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Review

LOW-VALENT ORGANOTITANIUM SPECIES AND THEIR APPLICATIONS TO ORGANIC SYNTHESIS

Yi Dang[1] and Herman J. Geise*
University of Antwerp (UIA), Department of Chemistry
Universiteitsplein 1, B-2610 Wilrijk, Belgium

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ABSTRACT

Low-valent organotitanium complexes and their synthetic applications are reviewed with emphasis on carbon-carbon bond formation. The survey covers (1) reductive coupling, (2) elimination, (3) carbonyl methylenation and general alkylidenation, (4) reduction and (5) fixation and/or reduction of small molecules.

INTRODUCTION

Over the past 15 years low-valent titanium reagents, prepared from $TiCl_3$ or $TiCl_4$ and a strong reducing agent, have been developed into powerful tools to induce carbonyl coupling reactions. The state-of-the-art of these purely inorganic reagents is presently well-documented [1-8].

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* Author to whom correspondence should be addressed

[1] Permanent address : Department of Chemistry, Shaanxi Teachers University, Xi'an (P.R. of China)

Organometallic derivatives of low-valent titanium - i.e. containing Ti with formal oxidation state below 4, and bonded to one or more organic ligands - are, however, also of considerable interest as reagents and/or catalysts in organic synthesis. Organotitanium compounds are even more readily prepared, isolated and characterized. A large number of such compounds is now available [9], yet their applications in organic chemistry are less documented. Two reviews have appeared recently, however focussing on organotitanium complexes containing neutral phosphorus donor ligands [10] and CO ligands [11], respectively. The last comprehensive review by Sato [12] on the use of low-valent C_5H_5-bound Ti-complexes in carbon-carbon bond formation, appeared in 1985. Since then many chiral titanocene derivatives have been synthesized [13-18], which have potential in asymmetric synthesis [17, 19-23]. This review is intended to highlight the achievements that have been accomplished in low-valent titanium chemistry since then, covering the literature mainly from 1985 to early 1990. The subject is addressed in two parts. The first concerns the synthesis of those low-valent organotitanium compounds which have been proved to be or potentially are valuable in organic synthesis. The second involves their uses in organic synthesis with emphasis on carbon-carbon bond formation.

PART I : SYNTHESIS OF LOW-VALENT ORGANOTITANIUM COMPLEXES

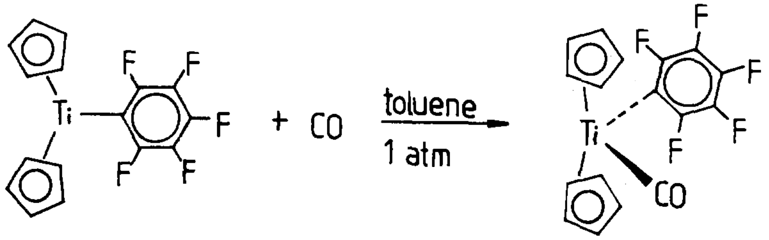
I.1. Ti(III)-COMPLEXES

Generally, Ti(III)-complexes are prepared either by reduction of Ti(IV) compounds or by direct interaction of Ti(III) compounds with appropriate ligand(s). A typical example is the generation of

$[Cp_2TiCl]_2$ by reduction of Cp_2TiCl_2 with Zn [24] or by reaction of $TiCl_3$ with C_5H_5Tl [25]. $[Cp_2TiCl]_2$ has been used as the starting material for most bis(cyclopentadienyl)titanium(III) chemistry, e.g. alkyl, aryl derivatives (Cp_2TiR) and allyl derivatives [(Cp_2Ti (η-allyl)]. Similar derivatives with substituted cyclopentadienyl ligands have also been reported. The related compounds $CpTiX_2$ and $CpTiX_2$.THF (X = Cl, Br) are obtained from $CpTiX_3$ with Zn reduction [26].

Since reduction is the most common route to low-valent organotitanium complexes and Cp_2TiCl_2 is a convenient starting material, its reduction has been examined extensively. The reducing agents employed include metals such as Na, Mg, Zn, Al, Na/Hg, Li/Hg and sometimes a metal in the presence of an appropriate ligand. Thus, organolithium, organoaluminium, and Grignard reagents as well as agents like Mg/MgI_2, MgH_2, $NaBH_4$, $LiAlH_4$ are used [9]. For synthetic purposes, C_5H_5-bound titanium(III) species are generated in situ by reaction of the corresponding Ti(IV) complexes with Grignard reagents [12, 27, 28]. Reaction of $(RCp)_2TiCl_2$ with K [29] or Al/Hg [30] affords the Ti(III) chlorides $(RCp)_2TiCl$. Lappert and co-workers have found $[Li[\mu\text{-}P(SiMe_3)_2](THF)_2]_2$ effective for converting Cp_2TiCl_2 into $Cp_2TiCl(THF)$ and $CpTiCl_2$ [31]. Active metal slurries are also employed in similar conversions [32]. Borohydride complexes of titanocene(III) [33] and 1,3-di-t-butyltitanocene(IV) [34] are conveniently obtained from MBH_4 (M = Na, Li) and the corresponding Ti(IV) complexes.

Teuben and co-workers found that titanocene complexes, Cp'_2TiR (Cp' = η-C_5H_5 or η-C_5Me_5), containing an electron-withdrawing group R yield carbonyl adducts, $Cp'_2Ti(R)(CO)$, on exposure to CO under mild conditions. For example, treatment of a toluene solution of $Cp_2Ti(C_6F_5)$ with CO gave the brown-green $Cp_2Ti(CO)(C_6F_5)$ in 60 % yield [35].



In addition to chemical reduction, electroreduction of Cp_2TiX_2 (X= Cl,Br,I) to Cp_2TiX has been studied recently [36-37].

I.2. Ti(II)-COMPLEXES

In recent years, the chemistry of Ti(II) complexes has become attractive and rich. For the sake of spatial requirements, however, we make a selection.

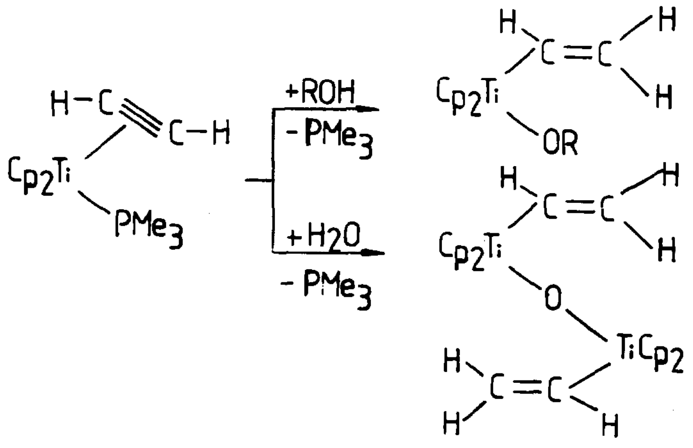
Carbonyl derivatives of titanium(II) have been reviewed recently [11, 38]. Reduction and subsequent treatment of Cp_2TiCl_2 with CO represents one of the most direct routes to $Cp_2Ti(CO)_2$, which is a useful reagent in homogeneous catalysis and stoichiometric organic synthesis. $Cp_2Ti(CO)_2$ is also applicable to the preparation of Ti(III) complexes and other Ti(II) complexes [11, 38-39].

