7)	19
						O 1.798 (0) [e]			
							180.0 (0)		
$\{[\eta^5\text{-}Cp)Ti^{IV}Cl_2]_2(\mu\text{-}O)\}$		$P2_1/c$	2	7.47		Cl 2.25 (4)		104 (2)	20
				9.86	127.56	(Cp)C 2.35 (5)	2.03 (5)	114 (2, 3)	
				12.58		O 1.78 (3) [e]	180		
$\{[\eta^5\text{-}Cp)Ti^{IV}Cl_2]_2(\mu\text{-}O)\}$	m	$P2_1/n$	2	7.566 (1)		Cl 2.239 (2, 0)		102.7 (2, 4)	21
				9.909 (2)	91.83 (2)	(Cp)C 2.314 (9, 26)	2.010	115.3 (–, 1.7)	
				9.914 (2)		O 1.777 (1) [e]	180		
$[(EtO)_2Ti^{IV}(CH_2Ph)_2]_2$	m	$P2_1/c$	4	7.93 (2)		C 2.119 (13, 28)	3.197 (3)	72.9–169.8 (2)	22
				15.99 (2)	92.7 (3)	O 1.837 (8)			
				13.40 (2)		O 1.985 (7, 120) [e]	107.1 (1)		
$\{[(\eta^5\text{-}Cp)TiCl_2]_2(\mu\text{-}NPh)_2\}$	or	*Pbca*	4	8.705 (3)		Cl [d]			23
				14.595 (7)		(Cp)C [d]			
				17.166 (3)		N [d,e]			
$[(\eta^5\text{-}CpTi^{III}Cl)_2(\mu\text{-}NPh)$ $(\mu\text{-}N_2Ph_2)]$	m	$C2/c$	4	14.041 (2)		Cl 2.332 (2)	2.829 (2)	37.0–116.6 (1)	12, 24
				12.743 (2)	115.23 (2)	(Cp)C [d]	2.040 (9)	110.0–151.9 (3)	
				15.875 (3)		(NPh)N 1.920 (4) [e]	81.4, 94.9 (1)		
						$(N_2Ph)N$ 2.157 (4, 207) [e]			
$[(\eta^5\text{-}CpTi^{III}Cl)_2$ $(\mu\text{-}N_2CPh_2)_2]$	m	$P2_1/c$	4	18.704 (2)		Cl 2.327 (3, 27)	2.837 (3)	36.9–145.7 (2)	12
				8.785 (1)	100.57 (1)	(Cp)C [d]	2.033 (7, 22)	115.4 (3, 9.0)	
				21.049 (2)		N 2.171 (6, 8)	94.7 (2, 4)		
						N 1.927 (6, 79) [e]			
$[(\eta^5\text{-}Cp)Ti^{III}Cl(BH_4)]_2$	m	$B2/b$	8	18.710 (8)		$(BH_4)H$ 1.95 (2, 10)		51–134 (2)	25
				13.826 (5)		(Cp)C 2.315 (7, 14)		107–156 (2)	
				7.144 (3)	125.70 (5)	Cl 2.437 (1, 1) [e]	90.00 (3)		
$[(\eta^7\text{-}C_7H_7)Ti^{II}(thf)(\mu\text{-}Cl)]_2$	m	$P2_1/n$	2	6.630 (3)		O 2.187 (1)	3.883 (1)	81.07 (3, 1.12)	8
				17.729 (3)	98.82 (3)	C 2.238 (5)	1.545		
				9.370 (1)		Cl 2.542 (1, 2) [e]	99.58 (2)		
$[(\eta^8\text{-}C_8H_8)Ti(thf)(\mu\text{-}Cl)]_2$ [f,g]	m	$P2_1/c$	4	10.779 (1)		O 2.254 (2)		82.4	26
				14.304 (1)	100.84 (2)	C 2.382 (3, 13)	1.518		

				15.478 (3)		Cl 2.531 (1, 6) [e]	97.6		
						O 2.258 (2)		81.6	
						C 2.387 (3, 16)	1.530		
						Cl 2.549 (1, 2) [e]	98.4		
$[(\eta^5\text{-Cp})\text{Ti}^{II}(C_6H_5COO)_2]_2$ [f]	m	$P2_1/b$	4	16.35 (3)		(Cp)C 2.48 (–, 13)	3.63	83(–, 3)	27
				21.35 (4)	92 (1)	O 2.00 (–, 5) [e]	2.16		
				11.27 (2)					
						(Cp)C 2.38 (–, 11)	3.74	83 (–, 7)	
						O 2.09 (–, 6) [e]	2.06		
$\{[\eta^5\text{-Cp})\text{Ti}^{IV}Cl_2]_2(O_2C_2Me_4)\}$ [h]		$P2_1/c$	2	9.066 (3)		Cl 2.276 (1)		102.2 (1, 1.1)	28
				6.798 (2)	94.60 (3)	(Cp)C 2.345 (3, 30)	2.019	116.0 (–, 2.8)	
				16.613 (5)		O 1.750 (2)			
$[(\eta^5\text{-Cp})\text{Ti}^{IV}\text{Cl}(\mu\text{-O})]_4$	or	$Cmc2_1$	4	15.320 (5)		Cl 2.266 (4, 4)	4.882 (–, 36)	102.8 (4, 1.6)	29
				11.715 (5)		C 2.37 (2, 7)	2.034 (–, 14)	115.7 (–, 1.4)	
				14.515 (5)		O 1.788 (6, 12) [e]	162.3 (5, 2.6)		
$[(\eta^5\text{-CpMe})\text{Ti}^{IV}\text{Cl}(\mu\text{-O})]_4$	m	$C2/c$	4	18.344 (4)		Cl 2.269 (3, 4)	3.899 (1, 1.06)	103.0 (1, 2.2)	30
				10.195 (2)	114.68 (1)	(Cp)C 2.357 (8, 54)	2.034 (–, 6)	115.3 (3, 5.2)	
				17.178 (3)		O 1.798 (2, 6)	161.5 (2, 7.6)		
$[(\eta^5\text{-}C_9H_{11})\text{Ti}^{IV}\text{Cl}(\mu\text{-O})]_4$	tg	$P\bar{4}2_1c$	2	15.704 (7)		Cl 2.281 (3)		103.4 (3, 2.0)	31a
				15.704 (7)		C 2.373 (9, 64)	2.049	114.9 (–, 2.1)	
				7.776 (4)		O 1.805 (5, 4) [e]	158 (2)		
$[(\eta^5\text{-}C_8H_8)\text{TiCl}]_4$ [h]	tg	$I\bar{4}2m$	4	10.763		C 2.348 (7, 30)		80.28 (4, 2.49)	26
				10.763		Cl 2.583 (2, 26) [c]			
				13.657			100.47 (4, 3.31)		
$\{[\eta^5\text{-Cp})\text{Ti}]_5(\mu_3\text{-S})_6\}$		$P2_1/n$	4	16.978 (5)		C [d]	3.157 (5, 81)		31b
				17.008 (9)	92.44 (2)	S 2.409 (7, 146) [e]			
				10.122 (3)					
$\{[(\eta^5\text{-Cp})\text{Ti}]_6(\mu_3\text{-O})_8\}$ [i]		$Pnam$	4	18.367 (4)		C 2.381 (5, 26)	2.891 (1, 28)		32
				9.635 (2)		O 1.973 (3, 15) [e]			
				16.758 (4)					
$\{[\text{Ti(dea)}_3]_2(\eta^5\text{-Cp})_2\text{Fe}\}$		$P2_1/n$	4	9.408 (5)		N 1.89 (2, 3)		110.1 (2, 4.5)	33
				25.111 (12)	106.83 (8)	C 2.15 (2, 2)			
				18.488 (18)					
$[(CO)_9Co_3(CO)]_2(\eta^5\text{-Cp})\text{TiCo(CO)}_4$		$P\bar{1}$	2	17.763 (5)	99.0	(Cp)C 2.375 (–, 1.2)		103.1 (–, 1.9)	34
				13.094 (4)	101.1	Co 2.614	2.044	115.0 (–, 3.5)	
				9.020 (6)	76.9	O 1.830 (–, 9) [d]			

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[a] Where more than one chemically equivalent distance or angle present, the mean value is tabulated. The first number in parentheses is the estimated standard deviation, and the second is the maximum deviation from the mean value. [b] The chemical identity of the coordinated atom or ligand is specified in this column. [c] The centroid of ring. [d] Value not given. [e] The bridging atom. [f] There are two independent molecules. [g] At 100 K. [h] At 135 K. [i] At 113 K.

in (η^5-Cp)TiCl$_2$(thf) is distorted tetrahedral (Fig. 1(a)) in (η^5-Cp)TiCl$_2$(thf)$_2$ it is a distorted trigonal bipyramid (Fig. 1(b)). The mean Ti–L bond distances in the latter are somewhat longer than those in the former (Table 1), as was expected.

X-Ray analysis of the bright-red air-stable crystals of (η^5-Cp)TiCl(quin)$_2$ [15] shows the geometry around the titanium(IV) atom to be distorted octahedral. In the remaining two examples (Table 1), the [(C$_4$Ph$_4$)TiCl$_3$]$^-$ ion [16] and (η^5-Cp)Ti(S$_2$CNMe$_2$)$_3$ [17], a hepta-coordinated geometry is found about each titanium atom.

Examination of the data in Table 1 reveals that the mean Ti–C(Cp) and Ti–CNT(Cp) bond distances are dependent on the coordination polyhedra, and increase with coordination number in the order: four- < five- < six- < seven-coordinate compounds, corresponding to the values, 2.31 and 2.01 Å < 2.38 and 2.055 Å < 2.41 and 2.101 Å < 2.422 and 2.103 Å, respectively. On the other hand, the Ti–Cl bond distance does not follow this order: 2.24 Å (seven-coordinate) < 2.27 Å (four-coordinate) < 2.369 Å (five-coordinate) < 2.372 Å (six-coordinate). In general, the Ti–L bond distances increase as the size of the ligating group increases. For example, the Ti–CNT distance in four-coordinated compounds is 2.01 Å (Cp) and 2.243 Å (C$_7$H$_7$).

(ii) Bi- and oligometallic compounds

Crystal and structural data for bi- and oligometallic titanium organometallics are gathered in Table 2. A characteristic feature in these structures is the omnipresence of bridging atoms or ligands. In several cases sufficiently short Ti–Ti distances (2.83–3.00 Å) for metal–metal bonding or orbital interactions to occur are encountered. Nevertheless, as for bimetallic compounds with at least two aromatic rings (see Table 4), short metal–metal distances should also be viewed as a consequence of bridging constraints as well as a bonding necessity.

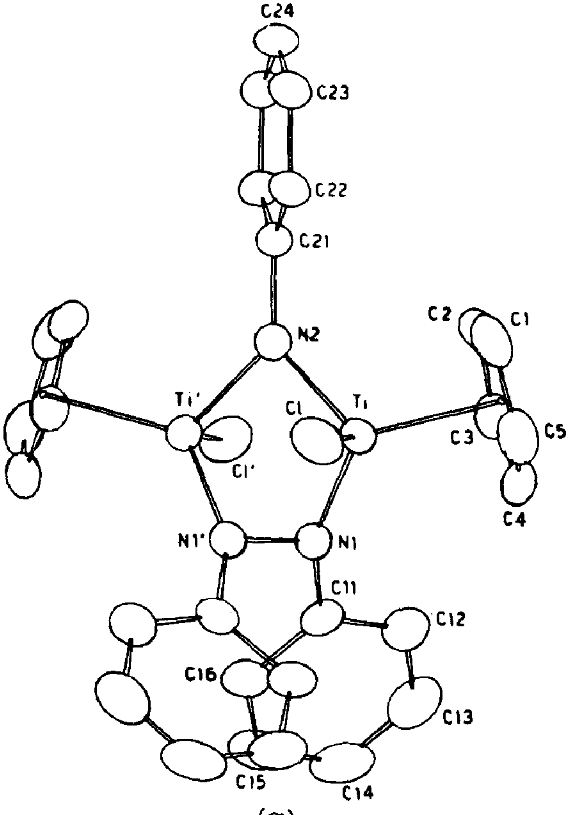
The homometallic examples can be divided into several groups based on the nature of the bridging. In [(η^8-C$_8$H$_8$)TiMeC$_2$Ph]$_2$ [18], the two C$_8$H$_8$ rings are planar and both are π-bonded to a central atom; one Ti atom is part of a titanole ring, the other Ti atom is π-bonded to this ring. The Ti–Ti bond distance of 2.94(4) Å indicates metal–metal bonding.

In the two structures {[Ti(CH$_2$Ph)$_3$]$_2$(μ-O)} and {[(η^5-Cp)TiCl$_2$]$_2$(μ-O)} [19–21], the two titanium(IV) atoms are bridged singly by oxygen atoms. The four nearest neighbours to the titanium(IV) atom form approximately tetrahedral coordination. These three tetrahedrally coordinated bimetallic titanium(IV) compounds were the first examples found with linear Ti–O–Ti bridges.

Doubly-bridged titanium atoms are the most common of the bimetallic derivatives listed in Table 2. Examples include compounds containing oxygen ligands (OEt) [22], nitrogen ligands (NPh) [23], and chlorine atoms [8, 25 and 26].

In $[(\eta^5\text{-CpTiCl})_2(\mu\text{-NPh})(\mu\text{-N}_2\text{Ph}_2)]$ [12 and 24] and $[(\eta^5\text{-CpTiCl})_2(\mu\text{-N}_2\text{CPh}_2)_2]$ [12], two titanium(III) atoms are bridged as shown in Figs. 2(a) and 2(b). In the former, the two [CpTiCl] moieties are bridged by a phenylimido ligand. The Ti–Ti distance of 2.829(2) Å is somewhat shorter than that in the latter (2.837(3) Å) and indicates a direct bond between the metal atoms. The Ti–L bond distances found in these two bimetallics also differ slightly from each other (Table 2).

By contrast, the distance between the titanium atoms in $[(\eta^5\text{-Cp})\text{Ti}(\text{C}_6\text{H}_5\text{COO})_2]_2$ [27] (3.63 or 3.74 Å; there are two independent bimetallic molecules) indicates no direct bonding interaction. This compound is bimetallic with a structure similar to that of copper(II) acetate



(a)

Fig. 2. Structure of $[(\eta^5\text{-CpTiCl})_2(\mu\text{-NPh})(\mu\text{-N}_2\text{Ph}_2)]$ (a); and $[(\eta^5\text{-CpTiCl})_2(\mu\text{-N}_2\text{CPh}_2)_2]$ (b), page 62. Reproduced with permission from ref. 12.

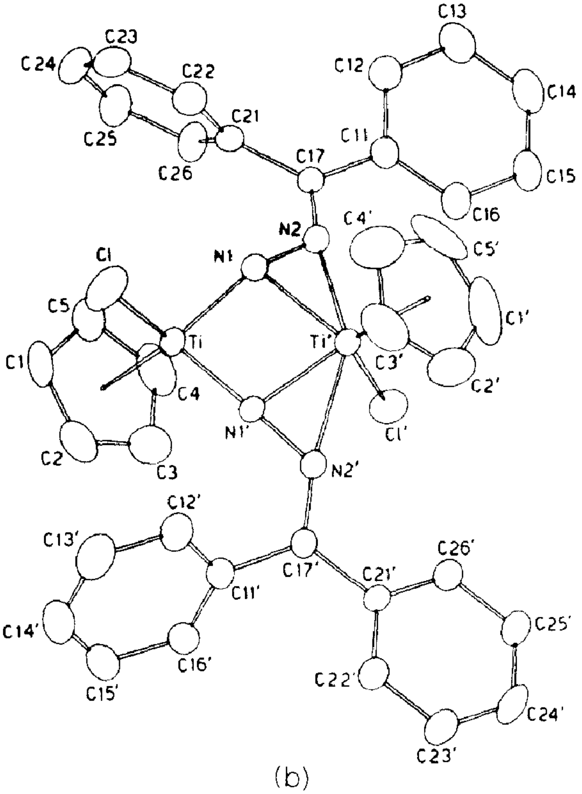


Fig. 2. (continued)

monohydrate [144], having two titanium(III) atoms bridged to four carboxylate groups. Each titanium atom has square pyramidal coordination, with the π-cyclopentadienyl ligand in the axial position. The absence of metal–metal bonds in a dimer of this type is rare, but there is probably considerable steric hindrance between the bulky cyclopentadienyl ligands in the axial positions and the carboxylate ligands bonded to titanium.

