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Titanocene derivatives containing titanium – carbon σ-bonds

V A Knizhnikov, N A Maier

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Abstract. The published data on the major methods for the synthesis and chemical conversions of titanocene derivatives containing titanium – carbon σ-bonds are systematised. The bibliography includes 288 references.

I. Introduction

The chemistry of dicyclopentadienyltitanium (titanocene) derivatives is one of the most rapidly developing branches of the chemical science. The interest in titanocene derivatives is partly due to their ability to catalyse various chemical processes, *e.g.*, polymerisation, isomerisation and hydrogenation of alkenes, cyclotrimerisation of acetylene derivatives, fixation of molecular nitrogen under mild conditions and many other reactions. These compounds acquire increasing popularity as additives to fuels and high-temperature lubricants, rubber accelerators, lacquer and water-repellent components, antiknock compounds, *etc.*

Among other compounds of the titanocene series, titanocene derivatives containing Ti – C σ-bonds are still the least known due to the thermal instabilities of the majority of representatives of this class and, to some extent, their high sensitivities to oxygen and atmospheric moisture. High reactivities of titanocene derivatives containing Ti – C σ-bonds with various organic and inorganic substrates and the presence of several reaction centres in some of them open broad prospects for their application in both organic synthesis and in the preparation of diverse organometallic compounds including novel representatives of the known types of titanocene derivatives. The published data on the major methods for the synthesis of titanocene derivatives containing Ti – C σ-bonds isolated from various reaction mixtures in individual state and the most typical chemical transformations are considered. The principal characteristics of titanocene derivatives (colour, solubility, air resistance, thermal stability, structure, *etc.*) have been described in the majority of the original papers and therefore fall outside the scope of this review.

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II. Methods for the synthesis of titanocene derivatives containing Ti – C σ-bonds

1. Reactions of titanocene halides with organic derivatives of non-transition metals

Reactions of titanocene dihalides with organolithium, -sodium, -magnesium or -aluminium compounds constitute a classical method for the synthesis of titanocene σ-derivatives; depending on the reagent ratio, both mono- and dialkyl- or diaryl derivatives can be prepared.

Dimethyltitanocene (**1**) was prepared by the reaction of titanocene dichloride (**2**) with an excess of methyllithium, methylmagnesium halides or lithium tetramethylaluminium at reduced temperatures. Diethyl ether is the most convenient solvent for such syntheses.[1 – 5]

$$\underset{\mathbf{2}}{Cp_2TiCl_2} + MeX \xrightarrow{Et_2O} \underset{\mathbf{1}}{Cp_2TiMe_2}$$

Cp = C_5H_5; MeX = MeLi, MeMgHal, $LiAlMe_4$.

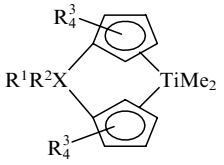
Dimethyltitanocene derivatives **3** containing various substituents in π-bound cyclopentadienyl ligands are prepared from the corresponding dichlorides.

$$Cp^1Cp^2TiCl_2 + MeX \longrightarrow \underset{\mathbf{3}}{Cp^1Cp^2TiMe_2}$$

MeX = MeLi, MeNa, MeMgHal, Me_3Al.

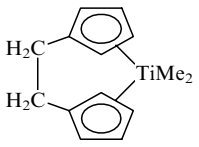
Cp^1	Cp^2	Ref.
C_5H_4Me	C_5H_4Me	6
C_5Me_5 (Cp*)	C_5Me_5	2, 6
1,2,3-$Me_3C_5H_2$	1,2,3-$Me_3C_5H_2$	6
C_5Me_4H	C_5Me_4H	6 – 8
$C_5Me_4(CH_2CH_2CH=CH_2)$	$C_5Me_4(CH_2CH_2CH=CH_2)$	9
C_5H_5	C_5Me_5	10
$C_5H_3(SiMe_3)_2$	$C_5H_2(SiMe_3)_3$	11
1,3-$Bu^t_2C_5H_3$	C_5H_5	12
C_5Me_5	$C_5Me_4(CH_2)_2NMe_2$	13
C_5Me_5	$C_5H_4CMe_2C_{13}H_9$	14

Dimethyltitanocene derivatives with bridges between the cyclopentadienyl ligands, such as compounds **4**,[15 – 19] **5a**[20] and **5b**,[21, 22] are known.

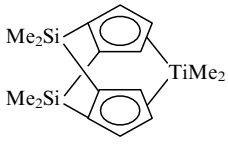


4

R^1	R^2	R^3	X	Ref.
Me	Me	H	C	15
H	Bu^n	H	C	16
Me	Me	H	Si	17, 18
Me	Me	Me	Si	19

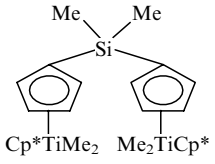


5a

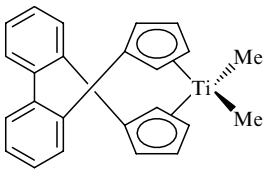


5b

The binuclear titanocene-like complex **6**[23] with a bridging (dimethylsilylidene)dicyclopentadiene ligand and the complex **7**[24] in which the role of a bridge is played by biphenyl-2,2′-diyl have been synthesised.

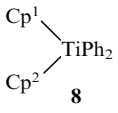


6

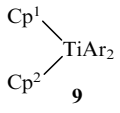


(±)-**7**

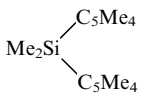
The reaction of titanocene dichloride (**2**) with phenyllithium or phenylmagnesium halides gave diphenyltitanocene Cp_2TiPh_2.[4,25–28] Diphenyltitanocene derivatives containing substituents in both π-bound cyclopentadienyl ligands, such as compound **8**, and σ-bound phenyl rings, such as compounds **9**, have been described.



8



9

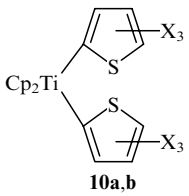
Cp^1	Cp^2	Ref.
C_5H_5	C_5Me_5	10
C_5H_5	C_5HMe_4	7, 8
C_5Me_5	C_5Me_5	7, 8
		19

Cp^1	Cp^2	Ar	Ref.
C_5H_5	C_5H_5	3(4)-MeC_6H_4	27, 28
C_5H_5	C_5H_5	2-$Me_2NC_6H_4$	27
C_5H_5	C_5H_5	C_6F_5	4, 29, 30
C_5HMe_4	C_5HMe_4	4-MeC_6H_4	7, 8
C_5H_5	C_5Me_5	4-MeC_6H_4	7, 8

The reaction of titanocene dichloride (**2**) or its derivatives with benzylmagnesium chloride or benzyllithium results in dibenzyltitanocene derivatives Cp_2TiBn_2,[31–33] $(C_5H_4Me)_2TiBn_2$,[33] $(C_5H_4SiMe_3)_2TiBn_2$[33] and $[(C_5H_4)_2SiMe_2]TiBn_2$.[16]

Syntheses of titanocene derivatives in which σ-bound organic radicals contain a heteroatom, *e.g.*, $Cp_2Ti(CH_2SiMe_3)_2$,[34–37] $[(C_5Me_4)_2SiMe_2]Ti(CH_2SiMe_3)_2$,[19] $[(C_5H_4)_2SiMe_2]Ti.(CH_2SiMe_3)_2$,[21] $Cp_2Ti(CH_2GeMe_3)_2$,[37] $Cp_2Ti(CH_2SPh)_2$,[38,39] $Cp_2Ti(CH_2PPh_2)_2$,[40] $Cp^*(Cp)Ti(CH_2PPh_2)_2$,[41] *etc.*, have been described.

Thiophene[42] or trichlorothiophene (compounds **10a**,**b**) can be used as σ-bound substituents.[43]

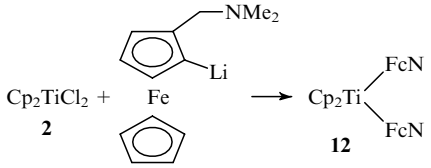


10a,**b**

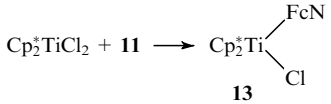
X = H (**a**), Cl (**b**).

The reaction of titanocene dichloride (**2**) with cyclopentadienylsodium afforded tetracyclopentadienyltitanium in which two cyclopentadienyl ligands were linked by π-bonds, whereas the other two ligands, by σ-bonds.[44–47] Presumably, this complex underwent rapid (on an NMR time scale) π ⇄ σ rearrangement of the ligands at 20 °C.[46,48]

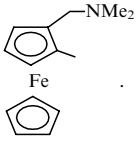
The reaction of an excess of ferrocenyllithium with titanocene dichloride (**2**) results in diferrocenyltitanocene Cp_2TiFc_2 (Fc = $C_5H_5FeC_5H_4$).[49] The reaction of titanocene dichloride (**2**) with an excess of 2-(dimethylaminomethyl)ferrocenyllithium (**11**) yields the symmetrical complex **12**. Under similar conditions, bis(pentamethylcyclopentadienyl)titanium dichloride yields the monoferrocenyl-substituted complex **13**.[50]



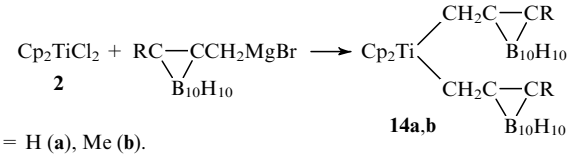
11



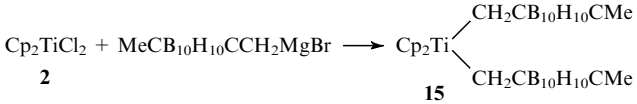
13

FcN = 

The reaction of titanocene dichloride (**2**) with *o*(*m*)-carboran-1-ylmethylmagnesium bromides leads to carboranylmethyl-substituted titanocenes **14a**,**b** and **15**.[51,52] Dicyclopentadienylbis(*o*-carboranylmethyl)titanium **14a**, contrary to the majority of titanocene derivatives containing Ti–C σ-bonds, is stable in air at 20 °C over a long period of time and is decomposed only on melting at 185 °C.



R = H (**a**), Me (**b**).



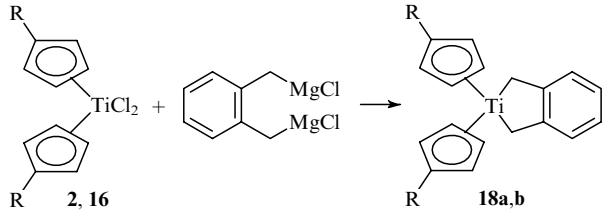
15

Titanocene dichloride (**2**) reacts with an excess of sodium, lithium or magnesium acetylenide to give titanocene diacetylenides $Cp_2Ti(C{\equiv}CR)_2$, where R = Ph,[53–55] $SiMe_3$,[56,57] CF_3,[58] Et, Pr^n, Bu^n, Bu^t (see Ref. 56), cyclo-C_6H_{11}, Ph_2CHCH_2, *n*-C_6H_{13},[55] Fc, Rc (Rc = $C_5H_5RuC_5H_4$);[59] $(C{\equiv}CR)_2$ = $(C{\equiv}C{-}2\text{-}C_6H_4{-}C{\equiv}C{-}2\text{-}C_6H_4{-}C{\equiv}C)$.[60] Similar compounds were prepared from titanocene dichloride derivatives containing substituents in cyclopentadienyl rings, *viz.*, $Cp'_2Ti(C{\equiv}CR)_2$, where Cp′ = C_5H_4Me: R = Ph, cyclo-C_6H_{11}, n-C_6H_{13}, Ph_2CHCH_2,[55] $SiMe_3$;[56] Cp′ = $C_5H_4SiMe_3$: R = Ph, $SiMe_3$,[56] $C{\equiv}C{-}C{\equiv}CEt$,[61] Fc,[59,62] Rc;[59] Cp′ = $C_5H_2Me_3$, R = $SiMe_3$;[63] Cp′ = Cp*, $(C{\equiv}CR)_2$ = $(C{\equiv}C{-}2\text{-}C_6H_4{-}C{\equiv}C{-}2\text{-}C_6H_4{-}C{\equiv}C)$;[60] Cp′ = $C_5H_4CH_2CH_2NMe_2$: R = $SiMe_3$;[64] Cp′ = C_5H_4X (X = Ph_2P, $Ph_2P{=}O$, $Ph_2P{=}S$), R = Bu^t (see Ref. 65).

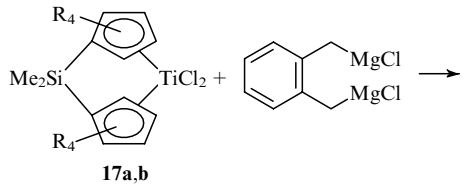
Symmetrical dicyclopentadienyltitanium derivatives with other σ-bound organic groups, *e.g.*, $Cp_2TiBu^n_2$ (see Ref. 66), Cp_2TiEt_2,[67] $Cp_2Ti[C(Ph){=}CMe_2]_2$,[68] $Cp_2Ti(CF{=}CF_2)_2$[69] and $[Me_2Si(C_5H_4)_2]TiBu^n_2$ (see Ref. 18), have been synthesised.

The reactions of titanocene dichloride (**2**) or its derivatives containing substituents in the cyclopentadienyl ligands with

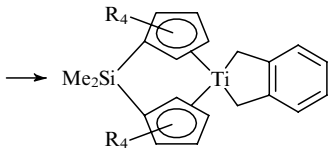
organodilithium or -dimagnesium compounds yield metallacycles. Thus titanaindans **18a**,**b**,[70] **19a** [18] and **19b** [19] were prepared from the dichlorides **2**, **16**, **17a**,**b** and 1,2-bis(chloromagnesiomethyl)benzene.



R = H (**2**, **18a**), $SiMe_3$ (**16**, **18b**).