Phosphines and phosphites have been used extensively to stabilize the titanocene fragment $Cp_2Ti(II)$ thereby resulting in stable, isolable 18-electron complexes of the general formula $Cp_2TiL'_2$. The derivatives containing PMe_3 [40, 41], $P(OMe)_3$ [42] and dmpe [43] have been prepared by the reduction of titanium(IV) halide precursors, while the PF_3 complex, $Cp_2Ti(PF_3)_2$ [44] has been prepared by photochemical ligand substitution of $Cp_2Ti(CO)_2$.

$$Cp_2TiCl_2 + Mg + 2PMe_3 \xrightarrow{THF} Cp_2Ti(PMe_3)_2 + MgCl_2$$

Bis(phosphine)titanocene, $Cp_2Ti(PMe_3)_2$, has proven to be a versatile starting material in the synthesis of other titanocene (II) complexes. Its rich chemistry is primarily due to the high lability of the phosphines, which allows facile substitution by a large number of substrates under very mild conditions. Thus, $Cp_2Ti(PMe_3)_2$ [45] reacts readily with CO to produce $Cp_2Ti(PMe_3)CO$. Acetylenes also easily replace one phosphine ligand of $Cp_2Ti(PMe_3)_2$ giving $Cp_2Ti(PMe_3)(RC{\equiv}CR')$ [40, 46, 47]. The chemistry of $Cp_2Ti(PMe_3)$ $(CH{\equiv}CH)$ has been studied in some detail [48, 49].

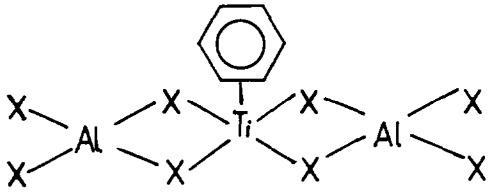
Stoichiometric reaction of this complex with alcohols results in protonation of the alkyne unit to form a titanium(IV) vinylalkoxide species, $Cp_2Ti(CH{=}CH_2)(OR)$, while reaction with one equivalent of H_2O gives a binuclear vinyl-bridged μ-oxo complex, $[Cp_2Ti(CH{=}CH_2)]_2$ $(\mu\text{-}O)$.



R=Me, Et, Ph

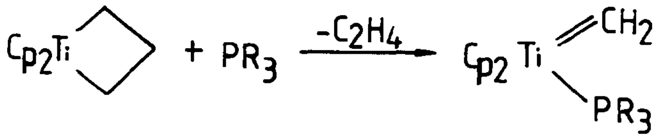
Polymerization of acetylene by $Cp_2Ti(PMe_3)_2$ gives predominantly trans-polyacetylene [50].

The diamagnetic titanium(II)-arene complexes are readily obtained from the reaction between TiX_4, Al and AlX_3 in refluxing arenes [51] (X = Cl, Br, I).

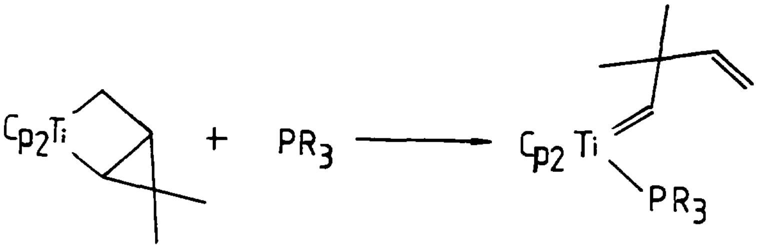


They have been used as catalysts in cyclo-oligomerization reactions [52, 53]. Titanocene methylene [$Cp_2Ti=CH_2$], first reported by Tebbe et al. [54], has been extensively investigated by Grubbs and co-workers leading to a number of publications [55]. The authors describe the synthesis of a series of titanocene metallocyclobutanes and a variety of reactions of the complexes with organic and inorganic reagents. The reactions include methylene transfer to organic carbonyls, formation of enolates, electron transfer from activated alkyl chlorides, olefin metathesis, ring-opening polymerization and complexation with metal halides.

Recently, phosphine-stabilized carbene complexes, $Cp_2Ti=CH_2(L)$, (L = PMe_3, PMe_2Ph) [55b, 56] and $Cp_2Ti=CHCMe_2CH=CH_2(L)$ (L = PMe_3, PMe_2Ph



$PR_3 = PMe_3, PMe_2Ph, PEt_3$

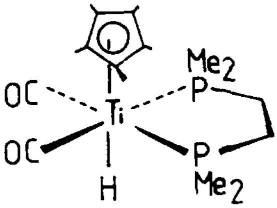


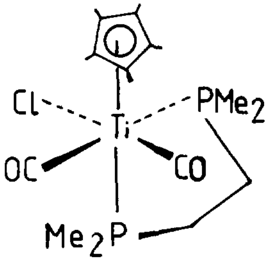
$PR_3 = PMe_3, PMePh_2$

and $PMePh_2$) [55d, 57] have been obtained by the phosphine-induced rearrangement of the appropriate metallocyclobutane and by cleavage of the binuclear carbene species $[Cp_2Ti]_2[\mu\text{-}CH_2]_2$ with PMe_3.

Additionally, a series of titanium/platinum and palladium heterobinuclear μ-methylenes has been prepared [58].

Two closely related mono(cyclopentadienyl)titanium(II)phosphine complexes have been reported. $CpTi(CO)_2H(dmpe)$ [59] was synthesized by protonation of the titanium(0) species $[K(2.2.2)]^+[CpTi(CO)_2dmpe]^-$ with acetic acid. This red-violet hybrid has been fully characterized both in solution and in the solid state. $Cp^*Ti(CO)_2Cl(dmpe)$ [60] was prepared by sodium naphthalenide reduction of Cp^*TiCl_3 in the presence of dmpe and CO.





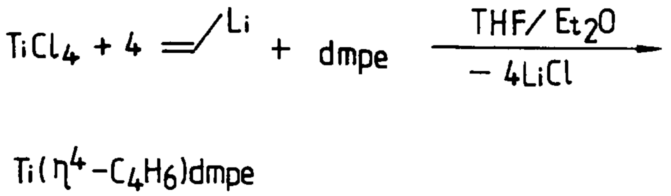
Finally, the existence of the titanium(II) species $[Cp_2TiX(PMe_2Ph]^-$ has been postulated in the two-electron reduction of Cp_2TiX_2 during cyclic voltammetry studies [61].

I.3. Ti(0) AND OTHER HIGHLY REDUCED ORGANOTITANIUM COMPLEXES

Some zero-valent titanium arene compounds $(\eta\text{-arene})_2Ti$ (arene = benzene, toluene, mesitylene, 1,3,5-tri-t-butylbenzene) have been prepared by metal-vapor synthesis [62-64].

A number of formally titanium(0) phosphine complexes, incorporating 1,3-butadiene or carbonyl ligands, have been reported. All the known titanium(0) dienephosphine derivatives are of the general formula $Ti(\eta^4\text{-}C_4H_6)_2L$, where L is a chelating bidentate phosphine or phosphinite, such as 1,2-bis(dimethylphosphino)ethene (dmpe), 1,2-bis(diethylphosphino)ethane (dppe) or 1,2-bis(dimethoxyphosphino) ethane (dmope) [65, 66].

The synthesis of these compounds is generally achieved by reduction of $TiCl_4(THF)_2$ with "magnesium butadiene" $([Mg.C_4H_6.2THF]_n)$ in the presence of the diphosphine. The dmpe derivative has also been prepared by the reductive coupling of four equivalents of vinyllithium with $TiCl_4$ and dmpe [65]. $Ti(\eta^4\text{-}C_4H_6)_2(dmpe)$ catalyzes the dimerization and trimerization of ethylene, while the dppe complex polymerizes the same substrate [66].

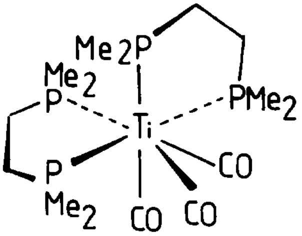


The dmpe and depe-butadiene complexes react with CO at 0°C to produce the seven-coordinated derivatives $Ti(CO)_3L_2$ (L = dmpe, depe). Addition of PF_3 to $Ti(CO)_3$(dmpe), readily displaces one carbonyl to give $Ti(CO)_2PF_3(dmpe)_2$ [67].