The bright-yellow compound $\{[(\eta^5\text{-Cp})TiCl_2]_2(O_2C_2Me_4)\}$ [28] has two $[CpTiCl_2]^+$ units held together by a pinacolate dianion ligand (Ti–O–C–C–O–Ti).

There are four tetrametallic examples of titanium complexes (Table 2). In the centre of the tetrametallic molecule, $[(C_8H_8)TiCl_2]_4$ [26], is a hexahedron of Ti and Cl atoms lying on alternate vertices. The four cyclooctatetraenyl rings which are π-bonded to the metal are tetragonally disposed around the approximate cube formed by the eight Ti and Cl atoms and lie roughly perpendicular to the body diagonals. In this compound the Ti–Ti distances are greater than 3.5 Å. In the remaining three examples ($[RTi^{IV}Cl(\mu\text{-}O)]_4$, R = η^5-Cp [29], η^5-CpMe [30], and η^5-C_9H_{11} [31a]), four RTiCl moieties are linked by four oxo bridges to produce an eight-membered central ring of

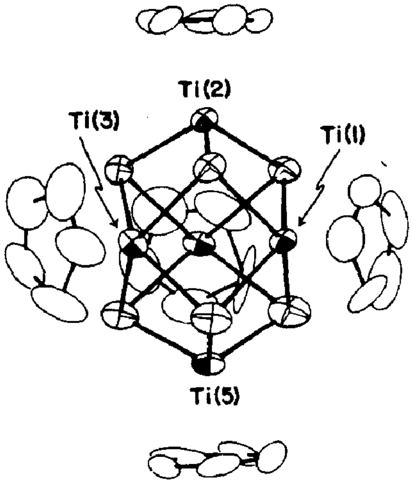


Fig. 3. Structure of $[(\eta^5\text{-CpTi})_5S_6]$. Reproduced with permission from ref. 31(b).

alternating Ti and O atoms. The pseudotetrahedral arrangement about each Ti(IV) atom is comprised of a multidentate R ring, a chlorine ligand, and two oxo bridges.

In general, the mean Ti–O–Ti and L–Ti–CNT angles decrease with increasing size of the R ligand, whereas the L–Ti–L angle decreases. In addition the Ti–L bond distances decrease as the size of the ligating R ring decreases (Table 2).

The crystal structure of dark green-brown $(\eta^5\text{-CpTi})_5S_6$ [31b] shows five titanium atoms forming a distorted trigonal bipyramid. One cyclopentadienyl ring is π-bonded to each titanium. The sulfur atoms are placed over the six triangular faces of the polyhedron, each bridging three titanium atoms (Fig. 3). Similarly, the titanium atoms in $(\eta^5\text{-CpTi})_6O_8$ [32] describe an octahedron. The six cyclopentadienyl rings cap all apices and the eight oxygen atoms each occupy a face of the polyhedron (Fig. 4). The mean Ti–Ti distance (3.157(5,21) Å) in the former pentametallic cluster is longer than that found in the latter (2.891(1,28) Å). The smaller covalent radius of oxygen (0.73 Å) versus sulfur (1.02 Å) has been proposed to be the main reason for the difference [31b].

There are two examples of heterometallic compounds (Table 2). In $[\text{Ti(dea)}_3]_2(\eta^5\text{-Cp})_2\text{Fe}$ [33], the crystal unit CpFe "holds" two Ti(dea)_3 moieties by a single carbon atom of the Cp ligand, and completes an approximately tetragonal environment about the titanium atoms. A tetrahedrally-surrounded titanium metal atom has been found in the cobalt cluster, $[(\text{CO})_9\text{Co}_3\text{CO}]_2(\eta^5\text{-Cp})\text{TiCo(CO)}_4$ [34] (Table 2). The coordination sphere about titanium is comprised of, two oxymethylidynenonacarbonyltricobalt groups, one π-bonded Cp ring, and one Co(CO)_4 group.

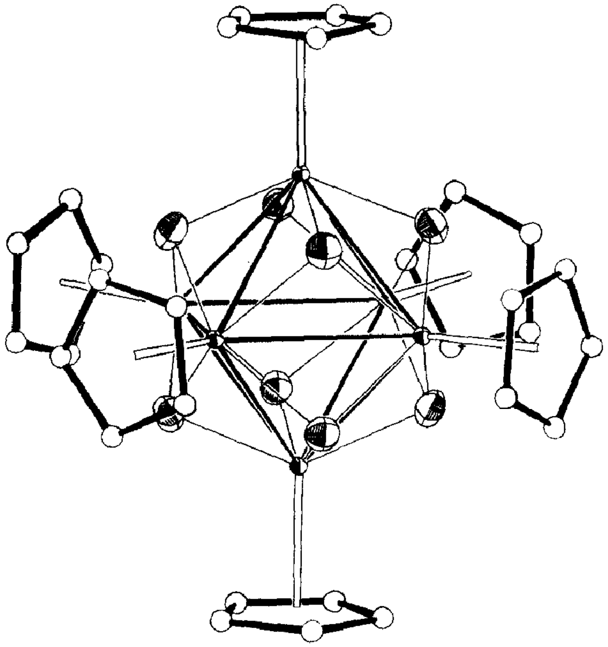


Fig. 4. Structure of $[(\eta^5\text{-CpTi})_6O_8]$. Reproduced with permission from ref. 32.

Inspection of the data in Table 2 shows that there is a tendency for the Ti–L bond distances to elongate with nucleation. For instance, while the mean Ti–L distances in bimetallic compounds are 1.785 Å (L = O, bridge), 2.364 Å (L = C, Cp), and 2.512 Å (L = Cl, bridge), in tetrametallic compounds they are 1.795, 2.370 and 2.583 Å, respectively. However, the mean Ti–Cl(terminal) distance of 2.292 Å in bimetallic compounds is somewhat longer than that in tetrametallic compounds (2.269 Å).

C. TITANIUM COMPOUNDS WITH TWO MULTIDENTATE RING LIGANDS

(i) Monometallic compounds

Crystal and structural data for monometallic titanium organometallics with at least two multidentate ligands are listed in Table 3 Almost half of the known structures for organotitanium compounds belong to this group. The cyclopentadienyl radical is one of the most widely found π-electron donors, and the vast majority of the titanium organometallic derivatives have at least one of these ligands. The Table has been arranged so that the structures are in increasing order of coordination number, increasing atomic number of the principal coordinating ligand, and increasing order of complexity of the coordination sphere.

TABLE 3

Structural data for mononuclear titanium compounds with two multidentate ligands [a]

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–CNT (Å) [c] CNT–Ti–CNT (°)	L–Ti–L (°) CNT–Ti–L [c] (°)	Ref.
$[Me_4N]_2[Ti(Me_2C_2B_{10}H_{10})_2]\cdot 2(Me_2CO)$ [d]	tr	$P\bar{1}$	2	13.412 (3) 9.325 (2) 16.781 (5)	95.21 (2) 106.15 (2) 81.55 (2)	C 2.324 (5, 148) B 2.400 (6, 62) C 2.326 (5, 141) B 2.398 (7, 60)			35
$(\eta^8-C_8H_8)Ti^{IV}(Et_2C_2B_4H_4)$		$Pna2_1$	4	14.309 (3) 12.660 (2) 8.476 (2)		C 2.304 (11, 38) B 2.371 (9, 16) (C_8H_8)C 2.291 (12, 35)			36
$(\eta^5-Cp)Ti(\eta^7-C_7H_7)$	or	$Pnma$ $(Pna2_1)$	4	11.040 (2) 10.805 (2) 8.040 (4)		(Cp)C 2.321 (3, 6) (C_7H_7)C 2.194 (3, 29)	1.994 (3)	177.8 (3)	37
$(\eta^5-Cp)Ti(\eta^8-C_8H_8)$		$Pnma$	4	11.178 (3) 10.993 (3) 8.469 (2)		(Cp)C 2.353 (4, 8) (C_8H_8)C 2.323 (4, 5)		178.1 (2)	38
$(\eta^8-C_8H_8)Ti(\eta^8-C_8H_8)$	m	Pb	2	7.00 12.26 7.92	114.85	C 2.32 (2, 18)			39
$(\eta^5-Cp)_2Ti^{III}(OPh)$	m	$P2_1/c$	4	8.010 (6) 15.919 (8) 17.640 (8)	98.15 (5)	O 1.892 (2) (Cp)C 2.362 (10, 18)	135.5		40
$(\eta^5-Cp)_2Ti^{III}(BH_4)$ [f]						H 1.89 B 2.31 (Cp)C 2.382	137		41
$(\eta^5-Cp)_2Ti^{III}(BH_4)$	or	$Fm2m$	4	9.336 (3) 7.991 (3) 13.467 (9)		H 1.75 (8) B 2.37 (1) (Cp)C 2.35 (2, 7)	2.03 (–, 3) 136.7	60(5)	42
$(\eta^5-Cp)_2Ti^{III}H_2AlCl_2\cdot(OEt_2)$	rh	$Pbca$	16	12.322 (2) 15.090 (3) 37.941 (7)		H 1.80 (7, 11) (Cp)C 2.33 (1, 5)	137.1 (–, 1)	75 (3, 5)	43
$[(\eta^5-Cp)_2Ti^{IV}(H_2O)_2](NO_3)_2$ [g]	or	$Pnma$	4	7.601 (2) 13.458 (4) 13.139 (4)		(H_2O)O 2.005 (4) (Cp)C 2.356 (7, 25)	2.031 (–, 5) 133.6	92.7 105.8 (–, 6)	44

TABLE 3 (continued)

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–CNT (Å) [c] CNT–Ti–CNT (°)	L–Ti–L (°) CNT–Ti–L [c] (°)	Ref.
				7.689 (3) [h] 13.828 (6) [h] 12.908 (4) [h]					
$[(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{H}_2\text{O})_2(\text{thf})][\text{ClO}_4]_2$ [g]	m	$P2_1/c$	4	15.324 (5) 10.848 (5) 18.325 (5)	 110.75 (3)	(H_2O)O 2.006 (5, 19) (Cp)C 2.361 (8, 23)	2.034 (–, 4) 133.3	90.4 (2) 106.2 (–, 1.2)	45
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{NO}_3)_2$	or	$Pbcm$	4	6.511 (2) 14.333 (4) 12.955 (4)		(NO_3)O 2.146 (7) (Cp)C 2.363 (12, 16)	2.048 (–, 1) 131.3	69.5 109.8 (–, 6)	46
$(\eta^5\text{-Cp})(\eta^5\text{-Cp}')\text{Ti(ClPhO)}\cdot(\text{Me}_2\text{PhO})$ [i]	or	$Pna2_1$	4	16.42 (3) 12.45 (2) 12.14 (2)		O 1.93 (Cp)C 2.43	2.13 125	62 97	47
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{C}_6\text{H}_5\text{COO})_2$	m	$P2_1/c$	4	16.078 (2) 12.853 (3) 16.076 (2)	 142.685 (7)	O 1.926 (6, 4) (Cp)C 2.373 (12, 36)	2.061 (10, 4) 131.7 (5)	91.4 (3)	48
$(\eta^5\text{-Cp})_2\text{Ti}^{III}(\text{C}_6\text{H}_5\text{COO})$ [j]	m	$P2_1/n$	8	11.388 (2) 11.564 (2) 22.673 (3)	 105.09 (1)	O 2.143 (4, 9) (Cp)C [e]	2.037 (9, 3) 136.0 (4)	60.9 (1) 108.8 (3, 1.8)	49
						O 2.151 (3, 4) (Cp)C [e]	2.036 (7, 2) 135.1 (3)	60.5 (1) 109.2 (2, 2.0)	
$[(\eta^5\text{-Cp})_2\text{Ti(thf)}(\text{Me}_2\text{CO})]_2[\text{Zn}(\text{B}_{10}\text{H}_{12})_2]\cdot(\text{thf})$	m	$P2_1/a$	4	22.920 (9) 16.608 (7) 14.360 (6)	 97.475 (15)	(thf)O 2.21 (1, 0) (Me_2CO)O 2.13 (1, 0) (Cp)C 2.36 (2, 6)	2.06 (–, 1) 135.6 (–, 4)	77.8 (–, 9) 106.9 (–, 2.7)	50
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{CF}_3\text{SO}_3)_2$	m	$P2_1/n$	4	16.137 (6) 12.851 (5) 8.299 (4)	 91.97 (5)	O 2.001 (7, 2) (Cp)C 2.368 (10, 38)	2.038 (–, 9) 131.0	91.2	51
$(\eta^5\text{-Cp})_2\text{Ti}(p\text{-NO}_2\text{C}_6\text{H}_4\text{COO})_2$	tr	$P\bar{1}$	2	12.96 (2) 11.53 (2) 7.62 (1)	84.3 (1) 95.2 (5) 90.5 (5)	O 1.99 (–, 5) (Cp)C 2.39 (–, 2)	2.05 (–, 1) 132	92 106 (–, 3)	52
$(\eta^5\text{-Cp})_2\text{Ti}^{III}(\text{Me}_3\text{CCOO})$ [j]		$Pnam$		11.343 (3) 9.646 (2) 12.619 (2)		O 2.13 (1, 1) (Cp)C 2.40 (1, 11)	 135 (1)	60.9 (2)	53
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{N}_3)_2$	or	$Pnam$	4	7.879 (5) 12.169 (8) 12.046 (8)		N 2.03 (1) (Cp)C 2.37 (2, 2)	2.04 (–, 2) 132.2	94.1 (6) 106.1 (–, 6)	54