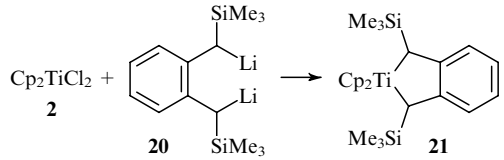
17a,**b**



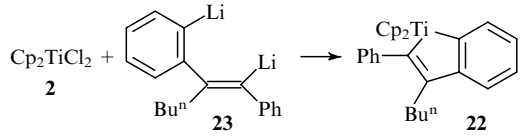
19a,**b**

R = H (**a**), Me (**b**).

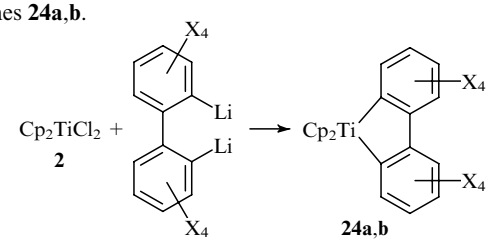
The dilithium derivative **20** was used for the preparation of substituted titanaindan **21**.[71]



Titanaindene **22** is produced by the reaction of titanocene dichloride (**2**) with the dilithium derivative **23**.[72]

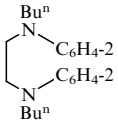
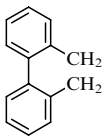


The reaction of titanocene dichloride (**2**) with 2,2′-dilithiobiphenyl [72] or 2,2′-dilithiooctafluorobiphenyl [73] gave titanafluorenes **24a**,**b**.

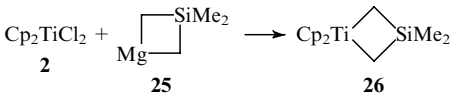


X = H (**a**), F (**b**).

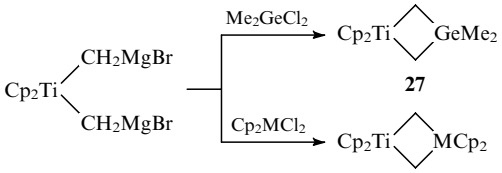
Diverse titanacyclic compounds Cp_2TiL_2 have been described in which the cyclic structures are formed owing to the ligands L_2.

L_2	Ref.	L_2	Ref.
	74	$(CH_2)_4$	77, 78
		$CH_2CH(Me)CH_2$	79
		$CH_2SiMe_2XSiMe_2CH_2$ ($X = CH_2$, O, $SiMe_2$)	80
	75, 76	$CH_2SiMe_2SiMe_2CH_2$	80

Titanocene dichloride (**2**) reacts with 1,1-dimethyl-1-sila-3-magnacyclobutane (**25**) to give thermally stable 3,3-dimethyl-1,1-dicyclopentadienyl-1-titana-3-silacyclobutane (**26**).[81]

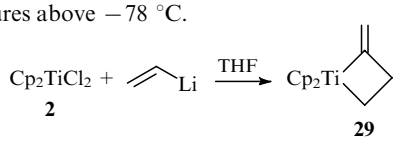


1-Titana-3-metallacyclobutanes **27** and **28** were prepared by the reactions of bis(bromomagnesiomethyl)titanocene with dichlorodimethylgermane [82] or titanocene, zirconocene and hafnocene dichlorides.[83]

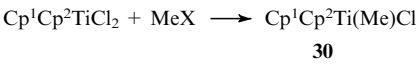


M = Ti, Zr, Hf.

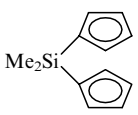
1,1-Dicyclopentadienyl-1-titana-2-methylidenecyclobutane (**29**) was synthesised by the reaction of titanocene dichloride (**2**) with vinyllithium in THF in the reagent ratio of 1 : 2.[84,85] Presumably, this reaction proceeds *via* divinyltitanocene, which is rearranged into 2-methylidenetitanacyclobutane **29** at temperatures above −78 °C.



Monoalkyl- or monoaryl titanocene chlorides are formed upon treatment of titanocene dichloride (**2**) with equimolar amounts of organolithium or -magnesium compounds. Thus methyltitanocene chloride derivatives **30** were prepared using methyllithium, methylmagnesium chloride or trimethylaluminium.



MeX = MeLi, MeMgCl, Me_3Al.

Cp^1	Cp^2	Ref.	Cp^1	Cp^2	Ref.
C_5H_5	C_5H_5	86–89	C_5H_5	1,3-$Bu^t_2C_5H_3$	12
C_5H_5	$C_5H_4CH(Me)Ph$	90			
C_5H_5	C_5H_4Me	91			17, 18
C_5H_4Me	C_5H_4Me	91			

The complexes $Cp^1Cp^2Ti(Me)ClAlMe_2Cl$ where $Cp^1 = C_5H_5$, $Cp^2 = C_5H_4Me$, $C_5H_4SiMe_3$; $Cp^1 = Cp^2 = C_5H_4SiMe_3$, have also been synthesised.[92]

Reactions of titanocene dichloride (**2**) or its derivatives containing substituents in the cyclopentadienyl ligands with trimethylsilylmagnesium chloride (1 : 1) yield the trimethylsilylmethyl derivatives **31a**–**d**. Compounds **31e**–**h** were prepared in a similar way.

$Cp^1Cp^2Ti(CH_2EMe_3)Cl$

31a–**h**

Compound **31**	Cp^1	Cp^2	E	Ref.
a	C_5H_5	C_5H_5	Si	33, 93, 94
b	C_5H_4Me	C_5H_4Me	Si	33
c	$C_5H_4SiMe_3$	$C_5H_4SiMe_3$	Si	33
d	$Me_2Si(C_5H_4)_2$		Si	17, 18
e	C_5H_5	C_5H_5	C	93
f	C_5H_5	C_5H_5	Ge	93
g	C_5H_5	C_5H_5	Sn	93
h	C_5H_4Me	C_5H_4Me	C	33

The reaction of titanocene dichloride (**2**) or its analogue containing a bridging dimethylsilylene group with an equimolar amount of benzylmagnesium chloride gave $Cp_2Ti(Bn)Cl$ (see Ref. 86) and $[Me_2Si(C_5H_4)_2]Ti(Bn)Cl$.[17]

Chlorotitanocene derivatives $Cp_2TiCl(L)$ containing bulky ligands [*e.g.*, $L = CH_2CH_2CHR^1CR^2{=}CH_2$, where $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = Ph$, $R_2 = H$; $L = CH_2CMe_2CHCR^1{=}CR^2CR^3{=}CH_2$, where $R^1 = R^2 = R^3 = H$; $R^1 = R^2 = H$, $R^3 = Me$; $R^1 = Me$, $R^2 = R^3 = H$; $R^1 = R^3 = H$, $R^2 = Me$; $R^1 = R^2 = Me$, $R_3 = H$] were synthesised by the reaction of titanocene dichloride (**2**) with the corresponding organomagnesium compounds.[95]

Titanocene dichloride derivatives containing substituents in the cyclopentadienyl ligands react with sodium acetylenides (charge ratio 1 : 1) to give the monoacetylenides $Cp'_2TiCl(C{\equiv}CR)$ [$Cp' = C_5H_4Me$, $C_5H_4SiMe_3$, $R = Ph$, $SiMe_3$ (see Ref. 56); $Cp' = C_5H_4SiMe_3$, $R = C{\equiv}CEt$ (see Ref. 61)].

The reaction of titanocene dichloride (**2**) with pentafluorophenyllithium in ether yields bis(pentafluorophenyl)titanocene (**32**) and pentafluorophenyltitanocene chloride (**33**).[29] The monopentafluorophenyl titanocene derivative **34** was prepared by treatment of cyclopentadienyl(*tert*-butylcyclopentadienyl)titanium dichloride with pentafluorophenylmagnesium bromide.[96]

$$Cp_2TiCl_2 + C_6F_5Li \longrightarrow Cp_2Ti(C_6F_5)_2 + Cp_2Ti(C_6F_5)Cl$$

2 **32** **33**

$$Cp(Bu^tC_5H_4)TiCl_2 + C_6F_5MgBr \longrightarrow Cp(Bu^tC_5H_4)Ti(C_6F_5)Cl$$

34

The chlorotitanocene derivatives **35** containing various alkyl-, aryl-, alkenyl- and other σ-bound ligands were synthesised by reactions of equimolar amounts of the corresponding dichlorides with organomagnesium or -lithium compounds.

$Cp^1Cp^2Ti(R)Cl$

35

Cp^1	Cp^2	R	Ref.
C_5H_5	C_5H_5	Ph	86
C_5H_5	C_5H_5	Et	86, 97
C_5H_5	C_5H_5	Pr^n	86
C_5H_5	C_5H_5	CH_2PPh_2	40
C_5H_5	C_5H_5		98
C_5H_5	C_5H_5	CH_2OMe	99
C_5H_5	C_5H_5	$CF_2{=}CF$	69
C_5H_5	C_5H_5	Fe, CH_2NMe_2	100
C_5H_5	C_5Me_5	CH_2PPh_2	41
C_5H_4Me	C_5H_4Me	CH_2OMe	99
C_5Me_5	$C_5Me_4(CH_2)_2NMe_2$	$CH_2{=}CH$	13

The bromotitanocene derivative $Cp_2TiBr(CH_2MgBr)$ was prepared from titanocene dibromide and $CH_2(MgBr)_2$.[101]

The alkyl- and aryl(dicyclopentadienyl)titanium(III) derivatives **36**–**38** have been described. They are prepared by treating dicyclopentadienyltitanium(III) chloride or its derivatives containing substituents in the cyclopentadienyl ligands with organolithium, -sodium or -magnesium compounds at −78 °C.

TiR

36

R	Ref.	R	Ref.
Me	102–104	$CHCMe_2CH_2CH_2C(R){=}CH_2$ (R = H, Me)	95
Et	102		
Bu^n	102	2(3,4)-MeC_6H_4	105
Ph	105	2,6-$Me_2C_6H_3$	105, 106
2,4,6-$Me_3C_6H_2$	105	C(Me)=CHMe	107
C_6F_5	104, 105	Bn	108

Me_5, TiR, Me_5

37

R	Ref.	R	Ref.	R	Ref.
Me	108, 109	Pr^n	108	C_2D_5	108
Et	108, 109	Bn	108	C_3D_7	108
CH_2Bu^t	108	$CH_2{=}CH$	108	CMe=CHMe	109
Ph	108	CD_3	108		

R^1_n, TiR^2, R^1_n

38

R^1_n	R^2	Ref.
Me_4	Me	110
Me_4	Ph	110
1,3-Bu^t_2	Me	111

The dicyclopentadienyltitanium(III) derivatives **39a**–**e** containing a heteroatom in the alkyl substituent have been obtained.

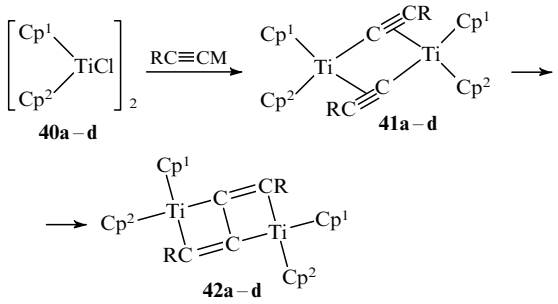
$TiCH_2R$

39a–**e**

Compound **39**	R	Ref.
a	$SiMe_3$	104
b	PPh_2	40
c	$(CH_2)_2OMe$	112
d	$(CH_2)_2SMe$	112
e	CH_2OMe	112

It is assumed that the titanium atom in compounds **39b–e** is additionally coordinated by the heteroatom of the σ-bound ligand.[40, 112]

Treatment of the dicyclopentadienyltitanium(III) chloride dimer or its derivatives containing substituted cyclopentadienyl ligands **40a–d** with lithium or sodium phenyl- or trimethylsilylacetylenides at −78 °C yields the paramagnetic complexes **41a–d** which are converted into the dimagnetic complexes **42a–d** upon heating.[17, 54, 57, 113, 114]



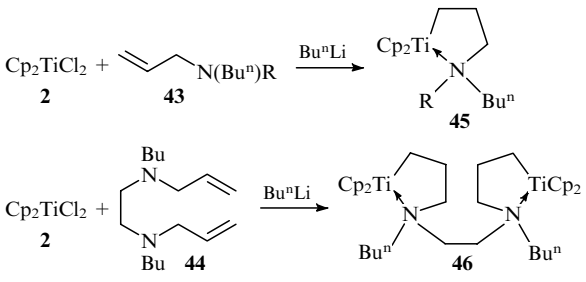
40a–d **41a–d** **42a–d**

M = Na, Li.