Ellis and co-workers [9d] have developed a useful synthetic methodology : a two-step reductive carbonylation of a variety of group 4 halides by alkali metal naphthalenides at low temperatures. They have synthesized and characterized a series of highly reduced organo-Ti compounds for the first time. For example, the complex $Ti(CO)_3(dmpe)_2$ can be prepared by the sodium naphthalenide reduction of $TiCl_4$(dmpe) followed by exposure to CO [68].

$TiCl_4$(dmpe)

1) 4 equiv. $Na.C_{10}H_8$/THF
   -70°C/dmpe
2) CO/atm/-70°C → 0°C
3) Ar



Treatment of $Ti(CO)_3(dmpe)_2$ with two equivalents of BH_3.THF in the presence of CO results in the formation of $Ti(CO)_5$dmpe [68]. The anionic Ti(0) complexes $Ph_4As^+[(Ti(CO)_4(EPh_3)(dmpe]^-$ have been isolated by reaction of $Ti(CO)_5$dmpe with $NaEPh_3$ (E = Ge, Sn) followed by metathesis [69]. Ellis' method has also been used to prepare very stable carbonyl complexes of the formula $Ti(CO)_4L$ (L = 1,1,1-tris(dimethylphosphinomethyl)ethane (trmpe), 1,1,1-tris(dimethylphosphinomethyl)-1-*t*-butylsilane (trimpsi)) [68, 70, 71]. In hexacarbonyltitanate, $Ti(CO)_6{}^{2-}$, titanium is in its lowest known formal oxidation state of 2- [72].

As a summary of Part I and an introduction into Part II, we give in Table 1 low-valent organotitanium reagents together with the corresponding inorganic titanium reagents. All the reagent systems in the table have been found applicable to organic synthesis. For the chemistry of inorganic-Ti reagents, see refs. [1-8, 73].

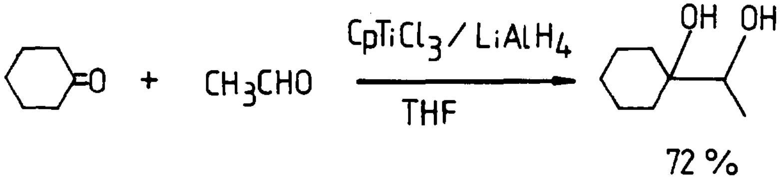
TABLE 1 : Low-valent titanium reagents starting from organo-titanium compounds and their inorganic counterparts.

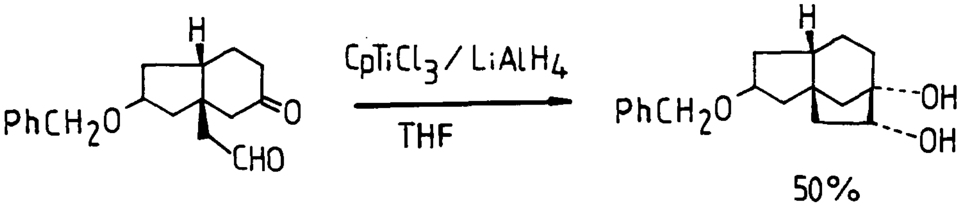
Organo-Ti reagent	Ref.	Inorg.-Ti	Inorg.-Ti
Cp_2TiCl_2/Zn	74-77	$TiCl_4/Zn$ or Zn-Cu	$TiCl_3$/Zn-Cu
Cp_2TiCl_2/Mg	78-85	$TiCl_4/Mg$ or Mg(Hg)	$TiCl_3/Mg$
Cp_2TiCl_2/Na or Na(Hg)	86-90	$TiCl_4/K$	$TiCl_3/K$
$CpTiCl_3$/Na,Mg,Ce	91	-	$TiCl_3$/Na-naphthalene
Cp_2TiCl_2/MH(Li,Na,K)	92	$TiCl_4$/MH (Li,Na,K)	-
$CpTiCl_3$ or $Cp_2TiCl_2/LiAlH_4$	93-96	$TiCl_4/LiAlH_4$	$TiCl_3/LiAlH_4$
-		$TiCl_4/C_8K$	$TiCl_3/C_8K$
$Cp_2TiCl_2/NaBH_4$	95	$TiCl_4/NaBH_4$	$TiCl_3/NaBH_4$
$Cp_2TiCl_2/RMgX$	12,19,20,21,27,28, 75,77,97-102	$TiCl_4/RMgX$	-
$CpTiX_2$, Cp_2TiR	103-107	-	$TiCl_3$
$[Cp_2Ti{=}CH_2]$	6,54-58,97,109-110	$TiX_4/Zn/CH_2X_2$	-
$Cp_2Ti(CO)_2$	9,38,39,111-116	-	-
$Cp_2Ti(PMe_3)_2$	10,40,41,45-47,50	-	-
$(C_6H_6)_2Ti$	117	-	-

PART II : APPLICATION OF LOW-VALENT ORGANO-Ti REAGENTS IN ORGANIC SYNTHESIS

II.1. REDUCTIVE COUPLINGS

In 1973, three separate research groups independently observed that low valent titanium reagents ($CpTiX_2$ [103], $TiCl_4/Zn$ [118], $TiCl_3/Mg$ [119]) reductively dimerize ketones and aldehydes to diols and alkenes. McMurry et al. soon found that the reductive coupling can also be achieved using $TiCl_3/LiAlH_4$ [120].
In 1976, Corey and co-workers reported that both the organotitanium reagents $CpTiCl_3/LiAlH_4$ and $(C_6Me_6)Ti(AlCl_4)_2$ and the inorganic titanium reagent $TiCl_4$/Mg-Hg can be successfully used in the pinacolic coupling of carbonyl compounds [93]. The $CpTiCl_3/LiAlH_4$ system induces the intramolecular coupling of ketones and aldehydes in fair to excellent yields.

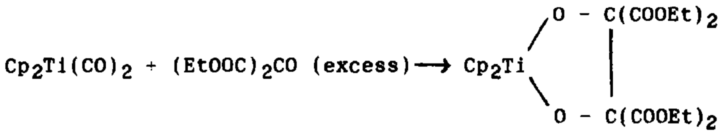




Optimum reaction conditions involve reduction of 6 equiv. of $CpTiCl_3$ with 4.5 equiv. of $LiAlH_4$ at 50°C in tetrahydrofuran (THF) followed by rapid addition of 1 equiv. of carbonyl compound. Corey et al. also found that the reagents $CpTiX_2$ [103] are ineffective in intramolecular reductive coupling reactions.

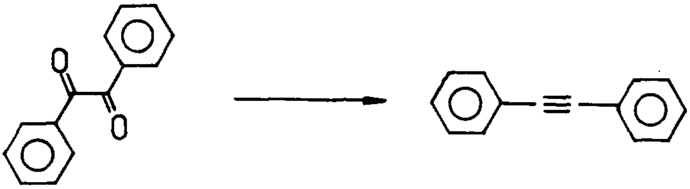
In order to devise the pinacolic coupling mechanism, they used well-defined Ti(II) species and found that the Ti(II) complex $(C_6Me_6)Ti(AlCl_4)_2$, prepared by reaction of $Al-AlCl_3$, $TiCl_4$ and hexamethylbenzene is capable of effecting the coupling. Another Ti(II) species, $Cp_2Ti(CO)_2$ [111], is also an effective reagent for the carbonyl coupling of aromatic aldehydes producing olefins and pinacols in good yields. Interestingly, the reaction of $Cp_2Ti(CO)_2$ with benzophenone gave diphenylmethanol (26 %), diphenylmethane (44 %) and 1,1,2,2-tetraphenylethane (17 %) after 30 h in refluxing THF, but no tetraphenylethylene was observed.

Reaction of $Cp_2Ti(CO)_2$ with diethyl ketomalonate, $(EtOOC)_2CO$, resulted in reductive coupling of the carbonyls and isolation of a mononuclear metallopinacol [114]. The maximum yield (40 %) of the complex was only obtained when a large excess of diethyl ketomalonate over $Cp_2Ti(CO)_2$ was used. This complex was structurally characterized and showed the expected structure for a mononuclear metallopinacol. Such mononuclear metallopinacol. Such mononuclear metallopinacols have



also been obtained from reaction of Cp_2MCl_2 (M = Ti, Zr) with R_2CO (R = Me, Ph) in the presence of Mg [85].