$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{NCO})_2$	or	*Pbca*	8	9.689 (3)		N 2.013 (3, 6)	2.056 (–, 3)	94.7 (2)	55
				13.265 (4)		(Cp)C 2.377 (4, 31)	132.8		
				17.500 (6)					
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{S}_3\text{N}_4)$ [f]	m	$P2_1/c$	12	7.802 (2)		N 1.954 (4, 8)		94.4 (2)	56
				20.012 (4)	92.75 (2)	(Cp)C [e]	132.8		
				25.099 (4)					
						N 1.957 (4, 6)		94.8 (2)	
						(Cp)C [e]	133.0		
						N 1.942 (4, 20)		94.6 (2)	
						(Cp)C [e]	133.3		
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{NCS})$	or	*Imma*	4	13.58 (1)		N 2.021 (7)	2.044	93.9 (3)	57
		(*Ima*2)		8.14 (1)		(Cp)C 2.358 (9, 5)	133.7		
				11.81 (1)					
$(\eta^5\text{-Cp})_2Ti^{III}(\text{Rphen})$	m	$P2_1/c$	4	14.786 (5)		N [e]			58
				9.835 (4)	107.35 (2)	(Cp)C [e]			
				14.902 (4)					
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{NC}_4\text{H}_4)_2$	m	$P2_1$	2	7.986 (4)		N 2.085 (5, 15)		90.4 (2)	59
				10.660 (5)	113.77 (4)	(Cp) 2.394 (7, 17)	128.5	107.8 (–, 1.3)	
				9.726 (5)					
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{NC}_6\text{H}_5)_2$	or	$P2_12_12_1$	4	18.034 (10)		N 1.968 (6, 3)	2.078 (–, 5)	39.8 (5)	60a
				8.904 (4)		(Cp)C 2.384 (12, 38)	133.03	112.09 (–, 5.24)	
				11.426 (7)					
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}^{IV}\text{Cl(Pu)}$	m	$P2_1/c$	4	7.484 (2)		N 2.131 (5)	2.052 (–, 2)	92.1 (1)	60b
				25.85 (1)	127.53 (3)	Cl 2.338 (2)	132.3	106.3 (–, 1.7)	
				9.134 (3)		(Cp)C 2.366 (10, 27)			
$(\eta^5\text{-Cp})_2\text{Ti}^{III}(\text{theo})$	m	$P2_1/c$	4	7.869 (5)		N 2.211 (3)	2.063 (–, 9)	79.6 (1)	60c
				7.745 (6)	100.37 (6)	O 2.278 (2)	135.0	107.1 (–, 1.1)	
				26.86 (2)		(Cp)C 2.377 (4, 33)			
$(\eta^5\text{-Cp})_2\text{Ti}^{II}(\text{CO})_2$	or	*Pnma*	4	7.837 (9)		(CO)C 2.030 (11)	2.025 (–, 7)	87.9 (6)	61
				11.475 (8)		(Cp)C 2,348 (12, 38)	138.6	104.8 (–, 7)	
				12.232 (8)					
$(\eta^5\text{-Cp}^*)_2\text{Ti}^{II}(\text{CO})_2$	or	$P2_12_12_1$	4	8.517 (3)		(CO) 2.01 (1)	2.06 (–, 1)	83.3 (3)	62
				10.774 (4)		(Cp*)C 2.384 (12)	147.9		
				22.195 (6)					
$(\eta^5\text{-Cp}^*)_2\text{Ti}^{II}(\eta^2\text{-C}_2\text{H}_4)$	tg	$P\bar{4}2_1m$	2	10.8621 (4)		(C_2H_4)C 2.160 (4)	2.092 (5)	38.9 (1)	63

TABLE 3 (continued)

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–CNT (Å) [c] CNT–Ti–CNT (°)	L–Ti–L (°) CNT–Ti–L [c] (°)	Ref.
				10.8621 (14)		(Cp*)C 2.407 (10, 57)	143.6 (5)	107.2 (3, 8)	
				8.5008 (5)					
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}(\eta^2\text{-Cp})$	or	*Pbca*	8	13.468 (6)		$(\eta^2\text{-Cp})$C 2.465 (5, 17)	2.049 (–, 12)		64
				10.229 (5)		$(\eta^5\text{-Cp})$C 2.357 (5, 45)	133.2		
				17.180 (7)					
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{IV}}(\eta^1\text{-Cp})_2$	or	*Cmca*	4	12.854 (8)		$(\eta^1\text{-Cp})$C 2.272 (14)		97.3 (1.1)	65
				16.480 (8)		$(\eta^5\text{-Cp})$C 2.31		104.4 (–, 2.3)	
				8.132 (5)					
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{IV}}(\eta^1\text{-Cp})_2$	hx	$P6_122$	6	9.214 (3)		$(\eta^1\text{-Cp})$C 2.332 (2)	2.078	86.3	66
				9.214 (3)		$(\eta^5\text{-Cp})$C 2.381 (4, 22)	129.9		
				21.895 (6)					
$(\eta^5\text{-C}_9\text{H}_7)\text{Ti}^{\text{IV}}(\text{CH}_3)_2$	or	$P2_12_12$	2	14.124 (7)		(CH_3)C 2.21 (2)	2.05	92.8 (12)	67
				8.073 (5)		(C_9H_7)C 2.44 (2, 9)	119.8 (14)	110.3 (13, 8)	
				6.929 (3)					
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}(\text{Me}_2\text{Ph})$ [m]	m	$P2_1/n$	4	7.72 (2)		(Me_2Ph)C 2.178 (7)	2.030		68
				14.66 (3)	101.01 (6)	(Cp)C 2.349 (9, 38)	140.9	109.3 (–, 3)	
				12.73 (2)					
$(\eta^5\text{-Cp})_2$Ti(pfpb) $\cdot 0.5\ (\text{C}_6\text{H}_{14})$	m	$C2/c$	8	27.953 (7)		(C_6H_4)C 2.132 (10)	2.052 (2)	78.3 (4)	69
				14.912 (5)	119.14 (2)	(C_2)C 2.219 (9)	136.7	106.6 (–, 1.7)	
				15.783 (5)		(Cp)C 2.370 (11, 54)			
$(\eta^5\text{-Cp})_2$Ti(tSipb)	or	*Pbca*	8	10.521 (7)		(C_6H_4)C 2.161 (3)	2.063 (6)	81.8 (1)	69
				15.207 (7)		(C_2)C 2.170 (3)	136.7	106.1 (–, 2.7)	
				28.636 (7)		(Cp)C 2.379 (4, 24)			
$(\eta^5\text{-Cp})_2\text{TiC}_4\text{Ph}_4$	m	$P2_1/n$	4	13.758 (5)		C 2.157 (5, 16)	2.06 (–, 1)	80.3 (2)	70
				11.059 (5)	93.76 (3)	CpC 2.386 (6, 22)	134.8 (3)	107.1 (3, 3.9)	
				18.492 (6)					
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{IV}}\text{Cl}_2$ [f]						Cl 2.318 (8)		97.1 (1.0)	71
						(Cp)C 2.372 (6)	128.1 (2, 4)		
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{IV}}\text{Cl}_2$ [j]		$P\bar{1}$	4	7.94 (2)	107.40 (20)	Cl 2.35 (1, 1)		95.6 (4)	72
				11.62 (2)	102.30 (20)	(Cp)C 2.46 (3, 7)			
				12.20 (3)	89.20 (20)				
						Cl 2.37 (1, 0)		94.8 (4)	
						(Cp)C 2.44 (4, 4)			

$(\eta^5\text{-Cp})_2\text{Ti}^{\text{IV}}\text{Cl}_2$ [j]	tr	$P\bar{1}$	4	7.882 (5)	90.46 (2)	Cl 2.364 (2, 3)	2.058– (–, 2)	94.43 (6)	73
				19.478 (10)	102.58 (2)	(Cp)C 2.370 (7, 24)	130.89 (5)	106.40 (6, 33)	
				12.156 (9)	143.49 (2)				
						Cl 2.364 (2, 1)	2.059 (–, 0)	94.62 (6)	
						(Cp)C 2.369 (7, 43)	131.04 (6)	106.32 (5, 93)	
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}\text{Cl}_2\text{Al}(\text{C}_2\text{H}_5)_2$		*Pnma*	4	15.77 (8)	90	Cl 2.5			74
		($Pna2_1$)		14.24 (7)	90	(Cp)C 2.3			
				7.54 (4)	90				
$(\eta^5\text{-CpMe})_2\text{Ti}^{\text{IV}}\text{Cl}_2$	or	*Pnma*	4	11.928 (5)		Cl 2.361 (2, 2)	2.067	93.15 (8)	75
				15.147 (6)		(CpMe)C 2.317 (1, 37)	130.2	106.8 (–, 2)	
				6.848 (4)					
$(\eta^5\text{-Cp})(\eta^5\text{-Cp*})\text{Ti}^{\text{IV}}\text{Cl}_2$		$Pna2_1$	4	9.84 (2)		Cl 2.329 (8, 5)	2.06 (2)	94.8 (9)	76
				11.29 (3)		(Cp)C 2.39	2.09 (2)	106.0 (1.3, 2.4)	
				12.88 (3)		(Cp*)C 2.41		118.2 (1.6, 6.5)	
$(\eta^5\text{-CpBu})_2\text{Ti}^{\text{IV}}\text{Cl}_2$	or	$P2_12_12_1$	2	12.862 (14)		Cl 2.370 (2)	2.093	92.5	77
				10.709 (9)		(CpBu)C 2.402 (5, 73)	131.5		
				6.602 (9)					
$(\eta^5\text{-Cp})(\eta^5\text{-MCp})\text{Ti}^{\text{IV}}\text{Cl}_2$	or	$P2_12_12_1$	4	6.501 (1)		Cl 2.368 (1, 1)	2.063 (3, 1)	94.8 (1)	78
				13.335 (3)		(Cp)C 2.370 (6, 23)	132.9 (1)	105.7 (1, 5)	
				23.320 (3)		(MCp) C 2.385 (4, 65)			
$(\eta^5\text{-DPhCp})_2\text{Ti}^{\text{IV}}\text{Cl}_2$		*Pc*	2	8.32		Cl 2.334 (4)			79
				12.92	74.6	C 2.43 (1)			
				13.03					
$(\text{CH}_3)_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2\text{TiCl}_2$	m	$C2/c$	4	13.329 (3)		Cl 2.361 (1)	2.078	95.8 (1)	80
				9.887 (3)	113.43 (2)	C 2.400 (3, 46)	128.9		
				10.689 (3)					
$(\text{CH}_2)_3(\eta^5\text{-Cp})_2\text{Ti}^{\text{IV}}\text{Cl}_2$	m	$P2_1/n$	4	8.490 (2)		Cl 2.368 (2, 4)	2.060 (–, 1)	93.69 (5)	81
				14.209 (4)	90.43 (2)	C 2.382 (4, 26)	132.64	105.95 (–, 25)	
				10.185 (2)		Cl 2.367 (9, 2) [n]	2.057 (–, 2)	93.20 (32)	82
						C 2.384 (9, 44)	133.12	105.89 (–, 22)	
$(\text{CH}_2)_2(\eta^5\text{-Cp*})_2\text{Ti}^{\text{IV}}\text{Cl}_2$	m	$C2/c$	4	16.796 (8)		Cl 2.325 (2)	2.086 (–, 2)	96.1 (1)	83
				7.923 (3)	124.69 (3)	C 2.406 (4, 63)	131.0		
				16.136 (7)					
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{IV}}(\text{SPh})_2$	m	$C2/c$	8	31.76 (10)		S 2.410 (8, 15)	2.069 (–, 3)	99.3 (3)	84
				7.97 (2)	104.87 (17)	(Cp)C 2.39 (–, 1)	132.4	105.2 (–, 3.5)	
				15.45 (5)					
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{IV}}(\text{mnt})$		$P2_1/n$	4	13.35 (1)		S 2.447 (3, 8)	2.051 (–, 2)	81.9 (1)	56
				6.88 (1)	105.6 (1)	(Cp)C 2.362 (5, 31)	130.7		
				15.38 (1)					

TABLE 3 (continued)

Compound	Crys- tal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–CNT (Å) [c] CNT–Ti–CNT (°)	L–Ti–L (°) CNT–Ti–L [c] (°)	Ref.
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}(S_2C_6H_4)$ [i]	m	$P2_1/c$	8	14.366 (8)		S 2.416 (6, 6)	2.05 (–, 2)	82.1 (2)	85
				15.380 (9)	90.20 (5)	(Cp)C 2.37 (2, 5)	130.6 (–, 1)	115 (–, 2)	
				12.736 (8)					
						S 2.417 (6, 11)	2.06 (–, 1)	82.3 (2)	
						(Cp)C 2.37 (2, 4)	129.1	115 (–, 2)	
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}S_2(CH)_2$	or	$Pcab$	8	22.000 (8)		S 2.417 (1, 14)	2.068 (–, 12)	83.23 (4)	86
				13.470 (6)		(Cp)C 2.387 (2, 46)	130.9	114.6 (–, 1.8)	
				7.737 (4)					
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}S_5$	m	$P2_1/n$	4	9.019 (3)		S 2.4351 (13, 132)	2.069 (–, 3)	94.59 (4)	87
				13.089 (6)	93.62 (4)	(Cp)C 2.373 (5, 32)	133.7	105.4 (–, 5.8)	
				11.294 (3)					
$(\eta^5\text{-Cp})_2\text{Ti}^{IV}S_5$ [j]	m	$P2_1/c$	8	22.843 (2)		S 2.426 (3, 26)	2.063 (–, 11)	95.4 (1)	88
				7.958 (1)	90.074 (4)	(Cp)C 2.374 (–, 33)	132.6	105.6 (–, 6.0)	
				14.465 (1)					
						S 2.429 (4, 10)	2.63 (–, 11)	94.6 (1)	
						(Cp)C 2.381 (–, 34)	132.7	105.7 (–, 6.8)	
$(\eta^5\text{-Me}_3\text{SiCp})_2\text{Ti}^{IV}S_5$	m	$P2_1/c$	4	7.884 (5)		S 2.433 (5, 17)	20.68 (–, 9)	93.4 (2)	89
				14.018 (14)	96.28 (7)	C 2.398 (15, 59)	131.0	106.4 (–, 6.2)	
				22.352 (24)					
$(\eta^5\text{-CpPr})_2\text{Ti}^{IV}S_4CH_2$	m	$P2_1/c$	4	11.584 (5)		S 2.438 (1)		91.6 (1)	90
				11.044 (4)	102.95 (4)	(CpPr)C [c]	130.1		
				15.252 (8)					
$(\eta^5\text{-Cp})_2\text{Ti}^{II}(PF_3)_2$ [j]	or	$C2cm$	12	7.811 (4)		P 2.345 (6, 5)	2.018	88.1 (2)	91
				13.724 (5)		(Cp)C 2.34 (1, 3)	137.09	105.25 (–, 40)	
				37.649 (11)					
						P 2.344 (4, 1)	2.016 (–, 4)	87.3 (3)	
						(Cp)C 2.34 (1, 2)	138.02	105.02 (–, 60)	
$(\eta^5\text{-Cp})_2\text{Ti}^{II}(PMe_3)_2$ [j]		Fdd_2	4	44.018 (15)		P 2.526 (4, 2)	2.060 (14, 3)	92.9 (1)	92
				28.755 (6)		(Cp)C 2.338–			
				8.603 (3)		2.412 (13)		133.2 (5)	
						P 2.527 (2)	2.049 (12)	91.5 (2)	
						(Cp)C 2.338–			
						2.412 (13)	134.3 (6)		