Compound	Cp^1	Cp^2	R	Ref.
a	C_5H_5	C_5H_5	Ph	54
b	MeC_5H_4	MeC_5H_4	Ph	113
c	C_5H_5	C_5H_5	$SiMe_3$	57
d	$Me_2Si(C_5H_4)_2$		Ph	17, 114

Dicyclopentadienyltitanium(III) monoacetylenides are formed as side products upon treatment of titanocene dichloride (**2**) with an excess of acetylenides EC≡CR (E = BrMg, Na, Li; R = Ph, Et, Pr^n, Bu^n, Bu^t, $SiMe_3$).[56] The formation of a dicyclopentadienyltitanium(III) derivative $Cp_2Ti(2\text{-}MeOCH_2C_6H_4)$ proceeds through preliminary reduction of Ti(IV) to Ti(III) in the reaction of titanocene dichloride (**2**) with an equimolar amount of bis(2-methoxymethylphenyl)magnesium in THF. This is the first Ti(III) derivative in which the titanium atom is coordinated by oxygen. A similar reaction with bis(2-*N*,*N*-dimethylaminomethylphenyl)magnesium[115] affords the Ti(III) complex $Cp_2Ti(2\text{-}Me_2NCH_2C_6H_4)$. Reactions of Cp_2TiCl_2 with sterically hindered lithium alkyls devoid of β-hydrogen atoms, such as $LiCHPh_2$ or $LiCH(SiMe_3)_2$ yield the Ti(III) complexes Cp_2TiR [R = Ph_2CH, $(Me_3Si)_2CH$]. Dicyclopentadienyltitanium(III) chloride was found to be the intermediate product of these reactions.[116]

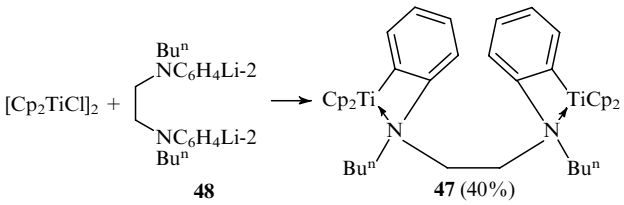
Treatment of titanocene dichloride (**2**) with n-butyllithium yields Cp_2TiH which adds to allylamines **43** and **44** to give 1-titana-2-azacyclopentanes **45** and **46**.[117]



2 **43** **45**

2 **44** **46**

The binuclear complex **47** was prepared by the reaction of dicyclopentadienyltitanium(III) chloride with *N*,*N*′-bis(*o*-lithiumphenyl)-*N*,*N*-di(n-butyl)ethylenediamine **48**.[74]

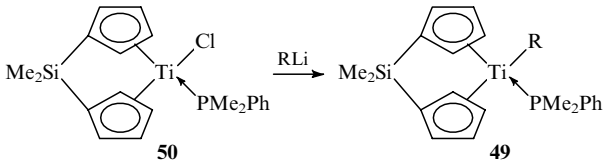


48 **47** (40%)

The reaction of dicyclopentadienyltitanium(III) chloride with lithium tetramethylaluminate in toluene at 0 °C was used to prepare the complex $Cp_2Ti(\mu\text{-}Me)_2AlMe_2$ containing two bridging methyl groups.[118] The titanocene derivatives $Cp_2Ti.(\mu\text{-}Cl)(\mu\text{-}CH_2)AlMe_2$ (see Ref. 119) and $Cp_2Ti(\mu\text{-}CH_2)_2PPhR$ (R = Me, Ph)[120] containing bridging methylene groups have also been synthesised.

The reaction of titanocene dichloride (**2**) with isopropylmagnesium chloride in a nitrogen atmosphere at temperatures below −78 °C affords $[Cp_2TiPr^i]_2N_2$ with a coordinated nitrogen molecule.[121] The complexes $[Cp_2TiR]_2N_2$ [R = CH_2Bu^t, CH_2SiMe_3 , 3-MeC_6H_4, 2,6-$Me_2C_6H_3$,[122] C(Me)=CHMe (see Ref. 107)] were prepared from dicyclopentadienyltitanium(III) chloride and organomagnesium compounds under similar conditions.

The phosphine titanocene derivatives **49** containing σ-bound methyl- or trimethylsilylmethyl groups were synthesised by the reaction of the phosphine complexes **50** with organolithium compounds.[123]



50 **49**

R = Me, Me_3SiCH_2.

It was shown that the complexes $[Cp_2TiR_2]M$ (M = Li, Na; R = Me, Et, Pr^i) stable only at low temperatures are formed upon treatment of titanocene dichloride (**2**) with an excess of organolithium or -sodium reagents at temperatures below −70 °C.[124] The complex $[\eta^5\text{-}(C_5HMe_4)_2Ti(\eta^1\text{-}C{\equiv}C{-}C{\equiv}CSiMe_3)_2]^-[Li(THF)_2]^+$ was isolated and characterised by X-ray diffraction analysis. This is the first complex in which the Li atom is located between the inner triple bonds of the ethynyl ligands.[125]

2. Synthesis of titanocene σ-derivatives using unsaturated organic compounds

Reactions resulting in metallacyclic titanocene complexes containing Ti–C σ-bonds can arbitrarily be divided into three groups:

1. Formation of a metallacycle by cross-linking of two unsaturated compounds including those π-coordinated by a metal atom;

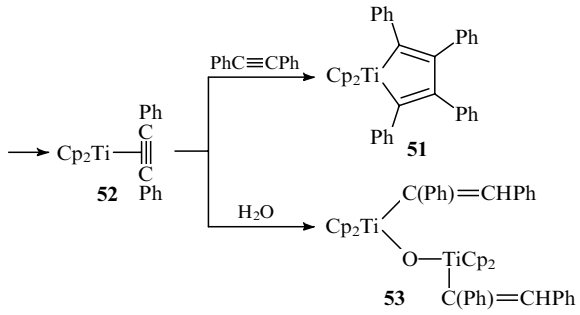
2. Formation of a titanacycle by incorporation of an unsaturated compound into the Ti–C σ-bond;

3. Addition of molecules containing several multiple bonds to dicyclopentadienyltitanium derivatives.

The first type of reactions include reduction of titanocene dichloride (**2**) with naphthalenesodium[126] or metallic magnesium[127, 128] in the presence of diphenylacetylene resulting in 1,1-dicyclopentadienyl-2,3,4,5-tetraphenyl-1-titanacyclopentadiene (**51**).

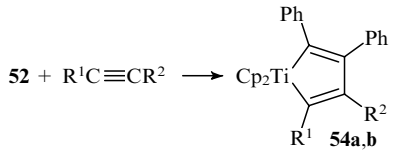


2



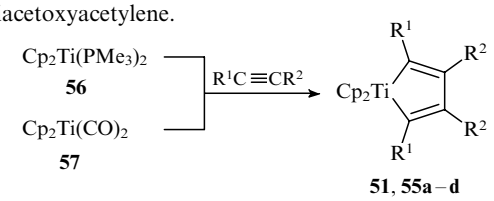
It is believed [129] that this reaction proceeds through the reduction of titanium(IV) to titanium(II) with subsequent formation of the tolan – titanocene π-complex **52**. Supporting evidence is provided by the fact that 1,1-dicyclopentadienyl-2,3,4,5-tetraphenyl-1-titanacyclopentadiene **51** is formed as a result of interaction of the complex **52** with tolan,[129] while treatment of the intermediate compound **52** with water gives the binuclear complex **53**.[127]

Titanacyclopentadienes **54a**,**b** were synthesised by the reaction of the tolan – titanocene complex **52** with phenylacetylene or hex-3-yne.[130]



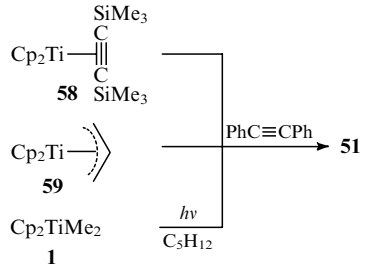
R^1 = Ph, R^2 = H (**a**); R^1 = R^2 = Et (**b**).

The dimerisation of alkynes and the formation of titanacyclopentadienes **51** and **55a – d** occur in the reaction of the diphosphine – titanocene complex **56** with acetylene, dimethylacetylene or methylacetylene or of the titanocenedicarbonyl **57** with tolan or diacetoxyacetylene.

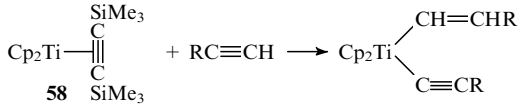


Compound	R^1	R^2	Ref.
55a	H	H	131 – 133
55b	Me	Me	134
55c	Me	H	133
55d	OC(O)Me	OC(O)Me	135
51	Ph	Ph	135

1,1-Dicyclopentadienyl-2,3,4,5-tetraphenyl-1-titanacyclopentadiene (**51**) was prepared by treatment of the titanocene complex with bis(trimethylsilyl)acetylene **58**[136] or of the π-allyl titanium(III) complex **59**[137] with an excess of tolan. The titanacycle **51** is also formed in a photochemical reaction of dimethyltitanocene (**1**) with tolan in pentane.[138 – 140]

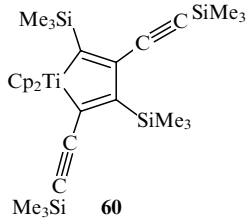


In contrast to the reaction of the bis(trimethylsilyl)acetylene – titanocene complex **58** with tolan, its reaction with monosubstituted acetylenes yields alkenyltitanocene acetylenides.[141]

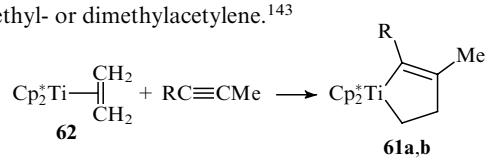


R = Ph, Me_3Si, $Me(CH_2)_3$.

The reaction of titanocene with bis(trimethylsilyl)butadiyne gives the titanacyclopentadiene derivative **60**.[142]



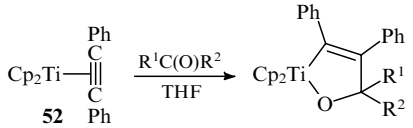
Cross-linking of ethylene and acetylene ligands and the formation of 1,1-bis(pentamethylcyclopentadienyl)-1-titanacyclopent-2-ene derivatives **61a**,**b** take place in the reaction of bis(pentamethylcyclopentadienyl)(ethylene)titanium (**62**) with methyl- or dimethylacetylene.[143]



R = H (**a**), Me (**b**).

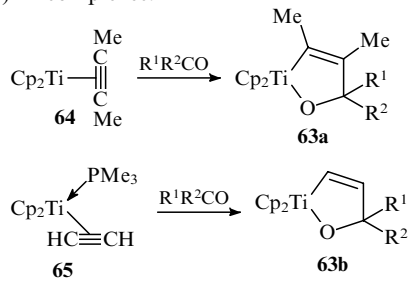
Compounds containing a titanacyclopentene fragment were prepared by reactions of (acetylene)(trimethylphosphine)di(cyclopentadienyl)titanium with ethylene [144] and by reactions of (diphenylacetylene)di(cyclopentadienyl)titanium with tricyclo-[5.2.1.$0^{2,8}$]deca-2,5,8-triene.[145]

Acetylene – titanocene complexes enter into heterocyclisation reactions with carbonyl compounds. Thus the tolan – titanocene complex **52** reacts with an equimolar amount of acetone [146, 147] or benzaldehyde [147] to yield titanadihydrofuran metallacycles.



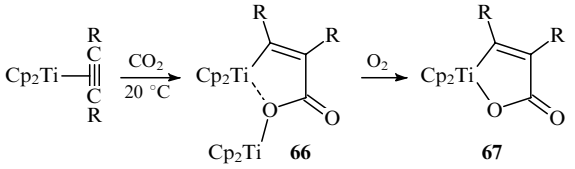
R^1 = R^2 = Me; R^1 = Ph, R^2 = H.

The titanadihydrofuran derivatives **63a**,**b** are formed by reactions of acetone or acetaldehyde with dimethylacetylene – titanocene (**64**)[134] or acetylene(trimethylphosphine) – titanocene (**65**)[144] complexes.



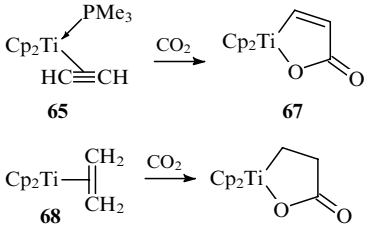
R^1 = H, R^2 = Me; R^1 = R^2 = Me.

The reaction of carbon dioxide with alkyne – titanocene π-complexes results in the binuclear σ-vinylcarboxylate complexes **66**. Their oxidation by atmospheric oxygen gives titanadihydrofuranones **67**.

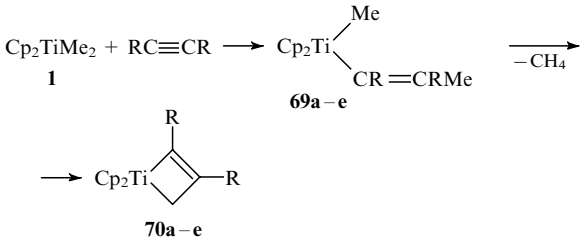


R = Ph,[148–150] $SiMe_3$,[149, 150] Me.[134]

Titanadihydrofuranone (**67**) (R = H) was prepared by the reaction of carbon dioxide with the trimethylphosphinacetylene–titanocene complex **65**.[144] The reaction of the ethylene–titanocene complex **68** with CO_2 yields titanatetrahydrofuranone.[143]

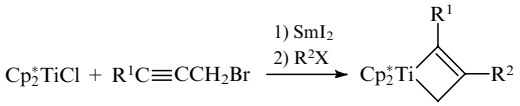


The reaction of dimethyltitanocene (**1**) with alkynes in boiling benzene in the dark is a typical reaction of the second type, which consists in the formation of titanacycles due to incorporation of unsaturated compounds into the Ti–C σ-bond. In the first step, methyl(vinyl)titanocene complexes **69a–e** are formed; in the case of R = Ph [151] and C_6F_5 (see Ref. 152), these complexes were isolated in an individual state. In the second step, methane is abstracted from the complexes **69a–e** resulting in the titanacyclobutene derivatives **70a–e.**[151, 153] In-depth studies of these reactions have been carried out.[154]



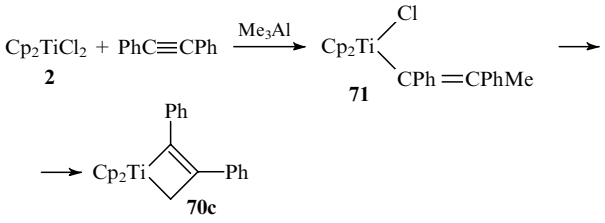
R = Et (**a**), Pr^n (**b**), Ph (**c**), Me_3Si (**d**), C_6F_5 (**e**).

Titanacyclobutene derivatives were prepared by the reaction of bis(pentamethylcyclopentadienyl)titanium chloride with propargyl bromides in the presence of samarium diiodide with subsequent treatment of the reaction mixture with an equimolar amount of the corresponding halide.[155, 156]

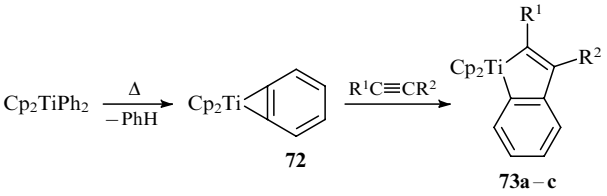


R^1 = H; R^2 = Bn; R^1 = Me, R^2 = $MeC{\equiv}CCH_2$, Bn;
R^1 = Ph, R^2 = Bn, $PhC{\equiv}CCH_2$; X = Hal.