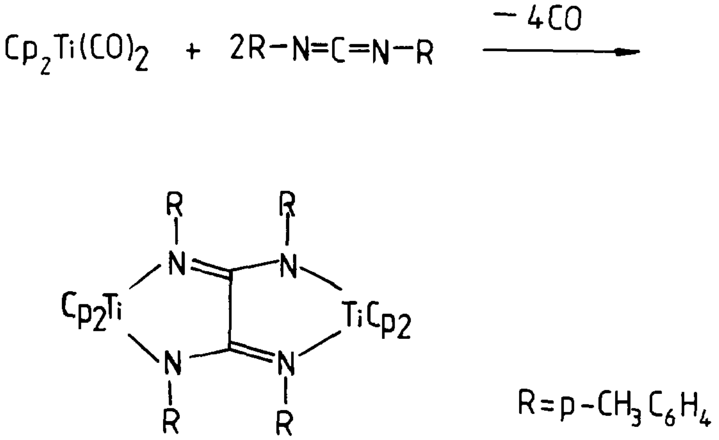
The Ti(II) compound $[CpTiCl_2(THF)_{1.5}]$ formed ethylene together with $[CpTiCl_2]_2O$ upon reaction with an excess of paraformaldehyde [104]. The compound $[CpTiCl(\mu-O)]_4$ co-crystallized with $[CpTiCl_2]_2O$, and its formation was suggested to occur via hydrolysis of $[CpTiCl_2]_2O$ in the reaction workup.



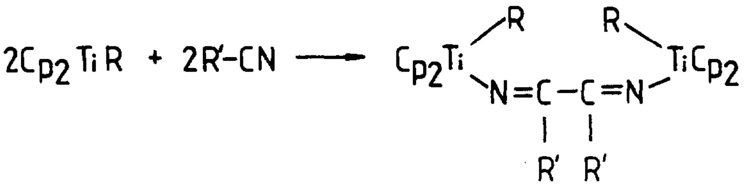
The zero-valent titanium compound $(\eta-C_6H_6)_2Ti$ was shown to be highly active towards reductive ketone coupling reactions for both aromatic and aliphatic ketones [117]. In addition, it is the only metal complex known that will reduce the α-diketone benzil to diphenylacetylene. There are some important mechanistic differences between this reagent and heterogeneous systems like those prepared by McMurry. In the coupling reaction of ketones, no pinacols were ever seen when $(\eta-C_6H_6)_2Ti$ was used. Furthermore, the reaction of pinacols with $(\eta-C_6H_6)_2Ti$ was much slower than the reaction of ketones. This is markedly different from the heterogeneous low-valent titanium systems where the ratedetermining step in the reduction of ketones was shown to be the deoxygenation of the metallopinacol to form the alkene [121, 122].

As previously mentioned, the reaction of the carbonyl compounds $(CH_3)_2CO$, $Ph(CH_3)CO$ and PhCHO with $CpTiX_2$ (X = Cl, Br) or their THF complexes gave rise to yellow crystalline products [103]. These colourful complexes were formulated as dinuclear metallopinacols which was later confirmed by X-ray crystallography was [123-125].

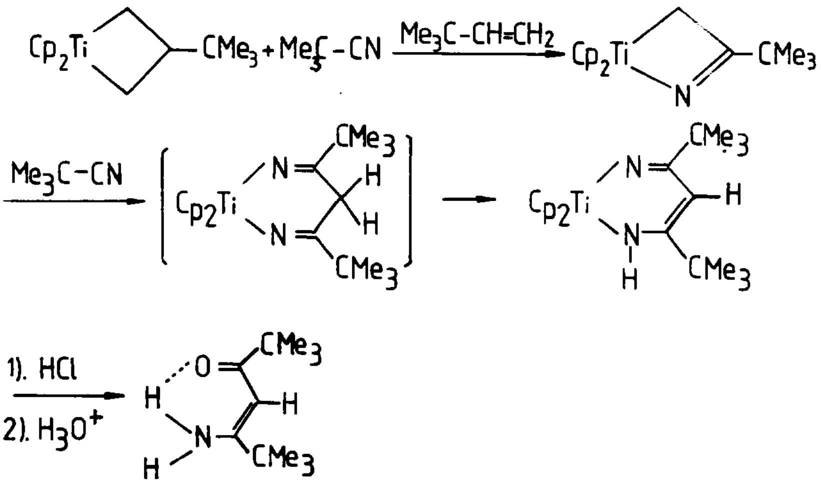
Floriani et al. reported the reductive coupling of p-tolyl carbodiimide $CH_3C_6H_4-N=C=N-C_6H_4CH_3$ by $Cp_2Ti(CO)_2$ as well as the X-ray structural analysis of the dinuclear complex [112]. Other N-bonded



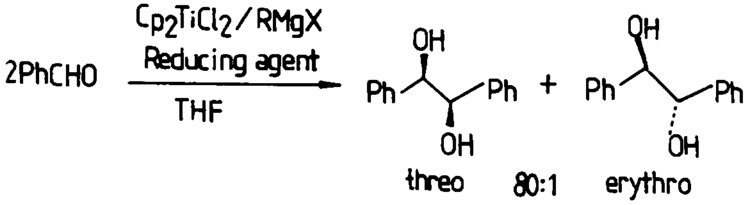
dinuclear titanium(IV) complexes have been obtained from coupling reactions of organic nitriles and Cp_2TiR [105].



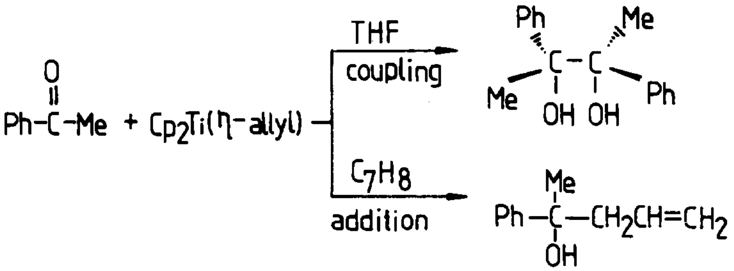
Reductive coupling of nitriles with titanocene metallocyclobutane is unusual, affording azametallocyclobutenes, diazametallacyclohexadienes and the β-ketoenamines upon acidolysis [109]. The course of the reaction critically depends on the nature of the nitrile employed.



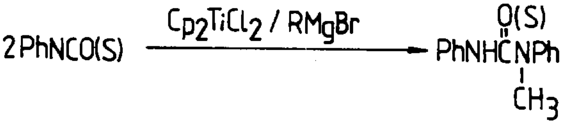
Electron rich nitriles led immediately to 2:1 complexes, while electron deficient or sterically hindered nitriles gave comparatively stable 1:1 complexes, with slower conversion to the 2:1 complexes. The combination of Cp_2TiCl_2 with Grignard reagents provides a very effective approach to reductive coupling. For example, low-valent organotitanium species generated in situ by reduction of Cp_2TiCl_2 with sec-BuMgCl has been found to promote the pinacolic homocoupling of aromatic and α,β-unsaturated aldehydes, giving rise to symmetric 1,2-diols with high threo-selectivity. Interestingly, aromatic aldehydes bearing less electron-donating groups showed lower reactivity and selectivity. Aliphatic aldehydes hardly reacted under the reaction conditions [75, 102].



Eisch et al. have observed effects of Lewis acids and bases on the reactivity of allyltitanocene(III) towards methyl phenyl ketone [126]. In THF solution, the reaction of $Cp_2Ti(\eta\text{-allyl})$ with methyl phenyl ketone in a 1:1 molar ratio yielded the pinacolic coupling product (d,l)-2,3-diphenyl-2,3-butane- diol, while in toluene solution, the reaction produced chiefly (> 70 %) the carbotitanation product, 2-phenyl-4-pentene-2-ol.