$(\eta^5\text{-CpMe})_2\text{Ti}^{\text{II}}(\text{dmpe})$	m	$P2_1/n$	4	8.073 (1)		P 2.543 (4, 7)		76.9 (2)	93
				14.782 (2)	93.34 (3)	C 2.371 (5, 70)	135.3 (2)	107.4 (2, 1.2)	
				15.777 (2)					
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}(\text{C}_6\text{H}_4\text{COO})$	rh	$Pbca$	8	13.744 (2)		C 2.20 (2)	2.04 (–, 1)	78	94
				14.410 (2)		O 1.95 (1)	134	107.5 (–, 3.5)	
				13.774 (2)		(Cp)C 2.39 (2, 4)			
$(\eta^5\text{-Cp})_2\text{Ti}(\text{Ph}_2\text{C}_2\text{O})$	m	$I2/a$	8	24.527 (4)		C 2.18 (1)	2.03 (–, 1)	77.0 (4)	95
				11.327 (2)	95.45 (2)	O 1.92 (1)	134.3 (7)	107.7 (–, 2.7)	
				20.370 (3)		(Cp)C 2.35 (2, 3)			
$(\eta^5\text{-Cp})(\eta^5\text{-Me}_3\text{BCp})$									
$\text{Ti}(\text{Me}_2\text{PhO})\text{Cl}$	m	$P2_1/n$		14.16 (2)		O 1.862 (5)	2.105 (9, 15)	98.5 (2)	96
				12.91 (2)	96.9 (5)	Cl 2.375 (2)	130.8 (2)	105.7 (2, 2.2)	
				13.18 (2)		(Cp)C 2.403 (9, 32)			
						(Me_3BCp)C 2.437 (7, 73)			
$(\eta^5\text{-Cp})(\eta^5\text{-Cp}')\text{Ti}(\text{Me}_2\text{PhO})\text{Cl}$	or$^{\text{p}}$	$Pbca$	8	19.51 (3)		O 1.88	2.11	64	47
				13.08 (2)		Cl 2.38	129	97	
				15.91 (3)		(Cp)C 2.44			
$(\eta^5\text{-Cp})(\eta^5\text{-Cp}')\text{Ti}$	m	$P2_1/c$	8	14.50 (2)		O 1.88	2.11	64	47
$(\text{ClPhO})\text{Cl}^{\text{p}}$				13.02 (2)	98.4 (4)	Cl 2.40	131	94	
				19.38 (3)		(Cp)C 2.42			
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{IV}}(\text{OEt})\text{Cl}$		$P2_1/n$	4	8.003 (2)		O 1.855 (2)	2.087 (–, 5)	93.1 (1)	28
				17.708 (6)	90.66 (2)	Cl 2.405 (2)	130.5	106.7 (–, 3.1)	
				7.997 (2)		(Cp)C 2.404 (3, 35)			
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}(\text{MAPh})$	m	$P2_1$	4	8.00 (2)		C 2.22 (3)	2.08 (–, 1)	73(1)	97
				14.92 (2)	112.5 (2)	N 2.46 (2)	131	109 (–, 2)	
				8.10 (3)		(Cp)C 2.41 (3, 8)			
$(\eta^5\text{-Cp})\text{Ti}^{\text{III}}(\text{MIPh})$	m	$P2_1/c$	4	14.370 (16)		C 2.096 (4)	2.065 (–, 4)	35.1 (2)	98
				7.804 (5)	105.44 (6)	N 2.149 (4)	135.0		
				18.459 (10)		(Cp)C 2.378 (7, 22)			
$(\eta^5\text{-Cp})_2\text{Ti}^{\text{II}}(\text{CO})(\text{PEt}_3)$	or	$Pbca$	8	11.972 (5)		(CO)C 2.009 (4)	2.052 (–, 4)	90.3 (1)	91

TABLE 3 (continued)

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–CNT (Å) [c] CNT–Ti–CNT (°)	L–Ti–L (°) CNT–Ti–L [c] (°)	Ref.
				16.977 (7)		P 2.585 (1)	138.73	104.28 (–, 2.90)	
				16.674 (7)		(Cp)C 2.373 (5, 48)			
(η^5-Cp)$_2$Ti(SiMe$_3$)Cl	or	*Pnma*	4	13.26		Cl 2.31 (1)		87 (1)	99
				12.71		Si 2.67 (1)	132 (3)	107 (3, 4)	
				8.69		(Cp)C [e]			
(η^5-Cp)$_2$Ti^{III}(η^3-Me$_2$al)	m	$P2_1/c$	4	11.521 (3)		η^3-C$_3$ 2.37 (4, 6)	2.06 (–, 2)	90.4	100
				13.224 (3)		(Cp)C 2.40 (4, 9)	132	114 (–, 2)	
				8.445 (2)					
(η^5-Cp)$_2$Ti(CO)(C$_2$Ph$_2$)	or	$P2_12_12_1$	4	18.464 (5)		(CO)C 2.050 (8)	2.083 (–, 1)	[q]	101
				13.301 (4)		(C$_2$Ph$_2$)C 2.169 (7, 62)	133.5 (5)		
				7.822 (4)		(Cp)C 2.389 (10, 36)			
(η^5-Cp)$_2$Ti^{II}(dedm)	tg	$I4_1/a$	16	31.369 (3)		O 2.247 (4)	2.071 (7, 6)	[r]	102
				31.369 (3)		N 2.100 (6, 120)	134.3 (3)	106.6 (2, 5.5)	
				7.760 (1)		(Cp)C [e]			
(η^5-Cp)$_2$Ti^{IV}(COMe)Cl		*Pnma*	4	13.85 (2)		Cl 2.494 (6)	2.06	[s]	103
		($Pn2_1a$)		12.07 (2)		(COMe)C 2.07 (2)	131.6		
				6.74 (1)		(COMe)O 2.194 (14)			
						(Cp)C 2.39 (2, 3)			

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the estimated standard deviation, and the second is the maximum deviation from the mean value. [b] The chemical identity of the coordinated atom or ligand is specified in this column. [c] The centroid of a ring. [d] At 113 K. There are two crystallographically independent molecules. [e] Value not given. [f] A gaseous electron diffraction study. [g] At 173 K. [h] At 295 K. [i] At 102 K. [j] There are two crystallographically independent molecules. [k] At 153 K. [l] There are three crystallographically independent molecules. [m] At 113 K. [n] By neutron diffraction. [o] At 123 K. [p] At 139 K. [q] The (PhC)C–Ti–C(Cph) angle is 34.3(3)°; the (CO)C–Ti–C(C$_2$Ph$_2$) angles are 71.9(3) and 106.1(3)°. [r] The N–Ti–N angle is 33.0(2)°; the N–Ti–O angle are 70.6(2) and 103.6(2)°. [s] The (COMe)C–Ti–O(COMe) angle is 32.0(4)°; the Cl–Ti–L, L = C and O from COMe, are 80.2(2) and 112.2(3)°, respectively.

From the structural point of view, the titanium organometallics summarized in Table 3, can be divided into two groups: π-bonded ring compounds with a "sandwich" or parallel ring arrangement, and "clino-sandwich" structures for those molecules with a bent arrangement of ring planes.

There are five examples (Table 3) in which a titanium atom is "sandwiched" by two parallel ligands. These complexes contain two π-bonded carborane or two cyclooctatrienyl rings or an admixture of these including π-bonded cyclopentadienyl and cycloheptatrienyl rings [35–39a]. Notable are the mean Ti–C bond distances which increase in these compounds in the order: 2.194 Å (C_7H_7) < 2.311 Å (C_8H_8) < 2.337 Å (C_5H_5). The mean Ti–C(C_7H_7) distance is by far the shortest compared with Ti–C(Cp), and no convincing explanation has yet been proposed for this anomaly. However, the corresponding shortening of the metal–ring centroid distances has been explained from simple geometrical considerations assuming the M–C bond lengths are approximately the same [39b]. This assumption seems quite inadequate for the molecules discussed, and a more likely explanation would be that lowering of the ring 3π molecular orbitals as the ring size increases favours the C_7H_7 and C_8H_8 over C_5H_5 bonding with respect to the $3d$ atomic orbitals of Ti(0) and Ti(III) metals.

Three types of complexes for the "clino-sandwich" structure have been found. These metallocenes have either one additional ligand, two ligands (atoms), and even three additional ligands on the open side of the tilted aromatic rings. Examination of the data in Table 3 reveals that the additional ligands cause the CNT–Ti–CNT angle to decrease from its ideal value of 180° for parallel rings. The value of this angle, in "clino-sandwich" compounds, ranges from 147.9° to 119.8°.

In (η^5-Cp)$_2$Ti(OPh) [40] the titanium(III) atom is η^5-bonded to two Cp ligands, and to the OPh anion via its oxygen atom. This is the only known example for a titanium "clino-sandwich" structure with one additional monodentate ligand.

The "clino-sandwich" structures with two additional ligands (atoms) are by far the most common found for the monometallic derivatives listed in the Table. The examples include hydrogen atoms [41–43], O ligands [44–53], N ligands [54–60], C ligands [61–70], Cl atoms [71–83], S ligands [56,84–90], P ligands [91–93], O, C ligand [94,95], O ligand and Cl atom [28,47,96], N, C ligand [97,98], C and P ligand [91,92], and Cl atom and Si ligand [99]. The crystal structure of (η^5-Cp)$_2$Ti(NO_3)$_2$ [46] is shown in Fig. 5 as a representative example. A nearly tetrahedral environment about the titanium(IV) atom is built up by two rings and two nitrate groups. Approximate tetrahedral symmetry is found around the titanium(IV) metal in the purinate derivative (η^5-Cp)$_2$TiCl(Pu) [60b]. In this structure the purine heterocycle is *N*-bonded and its plane is parallel to the Cl–Ti–N plane and directed away from the

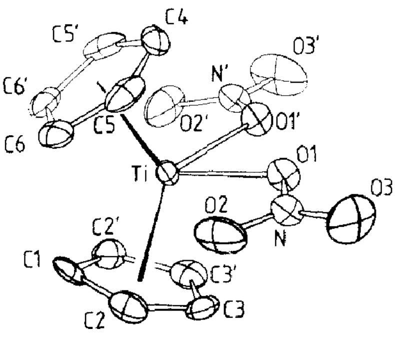


Fig. 5. Structure of $(\eta^5\text{-Cp})_2\text{Ti}(\text{NO}_3)_2$. Reproduced with permission from ref. 46.

open face of the tilted cyclopentadienyl rings. In the theophylline derivative $(\eta^5\text{-Cp})_2\text{Ti(theo)}$, *O,N*-chelation of the ligand results in a planar five-membered Ti–O–C–C–N metallocycle involving a titanium(III) atom [60c].

There are four examples (Table 3), in which an additional three atoms are coordinated to a central titanocene unit. They are comprised of either one or two additional ligands which are bonded to titanium as either a *C,C,C*-tridentate allyl ligand [100], a *C*-unidentate carbonyl plus a *C,C*-bidentate diphenylacetylene [101], a *N,N,O*-tridentate diethyldiazomalonate ligand, or as a Cl atom plus a *C,O*-bidentate COMe ligand [103].

The degree of occurrence of titanium oxidation states for the compounds tabulated decreases in the order: four > three > two. Although the comparison is obviously not strictly relevant, the Ti–L bond distances appear to show a slight increase with increasing formal oxidation state of the titanium atom. For example, the mean Ti–C(Cp) and Ti–CNT distances of 2.350 Å (range 2.310–2.422 Å) and 2.041 Å (range 2.018–2.071 Å) for Ti(II), are shorter than those for Ti(III), which are 2.375 Å (2.300–2.510 Å) and 2.048 Å (2.03–2.08 Å), and these are again somewhat smaller than those for Ti(IV), which are 2.377 Å (2.310–2.490 Å) and 2.058 Å (2.031–2.087 Å), respectively.

Comparison of the Ti–C(Cp) distance for the mono- and bis-cyclopentadienyl compounds reveals that the mean value is similar for both, 2.378 Å and 2.379 Å respectively. In a series of compounds with multidentate ligands, the mean Ti–C bond distance increases in the order: 2.350 Å(Cp) < 2.371 Å(CpMe) < 2.395 Å(Cp*) for Ti(II)–C; and 2.377 Å(Cp) < 2.382 Å($(\text{CH}_2)_3\text{Cp}_2$) < 2.385 Å(MCp) < 2.402 Å(CpBu) < 2.43 Å(DPhCp) < 2.44 Å(C_9H_7) for Ti(IV)–C. The mean Ti–C bond distance in the series of bidentate ligands is in the order: 2.157 Å(C_4Ph_4) < 2.160 Å(C_2H_4) < 2.165 Å(tSipb) < 2.169 Å(C_2Ph_2) < 2.176 Å(pfpb) < 2.465 Å(Cp); and finally, with unidentate ligands is 2.025 Å(CO) < 2.178 Å(Me_2Ph) < 2.21 Å(CH_3) < 2.179 Å(Cp). These trends are governed by both steric and electronic factors. In addition, the mean Ti–P distance is observed to decrease from 2.585 Å in $(Cp)_2Ti(dmpe)$ [93] and 2.526 Å in $(\eta^5\text{-}Cp)_2Ti(PMe_3)_2$ [92], to 2.344 Å in $(\eta^5\text{-}Cp)_2Ti(PF_3)_2$ [91] which is the order of decreasing steric demand of the phosphine ligand itself i.e. $PEt_3 > dmpe > PMe_3 > PF_3$.

In general, the Ti–L distance increases with increasing van der Waals radius of the ligated atom: 2.003 Å (range 1.860–2.155 Å) (O, 1.52 Å) < 2.007 Å (1.922–2.100 Å) (N, 1.55 Å) < 2.359 Å(2.310–2.405 Å)(Cl, 1.75 Å) < 2.429 Å(2.395–2.455 Å)(S, 1.80 Å) < 2.497 Å(2.340–2.585 Å)(P, 1.80 Å).

(ii) Bimetallic compounds

Structural data for bimetallic compounds are summarized in Table 4. There are several types of bridged systems in this group. The crystal structure of $[(\eta^5\text{-}Cp)_2TiAl(C_2H_5)_2]_2$ [104] is the only example with a non-bridged hetero-atom between two titanium atoms. The $(\eta^5\text{-}Cp)_2TiAl(C_2H_5)_2$ units are linked through a Ti–Ti bond which intersects a two-fold symmetry axis.

In an attempt to isolate and resolve the structure of the still sought after neutral titanocene molecule, the structure $(\eta^5\text{-}Cp)_2Ti(\mu\text{-}\eta^1 : \eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}Cp)(thf)$ was instead found in the solid reaction product [105]. Two bis(cyclopentadienyl)titanium units are held together by a metal–metal linkage in this molecule. One of the cyclopentadienyl ligands, however, contains only four hydrogen atoms and serves to bridge the two titanium centers, in a mono*hapto*: penta*hapto*-bonding arrangement. The Ti–Ti distance of 3.336(4) Å is longer than that in the former aluminium ligated complex (3.110(7) Å).

In another set of six homometallic compounds, two titanium atoms are bridged via a single oxygen atom [106–111]. The Ti–O (bridge) distance ranges from 1.829 to 1.865 Å (mean 1.840 Å). In each example, the titanium atom exhibits pseudo-tetrahedral coordination with two Cp ligands, an oxo-bridged atom and the remaining fourth place is occupied either by a water molecule [106,107], a chlorine atom [108], a nitrate group [109], C(Ph)=CH(Ph) [110], or by a $CF_3C{=}CHCF_3$ molecule [111]. The Ti–L–Ti angles range from 168.8 to 177.0(3)°, and Ti–C(Cp) distances vary from 2.302(10) to 2.467(10) Å (mean 2.398 Å). The mean Ti–C(Cp) distance is about 0.019 Å longer than that found in monometallic bis(cyclopentadienyl) derivatives (2.379 Å).