Diphenyl-substituted titanacyclobutene **70c** was synthesised by the reaction of titanocene dichloride (**2**) with tolan and trimethylaluminium. This reaction proceeds *via* the intermediate vinyl derivative **71**.[156]

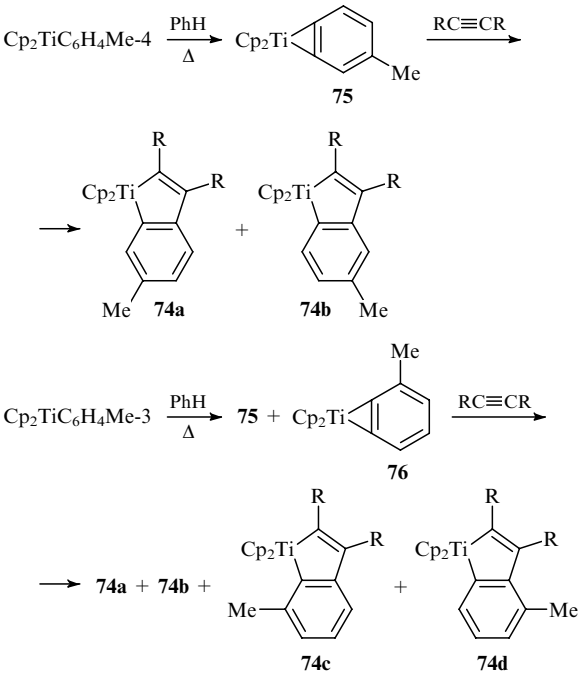


Thermal reactions of alkynes with diphenyltitanocene are also accompanied by insertion of alkyne into the Ti–C σ-bond. It is believed [157, 158] that the phenylenetitanium complex **72** is formed in the first step as a result of splitting of the benzene molecule from diphenyltitanocene. Subsequent insertion of alkyne into one of the Ti–C σ-bonds results in titanaindenes **73a–c**.



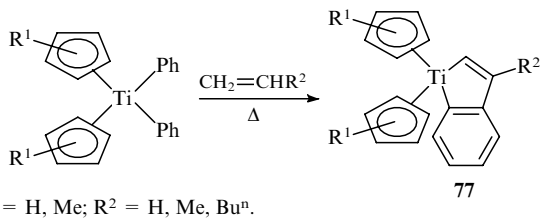
R^1 = R^2 = Ph (**a**), R^1 = R^2 = C_6F_5 (**b**), R^1 = $SiMe_3$, R^2 = Ph (**c**).

Analogous reactions yielding mixtures of substituted titanaindenes **74a–d** occur on heating of *m*- or *p*-tolyltitanocenes in the presence of alkynes.[159] The formation of a complex mixture of reaction products in the case of the *m*-tolyl derivative is explained by the fact that this compound yields a mixture of isomeric phenylenetitanium complexes **75** and **76** upon heating.[159]



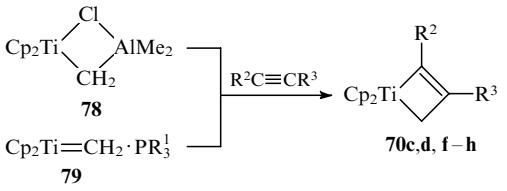
Titanaindene **73a** was prepared by reduction of titanocene dichloride (**2**) with magnesium in the presence of tolan and *o*-bromofluorobenzene.[128]

Heating of diphenyltitanocene derivatives in the presence of alkenes results in titanaindenes **77**.[160]



R^1 = H, Me; R^2 = H, Me, Bu^n.

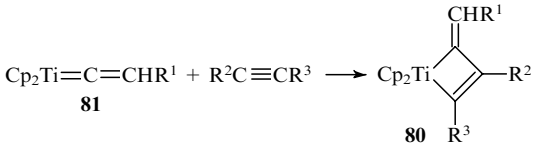
The 1,1-dicyclopentadienyl-1-titanacyclobut-2-ene derivatives **70c,d,f–h** were prepared by the reaction of alkynes with the titanium–aluminium complex **78** in the presence of pyridine [161, 162] or with carbene–titanocene complexes **79**.[163–165]



78 **79** **70c,d, f–h**

R^1_3 = Me_3, Me_2Ph, Et_3; R^2 = R^3 = Ph (**70c**), $SiMe_3$ (**70d**);
R^2 = CMe=CH_2, R^3 = Et (**70f**); R^2 = Et, R^3 = CMe=CH_2 (**70g**);
R^2 = CEt=CH_2, R^3 = Me (**70h**).

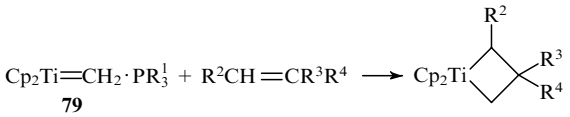
Alkylidenetitanacyclobutenes **80** are formed in reactions of alkynes with the titanocenevinylidene complexes **81**.[166]



81 **80**

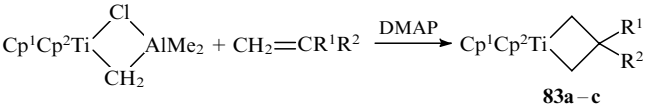
R^1 = Ph, Pr^n, n-C_5H_{11}; R^2 = H, Pr^n, n-C_5H_{11}, Ph; R^3 = Pr^n, Ph, $SiMe_3$.

The titanacyclobutane derivatives **82a–d** result from reactions of trisubstituted alkenes with the carbene–titanocene complexes **79**.[163–165] Titanacyclobutanes **83a–c** were prepared by the reaction of terminal alkenes with titanium–aluminium complexes in the presence of 4-dimethylaminopyridine (DMAP).[91, 167] The titanium–aluminium complex **78** yields the titanabicyclopentane derivative **84** in the reaction with 3,3-dimethylcyclopropene.[168]



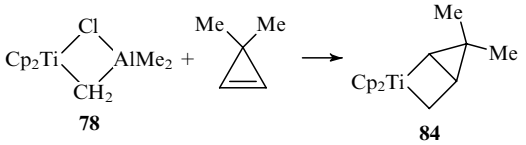
79 **82a–d**

R^1_3 = Me_3, Me_2Ph, Et_3; R^2 = R^3 = H; R^4 = Bu^n (**a**);
R^2 = R^3 = H, R^4 = Bu^t (**b**), R^2 = H, R^3 = R^4 = Me (**c**);
R^2 = R^4 = Me; R^3 = H (**d**).



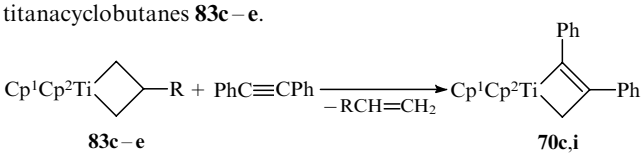
83a–c

Compounds **83**	Cp^1	Cp^2	R^1	R^2	Ref.
a	C_5H_5	C_5H_5	Me	Pr^i	167
b	C_5H_4Me	C_5H_4Me	Bu^t	H	91
c	C_5H_5	C_5H_4Me	Bu^t	H	91



78 **84**

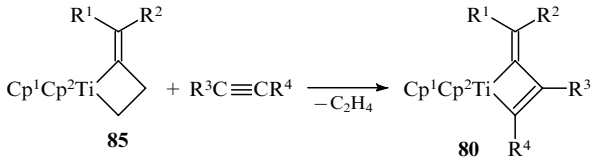
Titanacyclobutane derivatives react with alkynes to give titanacyclobutenes and the corresponding alkenes. Thus titanacyclobutenes **70c,i** were synthesised from diphenylacetylene and titanacyclobutanes **83c–e**.



83c–e **70c,i**

Titanacyclobutanes	Cp^1	Cp^2	R	Titanacyclobutenes	Ref.
83e	C_5H_5	C_5H_5	Bu^t	**70c**	169, 170
83d	C_5H_5	C_5H_5	Pr^i	**70c**	169, 170
83c	C_5H_5	C_5H_4Me	Bu^t	**70i**	91

Alkylidenetitanacyclobutanes **85** react with alkynes at 70 °C in benzene or toluene to give alkylidenetitanacyclobutenes **80**.[171, 172]

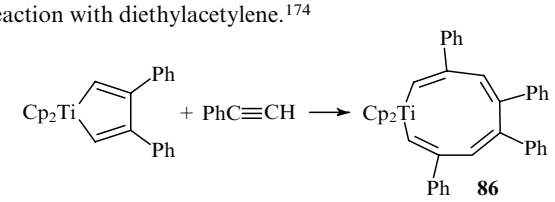


85 **80**

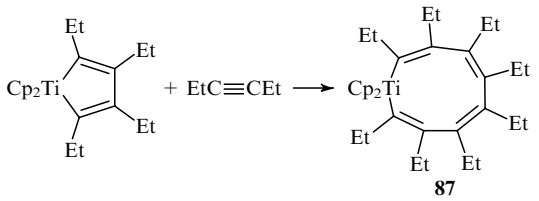
Cp^1 = Cp^2 = C_5H_5: R^1 = R^2 = Me; R^1 = Me, R^2 = Pr^i;
R^3 = R^4 = Me, Et; Cp^1 = Cp^2 = C_5Me_5: R^1 = R^2 = H;
R^3 = R^4 = H, Me, Ph, $SiMe_3$, $SiBu^n_3$; R^3 = Pr^n, R^4 = H;
R^3 = Me, R^4 = Et; R^3 = Et, R^4 = Me; R^3 = Me, R^4 = MeC≡C;
R^3 = Ph, R^4 = PhC≡C; R^3 = Me, R^4 = Ph;
R^3 = Ph, R^4 = Me; R^3 = Ph, R^4 = $SiMe_3$.

Reactions of titanacyclobutane complexes with 1,1-dimethyl- and 1-isopropyl-1-methylallenes result in the formation of alkylidenetitanacyclobutene derivatives **80** (R^1 = R^2 = Me, R^1 = Me, R^2 = Pr^i; R^3 = R^4 = H).[172, 173]

Some reactions of titanacyclic complexes with unsaturated or carbonyl compounds are accompanied by expansion of the metallacycle. Thus 1,1-dicyclopentadienyl-3,4-diphenyl-1-titanacyclopentadiene reacts with phenylacetylene to give a nine-membered titanacycle **86**. 1,1-Dicyclopentadienyl-2,3,4,5-tetraethyl-1-titanacyclopentadiene forms a similar cyclic derivative **87** in a reaction with diethylacetylene.[174]

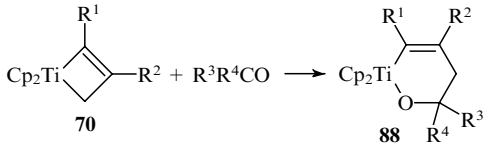


86



87

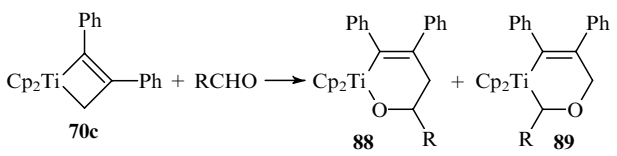
Insertion of aliphatic ketones into the Ti–C σ-bond of the titanacyclobutene derivatives **70** results in six-membered metallacycles **88**.[175]



70 **88**

R^1 = R^2 = Ph: R^3 = R^4 = Me; R^3 = Me, R^4 = Ph, CH_2=CH;
R^3 = Ph, R^4 = cyclo-C_3H_5; R^1 = Ph, R^2 = Me: R^3 = Me, R^4 = Me, Ph.

Reactions of 1,1-dicyclopentadienyl-1-titana-2,3-diphenylcyclobut-2-ene **70c** with aldehydes yield mixtures of isomeric titanadihydropyrans **88** and **89**.[175]

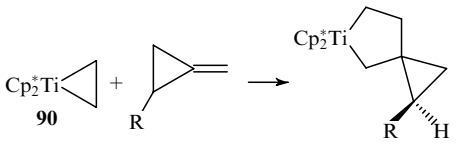


70c **88** **89**

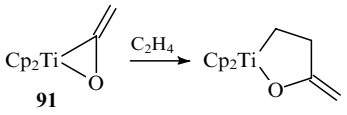
R = Me, Ph, Bn.

The expansion of the metallacycle also takes place in reactions of 1,1-bis(pentamethylcyclopentadienyl)-1-titanacyclopropane **90** with methylidenecyclopropane or 1-methylidene-2-phenylcyclo-

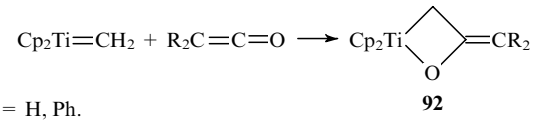
propane [176] and the ketene – titanocene complex **91** with ethylene.[177]



R = H, Ph.

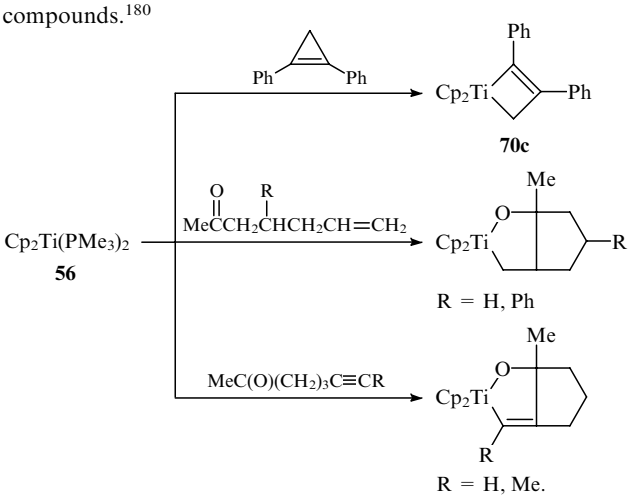


The metallacyclic compounds **92** were prepared by reactions of the carbene – titanocene complex with ketenes.[178]

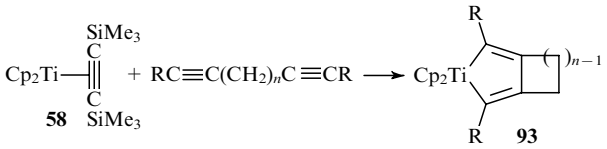


R = H, Ph.