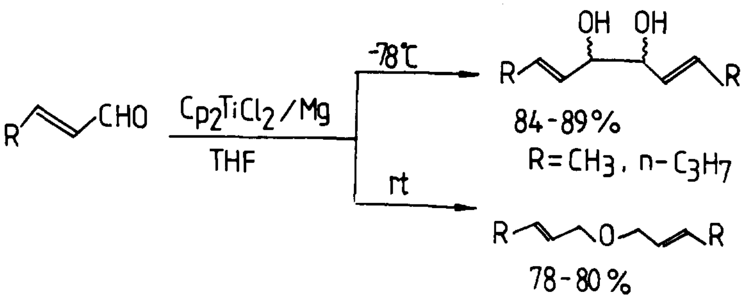
Phenylisocyanates and phenylthioisocyanates have been coupled to N-methyl- N,N'-diphenylureas and N-methyl-N,N'-diphenylthioureas, respectively [101]. It is of interest to note the influence of R on the



$$2PhNCO(S) \xrightarrow{Cp_2TiCl_2 / RMgBr} PhNH\overset{O(S)}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{N}}Ph$$

product yield. The Grignard reagents RMgBr with branched alkyls R give a higher yield than with unbranched alkyls R.

Schobert has found that α,β-unsaturated aldehydes are rapidly coupled by Cp_2TiCl_2/Mg at -78°C to give pinacols, which are formed as a diastereomeric mixture. At room temperature, however, the aldehydes are



reduced to the bis (allyl) ethers [81].

The intramolecular cyclization of diacetylenes has been achieved by using either the reagent combination $Cp_2TiCl_2/PMePh_2/Na(Hg)$ or $Cp_2ZrCl_2/Mg/HgCl_2$ in THF [89]. The procedures are compatible with a variety of saturated functionalities (O,N,Si) and in each case, acid hydrolysis of the initally formed organometallic intermediate affords exclusively the E,E exocyclic diene. For synthesis of simple five- and six-membered ring dienes, the titanium procedure is superior.

The titanium(III) compound Cp_2TiCl has been used to induce the cyclization of epoxyolefins [76] and the intermolecular addition of epoxides to activated olefins [127, 128].

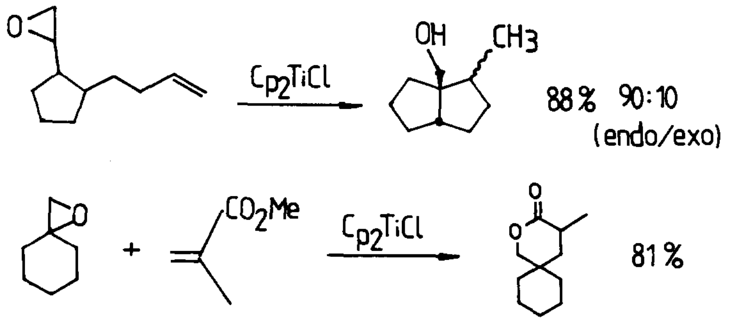


TABLE 2 : Titanium reagents for carbonyl coupling *

Reagent	alkene-forming		pinacol-forming		Ref.
	Ar	R	Ar	R	
$TiCl_3/LiAlH_4$	Y	Y	N	N	1-7,121,129
$TiCl_4/LiAlH_4$	Y	Y	Y	Y	1-7,130-134
$Cp_2TiCl_2/LiAlH_4$	N	N	N	N	8
$CpTiCl_3/LiAlH_4$	?	?	?	Y	93
$TiCl_4/Zn$	Y	Y	Y	Y	119,135-137
Cp_2TiCl_2/Zn	?	?	Y	N	77,75
$TiCl_4/Mg$	Y	Y	Y	Y	93,138-140
Cp_2TiCl_2/Mg	?	?	Y	Y	81,85
$Cp_2TiCl_2/RMgX$	N	N	Y	N	75,77,99,102
$Cp_2Ti(CO)_2$	Y	N	Y	N	111,112
$(C_6H_6)_2Ti$	Y	Y	N	N	118

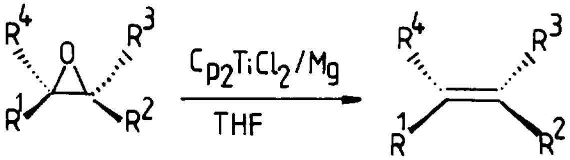
* Ar : aromatic and α,β-unsaturated ketones and aldehydes
R : aliphatic ketones and aldehydes
Y : yes; N : no; ? : no report.

It seems apparent that low-valent organo-Ti species are less effective than the corresponding inorganic titanium species in carbonyl coupling leading to alkenes. Examples given in Table 2 clearly show the different reactivity of the reagents towards carbonyl functionality. As can be seen from the table, the organotitanium reagents are most successful in the pinacol-forming coupling of aromatic, α,β-unsaturated ketones and aldehydes, and least successful in the alkene-forming coupling of aliphatic ketones and aldehydes, which are indeed harder to reduce. Low-valent inorganic titanium systems have been applied to induce carbonyl coupling of all kinds of ketones and aldehydes to pinacols and olefins. These observations are of interest for several reasons. First, it suggests that the organic ligands of the titanium complex play a key role in reducing its effectivity for carbonyl-coupling, e.g. Cp_2TiCl_2/Zn versus $TiCl_4/Zn$ and Cp_2TiCl_2/Mg versus $TiCl_4/Mg$. By adjusting the ligands, one may obtain interesting coupled products. For example, chiral organotitanium complexes could induce asymmetric coupling of carbonyl compounds. Second, highly reducing organotitanium species like $(C_6H_6)_2Ti(0)$ are effective in carbonyl coupling to olefins. Third, well-characterized low-valent organotitanium complexes should be useful for mechanistic studies of the carbonyl coupling.

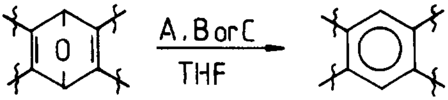
II.2. ELIMINATION REACTIONS

In the early seventies, Merijanian and co-workers observed dehalogenation of organic halides by titanocene [141]. At room temperature the system Cp_2TiCl_2/ $NaC_{10}H_8$ can abstract halogens readily from alkyl, allyl and certain vinyl halides, but not from aromatic halides. This is also the case when titanocene halides Cp_2TiX are employed in effecting the dehalogenation of benzylic, allylic halides and of α-bromoketones [28]. Benzylic and allylic halides are transformed into the coupled products, whereas the α-bromoketones are reduced to the corresponding ketones under mild conditions. Dehalogenation of aromatic halides has been achieved by $TiCl_3/LiAlH_4$ [142].

Davies et al. reported that Cp_2Ti debrominates vic-dibromides cleanly, but Cp_2TiCl, generated by zinc reduction of Cp_2TiCl_2, proved to be a more convenient and selective reagent for this conversion [74]. The ability to deoxygenate organic oxygen-containing molecules is unique to titanium owing to its high oxophilicity. Three titanium reagents $Cp_2TiCl_2/Na(Hg)$ [88], $(C_6H_6)_2Ti$ [118], and Cp_2TiCl_2/Mg [81], have been utilized to deoxygenate epoxides to alkenes. It is observed that trans-epoxides lead exclusively to trans-alkenes [81], and cis-epoxides furnish predominantly cis-alkenes [81, 88].