Doubly-bridged titanium atoms are those most common in the homo-bimetallic bis(cyclopentadienyl) derivatives listed in the Table. Examples include hydrogen and chlorine atoms [112], O ligands [95,114], N atoms [115], Cl atoms [116,117], Br atoms [117], and Si atoms [118]. Ti–Ti distances are in the range 2.910 to 4.125 Å and Ti–L–Ti angles vary from 98

TABLE 4

Structural data for binuclear compounds [a]

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–Ti (Å) Ti–CNT (Å) CNT–Ti–CNT (°)	Ti–L–Ti (°) L–Ti–CNT (°) L–Ti–L (°)	Ref.
$[(\eta^5\text{-Cp})_2\text{TiAl}(\text{C}_2\text{H}_5)_2]_2$		*Pbcn*	4	9.50		Al 2.792 (11)	3.110 (7)		104
				14.60 (3)		(Cp)C 2.35 (3, 13)	2.01 (–, 1)		
				19.40 (3)			136.2		
$(\eta^5\text{-Cp})_2\text{Ti}(\mu\text{-}\eta^1:\eta^5\text{-C}_5\text{H}_4)$ $\text{Ti}(\eta^5\text{-Cp})(\text{thf})\cdot(\text{thf})$	m	*I2/a*	8	28.567 (19)	90.0	(thf) O 2.26 (1)	3.336 (4)		105
				8.061 (2)	101.11 (2)	(C_5H_4)C 2.19 (2)			
				19.691 (7)	90.0	(Cp)C 2.38 (2, 6)			
$[\{\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}(\text{H}_2\text{O})\}_2\text{O}]\text{S}_2\text{O}_6$		*Pbcn*	4	15.827 (4)		μ-O 1.834 (5)		177.0 (3)	106
				11.922 (3)		(H_2O)O 2.086 (5)	2.075 (–, 8)	106.1 (3, 2.0)	
				12.152 (3)		(Cp)C [c]	131.3 (3)	95.1 (3)	
$[\{\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}(\text{H}_2\text{O})\}_2\text{O}]$- $(\text{ClO}_4)_2\cdot 2\,(\text{H}_2\text{O})$	or	*Fdd*2	8	28.893 (5)		μ-O 1.829 (2)		175.8 (5)	107
				17.433 (4)		(H_2O)O 2.2129 (6)	2.077 (–, 37)	105.0 (–, 3.9)	
				10.312 (3)		(Cp)C 2.386 (10, 84)	134.9	94.3 (3)	
$[\{(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}\text{Cl})_2\}\text{O}]$	hx	$P3_121$	3	7.742 (1)		μ-O 1.837 (2)		173.81	108
		$(P3_221)$		7.7421 (1)		Cl 2.409 (1)	2.090 (–, 6)	106.50 (–, 2.75)	
				27.177 (7)		(Cp)C 2.398 (4, 34)	129.61	95.95	
$[\{(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}(\text{NO}_3)\}\text{O}]$	m	$P2_1/c$	4	12.656 (4)		μ-O 1.835 (5, 6)		171.8 (3)	109
				10.181 (5)	93.57 (3)	(NO_3)O 2.072 (5, 13)	2.076 (–, 5)	106.7 (–, 1.2)	
				16.197 (3)		(Cp)C 2.384 (9, 37)	131.6 (–, 2)	88.4 (–, 5)	
$[\{(\eta^5\text{-Cp})_2\text{Ti}(\text{PhC}=\text{CHPh})\}_2\text{O}]$	m	$P2_1/a$	4	16.192 (2)		μ-O 1.85 (1, 1)		168.8 (7)	110
				11.041 (1)	106.99 (1)	C 2.25 (2, 1)			
				24.575 (3)		(Cp)C 2.31–2.49	128.6 (–, 2.1)	98.3 (6, 1.5)	
$[\{(\eta^5\text{-Cp})_2\text{Ti}(\text{CF}_3\text{C}$ $=\text{CHCF}_3)\}_2\text{O}]$ [d]	tr	$P\bar{1}$	4	11.522 (5)	77.52 (4)	μ-O 1.852 (3, 4)		171.0 (2)	111
				15.015 (6)	77.93 (4)	C 2.241 (5, 1)			
				17.959 (6)	70.27 (4)	(Cp)C 2.422 (5, 47)	129.7 (–, 2)	94.5 (1, 3)	
						μ-O 1.861 (3, 5)		169.0 (2)	
						C 2.236 (5, 3)			
						(Cp)C 2.420 (5, 48)	129.9 (–, 3)	95.3 (2, 1.2)	
$[(\eta^5\text{-Cp})_2(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)$ $\text{Ti}_2(\mu\text{-H})(\mu\text{-Cl})]$ [d]	m	$P2_1/c$	8	13.864 (5)		η-H 2.05 (6, 9)	3.124 (2)	77.6, 93	112
				15.481 (5)	110.02 (3)	μ-Cl 2.492 (2, 1)	2.04		
				16.331 (5)		(Cp)C 2.361 (9, 59)	137.3		
						$(\text{C}_{10}\text{H}_8)$C 2.353 (7, 41)			

						μ-H 2.29 (2)	3.128 (2)		
						μ-Cl 2.494 (2, 13)			
						(Cp)C 2.376 (9, 60)			
						($C_{10}H_8$)C 2.354 (8, 43)			
{η^5-Cp)$_2$(η^5 : η^5-$C_{10}H_8$) Ti_2(μ-H)(H_2AlEt_2)}	m	*C*2/*c*	8	33.310 (14)		μ-H 1.80	3.374	H 138	113
				8.407 (4)	117.89 (2)	H 1.69			
				17.921 (6)		($C_{10}H_8$)C 2.33–2.39	136.8		
						(Cp)C 2.353 (4)			
{[(η^5-C_5H_4)TiHAlEt$_2$]$_2$ (η^5 : η^5-$C_{10}H_8$)} · (tol)	m	*C*2/*c*	4	24.367 (18)		(C_5H_4)C 2.24	2.910		113
				9.090 (4)	123.77 (6)				
				17.832 (12)			134.1		
{[(η^5-Cp)Ti(μ-OH)]$_2$ (η^5 : η^5-$C_{10}H_8$)}	or	*Pna*2_1	4	10.143 (6)		μ-O 2.05 (1, 1)	3.195 (4)	100.8 (6, 2.0)	114
				23.571 (14)		μ-O 2.10(1, 2)		108.2 (7, 1.7)	
				9.009 (8)		($C_{10}H_8$)C 2.40 (2, 8)	133.5 (10, 1)	75.4 (5, 6)	
						(Cp)C 2.41 (2, 6)			
(η^5-Cp)$_2$Ti$_2$(μ-N)$_2$H$_3$	or	*Pca*2_1	4	15.029 (10)		μ-N 2.232 (16, 29)	3.392 (4)	98	115
		(*Pbcn*)		6.214 (3)		(Cp)C 2.404 (20, 123)			
				19.158 (11)				81.0 (6, 1)	
(η^5-Cp)$_2$(η^5 : η^5-$C_{10}H_8$)Ti$_2$Cl$_2$ [e]	or	*Fdd*2	8	20.423 (4)	90	μ-Cl 2.519 (1, 5)	3.638	92.47 (3)	116
				21.928 (5)	90	($C_{10}H_8$)C 2.387 (3, 18)	2.056 (–, 3)		
				7.691 (2)	90	(Cp)C 2.376 (3, 31)	134.42	81.29 (4)	
[(η^5-Cp)$_2$Ti^{III}Cl]$_2$ [d]	or	*P*2_1/*c*	6	13.422 (8)		μ-Cl 2.546 (2, 12)	3.943 (2)	101.50 (7, 30)	117
				15.666 (11)	94.21 (4)	(Cp)C 2.356 (6, 43)	2.049		
				13.083 (12)			131.2	78.42 (7, 21)	
						μ-Cl 2.537 (2, 3)	3.968 (2)	102.89 (5)	
						(Cp)C 2.340 (7, 44)	2.058		
							133.4	77.11 (5)	
[(η^5-CpMe)$_2$Ti^{III}Cl]$_2$	or	*Pbca*	8	16.357 (9)		μ-Cl 2.547 (2, 21)	3.926 (3)	100.81 (7, 7)	117
				19.194 (13)		(CpMe)C 2.380 (6, 67)	2.062 (–, 12)		
				14.232 (9)			130.9 (–, 1)	79.19 (6, 12)	
[(η^5-CpMe)$_2$Ti^{III}Br]$_2$	m	*P*2_1/*c*	2	6.746 (6)		μ-Br 2.714 (3, 9)	4.125 (4)	98.93 (7)	117
				10.591 (10)	112.22 (6)	(CpMe)C 2.383 (6, 71)	2.065 (–, 3)		
				17.164 (20)			134.2	81.07 (7)	
[(η^5-Cp)$_2$Ti(μ-SiH$_2$)]$_2$	tg	*P*4_2/*mnm*	2	8.018 (3)		μ-Si 2.159 (13)	3.368 (10)	102.8 (7)	118
				8.018		(Cp)C [c]	2.158 (50)		
				16.113			126 (1)	79.2 (6)	

TABLE 4 (continued)

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–Ti (Å) Ti–CNT (Å) CNT–Ti–CNT (°)	Ti–L–Ti (°) L–Ti–CNT (°) L–Ti–L (°)	Ref.
$[(\eta^5\text{-Cp})_2\text{Ti}^{\text{II}}(\text{Ph}_2\text{C}_2\text{O}]_2 \cdot 2(\text{thf})$	tr	$P\bar{1}$	1	9.990 (1)	73.86 (2)	μ-O 2.037 (2)		116.0 (1)	95
				11.058 (2)	94.98 (2)	μ-O 2.250 (3)	2.092 (4, 4)	107.6 (2, 6.6)	
				10.820 (2)	98.85 (1)	C 2.099 (3)	131.2 (2)	67.7 (1)	
						(Cp)C 2.407 (5, 19)			
$\{[(\eta^5\text{-Cp}^*)_2\text{Ti}^{\text{II}}]_2(\mu\text{-N}_2)\}$ [d]	tr	$P\bar{1}$	4	18.867 (1)	98.22 (1)	μ-N 2.011 (10, 11)			119
				8.968 (2)	101.83 (1)	(Cp*)C 2.374 (10, 29)	2.067 (7, 11)	107.2 (3, 7)	
				22.767 (1)	93.86 (1)		145.7 (3, 4)		
						μ-N 2.023 (10, 20)			
						(Cp*)C 2.391 (10, 53)	2.067 (7, 8)	107.1 (3, 8)	
							145.7 (3, 8)		
$\{[(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}(p\text{-MeC}_6\text{H}_4)]_2(\mu\text{-N}_2)\}$ [f]	m	$P2_1/c$	2	8.093 (3)		μ-N 1.962 (6)			120
				17.799 (10)		C 2.216 (7)	2.048 (–, 1)	104.6 (–, 1.6)	
				9.678 (5)		(Cp)C 2.371 (8, 16)	137.9	91.1 (2)	
$[(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}(\mu_2\text{-pz})]_2$	m	$P2_1/n$	2	8.073 (2)		μ-N 2.195 (5, 12)	4.339 (3)		121
				7.961 (3)	94.54 (2)	(Cp)C 2.379 (8, 52)	2.082 (–, 5)		
				17.834 (5)			110.9 (11)	91.6 (2)	
$(\eta^5\text{-CpMe})_4\text{Ti}_2^{\text{IV}}\text{S}_6$	m	$P2_1/c$	4	12.559 (2)		μ-S 2.425 (1, 9)			122
				15.054 (3)	99.24	(CpMe)C [c]	2.063 (4, 4)		
				14.211 (2)			132.6 (2)	96.08 (3)	
$(\eta^8\text{-C}_8\text{H}_8)_3\text{Ti}$	rh	$Fdd2$	8	14.41		μ-C 2.40 (–, 14)			123
				35.99		C 2.35 (–, 5)			
				7.25					
$(\eta^5\text{-CpMe})_3\text{Ti}_2\text{OAsS}_3$	m	$P2_1/m$	2	10.404 (6)		μ-O 1.833 (2, 39)		145.2 (1)	124
				12.932 (9)		μ-S [c]			
				7.491 (6)		(Cp)C [c]		93.71 (3)	
$[\{(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}\}_2\{\text{OC(NPh)}_2\}] \cdot 0.5(\text{tol})$	or	$Fdd2$	16	19.138 (2)		μ-O 2.180 (9, 16)		175.3 (2)	125
				75.184 (10)		μ-N 2.131 (6, 5)	2.071 (9, 43)	109.9 (3, 3.3)	

				8.553 (2)		(Cp)C 2.388 (9, 50)	133.3 (4, 6)	61.2 (2, 5)	
$[\{(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}\}_2\{\mu\text{-}(\text{C}_2\text{O}_4)\}]$ $\cdot 0.5(\text{OEt}_2)$	or	*Pbcn*	12	17.228 (13)		μ-O 2.163 (6, 13)			126
				12.224 (13)		(Cp)C 2.374 (11)	2.058 (4)		
				30.309 (23)			135.4 (3)	75.8 (2, 1)	
						μ-O 2.156 (6, 10)			
						(Cp)C 2.374 (11)			
								75.1 (2)	
$[(\eta^5\text{-Cp})_2\text{Ti}(p\text{-tcd})_2]_2$	tr	$P\bar{1}$	1	12.404 (1)	103.56 (1)	μ-N 2.174 (2, 2)			127
				10.449 (1)	94.29 (1)	(Cp)C 2.407 (11)	2.095 (4, 6)		
				8.179 (1)	94.23 (1)	(Cp)C 2.414 (13)	131.6 (2)	73.6 (1)	
$[\{(\eta^5\text{-CpMe})_2\text{Ti}\}_2(\text{C}_4\text{Ph}_2)]$	m	$P2_1/c$	2	10.133 (2)		μ-C 2.118 (2, 35)	4.227 (1)		128
				14.838 (4)	106.97 (1)	(Cp)C 2.403 (3, 35)	2.04 (1)		
				10.530 (3)			131.1	72.94 (8)	
$[\{(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}\}_2$ $(\text{O}_2\text{CPhCO}_2)]$	m	$P2_1/c$	4	8.136 (2)		μ-O 2.1628 (23, 6)	5.783	106.0	49
				10.671 (2)	124.4 (1)	(Cp)C [c]	2.047 (6, 5)	109.3 (2, 5)	
				17.553 (3)			135.1 (2)	60.38 (8)	
$[\{(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}\}_2$ $(\text{O}_2\text{CC}_4\text{H}_6\text{CO}_2)]$	or	$P2_12_12_1$	4	11.096 (2)		μ-O 2.1640 (34, 66)	5.932	110.0	49
				26.804 (5)		(Cp)C [c]	2.047 (8, 7)	108.76 (26, 1.11)	
				8.049 (1)			136.31 (35, 61)	60.28 (13, 8)	
$[\{(\eta^5\text{-CpMe})_2\text{Ti}^{\text{III}})_2$ $(\text{S}_2\text{N}_2\text{C}_4\text{H}_2)]$	or	*Pbca*	8	16.91 (2)		μ-N 2.206 (8, 32)	6.075 (2)		129
				22.22 (2)		μ-S 2.594 (3, 4)			
				13.93 (1)		(CpMe)C 2.383 (12, 155)	133	65.1 (2, 1)	
$[\{(\eta^5\text{-Cp})_2\text{Ti}^{\text{III}}\text{Cl}\}_2(\text{dppae})]$	m	$P2_1/n$	2	9.581 (1)		P, As 2.677 (3)			130
				14.678 (2)	98.29 (1)	Cl 2.462 (5)	2.06 (2, 1)	107.2 (6, 2.5)	
				14.523 (2)		(Cp)C 2.39 (2, 4)	134.2 (9)	81.0 (1)	
$\{[(\eta^5\text{-Cp})_2\text{Ti}(\mu\text{-H})_2\text{AlH}_2]_2$ $(\text{tmen})\cdot\text{C}_6\text{H}_6$	tr	$P\bar{1}$	2	8.406 (2)	112.01 (2)	μ-H 1.62 (10, 2)			131
				10.117 (2)	109.25 (2)	Al 2.788	2.04 (−, 0)		
				11.269 (3)	87.04 (2)	(Cp)C 2.36 (1, 4)	139.4	71 (5)	

---

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the estimated standard deviation, and the second is the maximum deviation from the mean value. [b] The chemical identity of the coordinated atom or ligand is specified in this column. [c] Value not given. [d] There are two independent molecules. [e] At 113 K. [f] At 90 K.