Reactions of bis(trimethylphosphine)titanocene (**56**) with 1,2-diphenylcyclopropene,[179] δ-enones and δ-inones belong to the third type of reactions leading to the formation of titanacyclic compounds.[180]

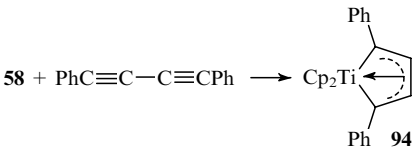


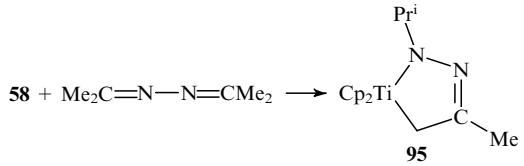
A reaction of the bis(trimethylsilyl)acetylene – titanocene complex **58** with diynes was used for the preparation of bicyclic titanacyclopentadiene derivatives **93**.[181]



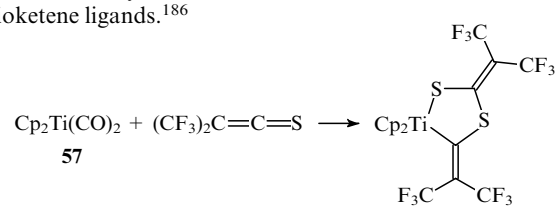
n = 2, R = Me, Bu; n = 4, R = Et.

The reaction of the bis(trimethylsilyl)acetylene – titanocene complex **58** with 1,4-diphenylbuta-1,3-diyne results in titanacyclocumulene **94**,[182] while the reaction with acetone azine gives the 1-titana-2,3-diazacyclopent-3-ene derivative **95**.[183, 184]





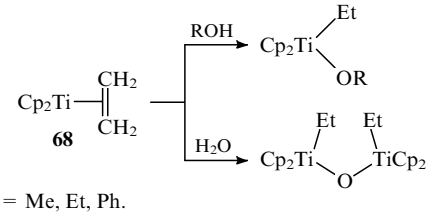
The reaction of di(carbonyl)di(cyclopentadienyl)titanium (**57**) with 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane gives a monomeric alkylidenetitanathiirane containing a η^2-(C–S)-bound thioketone ligand.[185] The reaction of di(carbonyl)di(cyclopentadienyl)titanium (**57**) with bis(trifluoromethyl)thioketene yields a titanacycle in which the titanium atom is bound to two thioketene ligands.[186]



3. Miscellaneous methods for the synthesis of titanocene σ-derivatives

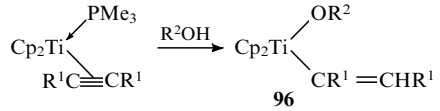
In some cases, addition of various substrates to π-bound organic ligands of titanocene derivatives results in the formation of Ti–C σ-bonds.

Treatment of di(η^5-cyclopentadienyl)(η^2-ethylene)titanium (**68**) with alcohols, phenols[187, 188] and water [188] gave mono- and binuclear derivatives of ethyltitanocene.



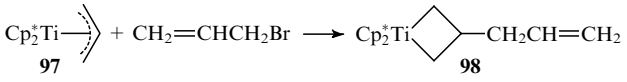
R = Me, Et, Ph.

The reactions of acetylene titanocene complexes with alcohols or phenols yielded σ-alkenyl complexes **96**.[187, 188]

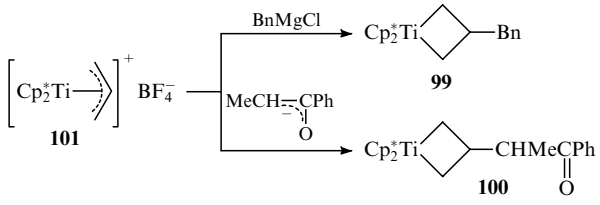


R^1 = Ph, Me; R^2 = Me, Et, Ph.

Bis(η^5-pentamethylcyclopentadienyl)(η^3-allyl)titanium (**97**) reacts with allyl bromide to give the titanacyclobutane complex **98**.[189]

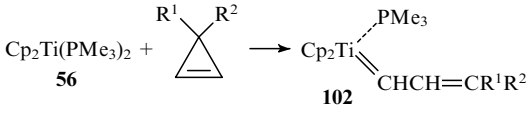


Reactions of the cationic π-allyl complex **101** with benzylmagnesium chloride or propiophenone enolate lead to the titanacyclobutane derivatives **99** and **100**.[190]



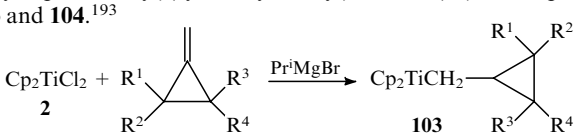
Bis(pentamethylcyclopentadienyl)titanium hydride reacts with alkenes to give the σ-alkyl derivatives $Cp^*_2TiCH_2CH_2R$ (R = H, Me).[108]

Reactions of bis(trimethylphosphine)titanocene (**56**) with an equimolar amount of 3,3-disubstituted cyclopropenes afford the titanocene(vinylcarbene) complexes **102**.[191] The complex **102** ($R^1 = R^2 = Ph$) was prepared together with the complex $Cp_2Ti(PMe_3)=C=C=CPh_2$ by treatment of titanocene dichloride with two equivalents of butyllithium in the presence of trimethylphosphine and 3,3-diphenylcyclopropene.[192]

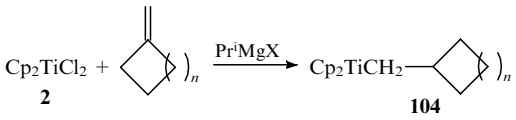


$R^1 = R^2 = Me, Ph$; $R^1 = Me$, $R^2 = Ph$.

Reduction of titanocene dichloride (**2**) by isopropylmagnesium halides in the presence of methylidenecyclopropanes, methylidenecyclobutane or methylidenecyclopentane results in the di(cyclopentadienyl)(cycloalkylmethyl)titanium(III) complexes **103** and **104**.[193]



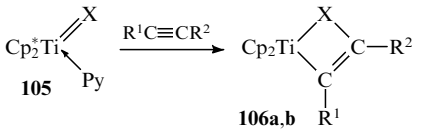
$R^1, R^2, R^3, R^4 = H, Me$.



$n = 1, 2$; X = Cl, Br.

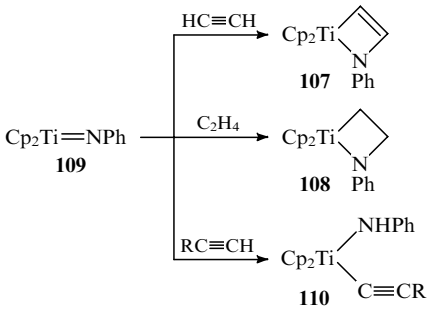
Titanium enolates of the formula $Cp^*_2TiMe(OCR^1=CR^2R^3)$ were prepared by heating bis(pentamethylcyclopentadienyl)dimethyltitanium(IV) in the presence of epoxides, *e.g.*, cyclohexene oxide, *cis*- and *trans*-but-2-ene oxides.[194]

The titanocene sulfide and titanocene oxide complexes **105** enter into [2 + 2]-cycloaddition reactions with alkynes to give titanaoxa- (**106a**) and titanathiacyclobutenes (**106b**).[195, 196]



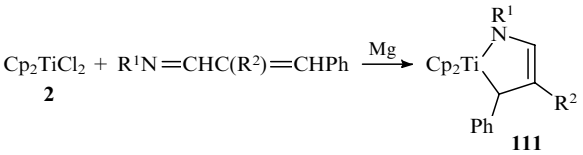
106a: X = O; $R^1 = H$; $R^2 = Me, Bu^t, Ph, 4\text{-}MeC_6H_4$; $R^1 = R^2 = Ph$;
106b: X = S; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Ph, Me_3Si$.

The azatitanacycles **107** and **108** are prepared by the reaction of the complex **109** with acetylene or ethylene, respectively. Reactions of the complex **109** with phenyl- or trimethylsilylacetylene yield acetylenides **110**.[197]



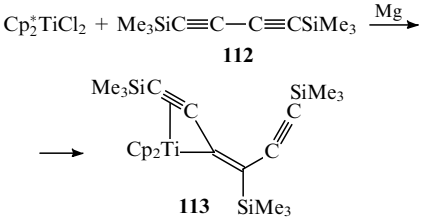
R = Ph, Me_3Si.

Some titanocene derivatives containing Ti–C σ-bonds were prepared by the reduction of titanocene dichloride (**2**) in the presence of unsaturated compounds. Thus its reduction by magnesium in the presence of Schiff's bases prepared from α,β-unsaturated aldehydes yields titanazacyclopentenes **111**.[198]



$R^1 = Bu^t, 4\text{-}MeC_6H_4$, $R^2 = H$; $R^1 = cyclo\text{-}C_6H_{11}$, $R^2 = Me$.

Reduction of bis(pentamethylcyclopentadienyl)titanium dichloride by magnesium in the presence of 1,4-bis(trimethylsilyl)buta-1,3-diyne (**112**) results in the η^3-enyne complex **113**.[199]



Reduction of bis(trimethylsilyltetramethylcyclopentadienyl)-titanium dichloride by magnesium in THF in the presence of bis(trimethylsilyl)acetylene gives $\eta^5:\eta^1$-[$C_5Me_4Si\text{-}Me_2CH_2$].[$\eta^5$-$C_5Me_4(SiMe_3)$]Ti(III).[200]

Reactions of ylides $Me_{3-n}(Me_2N)_nP=CH_2$ (n = 1, 2) with titanocene dichloride yield complexes $Cp^2TiCl(CH=PR^1R^2_2)$, where $R^1 = NMe_2$, $R^2 = Me$; $R^1 = Me$, $R^2 = NMe_2$.[201]

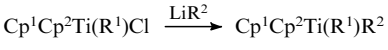
Reactions of the titanocene(dicarbonyl) **57** with alkyl iodides gave the acyl complexes $Cp_2TiI[C(O)R]$, where R = Me, Et, Pr^i, Bu^n (see Refs 202, 203). Acyl titanocene halide derivatives are also formed upon treatment of the titanocene(dicarbonyl) **57** by organic acid chlorides [202, 203] or by treatment of alkyl(titanocene) halides with carbon monoxide.[204]

III. Reactions of titanocene derivatives containing Ti–C σ-bonds

Reactions of titanocene derivatives containing Ti–C σ-bonds are little studied. The published data on the reactivities of these compounds are conventionally divided into two groups, *viz.*, reactions involving Ti–C σ-bonds and those with retention of these bonds.

1. Reactions with retention of Ti–C σ-bonds

Reactions of halide derivatives of titanocene σ-complexes with organometallic derivatives of non-transition metals belong to the most typical reactions of this type. Thus reaction of alkyl- or aryltitanocene chlorides with organolithium compounds was used for the preparation of the complexes **114**, which contain two different σ-bound organic radicals.



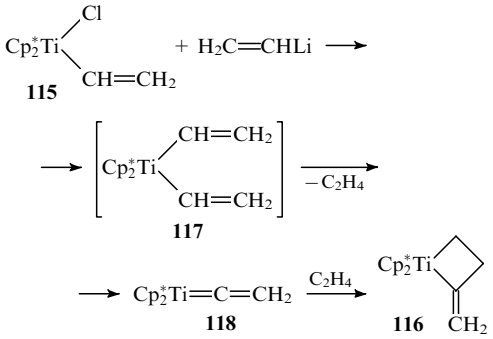
114

Cp^1	Cp^2	R^1	R^2	Ref.
C_5H_5	C_5H_5	Me	Ph	205
C_5H_5	C_5H_5	Me	$4\text{-}MeOC_6H_4$	205
C_5H_5	C_5H_5	Me	$4\text{-}MeC_6H_4$	205
C_5H_5	C_5H_5	2-thienyl	Me	206
C_5H_5	C_5H_5	2-thienyl	Ph	206
C_5H_5	C_5H_2	2-thienyl	C≡CPh	206
C_5H_5	C_5H_5	CH_2SiMe_3	C≡CX [a]	207
C_5Me_5	$C_5Me_4(CH_2)_2NMe_2$	$CH=CH_2$	Me	13

Cp^1	Cp^2	R^1	R^2	Ref.
C_5H_5	$Bu^tC_5H_4$	C_6F_5	$CH_2CH=CH_2$	208
C_5Me_5	C_5Me_5	$CH=CH_2$	Me	209

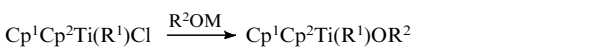
[a] X = $SiMe_3$, 3,5-$(Me_2NCH_2)_2C_6H_3$, 4-NCC_6H_4, 4-C_5H_4N, Fc, 4-I-3,5-$(Me_2NCH_2)_2C_6H_2$.

In some cases, synthesis of this type of compound is complicated by side reactions. Thus the attempts to prepare non-symmetrical ethyltitanocene derivatives by the reaction of bis(pentamethylcyclopentadienyl)ethyltitanium chloride with methyllithium, benzylpotassium or vinyllithium yielded only the ethylene complex $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$ concomitantly with the liberation of the corresponding hydrocarbon. Treatment of bis(pentamethylcyclopentadienyl)vinyltitanium chloride **115** with benzylpotassium or dimethylphosphinomethyllithium gave the complex $(\eta^5\text{-}C_5Me_5)(C_5Me_4CH_2)Ti-CH=CH_2$.[209] The reaction of the complex **115** with vinyllithium yields 1,1-bis(pentamethylcyclopentadienyl)-1-titana-2-methylidenecyclobutane (**116**).[209] Presumably, bis(pentamethylcyclopentadienyl)divinyltitanium (**117**), which is formed in the first step of this reaction, is decomposed to give the derivative **118**. The latter adds the ethylene molecule at the Ti=C bond to give the final product **116**.