The two systems, $CpTiCl_3/LiAlH_4$ and $Cp_2TiCl_2/LiAlH_4$ have been applied to deoxygenation of 1,4-endoxides [94]. The results have shown that the three methods generally provide comparable yields. But the use of $CpTiCl_3/LiAlH_4$ and $Cp_2TiCl_2/LiAlH_4$ improves the synthetic procedure,

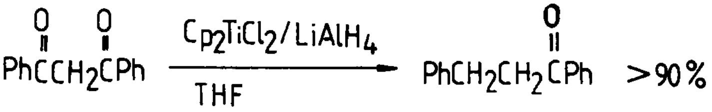


Method A : $CpTiCl_3/LiAlH_4$

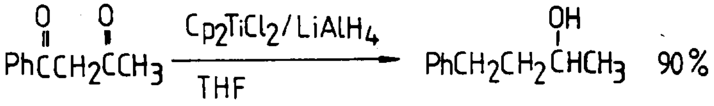
Method B : $Cp_2TiCl_2/LiAlH_4$

Method C : $TiCl_4/LiAlH_4/Et_3N$

because the extraction step becomes much easier than in the case of $TiCl_4/LiAlH_4$. Furthermore, $CpTiCl_3$ and Cp_2TiCl_2 are safer and more convenient to handle than $TiCl_4$. In addition to this type of deoxygenation, $Cp_2TiCl_2/LiAlH_4$ can also be applied to remove oxygen from aromatic ketones. Interestingly, an aliphatic ketone is simply reduced to the corresponding alcohol [95].

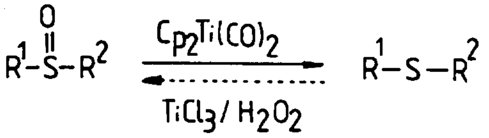


$$\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph} \xrightarrow[\mathrm{THF}]{\mathrm{Cp_2TiCl_2/LiAlH_4}} \mathrm{PhCH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph} \quad >90\%$$



$$\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow[\mathrm{THF}]{\mathrm{Cp_2TiCl_2/LiAlH_4}} \mathrm{PhCH_2CH_2}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_3} \quad 90\%$$

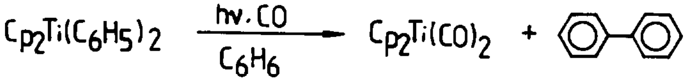
Aliphatic and aromatic sulfoxides are readily deoxygenated by $Cp_2Ti(CO)_2$ to give sulfides in high yield, while sulfones and phosphine oxides are inert [115]. The use of Cp_2TiCl_2/i-PrMgBr was also described [143]. Inorganic titanium reagents for this purpose include aqueous $TiCl_3$



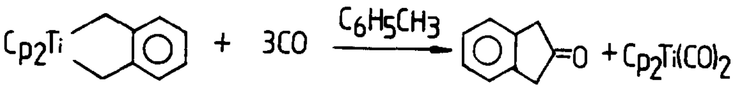
$$R^1-\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}-R^2 \underset{\mathrm{TiCl_3/H_2O_2}}{\overset{\mathrm{Cp_2Ti(CO)_2}}{\rightleftarrows}} R^1-\mathrm{S}-R^2$$

[122, 144, 145], $TiCl_4/NaBH_4$ [146], $TiCl_4/Te(iBu)_2$ [147] and $TiCl_4$/Zn [148, 149]. Reversely, sulfoxides are obtained from sulfides by using $TiCl_3/H_2O_2$ [150].

Lastly and perhaps interestingly, the elimination of one or more organic ligands from organotitanium derivatives (not necessarily leading to low-valent Ti-derivatives) has proven to be useful in mixed organic/ organometallic synthesis [11]. This is especially true in the preparation of $Cp_2Ti(CO)_2$ via titanocene alkyl and aryl complexes. Biphenyl is formed in 50 % yield upon irradiation of Cp_2TiPh_2 in a CO atmosphere [151]. The reaction of Cp_2TiMe with CO yields $Cp_2Ti(CO)_2$ and acetone,

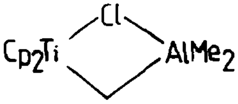


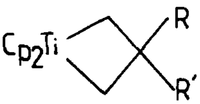
along with the reduced organics isopropanol and ethanol as minor products [152]. The carbonylation of bis(η-cyclopentadienyl) titanocenocyclopentene resulted in the formation of $Cp_2Ti(CO)_2$ and indan-2-one [153].

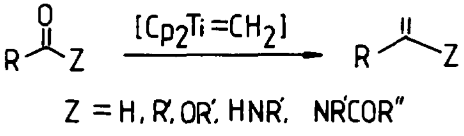


II.3. CARBONYL METHYLENATION AND GENERAL ALKYLIDENATION

In 1978 two separate research groups independently reported the carbonyl methylenation of ketones by $Cp_2TiCl_2/AlMe_3$ [54] and $TiCl_4/Zn/CH_2Br_2$ [154]. Two years later, ester methylenation was achieved using the organometallic reagent devised by Grubbs et al. [155], who later also developed the methodology and extended the applications to synthetic organic and organometallic chemistry [55, 57]. Their results have shown that the reactive species $[Cp_2Ti=CH_2]$, generated in situ from either its aluminium alkyl adducts or olefin adducts (metallacyclobutanes), is a very effective methylenating agent

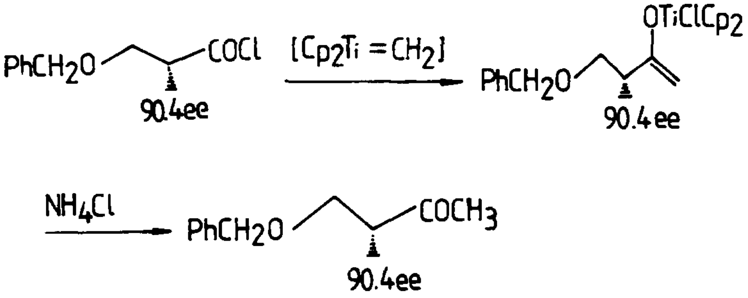




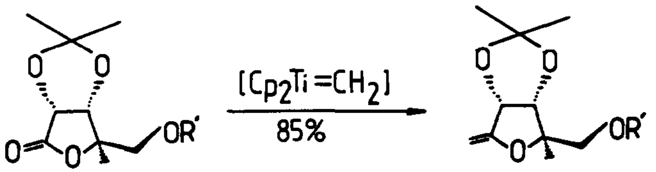


Z = H, R', OR', HNR', NR'COR''

for a variety of carbonyl groups. Easily enolizable ketones are methylenated quantitatively and isolated in high yield. This reagent also demonstrates chemoselectivity for ketones over esters and regioselectivity for less hindered ketones [55c]. It is unique in that the carbonyl groups of carboxylic acid derivatives are readily methylenated. Thus vinyl enol ethers are prepared from esters and enamines from amides [55a, 156]. A variety of acid chlorides can be converted into the enolates of the corresponding methyl ketones. The enolates did not isomerize and could thus be used to generate enolates that were chiral at the α-center and to generate unstable regio-isomers of enolates that are unavailable by other techniques [157, 158].



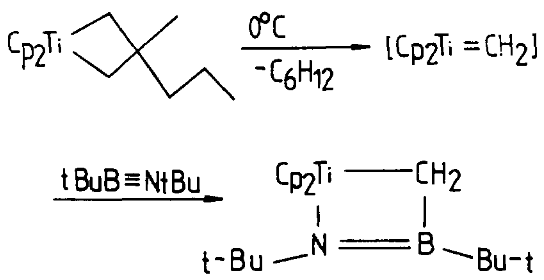
The methylenation methodology has found several applications in synthetic transformations (vide supra) and the synthesis of natural products [55, 159, 160]. It is used as a key step, e.g. in the synthesis of C-glycosides [160] and of capnellene [161, 162, 163]. $[Cp_2Ti=CH_2]$ is



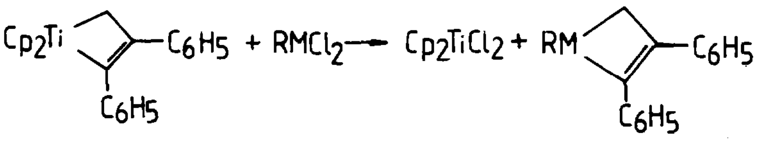
also utilized to prepare methylene sugars that can be converted to

C-linked disaccharides [108]. Two titanium reagents $TiCl_3/LiAlH_4/Et_3N$ and $[Cp_2Ti=CH_2]$ have been elegantly applied to the synthesis of capnellene in a short and efficient way [163].