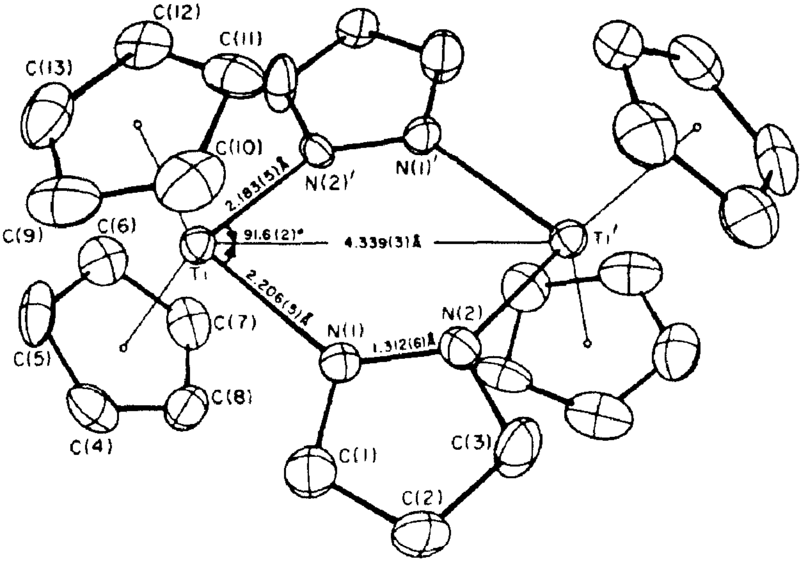


Fig. 6. Structure of $[(\eta^5\text{-Cp})_2\text{Ti}(\mu_2\text{-pz})]_2$. Reproduced with permission from ref. 121.

to 138° (Table 4). As pointed out by several authors, the observed short intermetallic distances are often a consequence of constraints due to the nature of the bridge rather than a bonding interaction as indicated by the magnetic or electronic properties of these molecules [113–117]. Interestingly, the mean Ti–C(Cp) distance of 2.377 Å (range 2.305–2.527 Å) found in these doubly-bridged bimetallic derivatives, is somewhat shorter than that in singly-bridged analogues (2.398 Å), the reverse of that expected. The angles CNT–Ti–CNT lie in the range 126 to 136° in the former and 126 to 127° in the latter.

There are two examples where two titanium metals are linked by the dinitrogen ligand in an essentially linear manner (Ti–N ≡ N–Ti). In $[(\eta^5\text{-Cp*})_2\text{Ti}]_2\text{N}_2$ [119], two (Cp*)Ti moieties bridged by the N_2 and the Ti(II) atoms are in a trigonal environment. This is the only known example of such a geometry in bis(cyclopentadienyl)titanium(II) derivatives.

A pseudo-tetrahedral environment about Ti(III) has been found in $[(\eta^5\text{-Cp})_2\text{Ti}(p\text{-MeC}_6\text{H}_4)]_2\text{N}_2$ [120], where two $\text{Cp}_2\text{Ti}(p\text{-MeC}_6\text{H}_4)$ units are held together in a manner similar to that in $[\eta^5\text{-Cp}_2^*\text{Ti}]_2\text{N}_2$ (Table 4).

In crystalline $[\eta^5\text{-Cp}_2\text{Ti}(\mu_2\text{-pz})_2]_2$ [121], the two titanium(III) atoms are bridged as shown in Fig. 6. The four nitrogen atoms from the pyrazolide groups are in the same plane and the titanium atoms of the metallocycle form a six-member chair configuration with one titanium atom occupying a position 0.40 Å above the plane of the pyrazolide groups and the other titanium atom 0.40 Å below the same plane.

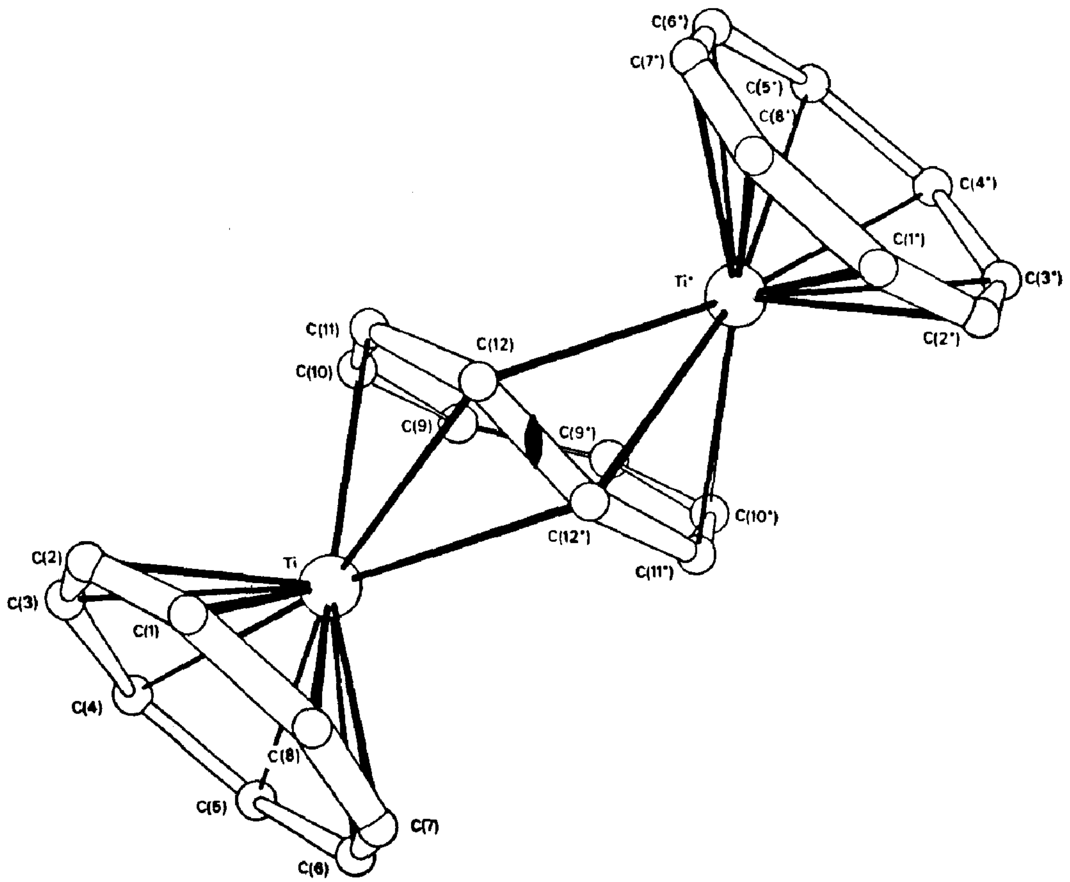


Fig. 7. Structure of $(\eta^8\text{-}C_8H_8)_3Ti_2$. Reproduced with permission from ref. 123.

X-Ray analysis of blue $(\eta^5\text{-CpMe})_4Ti_2S_6$ [122] shows that the structure consists of an eight-membered ring (Ti_2S_6) of approximate D_2 symmetry. Two $(CpMe)_2Ti$ fragments are held together by a doublet of three S atoms (Ti–[–S–S–S]$_2$–Ti). The mean Ti–S distance of 2.425 Å is not significantly different from that found in $(\eta^5\text{-Cp})_2TiS_5$ or $(\eta^5\text{-Me}_3SiCp)_2TiS_5$ (Table 3) (2.430 Å).

The crystal structure of tris(cyclooctatrienyl)dititanium [123] is shown in Fig. 7. This complex molecule has a double sandwich structure with a twofold polar axis across the boat-shaped ring. The mean Ti–C(bridge) bond distance 2.40 Å is about 0.05 Å longer than those in the terminal ligands, as expected. The C–Ti–C bond angles are in the range 32.7 to 37.7(3)° (mean 34.6°).

Bimetallic dark-brown $(\eta^5\text{-CpMe})_3Ti_2OAsS_3$ [124] exhibits a highly distorted tetrahedral configuration with two non-equivalent titanium atoms. One titanium has two S atoms, a CpMe ring, and an O atom in the inner

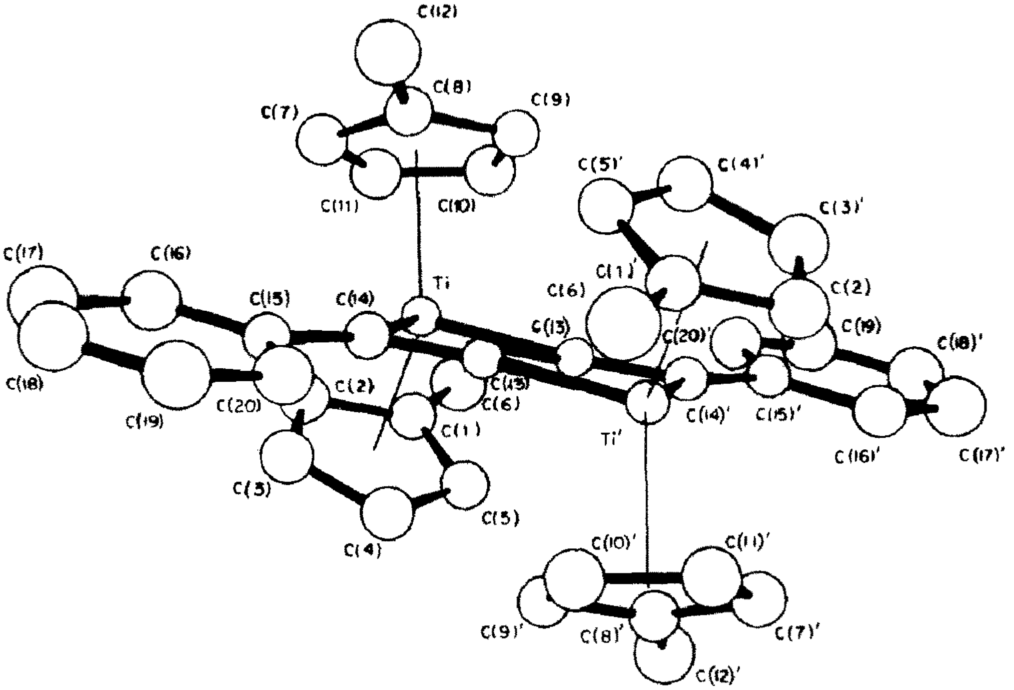


Fig. 8. Structure of $\{(\eta^5\text{-CpMe})_2\text{Ti}\}_2(\text{C}_4\text{Ph}_2)$. Reproduced with permission from ref. 128.

coordination sphere. The other, has two CpMe rings plus an S and O atom. The oxygen atom links the two titanium centers (Table 4).

In $\{(\eta^5\text{-Cp})_2\text{Ti}\}_2\{\text{OC(NPh)}_2\}$ [125], the diphenylureylene ligand bridges two Cp_2Ti units through the nitrogen and oxygen atoms and completes a tetrahedral environment around the titanium(III) atoms.

Other types of bridge have been found in $\{(\eta^5\text{-Cp})_2\text{Ti}\}_2\{\text{C}_2\text{O}_4\}$ [126] and $[(\eta^5\text{-Cp})_2\text{Ti}(p\text{-tcd})_2]_2$ [127]. Two Cp_2Ti moieties are held together by a planar tetradentate bridging oxalate ligand $\text{C}_2\text{O}_4^{2-}$ in the former and by the carbodiimide ligand *p*-tcd in the latter. In the latter, all Ti–L bond distances are somewhat longer than those in the former (Table 4) and reflect the more bulky bridged *p*-tcd ligand relative to $\text{C}_2\text{O}_4^{2-}$.

The crystal structure of dark green $\{(\eta^5\text{-CpMe})_2\text{Ti}\}_2(\text{C}_4\text{Ph}_2)$ [128] is shown in Fig. 8. In this complex the titanium is part of a four-membered metallocyclic ring and is the first organometallic compound involving an early transition metal reported to have such a structure.

There are two examples, $\{(\eta^5\text{-Cp})_2\text{Ti})_2(\text{O}_2\text{CPhCO}_2)$ and $\{(\eta^5\text{-Cp})_2\text{Ti}\}_2(\text{O}_2\text{CC}_4\text{H}_6\text{CO}_2)$ [49], in which each Cp_2TiO_2 fragment has normal pseudotetrahedral distances and angles (Table 4). These bimetallic compounds bridged by a dicarboxylate dianion have intermolecular distances of 5.783 and 5.932 Å, respectively.

In dark green $\{(\eta^5\text{-CpMe})_2\text{Ti}\}_2(\text{S}_2\text{N}_2\text{C}_4\text{H}_2)$ [129] the dianion of 2,4-dithiopyrimidine is acting as a bis-bidentate bridge between two $(\text{CpMe})_2\text{Ti}$ moieties, with a Ti–Ti distance of 6.075(2) Å (Table 4). μ-1-Diphenylphosphino-μ-2-diphenylarsinoethane occurs as a bridge between two $(\text{Cp})_2\text{TiCl}$ units (Ti–P(As)–C–C–P(As)–Ti) in the complex $\{(\eta^5\text{-Cp})_2\text{TiCl}\}_2(\text{dppae})$ [130].

The longest bridge between two titanium atoms to be identified by X-ray diffraction in a solid organometallic compound occurs in $\{(\eta^5\text{-Cp})_2\text{TiH}_2\text{AlH}_2\}_2(\text{tmen})$ [131]. The acidic (Lewis) aluminium atoms of the two $(\text{Cp})_2\text{TiH}_2\text{AlH}_2$ moieties are linked by the nitrogen atoms of the tetramethylethylenediamine ligand in this molecule.

There are three examples [111,112,117] of bimetallic structures in which two crystallographically-independent molecules are present. These isomers differ only by the degree of distortion, representing another example of distortion isomerization.

(iii) Tri-, tetra-, and hexametallic compounds

There are three known examples of structures for trimetallic titanium compounds (Table 5). The trimetallic complex $\{(\eta^5\text{-Cp})_5\text{Ti}_3\text{Cl}_3\}\text{O}_2$ [132] exhibits a distorted tetrahedral configuration with two non-equivalent titanium(IV) atoms. Two Cp_2Ti units are held to the center CpTiCl unit through a single almost linear oxo-bridge. The mean Ti(IV)–O(bridge) distance of 1.819(7, 61) Å is somewhat shorter than those found in more familiar bimetallic compounds (1.834 Å) (Table 4). However, in these bimetallic derivatives the titanium atom is in its 3+ oxidation state, which presumably affects bond distances.

The crystal structure of the monoclinic mixed-valency Ti(IV)–Ti(III) compound, $\{(\eta^5\text{-Cp})_2\text{Ti}\}_3\{\text{OC}(\text{NPh})_2\}_2$ [125] is shown in Fig. 9, where it can be seen that two $(\text{Cp})_2\text{Ti}\{\text{OC}(\text{NPh})_2\}$ moieties are linked symmetrically to the central Cp_2Ti unit through their carbonyl oxygen atom. There are two non-equivalent titanium atoms, which differ not only by their coordinated atoms, but the cyclopentadienyl rings also exhibit an almost staggered configuration around the N-bonded Ti(III) (Ti(2) in Fig. 9), while the configuration around the other O-bonded Ti(IV) (Ti(1) in Fig. 9) is neither staggered nor eclipsed. The bond distances and angles are given in Table 5.