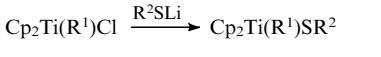


Apparently, reactions of phenyltitanocene chloride with butyl-, vinyl- or benzyllithium afford the intermediates $Cp_2Ti(Ph)R$ (R = Bu^n, $CH=CH_2$, Bn) which are further converted into phenyldicyclopentadienyltitanium(III).[209]

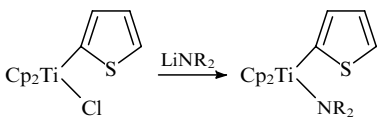
Treatment of alkyl- or aryltitanocene chlorides with alkali metals alcoholates[90,96,210–213] or thiolates[87,214] or with lithium amides[215] results in the replacement of chlorine atoms.

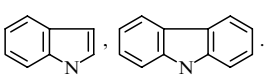


M = Na, Li; $Cp^1 = Cp^2 = C_5H_5$: $R^1 = C_6F_5$, R^2 = Me, Et;
R^1 = Me, $R^2 = CH=CH_2$; R^1 = 2-thienyl, R^2 = 2,4,6-$(NO_2)_3C_6H_2$, 3,4-$(NO_2)_2C_6H_3$; $Cp^1 = C_5H_5$, $Cp^2 = C_5H_4CH(Me)Ph$,
$R^1 = C_6F_5$, R^2 = 2-MeC_6H_4; $R^1 = R^2$ = Me.

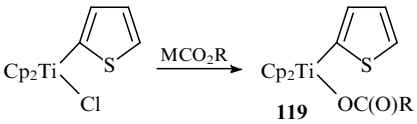


R^1 = Me, R^2 = 4-$NH_2C_6H_4$; R^1 = 2-thienyl, R^2 = Bn, 2-thienyl.





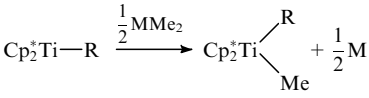
Reactions of 2-thienyltitanocene chloride with potassium 2,4-dichlorophenoxyacetate, mercury(I) benzoate or silver trifluoroacetate were used for the preparation of the corresponding 2-thienyltitanocene acylates (**119**).[216]



M = K, R = 2,4-$Cl_2C_6H_3OCH_2$; M = Hg, R = Ph; M = Ag, $R = CF_3$.

The reaction of pentafluorophenyltitanocene chloride with sodium hydroxide occurs with the retention of the Ti–C σ-bond and results in the substitution of the hydroxy group for the chlorine atom.[211]

Some transformations of dicyclopentadienyltitanium(III) derivatives under the action of various oxidants, which may even include dimethylzinc, dimethylcadmium and $PbCl_2$, occur with the retention of the Ti–C σ-bond. Thus reaction of ethyl-, phenyl- or vinylbis(pentamethylcyclopentadienyl)titanium with dimethylzinc[217,218] or dimethylcadmium[217] afforded methyltitanocene derivatives along with metallic zinc or cadmium.

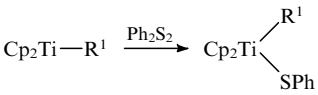


R = Et, Ph, $CH=CH_2$; M = Zn, Cd.

The methylbis(pentamethylcyclopentadienyl)titanium derivatives $Cp^*_2Ti(Me)X$, where X = Cl, OMe, N = $CHBu^t$, are also formed in the oxidation of the corresponding Cp^*_2TiX derivatives by dimethylzinc or -cadmium.[217,218] It is noted[217] that dimethylmercury does not enter into such reactions.

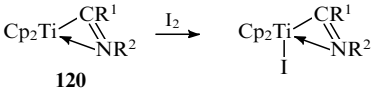
Alkyl- or acyldicyclopentadienyltitanium(IV) chlorides were prepared by oxidation of σ-alkyl- or σ-acyldicyclopentadienyltitanium(III) derivatives by lead dichloride.[109,219]

Treatment of dicyclopentadienyltitanium(III) derivatives with diphenyl disulfide is also accompanied by the oxidation of Ti(III) to Ti(IV) with the retention of the Ti–C σ -bond.[102,103,107]

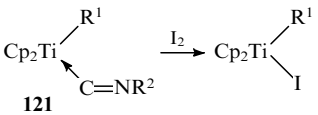


R^1 = C(O)CMe=CHMe; 2,6-$Me_2C_6H_3N=CR^2$,
R^2 = Me, Et, Bu^n.

In some cases, reaction of dicyclopentadienyltitanium(III) σ-derivatives, *e.g.*, complexes **120** and **121**, with iodine also occurs with the retention of the Ti–C σ-bond resulting in titanium(IV) derivatives.[103,220]

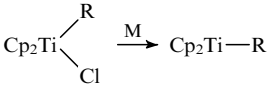


R^1 = Me, R^2 = 2,6-$Me_2C_6H_3$; R^1 = Ph, 2-MeC_6H_4,
R^2 = 2-MeC_6H_4, 2,6-$Me_2C_6H_3$.



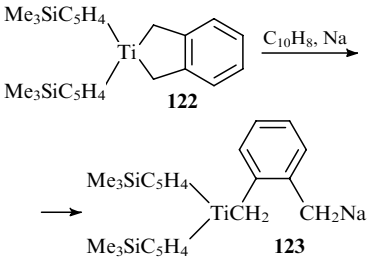
R^1 = Ph, 2-MeC_6H_4; R^2 = 2-MeC_6H_4, 2,6-$Me_2C_6H_3$.

Sometimes, reduction of titanocene σ-derivatives occurs with the retention of the metal–carbon σ-bond. Thus the reaction of alkyltitanocene chlorides with zinc or magnesium yields titanium(III) complexes.[40,104]

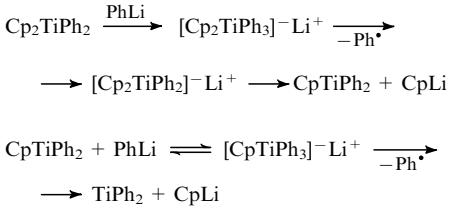


M = Zn, Mg; R = C_6F_5, Me, CH_2SiMe_3, CH_2PPh_2.

Reaction of titanaindan **122** with naphthalenesodium occurs with the opening of the metallacycle and the formation of the complex **123**.[221]



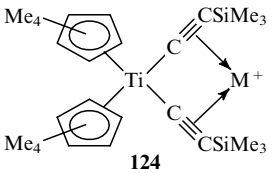
In some cases, the role of reducing agents for titanocene σ-derivatives is played by organolithium compounds. Thus the reaction of di(cyclopentadienyl)diphenyltitanium(IV) with phenyllithium in ether results in the reduction of Ti(IV) to Ti(III) and the formation of diphenyl(cyclopentadienyl)titanium(III) and diphenyltitanium(II). Diphenyl(cyclopentadienyl)titanium(III) is formed first. An excess of phenyllithium causes the decomposition of the Ti(III) complex, the diphenyltitanium being the final product.[222, 223]



Reactions with retention of the Ti–C σ-bond include the formation of complex bimetallic compounds based on titanocene σ-derivatives. Thus reactions of diphenyltitanocene with diphenylzinc or triethylaluminium yield the binuclear complexes $(C_5H_4)_4Ti_2Ph_2Zn$ (see Ref. 224) and $[Cp(C_5H_4)TiHAlEt_2]_2$ in which Ti and Al atoms are linked through a bridging hydride ligand (see Ref. 225).

It is of note that the derivatives of the type $Cp_2TiX_2AlR_2$ (X = Cl, I, Br; R = Alk, Ar) are the most well-studied titanium–aluminium complexes;[226] however, they do not contain Ti–C σ-bonds and are therefore not considered in this review.

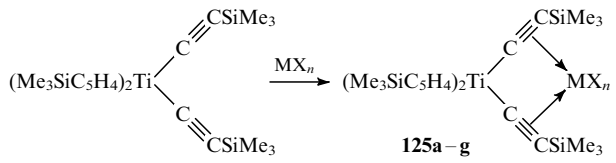
The bimetallic Ti(III) complexes in which the alkali metal ion was incorporated between the acetylenide fragments (tweezer complexes) were synthesised from titanocene acetylenides and its derivatives containing substituents in the cyclopentadienyl ligands. Thus the complexes **124** were prepared by the reaction of $(\eta^5\text{-}C_5HMe_4)_2Ti(\eta^1\text{-}C{\equiv}CSiMe_3)_2$ with alkali metals in toluene.[63, 227]



M = Li, Na, K.

A similar complex $[(\eta^5\text{-}C_5HMe_4)_2Ti(\eta^1\text{-}C{\equiv}CC{\equiv}CSiMe_3)_2^-[Li(THF)_2]^+$ (see Ref. 125) was prepared by treatment of bis(tetramethylcyclopentadienyl)(4-trimethylsilylbuta-1,3-diynyl)titanium in THF with an excess of 1-lithio-4-(trimethylsilyl)buta-1,3-diyne.

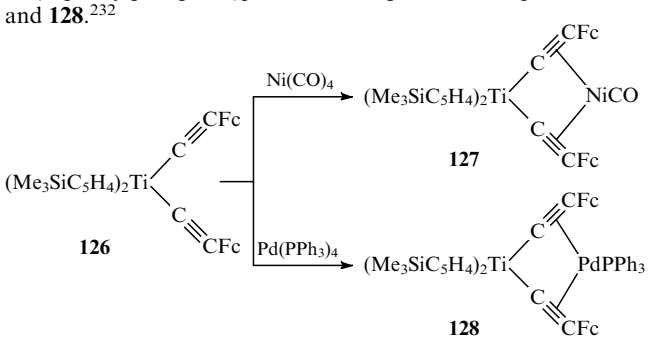
Bis(alkynyl)titanocenes are very good chelating ligands owing to their ability to form bimetallic complexes with copper(I), iron(II) and silver salts. Thus reactions of bis(trimethylsilylcyclopentadienyl)bis(trimethylsilylethynyl)titanium with CuCl, $FeCl_2$ and various silver salts yield the complexes **125a–g**.



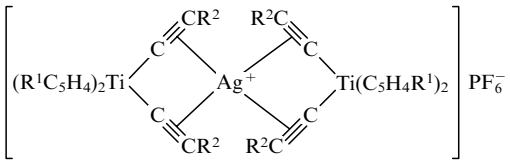
Compounds **125**	M	X	*n*	Ref.
a	Cu	Cl	1	228, 229
b	Fe	Cl	2	228, 230
c	Ag	Cl	1	230
d	Ag	CN	1	230
e	Ag	SCN	1	230
f	Ag	NO_2	1	230
g	Ag	ClO_4	1	230

In the reaction of the complex **125a** with lithium acetylenides, the chlorine atom is replaced by the ethynyl group to give complexes of the general formula $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti.(\eta^1\text{-}C{\equiv}CSiMe_3)_2CuC{\equiv}CR$, where R = $SiMe_3$, Bu^t, Ph.[229] The structurally similar copper and silver complexes $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\eta^1\text{-}C{\equiv}CSiMe_3)_2MR$, where M = Cu, Ag and R = 2,4,6-$Me_3C_6H_2$, have been synthesised.[231]

Bis(trimethylsilylcyclopentadienyl)bis(ferrocenylethynyl)titanium (**126**) reacts with nickel tetracarbonyl or tetrakis(triphenylphosphine)palladium to give the complexes **127**[69] and **128**.[232]



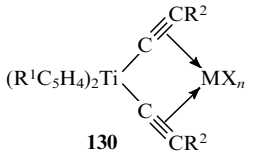
Reaction of the complex **126** with silver hexafluorophosphate yields the complexes **129a–c** in which the silver ion is bound to the four triple bonds of the acetylenic groups.[233] Compounds **129d,e** were prepared analogously.



129a–e

R^1 = H, R^2 = Fc (**a**); R^1 = Me_3Si, R^2 = Fc (**b**);
R^1 = H, R^2 = $(C{\equiv}C)_2Fc$ (**c**); R^1 = Me_3Si, R^2 = Ph (**d**);
R^1 = Me_3Si, R^2 = Rc.

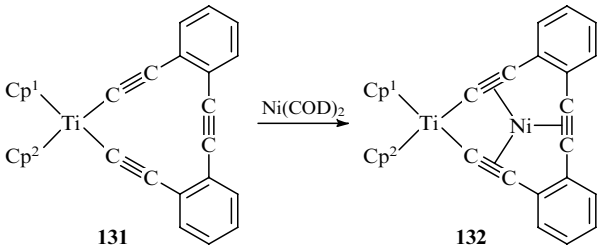
Bis(trimethylsilylcyclopentadienyl)(trimethylsilylethynyl)titanium and bis(trimethylsilylcyclopentadienyl)(hexa-1,3-diynyl)titanium chlorides form the complexes $[(C_5H_4SiMe_3)_2Ti(R)Cl].CuBr$ [R = $C{\equiv}CSiMe_3$,[234] $C{\equiv}C{-}C{\equiv}CEt$ (see Ref. 61)] with copper(I) bromide. The complexes **130** were synthesised from



R^1 = $Me_2NCH_2CH_2$, R^2 = Me_3Si, MX_n = AgCl;
R^1 = Ph_2P, $Ph_2P(O)$, $Ph_2P(S)$; R^2 = Bu^t, MX_n = CuCl, $Mo(CO)_4$;
R^1 = Me_3Si, R^2 = Ph, MX_n = CoCO.

dialkynyltitanocene derivatives containing various substituents in the cyclopentadienyl ligands.[65, 235]

The reaction of the triyne titanacycles **131** with bis(cyclooctadiene)nickel $Ni(COD)_2$ yields the binuclear complexes **132**.[60]

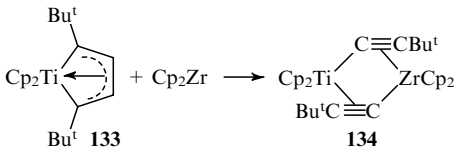


131 **132**

$Cp^1 = Cp^2 = C_5H_5, C_5Me_5$.