The use of titanocene methylidene in the synthesis of heterocycles has received much attention. The iminoborane tBuB≡NtBu reacts with $[Cp_2Ti=CH_2]$ to give 1-aza-2-bora-4-titanacyclobutane by [2+2]-cyclo addition [164].

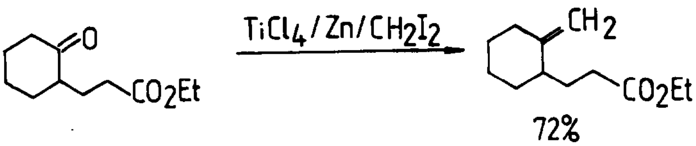


The formation of novel metallacycles has been observed in the reaction of the heterocyclic compounds benzothiazole and benzoxazole with $[Cp_2Ti=CH_2]$ [55c]. Two groups discovered almost simultaneously that phosphacyclobutenes [165, 166] and arsacyclobutene [166] can be synthesized by treatment of diphenyltitanacyclobutene with 1 equiv. of phenyldichlorophosphine or phenyldichloroarsine.

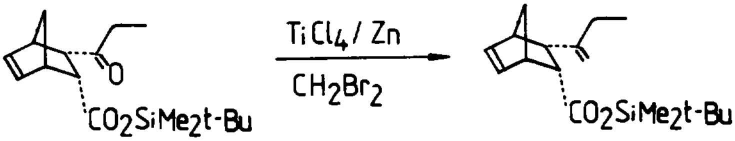


M = P, As. R=C_6H_5, CH_3CH_2, $(CH_3)_3C$, CH_3CH_2O

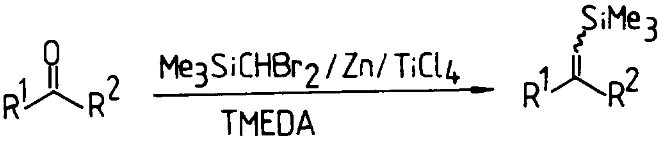
Compared to titanocene alkylidenes, the systems $TiCl_4/Zn/CH_2X_2$ are simple and readily available. Special techniques are not required. It has been found that carbonyl groups of aliphatic and aromatic ketones and aldehydes are methylenated, whereas the carbonyl group of an ester remains uneffected [154, 167, 168]. The simplicity and usefulness of



this reagent has been recognized by synthetic organic chemists when synthesizing natural products [169-171].

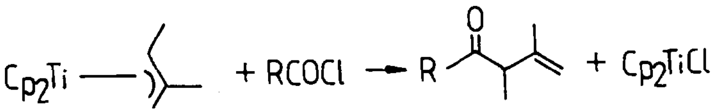


Additionally, the modified reagents $TiCl_4/Zn/RCHBr_2$ in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA) have been found effective in the conversion of esters into the corresponding alkenyl ethers with high Z-selectivity [172, 173]. Esters can also be converted into β-alkoxy- substituted alkenylsilanes [174]. Other synthetic examples include β-alkyl-thio-substituted alkenylsilanes from thioesters [174] and silyl-enol ethers from silyl esters [175].



II.4. REDUCTION

Some years ago, Sato et al. reported [9] that the Cp_2TiCl_2/Grignard reagent system can reduce ketones, aldehydes and esters to alcohols [176], and carboxylic acids to aldehydes [177]. However, no aldehydes were obtained from α,β-unsaturated carboxylic acids, e.g. trans-$C_6H_5CH{=}CHCO_2H$. Reduction of RCN with Cp_2TiCl_2/i-PrMgBr produced aldehydes [178]. Imines have been reduced to amines by Cp_2TiCl_2/i-PrMgBr [179]. Recent advances make the methodology even more synthetically useful. Allyltitanocene(III) complexes, prepared by the interaction of 1,3-dienes or trienes with Cp_2TiCl_2 and n-PrMgBr, react with carboxylic acid chlorides RCOCl (R = alkyl, aryl, alkenyl) to give



β,γ-unsaturated ketones in high yields. The reaction takes place at the most substituted carbon atom of the π-allylic ligand [27].

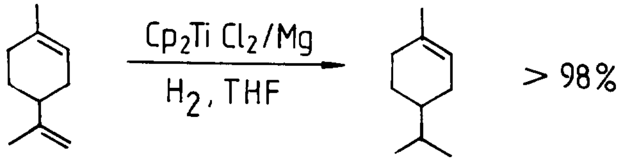
Collins and co-workers have demonstrated that substituted η^3-crotyltitanocene complexes $(RCp)_2Ti(\eta\text{-}C_4H_7)$, (R = H, Me, i-Pr) derived from titanocene dichlorides $(RCp)_2TiCl_2$, undergo addition reactions with aldehydes to provide anti-homoallylic alcohols with no apparent loss in yield. Furthermore, there is a correlation of the degree of diastereoselectivity with the size of the substituent on the cyclopentadienyl ring and on the aldehyde [14]. Collins et al. also investigated the diastereoselective synthesis of homoallylic alcohols with recyclable chiral titanocene reagents [20]. Martin and Li examined the stereochemistry of the anti-selective additions of crotyl organometallic reagents, including organo-Ti reagents, to α-alkoxy aldehydes [21].

Aliphatic aldehydes react with $Cp_2Ti(CO)_2$ to give mainly the corresponding alcohols [111].

Direct conversion of aldehydes, esters and epoxides to alkanes is achieved with Cp_2TiCl_2/Na. The reductions occur with carbon skeleton preservation in good yields at room temperature [87]. Reduction of organic halides with Cp_2TiCl_2/Mg [79] or i-PrMgBr [180] gives the corresponding hydrocarbons.

The application of titanium complexes to the hydrogenation of unsaturated hydrocarbons has been the subject of current interest [92]. Rapid reduction of terminal alkenes and internal alkynes has been observed with complex metal hydrides of aluminium and Cp_2TiCl_2 [181]. Disubstituted acetylenes react with Cp_2TiCl_2/RMgBr to yield cis-olefins after hydrolysis [182, 183]. Some saturated acids have been reduced to the corresponding saturated species upon reaction with $Cp_2Ti(CO)_2$. In the hydrogenation, the acidic hydroxyl groups of the unhydrogenated acids are found to be an effective source of hydrogen [39].

Various reductants such as $LiAlH_x(OR)_y$ [184], MgH_2 [185], RMgX [186], RLi [187] and sodium or other alkali metal naphthalenides [188, 189] have been used in the preparation of low-valent organotitanium species. Cp_2TiCl_2 and Mg in THF produce a stable solution, which under a H_2 atmosphere effectively hydrogenates various types of olefins and acetylenes under ambient conditions [84].

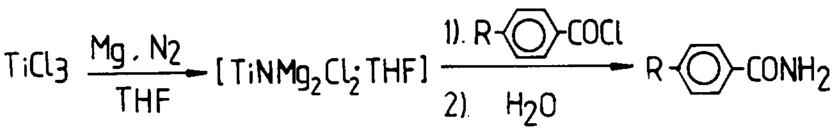


Some Chinese researchers reported the results of the hydrogenation of 1-hexene catalyzed by Cp_2TiCl_2 with active alkali metal hydrides [92]. They found that the use of active NaH and KH as co-catalysts is the key to high catalyst activities.

II.5. FIXATION AND/OR REDUCTION OF SMALL MOLECULES

Dilworth and Richards have reviewed reactions of dinitrogen promoted by transition metal compounds including organotitanium derivatives [190]. Therefore, we will address only some very recent advances in this field and in the development of reactivity of low-valent organotitanium species towards small molecules, such as CO, CO_2, CS_2, HC≡CH, CH_2=CH_2, etc.