Another trimetallic mixed-valency Ti(IV)–Ti(III) compound, $\{(\eta^5\text{-Cp})_2\text{Ti}\}_3\{\text{Ph}_2\text{CN}_2\text{C(O)N}_2\text{CPh}_2\}_2$ [102], having crystallographic C_2 symmetry, shows a familiar environment about the titanium atoms (Fig. 9).

Very air sensitive, the light-green crystals of $[\{(\eta^5\text{-Cp})_2\text{Ti}\}_2(\text{CO}_3)]_2$ [133] consist of tetrameric units having C_{2h} symmetry. The four $(\text{Cp})_2\text{Ti}$ units are bridged by two CO_3^{2-} ligands. As shown in Fig. 10(a), there are two

TABLE 5

Structural data for tri-, tetra-, and hexa-nuclear compounds [a]

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	Ti–Ti (Å) Ti–CNT (Å) CNT–Ti–CNT (°)	Ti–L–Ti (°) L–Ti–CNT (°) L–Ti–L (°)	Ref.
$[\{(\eta^5\text{-Cp})_5\text{Ti}_3^{IV}\text{Cl}_3\}(\mu\text{-O})_2]$	tr	$P\bar{1}$	2	15.184 (3) 12.731 (3) 7.843 (3)	85.04 (2) 90.83 (2) 98.62 (2)	O 1.819 (7, 61) Cl 2.367 (4, 37) (Cp)C 2.374 (17, 38)	 2.076 (–, 8) 130.8 (–, 3)	169.0 (4, 7.1) 106.4 (–, 1.2) [c] 100.0 (3, 7.0)	132
$[\{(\eta^5\text{-Cp})_2\text{Ti}\}_3\{\text{OC(NPh)}_2\}_2]$	m	$C2/c$	4	26.187 (1) 8.865 (3) 20.515 (5)		O 1.92 (2) N 2.14 (3, 1) (Cp)C 2.39 (3, 10)	 2.06 (3, 1) 133.6 (1.1, 4.2)	 107.9 (1.1, 2.3) 59.4, 92.5 (9)	125
$[\{(\eta^5\text{-Cp})_2\text{Ti}\}_3\{\text{Ph}_2\text{CN}_2\text{C(O)}$ $\text{N}_2\text{CPh}_2\}_2]\cdot 3(\text{C}_7\text{H}_8)$	or	$P2_12_12$	2	27.667 (2) 13.462 (1) 11.846 (1)		O 1.930 (4) N 2.216 (6, 6) (Cp)C [d]	 2.060 (6, 6) 132.5 (3, 1.2)	 108.5 (2, 5.8) 60.3, 98.2 (2)	102
$[\{(\eta^5\text{-Cp})_2\text{Ti}^{III}\}_2(\text{CO}_3)]_2$	or	$Cmca$	4	11.282 (1) 16.038 (1) 19.729 (2)	90.0 90.0 90.0	μ-O 2.156 (3, 28) (Cp)C 2.388 (12, 72)	3.597 (2) 2.069 (9, 25) 133.7 (5, 2.4)	111.0 (2) 109.3 (3, 8) 65.2 (1, 3.9)	133
$[\{(\eta^5\text{-Cp})_3(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{Ti}_2\}$ $\{(\eta^5\text{-Cp})_2(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Ti}_2\}$- $(\mu_3\text{-N}_2)][(\eta^5\text{-Cp})_2\text{Ti(bme)}]\cdot\text{(bme)}$	tr	$P\bar{1}$	2	14.516 (6) 15.509 (6) 12.695 (4)	91.07 (3) 101.27 (3) 88.62 (3)	μ-N 2.022 (11, 165) C 2.175 (13) (Cp)C 2.417 (17, 50) $(\text{C}_{10}\text{H}_8)$ 2.424 (14, 11) O 2.181 (15, 21) [f] (Cp)C 2.37 (2, 1) [f]	3.816 (4, 1.065) 2.077 (–, 51) 133.3 (–, 1) 2.035 (–, 8) [f] 134.3 [f]	103.1, 145.6 (6) 115.0 (–, 3.1) [e] 35.3 (3) 107.7 (–, 2.4) [f] 74.6 (6) [f]	134
$[(\eta^5\text{-Cp})_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\mu\text{-H})$- $(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{Ti}(\eta^5\text{-Cp})$ $(\mu_2\text{-H})]_2\cdot\text{(tol)}$	m	$P2_1/c$	4	11.753 (5) 15.701 (7) 23.95 (1)	 99.22 (4)				135

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[a] Where more than one chamically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the estimated standard deviation, and the second is the maximum deviation from the mean value. [b] The chemical identity of the coordinated atom or ligand is specified in this column. [c] The value of L–Ti–CNT moieties of $\text{Cp}_2\text{Ti(1)(3)L}$; the mean value of L–Ti–CNT in CpTi(2)L is 114.7 (–, 2.0)°. [d] Value not given. [e] The value of Ti–Ti–CNT(Cp); the Ti–Ti–CNT(fulvalenyl) is 98.6°. [f] Data for $(\eta^5\text{-Cp})_2\text{Ti(bme)}_2$.

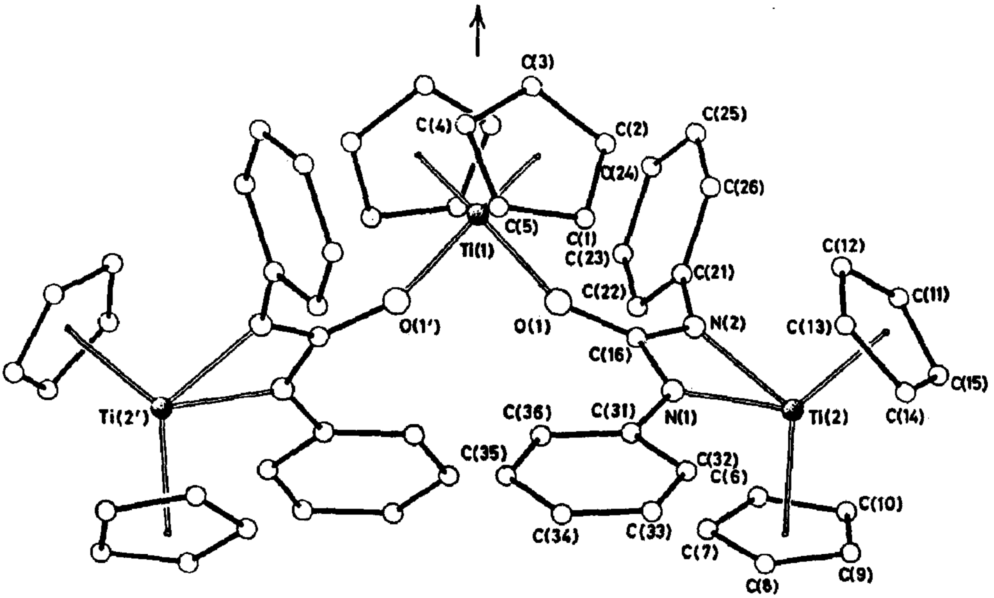

Fig. 9. Structure of $\{(\eta^5\text{-Cp})_2\text{Ti}\}_3\{\text{OC(NPh}_2)_2\}_2$. Reproduced with permission from ref. 125.

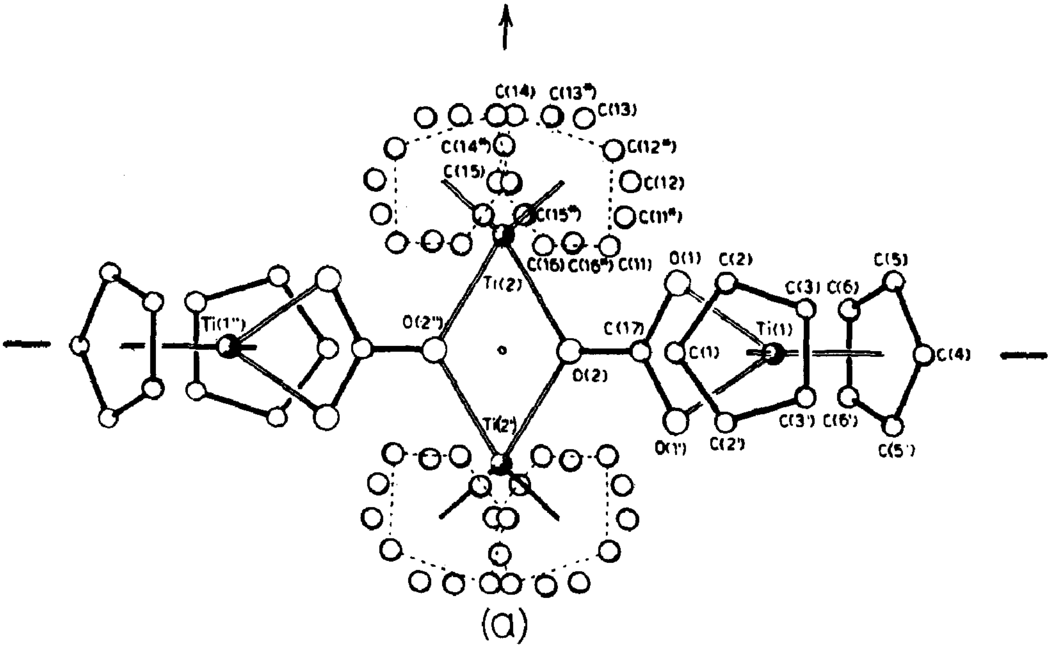

Fig. 10. Structure of $[\{(\eta^5\text{-Cp})_2\text{Ti}\}_2(\text{CO}_3)]_2$ (a) (ref. 133) and of $[\{(\eta^5\text{-Cp})_3(\eta^1{:}\eta^5\text{-C}_5\text{H}_4)\text{Ti}_2\}\{(\eta^5\text{-Cp})_2(\eta^5{:}\eta^5\text{-C}_{10}\text{H}_8)\text{Ti}_2\}(\mu_3\text{-N}_2)]$ unit (b) (page 88) (ref. 134). Reproduced with permission.

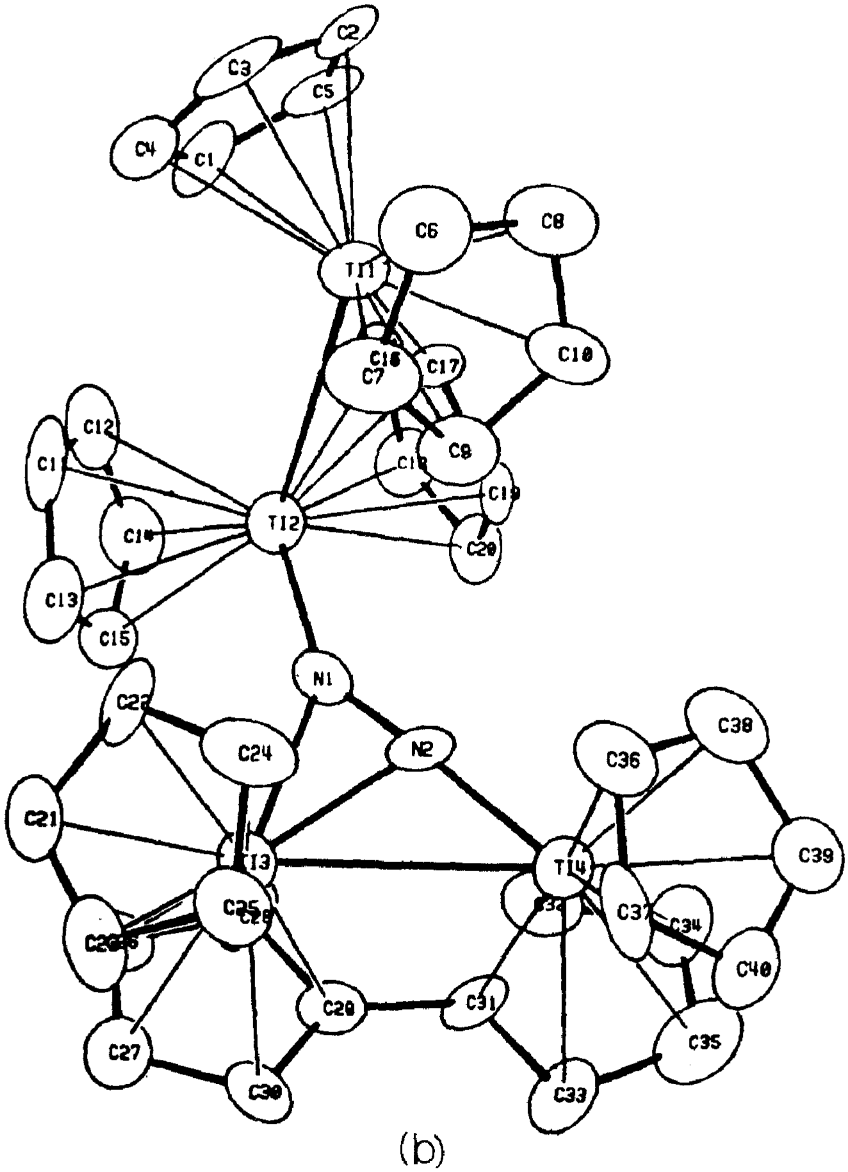

Fig. 10. (continued)

chemically different atoms of titanium(III) in this complex. The Ti(2)–Ti(2′) distance (3.597(2) Å) rules out a metal–metal interaction.

An unusual, and unique coexistence of tetra and monometallic structures in the air-sensitive, dark red-brown prismatic crystal of $[\{(\eta^5\text{-Cp})_3(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{Ti}_2\}\{(\eta^5\text{-Cp})_2(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Ti}_2\}(\mu_3\text{-N}_2)][(\eta^5\text{-Cp})_2\text{Ti(bme)}]$ has been found [134]. The crystal structure of the tetrametallic unit is shown in Fig. 10(b) (bottom). In the monometallic $\text{Cp}_2\text{Ti(bme)}$ unit (not shown in the Figure), the two cyclopentadienyl rings about titanium are tilted in a clino fashion hence forming a cavity in the equatorial plane for the bidentate bis(2-methoxyethyl)ether ligand. The bond distances and angles are given in Table 5.

D. HETEROMETALLIC COMPOUNDS

Structural data for heterometallic organometallic compounds of titanium are presented in Table 6. There are several polymetallic complexes including at least one titanium atom. However, few contain Ti–metal or Ti–Ti bonds. Most structures are of the polymeric type where the metal atoms are generally bridged by a ligand and there is one example of a resolved carbonyl Co cluster structure bonded to a titanocene unit.

For the heterometallic compounds, two types of bridged systems have been found. In $[(\eta^5\text{-Cp})_2\text{Ti(dppet)}_2\text{Cu}]\text{BF}_4$ [136] and in $(\eta^5\text{-Cp})_2\text{Ti(SMe)}_2\text{Mo(CO)}_4$ [137] the metal atoms are doubly bridged by the S atoms of the two ligands. The mean Ti–S–M angle 82.8° (M = Mo) in the former is larger than that of 78.1° (M = Cu) in the latter. The Ti–M bond lengths show a similar pattern with a value for Ti–Mo 0.297 Å longer than that of 3.024(1) Å for the Ti–Cu bond. This lengthening of the Ti–Mo bond can also be attributed to the covalent radius of Mo (1.45 Å) versus Cu (1.38 Å). The mean Ti–C(Cp) bond distance 2.371(9, 22) Å in the former and 2.39(2, 5) Å, in the latter, are in the range found in bis(cyclopentadienyl)titanium derivatives (Table 4).