Dicyclopentadienylbis(diphenylphosphinomethyl)titanium and bis(dicyclopentadienyldiphenylphosphinomethyltitanium) oxide form the complexes $[Cp_2Ti(CH_2PPh_2)_2Rh(CO)Cl]_2$ (see Ref. 40) and $O[Cp_2TiCH_2PPh_2]_2Rh(CO)Cl$[236] with dicarbonylrhodium chloride. The cationic complex $[Cp_2Ti(CH_2PPh_2)_2Rh.(COD)]^+[BPh_4]^-$ was prepared by treatment of dicyclopentadienylbis(diphenylphosphinomethyl)titanium with the rhodium complexes $[L_2Rh(COD)]^+[BPh_4]^-$, where L = Ph_3P, COD.[237]

The reaction of titanacumulene (**133**) with dicyclopentadienylzirconium occurs with the cleavage of the central C=C bond and results in the formation of the heterodimetallic titanocene–zirconocene complex **134** with a σ,π-alkynyl bridge.[142]

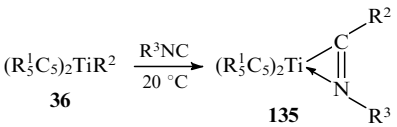


133 **134**

2. Insertion into Ti–C σ-bonds

Transformations of titanocene derivatives occurring with insertion of various fragments into Ti–C σ-bonds have been described.

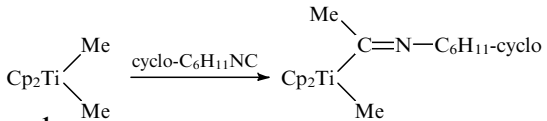
Thus isocyanides are inserted into the Ti–C σ-bonds of alkyl- or aryltitanocenes **36** to give the titanacycles **135** at 20 °C. At the same time, at −78 °C the reaction of the complexes **36** with isocyanides yields exclusively the adducts $Cp_2TiR^1{\cdot}R^2NC$.



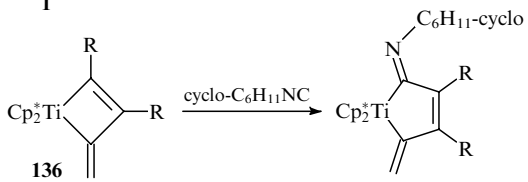
36 **135**

R^1	R^2	R^3	Ref.
H	Et	2,6-$Me_2C_6H_3$	102
H	Bu	2,6-$Me_2C_6H_3$	102
H	Me	2,6-$Me_2C_6H_3$	102, 103
Me	Me	2,6-$Me_2C_6H_3$	109
H	Ph	2-MeC_6H_4	220
H	Ph	2,6-$Me_2C_6H_3$	220
H	2-MeC_6H_4	2-MeC_6H_4	220
H	2-MeC_6H_4	2,6-$Me_2C_6H_3$	220

Insertion into the Ti–C σ-bond takes place in the reaction of cyclohexyl isocyanide with dimethyltitanocene (**1**)[238] or the methylidenetitanacyclobutene complexes **136**[169] as well as in reactions of *tert*-butyl isocyanide with 1-oxa-5-titanacyclopentanes **137**[239] or bis(methylethynyl)titanocene **138** in the presence of dimethylanilinium tetraphenylborate.[240]

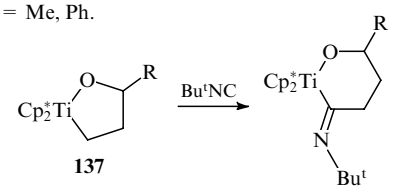


1



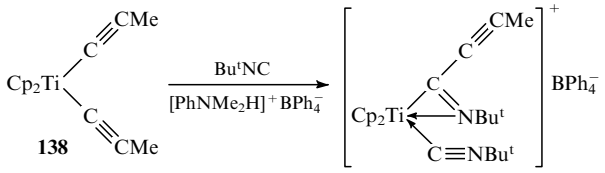
136

R = Me, Ph.



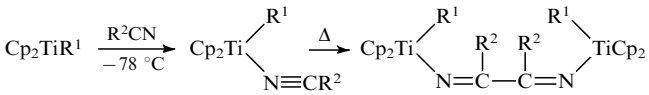
137

R = Me, Et, Pr^i.



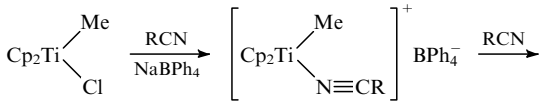
138

As in the case of isocyanides, reactions of alkyltitanocenes with nitriles at low temperatures give the adducts $Cp_2TiR^1 \cdot R^2CN$ (R^1 = Ph, 2-MeC_6H_4, Bn, C_6F_5; R^2 = Me, Bu^t, Ph, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$).[241] An increase in the temperature leads to dimerisation of the nitrile ligand.[242]

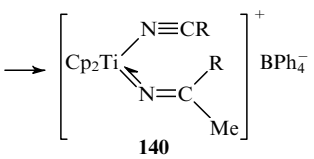


R^1 = Ph, 2-MeC_6H_4, Bn, C_6F_5; R^2 = Ph, Me, 2-MeC_6H_4.

Treatment of methyltitanocene chloride with equimolar amounts of nitriles in the presence of sodium tetraphenylborate gives the complexes **139** which further yield the azaalkylidene derivatives **140** due to the insertion of the nitrile molecule into the Ti–C bond.[243, 244]



139

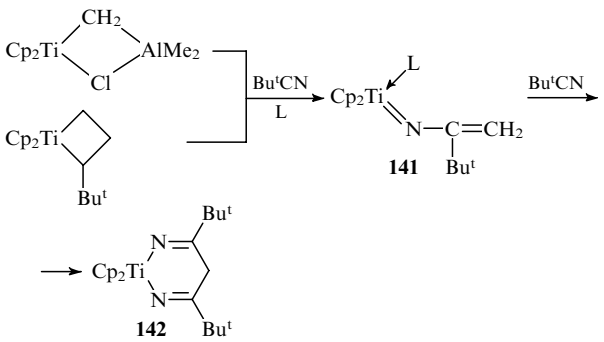


140

R = Me, Pr, Ph, Bu^t.

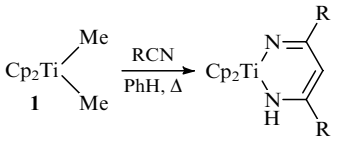
In this reaction, trimethylsilyl cyanide is isomerised into the corresponding isocyanide, which forms an η^2-iminoacyl complex $[Cp_2Ti(CMe{=}NSiMe_3)(C{\equiv}NSiMe_3)]^+BPh_4^-$ with methyltitanocene chloride (see Ref. 244).

Reactions of the titanaluminium complex $Cp_2Ti(\mu\text{-}Cl).(\mu\text{-}CH_2)AlMe_2$ or 2-*tert*-butyl-1,1-bis(cyclopentadienyl)-1-titanacyclobutane with *tert*-butyl cyanide in the presence of trimethylphosphine or 4-(*N*,*N*-dimethylamino)pyridine gives first the vinylimide complexes **141**, which react with an excess of nitrile to yield the 2,6-diaza-1-titanacyclohexa-2,5-diene derivative **142**.[245, 246]



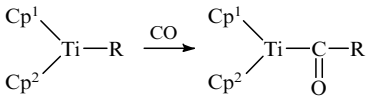
L = PMe_3, 4-$Me_2NC_5H_4N$.

2,6-Diazatitanacyclohexa-2,4-dienes **142** (R = Bu^t, Ph) are formed upon refluxing of *tert*-butyl or phenyl cyanide with dimethyltitanocene (**1**) in benzene.[151]



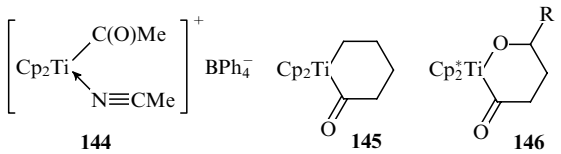
R = Bu^t, Ph.

The direction of reactions of titanocene σ-derivatives with carbon monoxide depends on the reaction conditions and the structure of the organometallic compound. Thus treatment of alkyl-, aryl- and vinyldicyclopentadienyltitanium(III) derivatives as well as ethyl- or methyltitanocene chlorides with carbon monoxide leads to the insertion into the Ti–C σ-bond eventually resulting in the acyltitanocene complexes **143**.[109, 204, 247, 248]



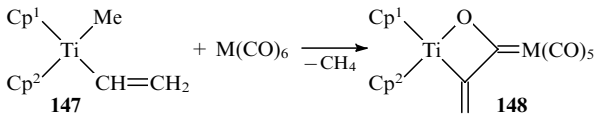
Cp^1	Cp^2	R	*T*/°C	Ref.
C_5H_5	C_5Me_5	Me	−70	106
C_5H_5	C_5Me_5	Et	−70	106
C_5H_5	C_5Me_5	Me	0	247
C_5H_5	C_5Me_5	n-C_5H_{11}	0	247
C_5H_5	C_5H_5	C(Me)=CHMe	20	106, 248
C_5H_5	C_5H_5	2-MeC_6H_4	20	106, 248

The products of CO insertion into the Ti–C bond (**144**–**146**) were prepared by treating acetonitrile(methyl)titanocene tetraphenylborate[243] or the corresponding titanacyclopentane and titanaoxacyclopentane derivatives[77, 239] with carbon monoxide.



R = Me, Et, Pr^i.

Reactions of chromium and tungsten hexacarbonyls with the methyl(vinyl)titanocene derivative **147** occur as the insertion of CO into the Ti–C σ-bond and the formation of the bimetallic complexes **148**.[13]

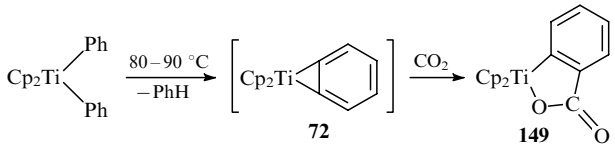


Cp^1 = $C_5Me_4(CH_2)_2NMe_2$, Cp^2 = C_5Me_5; M = Cr, W.

In contrast to alkyldicyclopentadienyltitanium(III) derivatives, pentafluorophenyltitanocene reacts with carbon monoxide (25 °C, 1 atm) with the formation of the carbonyl complex $Cp_2Ti(CO)C_6F_5$.[247] Photochemical reactions of dimethyl- or diphenyltitanocene with carbon monoxide[25, 140] or treatment of dibenzyltitanocene[204, 249] and titanaindan derivatives **18a**,**b**[70] in benzene with carbon monoxide gave the titanocenedicarbonyl $Cp_2Ti(CO)_2$. It was noted that the reaction of carbon monoxide with dibenzyltitanocene in pentane is sometimes associated with the intermediate formation of the benzylacyl complex $Cp_2Ti(COBn)Bn$.[249]

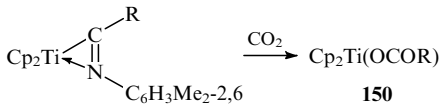
Reactions of some titanocene derivatives with carbon dioxide also occur by insertion into the metal–carbon σ-bond. Thus the photochemical reaction of dimethyltitanocene with carbon dioxide in pentane (16 °C, 20 h) results in methyltitanocene acetate $Cp_2Ti(Me)\cdot[OC(O)Me]$.[250] Passage of carbon dioxide through a solution of dimethyltitanocene in toluene at 80 °C leads to the insertion of CO_2 simultaneously into two Ti–C σ-bonds resulting in the titanocene diacetate $Cp_2Ti(OC(O)Me)_2$.[251]

Treatment of diphenyltitanocene with carbon dioxide in xylene at 80–90 °C gives the titanacyclic compound **149**.[251, 252]



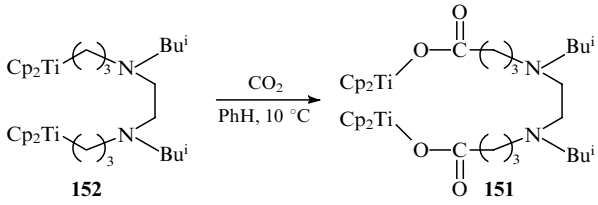
It is believed that compound **149** is formed as a result of insertion of carbon dioxide into the phenylenetitanium complex **72** formed upon splitting of the benzene molecule from diphenyltitanocene.

Reactions of η^2-iminoacyl complexes with carbon dioxide occur by insertion of CO_2 into the Ti–Alk bond and yield dicyclopentadienyltitanium(III) acylates **150**.[102]

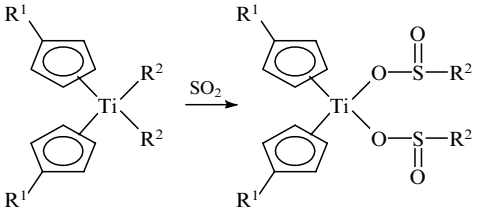


R = Me, Et, Bu^n.

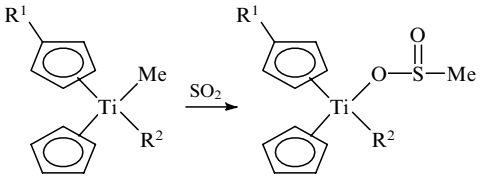
The product of insertion into the Ti–C σ-bond **151** was obtained in the reaction of the binuclear complex **152** with CO_2.[253]



The insertion into the Ti–C σ-bond and the formation of *O*-sulfinates take place in the treatment of dimethyl-, diphenyl- or bis(2-thienyl)titanocenes[254–256] and methylchloro- or methyl(pentafluorophenyl)titanocenes[254, 257, 258] with sulfur dioxide.



R^1 = H, R^2 = Me, Ph, 2-thienyl; R^1 = R^2 = Me.



R^1 = CH(Me)Ph, R^2 = C_6F_5; R^1 = H, R^2 = Cl, C_6F_5.

The reaction of carbon disulfide with vinyldicyclopentadienyltitanium(III) gives the paramagnetic insertion product $Cp_2Ti[SC(S)CMe=CHMe]$.[107]

3. Cleavage of Ti–C σ-bonds

Whereas the π-bond between the cyclopentadienyl ligand and the titanium atom is stable in acidic media, the Ti–C σ-bonds are easily cleaved by acids. Thus dialkyl- and diaryltitanocene derivatives react with an excess of hydrogen chloride to give the corresponding titanocene dichlorides.