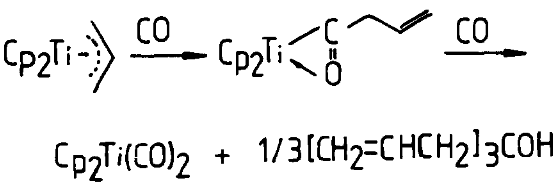
$TiCl_3$/Mg in THF can react with dinitrogen to afford $TiNMg_2Cl_2$.THF [191], which then reacts with benzoyl chloride to give benzamide [192].



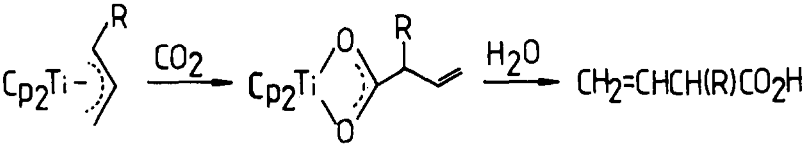
We found that treatment of benzoyl chloride with $TiCl_3/LiAlH_4$ in THF led to mainly stilbene and other coupled products [193]. The complex $[Cp_2Ti(PMe_3)]_2(\mu\text{-}N_2)$ has been isolated in 56 % yield from a petroleum ether slurry of $Cp_2Ti(PMe_3)_2$ under N_2 [194]. The crystal structure of this dimer shows a nearly linear N≡N bridge having an N-N distance of 1.191Å. The dinitrogen ligand is labile, and can be displaced by addition of excess CO or PMe_3 to yield Cp_2TiL_2 (L = CO, PMe_3). The complex $[Cp_2Ti(PMe_3)]_2$ $(\mu\text{-}N_2)$ slowly decomposes in benzene over a period of a few days to give the known binuclear complex $[CpTi(PMe_3)]_2(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4]_2$ [195].

As reviewed by Sikora, Macomber and Rausch [11], carbon monoxide has been widely used in the synthesis of carbonyl derivatives of titanium, zirconium and hafnium. In fact, a particularly fascinating aspect of the activation of carbon monoxide by transition metal compounds is the carbonylation of bicyclopentadienyl dialkyls (diaryls), haloalkyls and related derivatives of group 4d metals and actinides of the type Cp_2MR_2 and Cp_2MRX. The insertion processes of CO into the M-R bonds of these complexes are extremely facile and (although they are not catalytic) have served as models for the CO activation and reductive CO coupling steps of some catalytic processes of potential importance to industry [196]. Durfee and Rothwell have reviewed the chemistry of η^2-acyl organometallic complexes [197].

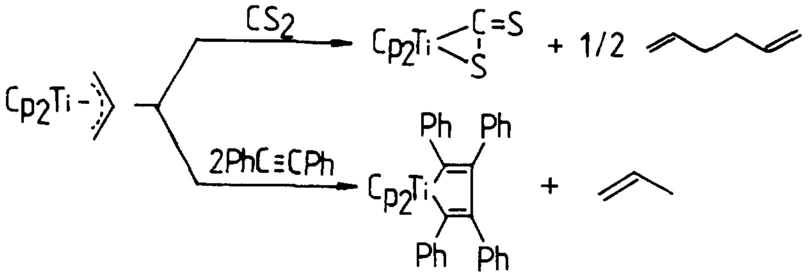
Teuben et al. reported the titanocene-promoted allyl transfer to carbon monoxide and other unsaturated molecules [198]. The carbonylation



of $Cp_2Ti(\pi$-allyl) yields $Cp_2Ti(CO)_2$ and trialkylmethanol. The insertion of CO_2 into a Ti-C bond followed by hydrolysis yields a carboxylic acid.

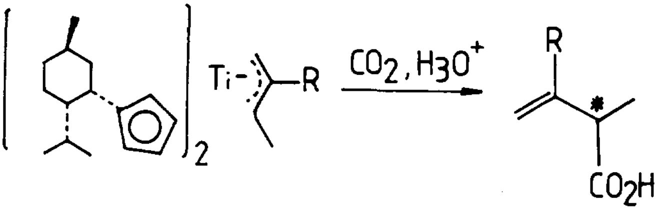


Allyl-elimination takes place between $Cp_2Ti(\pi$-allyl) and molecules like CS_2 and PhC≡CPh.

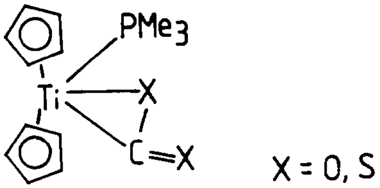


Labile acyl compounds Cp^*_2TiCOR ($Cp^* = C_5Me_5$, $R = CH_3$, neo-C_5H_{11}), prepared from Cp^*_2TiR and CO, react with $[CpMo(CO)_3]_2$ to give rise to complexes $Cp^*_2Ti(\eta^2\text{-COR})(\mu\text{-OC})MoCp(CO)_2$, which undergo acyl C-O bond scission with concommitant formation of benzene derivatives [199].

Asymmetric carbon dioxide fixation has been achieved by reaction of CO_2 with a chiral titanocene(III) complex [200].



The bis(trimethyl)phosphine titanocene complex $Cp_2Ti(PMe_3)_2$ reacts immediately with CO_2 and CS_2 yielding the new complexes $Cp_2Ti(CO_2)(PMe_3)$ and $Cp_2Ti(CS_2)(PMe_3)$ in high yield [201]. NMR and IR spectra indicate that the heteroalene is coordinated to the metal in a "side-on" manner.



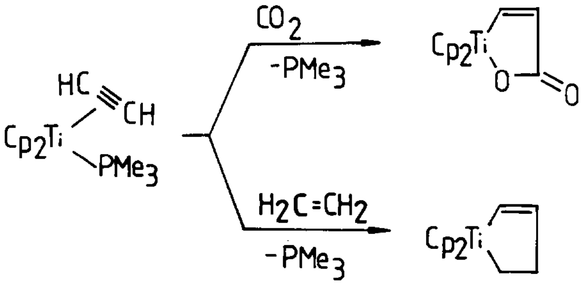
Reductive head-to-head dimerization of CS_2 can be achieved with $Cp_2Ti(CO)_2$, giving rise to $(Cp_2Ti)_2(C_2S_4)$ [202].

The reaction of $Cp_2Ti(PMe_3)_2$ and ethylene affords the 16-electron species $Cp_2TiC_2H_4$. In the reaction under pressure, 1-butene and trans-2-butene are formed catalytically. With water, $Cp_2TiC_2H_4$ reacts to give the dinuclear μ-oxo complex $(Cp_2TiEt)_2O$, the structure of which

$$2Cp_2TiC_2H_4 + H_2O \longrightarrow Cp_2EtTi{-}O{-}TiEtCp_2$$

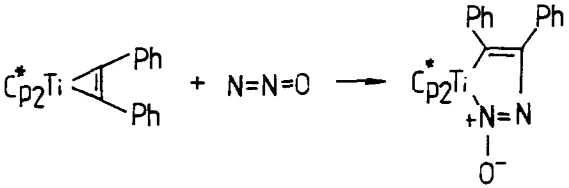
has been determined by X-ray diffraction showing a nearly linear Ti-O-Ti bond (173.3°) [203].

The acetylene complex $Cp_2Ti(PMe_3)(C_2H_2)$ is prepared from reaction of $Cp_2Ti(PMe_3)_2$ with CH≡CH [46]. The alkyne ligand readily undergoes carbon-carbon addition reactions with carbon dioxide, acetone, acetaldehyde and ethylene to give five-membered metallacycles [49].



As previously mentioned, acetylene can be polymerized by $Cp_2Ti(PMe_3)_2$ [50].

Finally, nitrous oxide (1 equiv., 20°C) reacts with toluene solutions of $Cp_2{}^*Ti(C_2Ph_2)(Cp^* = \eta\text{-}C_5Me_5)$ to afford ~70 % yield of



$Cp_2{}^*Ti[N(O)NCPh{=}CPh]$, a product of N_2O insertion into a Ti-C(alkyne) bond [204].

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