X-Ray analysis of the bright-green solid $(\eta^5\text{-Cp})_2\text{Ti(thf)(CO)-Mo(CO)}_2(\eta^5\text{-Cp})$ [138] shows the structure to consist of a $(\text{Cp})_2\text{Ti}$ unit coordinated by a molecule of thf(Ti–O = 2.197(5) Å) and by the oxygen atom of a μ-η^2-bridging carbonyl (Ti–O = 2.143(5) Å, and C–Mo = 1.874(7) Å) to the CpMo(CO)_2 fragment.

The molecular structure of hetero-trimetallic $\{(\eta^5\text{-Cp}_2\text{Ti}[(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{Mn(CO)}_3]_2\}$ [139] is shown in Fig. 11, and data are given in Table 6.

In another example of a hetero-trimetallic compound, two independent structure determinations for the zinc chloride derivative $\{[(\eta^5\text{-Cp})_2\text{TiCl}]_2\text{ZnCl}_2\}$ (Table 6) have been reported. The trimetallic molecule consists of a central ZnCl_4 tetrahedron linking the two other Cp_2Ti groups [140,141]. Moreover, the Cp_2Ti units are joined by the Cl...Cl edges of the ZnCl_4 unit in such a way that the metals are nearly colinear. The molecular structure of $[(\eta^5\text{-Cp})_2\text{Ti(dme)}_2(\text{Zn}_2\text{Cl}_6]$ consists of a $[\text{Cp}_2\text{Ti}]^+$ cation stabilized by a dme molecule, and a $(\text{Zn}_2\text{Cl}_6)^{2-}$ anion [142]. Two benzene molecules are present in each trimer solid as solvent of crystallization.

Two organometallic cluster structures containing titanium are reported. They have been described earlier and are shown in Figs. 3 and 4. Structures for two cobalt clusters also containing organometallic titanium, $[(\text{CO})_9\text{Co}_3.$

TABLE 6

Structural data for heteronuclear compounds [a]

Compound	Crystal class	Space group	Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Ti–L [b] (Å)	M–L–Ti (°) L–T–L (°) CNT–Ti–CNT(°) [c]	Ref.
$[(\eta^5\text{-Cp})_2\text{Ti}^{IV}(\text{dppet})_2\text{Cu}]\text{BF}_4$	m	$P2_1/c$	4	16.853 (3)		μ-S 2.474 (3, 10)	78.1 (1, 1)	136
				15.297 (1)	108.90	(Cp)C 2.371 (9, 22)	97.5 (1)	
				15.575 (3)		Cu 3.024 (1)		
$(\eta^5\text{-Cp})_2\text{Ti}(\text{SMe})_2\text{Mo}(\text{CO})_4$	or	$Pbca$	8	15.842 (8)		μ-S 2.460 (4, 15)	82.8 (–, 4)	137
				15.437 (12)		(Cp)C 2.39 (2, 5)	99.9 (1)	
				14.992 (8)		Mo 3.321 (2)		
$(\eta^5\text{-Cp})_2\text{Ti}^{III}(\text{thf})(\text{CO})\text{Mo}(\text{CO})_2(\eta^5\text{-Cp})$	m	$P2_1/c$	4	14.333 (2)		(CO)O 2.143 (5)		138
				10.783 (3)	109.19 (2)	(thf)O 2.197 (5)	79.89 (18)	
				14.051 (3)		(Cp)C [d]		
$\{(\eta^5\text{-Cp})_2\text{Ti}[(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3]_2\}$	m	$C2/c$	4	13.474 (2)		C 2.207 (2)	134.1 (2)	139
				8.085 (1)	105.08 (1)	(Cp)C 2.395 (2, 21)	88.6 (2)	
				22.327 (3)			128.1 (1)	
$\{[(\eta^5\text{-Cp})_2\text{Ti}^{III}\text{Cl}]_2\text{ZnCl}_2\}\cdot 2(\text{C}_6\text{H}_6)$	or	$Pbcn$	4	18.45 (5)		μ-Cl 2.605 (6, 6)	90.2 (2, 2)	140
				15.40 (6)		(CNT) 2.05 (1, 1) [e]	81.6 (2)	
				11.35 (3)		Zn [d]	137.0 (5)	
	or	$Pbcn$	4	18.236 (10)		μ-Cl 2.580 (2, 10)	89.87 (6, 19)	141
				15.513 (8)		(Cp)C 2.334 (7, 16)	82.09 (6)1	
				11.237 (6)		Zn 3.420 (2)		
$[(\eta^5\text{-Cp})_2\text{Ti}^{III}(\text{dme})_2(\text{Zn}_2\text{Cl}_6)]\cdot(\text{C}_6\text{H}_6)$	m	$P2_1/n$	4	11.810 (4)		(dme)O 2.115 (6)		141
				10.201 (5)	93.20 (2)	(Cp)C 2.360 (8, 81)	76.6 (2)	
				17.284 (7)		Zn [d]	133.5	
$\{[(\eta^5\text{-Cp})_2\text{Ti}^{III}\text{Cl}]_2\text{MnCl}_2\}\cdot 2(\text{thf})$	m	$P2_1/c$	2	8.167 (5)		μ-Cl 2.575 (2, 3)	97.85 (5, 7)	142
				11.453 (8)	91.64 (3)	(Cp)C 2.369 (6, 35) [f]	81.31 (6)	
				16.249 (12)		Mn 3.850 (2)	135.2	
$(\eta^5\text{-Cp})_2\text{TiCl}(\text{CO})\text{Co}_3(\text{CO})_9$	m	$P2_1/n$	4	13.532 (6)		(CO)O 1.938 (8)		143
				22.939 (10)	90.67 (4)	Cl 2.336 (5)	92.0	
				7.760 (8)		(Cp)C 2.39 (3, 5) [g]	132.0	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the estimated standard deviation, and the second is the maximum deviation from the mean value. [b] The chemical identity of the coordinated atom or ligand is specified in this column. [c] The centroid of the ring. [d] Value not given. [e] The value of Ti–CNT(centroid of Cp) distance. [f] The molecule has a Ti–CNT distance of 2.06 Å. [g] The molecule has a Ti–CNT distance of 2.07 Å, and a Cl–Ti–CNT angle of 106.5 (–, 1.6)°.

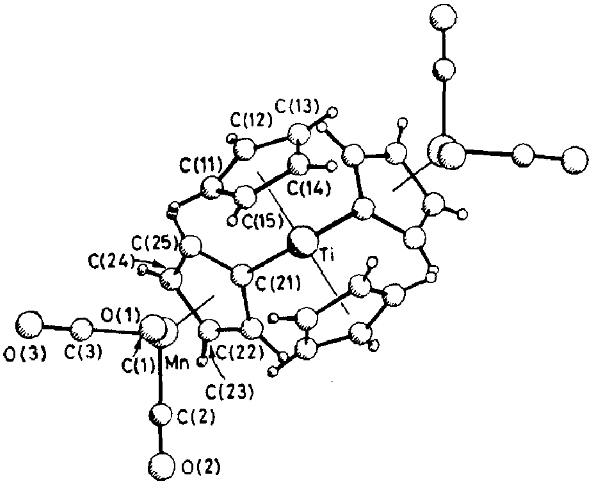

Fig. 11. Structure of $\{(\eta^5\text{-Cp})_2\text{Ti}[(\eta^1:\eta^5\text{-C}_5\text{H}_4)\text{Mn(CO)}_3]_2\}$. Reproduced with permission from ref. 139.

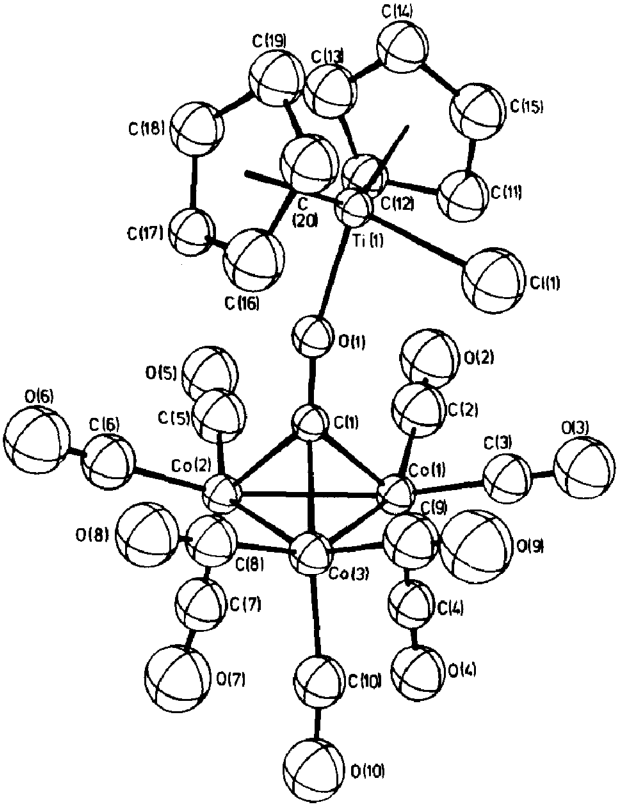

Fig. 12. Structure of $(\eta^5\text{-Cp})_2\text{TiCl(CO)Co}_3\text{(CO)}_9$. Reproduced with permission from ref. 143.

TABLE 7

Summary of the titanium–atom(ligand) and vanadium–atom(ligand) bond distances in Å [a]

Central atom	Coordinated atom	Mononuclear		Binuclear	
		mono-Cp	bis-Cp	mono-Cp	bis-Cp
Ti	H			1.89–2.05 (1.95) [b]	1.60–2.29 (1.86) [b]
V				1.63–1.69 (1.66) [b]	
Ti	O			1.777–1.798 (1.785) [b]	1.759–1.880 (1.839) [b]
				1.776–1.809 (1.795) [b,c]	
				1.973 [d]	
V				1.861–2.003 (1.948) [d]	
Ti	O (ligand)	1.954–2.275 (2.083)	1.860–2.155 (2.003)	1.837–2.258 (2.141)	1.920–2.260 (2.137)
				1.865–2.104 (1.985) [b]	2.037–2.250 (2.134) [b]
V			1.955–2.081 (2.019)	2.04–2.06 (2.05)	2.006
Ti	N				1.857–2.181 (2.000) [b]
Ti	N (ligand)	1.877–2.270 (2.096)	1.922–2.100 (2.007)	2.163–2.176 (2.171)	2.126–2.222 (2.162)
				1.860–2.006 (1.927)	2.174–2.261 (2.202)
V			1.665–2.120 (1.916)		
Ti	C(CO)		2.009–2.050 (2.025)		
V		1.863–1.960 (1.920)	1.879–1.990 (1.950)	1.890–1.972 (1.929)	
Ti	C(Cp)	2.260–2.438 (2.378)	2.300–2.510 (2.379)	2.288–2.600 (2.364)	2.350–2.538 (2.384)
V		2.223–2.347 (2.278)	2.170–2.439 (2.279)	2.180–2.380 (2.269)	
Ti	C (ligand) [e]	2.197–2.211 (2.204)	2.070–2.247 (2.170)	1.980–2.380 (2.180)	2.175–2.260 (2.221)
					2.083–2.540 (2.25) [b]
V			2.032–2.213 (2.117)		
Ti	Cl	2.201–2.371 (2.306)	2.310–2.405 (2.359)	2.250–2.353 (2.292)	2.409–2.514 (2.477)
				2.437–2.547 (2.512) [b]	2.526–2.611 (2.557)
				2.557–2.609 (2.853) [b,c]	
V		2.401–2.405 (2.403)	2.390		
Ti	S (ligand)	2.565–2.666 (2.611)		2.395–2.455 (2.429)	
				2.416–2.598 (2.488) [b]	
V			2.415–2.470 (2.444)	2.210–2.280 (2.235)	
				2.380–2.430 (2.413) [b]	
Ti	P (ligand)	2.636–2.673 (2.655)	2.340–2.585 (2.497)		
V		2.303–2.510 (2.439)			
Ti	Br				2.705–2.722 (2.714) [b]
V		2.59			

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[a] The mean value is given in parentheses. The vanadium data was taken from ref. 146. [b] The values are for a bridging atom (ligand). [c] Intranuclear. [d] The values of a triple bridged atom (ligand). [e] The values are for unidentate C ligands, excluding CO.

CO]$_3$(η^5-Cp)TiCo(CO)$_4$ [34] (Table 2) and (η^5-Cp)$_2$TiClOCCo$_3$(CO)$_9$ [143] (Table 6) are known. The crystal structure of the latter is shown in Fig. 12 and consists of a CCo(CO)$_9$ tetrahedral unit to which a tetrahedral Cp$_2$Ti(O)Cl group is attached. In both these structures the titanium metal is not involved in the metal aggregate.

E. CONCLUSIONS

The crystal structural data gathered in this review represent over 150 titanium organometallic compounds. The majority of these are mono- and bimetallic, with six examples of trimetallic, five of tetrametallic, and one example each of penta-, and hexametallic clusters.

The occurrence of the three oxidation numbers in these derivatives shows a distinct Ti(II < Ti(III) < Ti(IV) order, with few examples of mixed-valency compounds.

Two crystallographically-independent molecules differing by their degree of distortion, are present in 14 examples [26,27,35,49,72,73,85,88,91,92,111, 112,117,126]. There is even an example, η^5-Cp$_2$Ti(S$_3$N$_4$) [56], in which three such molecules are present. The coexistence of two or more species with the same coordination number of the central atom, but different degrees of distortion within the same crystal, is typical of the general class of distortion isomerism [145].

The cyclopentadienyl ring is by far the most common ligand occurring here, and a tetragonal arrangement about the metal is the preferred molecular geometry. Binuclear titanium compounds with two linking ligands are the most common bridging structure encountered.

A summary of the structural data for organometallic titanium compounds is given in Table 7. Inspection of the data reveals that:

(a) In general, the mean Ti–L bond distance in monometallic compounds with one η^5-Cp ligand is somewhat longer than those with two η^5-Cp ligands. However, the mean Ti–Cl bond distance is reversed, and the mean Ti–C(Cp) distance is almost equal in both types of compound.

(b) The mean Ti–L bond distance in bimetallic compounds with one η^5-Cp ligand is shorter than those with two η^5-Cp ligands when L is Cl or C-bonded, but longer if L is either O- or N-bonded to titanium.

(c) In general, the mean Ti–L(bridge) bond distances in oligometallic compounds with one η^5-Cp ligand are found to be shorter than those with two η^5-Cp ligands.

(d) In general, the Ti–L(bridge) distances tend to be somewhat longer than the Ti–L(terminal) distances.

An overall summary of the structural data for organometallic compounds of titanium and vanadium is given in Table 7. Some points of comparison arising from these data are listed below.

In general, the Ti–L bond distances are longer than the corresponding V–L distances, with the exception of V–Cl distances which are found to be longer than Ti–Cl distances. However, it must be noted that there is only one example for each. This observation, (Ti–L) > (V–L), corresponds very well with the metallic covalent radii (1.32 Å versus 1.25 Å, respectively). Finally, the M–L distances increase with increasing van der Waals radius of the ligated atom.

This survey illustrates the rich variety found in over 300 titanium compounds for which structures have been defined by X-ray crystallography or related techniques. During the collection and oganization of the data it has become clear that, despite the increasing availability of data retrieval systems, the tracing of relevant material is not always a straightforward task. Some of the data surveyed were available only as supplementary material, and this can sometimes lead one to overlook some relevant structural features for comparative purposes. In view of the limitations inherent in information retrieval, we believe that such reviews will continue to serve a useful function by crystallizing available material, and delineating areas of both interest and weakness.

Despite the variability of the compounds, many systematic trends have been observed and outlined here. From these trends, directions for further inquiry are more apparent in this and related areas.

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