$Cp^1Cp^2TiR_2 \xrightarrow{HCl} Cp^1Cp^2TiCl_2$

Cp^1	Cp^2	R	Ref.
C_5H_5	C_5H_5	Ph	259
C_5H_5	C_5H_5	Me	260
C_5H_5	C_5H_5	Fc	49
$Me_2C(C_5H_4)_2$		Me	260
C_5H_4Me	C_5H_4Me	C≡CR [a]	56
$C_5H_4SiMe_3$	$C_5H_4SiMe_3$	C≡CR [a]	56

[a] R = Et, Pr^n, Bu^n, Bu^t, Me_3Si, Ph.

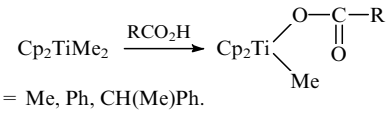
Titanocene dichloride is prepared by treatment of titanacycles, such as 1,1,-dicyclopentadienyl-1-titanacyclopentane,[78] 1,1-dicyclopentadienyl-1-titanafluorene,[73] titanacyclopentadienes **54a,b**[130] or titanabicyclopentane **84,**[168] with an excess of hydrogen chloride.

The complexes $Cp^1Cp^2TiCl_2$ containing two different π-bound cyclopentadienyl ligands were prepared by the reaction of hydrogen chloride with the titanocene derivatives $Cp^1_2Ti(Cp^2)Cl$ in which the two cyclopentadienyl ligands were linked by π-bonds and one cyclopentadienyl ligand, by σ-bonds.[261,262]

Reactions of dialkyl- or diaryltitanocenes with equimolar amounts of hydrogen chloride result in the cleavage of only one Ti–C σ-bond and yield alkyl- or aryltitanocene chlorides $Cp^1Cp^2Ti(R)Cl$ and $Cp^2_2Ti(R)Cl$, where $Cp^1 = C_5H_5$, $Cp^2 = C_5Me_4H$: R = Me, Ph, 4-MeC_6H_4;[7] $Cp^1 = Cp^2 = C_5H_5$, R = 2-thienyl,[214] 3,4,5-trichloro-2-thienyl.[43] The cationic complex $[Cp_2TiMe]^+BF_4^-$ was prepared by the reaction of dimethyltitanocene with an equimolar amount of fluoroboric acid.[263]

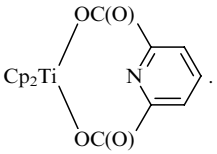
In contrast to the majority of titanocene σ-derivatives, bis(*o*-carboranylmethyl)- and bis(pentafluorophenyl)titanocenes are relatively stable in acidic media and are converted into titanocene dichloride only after prolonged boiling with hydrochloric acid.[24,45] The retention of the σ-bond between the titanium atom and the perfluorophenyl ligand was also observed in the treatment of methylsulfinate and perfluorophenyltitanocene alcoholates $Cp(C_5H_4CHMePh)Ti(C_6F_5)(O_2SMe)$ (see Ref. 257) and $Cp(C_5H_4CHMePh)Ti(C_6F_5)OR$ (R = Me, 2-MeC_6H_4) with hydrogen chloride.[96]

The cleavage of Ti–C σ-bonds takes place upon treatment of alkyl- or aryltitanocenes with organic acids. Thus dimethyltitanocene reacts with equimolar amounts of acetic,[205] benzoic or 2-phenylpropionic acids [264] with cleavage of one of methyl groups eventually resulting in the corresponding methyltitanocene acylates.



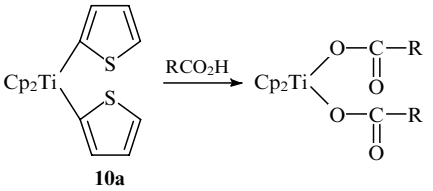
R = Me, Ph, CH(Me)Ph.

Treatment of dimethyltitanocene with an excess of phenylpropiolic or trifluoromethanesulfonic acid results in the replacement of two σ-bound methyl groups by acid residues.[265,266] The reaction of pyridine-2,6-dicarboxylic acid with dimethyltitanocene yields the complex **153**.[260]



153

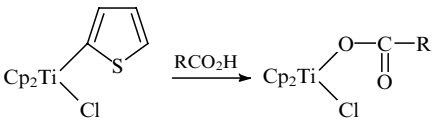
The formation of titanocene diacylates takes place in the reaction of bis(2-thienyl)titanocene **10a** with 3,5-dinitrobenzoic, perfluorobenzoic and trifluoro-, trichloro- and tribromoacetic acids.[42]



10a

R = 3,5-$(NO_2)_2C_6H_3$, C_6F_5, CF_3, CCl_3, CBr_3.

The reaction of methyltitanocene chloride with benzoic or phenylacetic acids afforded mixtures of titanocene dichloride with the corresponding titanocene diacylates $Cp_2Ti[OC(O)R]_2$; their formation is due to symmetrisation of the intermediate chlorotitanocene acylates $Cp_2TiCl[OC(O)R]$.[267] The formation of a Cp_2TiMe_2, $Cp_2TiMe[OC(O)CF_3]$ and $Cp_2Ti[OC(O)CF_3]_2$ mixture is also observed upon treatment of 1,1,3,3-tetracyclopentadienyl-1,3-dititanacyclobutane with trifluoroacetic acid.[167] Reactions of (2-thienyl)titanocene chloride with trichloro- and tribromoacetic, perfluorobenzoic or 2-nitrobenzoic acids gave the corresponding chlorotitanocene acylates.[216]



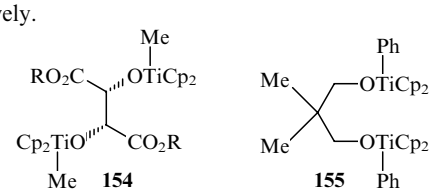
R = CCl_3, CBr_3, C_6F_5, 2-$NO_2C_6H_4$.

It is of note that treatment of some methyltitanocene alcoholates $Cp_2TiMe(OR^1)$ (R^1 is benzyl, menthyl, bornyl) with benzoic or diphenylacetic acids results in the cleavage of the alkoxide ligand (rather than the methyl ligand) and affords the methyltitanocene acylates $Cp_2Ti(Me)OC(O)R^2$, where R^2 = Ph, $CHPh_2$.[267]

Ti–C σ-bonds are cleaved upon the action of hydrogen chloride on alkyl- or aryl[dicyclopentadienyltitanium(III)] and their complexes with molecular nitrogen or

nitriles.[103, 105, 112, 241, 268] The titanocene monochloride formed at low temperatures (−78 °C) is oxidised to titanocene dichloride at 20 °C.

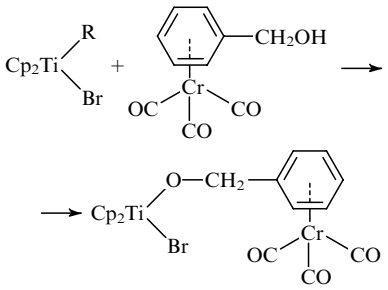
The Ti−C bond is also cleaved under the action of some alcohols and phenols on titanocene derivatives. Thus reactions of dimethyltitanocene with an equimolar amount of alcohols bearing bulky radicals gave the methyltitanocene alcoholates $Cp_2Ti(Me)OR$ [R is benzyl, menthyl, bornyl,[267] $CHMeC_8H_{17}$, $CMePh_2$, $CHPr^nPh$, CHPhBn, $CH_2CH=CHPr^n$ (see Ref. 264)]. Titanocene trifluoromethanesulfonate alcoholates $Cp_2Ti(O_3SCF_3)(OR)$, where R = Me, Me_3Si, Me_2Bu^tSi, are formed upon treatment of methyltitanocene trifluoromethanesulfonate with the corresponding alcohols.[265] Reactions of dimethyltitanocene with (+)-(2*R*,3*R*)-dimethyl and (+)-(2*R*,3*R*)-dibutyl tartrates[269] and reactions of diphenyltitanocene with 2,2-dimethylpropane-1,3-diol[270] yielded the binuclear complexes **154** and **155**, respectively.



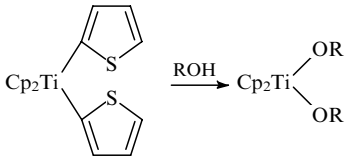
154 **155**

R = Me, Bu^n.

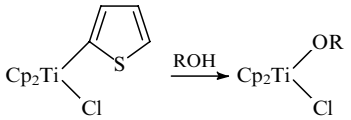
A bimetallic complex was also formed when chromotricarbonyl(hydroxymethyl)benzene was used.[271]



The reaction of bis(2-thienyl)titanocene (**10a**) or (2-thienyl)titanocene chloride with picric acid, 4-hydroxybiphenyl or 3,4-dimethylphenol afforded the corresponding titanocene diphenolates and chlorotitanocene phenolates.[213]

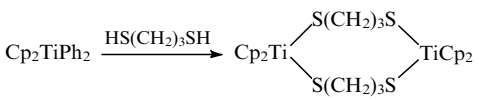


10a

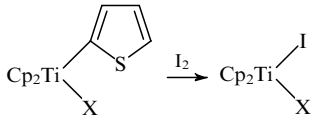


R = 2,4,6-$(NO_2)_3C_6H_2$, 4-PhC_6H_4, 3,4-$Me_2C_6H_3$.

The cleavage of the Ti−C σ-bond by propane-1,3-dithiol has been described.[272]



Treatment of dialkyl- or diaryltitanocene derivatives with halogens results in the cleavage of the metal–carbon σ-bonds to give the corresponding titanocene dihalides Cp_2TiX_2 (X = Cl, Br, I).[31, 42, 56, 73, 78, 79, 273, 274] It was shown that the reaction of (2-thienyl)titanocene derivatives with iodine proceeds in a stepwise manner; the σ-bound thienyl group is split off in the first step.[275, 276]



X = 3,4-$Me_2C_6H_3O$, PhS, Ph_2N, Cl, 2-thienyl.

Treatment of alkyl- or aryldicyclopentadienyltitanium(III) derivatives with an excess of halogens occurs as the cleavage of the Ti−C σ-bond and the oxidation of the titanium atom leading to the formation of titanocene dihalides.[105, 112, 268]

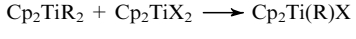
Substitution of chlorine atoms for σ-bound alkyl or aryl ligands takes place in the reaction of dialkyl- or diaryltitanocenes with mercury dichloride.



R	Ref.	R	Ref.
Me	251, 277	Bn	36
Ph	278, 279	*o*-carboranylmethyl	66

The cleavage of σ-bound pentafluorophenyl ligands in bis(pentafluorophenyl)titanocene under the action of $TiCl_4$ (see Ref. 255) or BCl_3 was observed.[35] The cleavage of Ti−C σ-bonds and the formation of titanocene dichloride takes place upon treatment of dicyclopentadienyl-2,4-bis(trimethylsilylethynyl)-3,5-bis(trimethylsilyl)titanacyclopenta-2,4-diene with S_2Cl_2,[280] as well as upon treatment of $Cp_2Ti[C\equiv CFc]_2$ with nickel chloride.[62]

Exchange reactions of methyl and phenyl groups for halogen atoms upon treatment of dimethyl- or diphenyltitanocene with titanocene dihalides have been studied.[251]



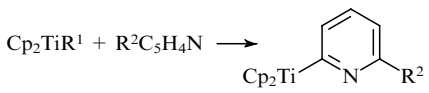
R = Me, Ph; X = F, Cl, Br, I.

It was found that reaction rates decrease in the following order: I > Br > F > Cl for dimethyltitanocene and I > Cl > Br > F for diphenyltitanocene.

Heating of dimethyl- or diphenyltitanocene with chloroform or carbon tetrachloride is also accompanied by the cleavage of Ti−C σ-bonds resulting in titanocene dichloride.[277, 279] Heating of diphenyltitanocene with benzyl chloride yields a titanocene dichloride–(cyclopentadienyl)titanium trichloride mixture.[281] 1,1-Dicyclopentadienyl-1-titanacyclobutane reacts with benzyl or allyl chloride to give alkyltitanocene chlorides $Cp_2Ti(CH_2R)Cl$ (R = Bn, All).[282]

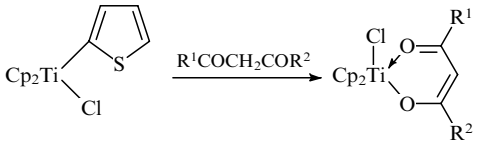
Cleavage of Ti−C σ-bonds takes place upon treatment of diphenyltitanocene with benzoyl peroxide.[283–285] When this reaction is carried out in isopropyl alcohol, titanocene dibenzoate $Cp_2Ti(O_2CPh)_2$ is formed as the major product. The dicyclopentadienyltitanium fragment is destroyed in ether or benzene to give the cyclopentadienyltitanium dibenzoate $CpTi(O_2CPh)_2$. In contrast to reactions of diphenyltitanocene with benzoyl peroxide, treatment with 3- or 4-nitrobenzoyl peroxides is not accompanied by the cleavage of the titanocene fragment and the corresponding titanocene bis(nitrobenzoates) are formed.[286]

The Ti−C σ-bonds of methyl- or butyltitanocenes are split off under the action of pyridine derivatives.[287]



R^1 = Me, Bu; R^2 = 2-Me, 2-Ph, 2-CH=CH_2.

Reactions of thienyltitanocene chloride with acetylacetone, benzoylacetone or dibenzoylmethane gave the corresponding chlorotitanocene β-diketonates.[288]



$R^1 = R^2$ = Me, Ph; R^1 = Ph, R^2 = Me.

* * *

The data presented demonstrate high reactivities of titanocene derivatives containing Ti–C σ-bonds. The ease and selectivity of reactions involving these bonds, the possibility of titanium to exist in different oxidation states and the formation of complex bimetallic compounds suggest that titanocene σ-derivatives are promising reagents for fine organic and organometallic syntheses.

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