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REDUCTIONS PROMOTED BY LOW VALENT TRANSITION METAL COMPLEXES IN ORGANIC SYNTHESIS

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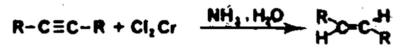
CONTENTS

1. INTRODUCTION

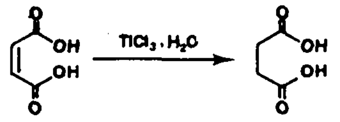
The increasing use of low valent transition metal species in organic chemistry, during the last 15 years, has been widely noted. In this report, we have endeavoured to collect the results concerning, in particular, the complexes, which result from the reduction of transition metal halides, used in stoichiometric ratio. Due to the importance of the reductive duplication of ketones or aldehydes in the presence of low valent titanium complexes, particular attention has been paid to this reaction.

1.1. *History*

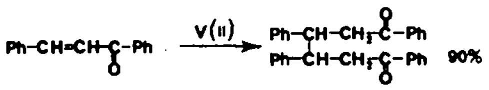
Berthelot seems to have been the first to use a low valent transition metal as a reducing agent: he observed that acetylene is reduced to ethylene by an ammoniacal solution of chromous chloride.[1] This reaction offers a general character, and the *E*-alkene can be obtained stereospecifically.[2]



Olefins are likewise reduced into alkanes.[3] In the early 1900s some works also revealed the reducing properties of Ti(III) on ethylenic acids.[4,5]

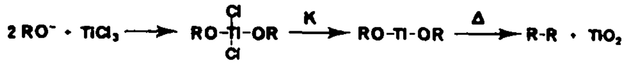


However, about 20 years then passed before V(II) was tested for the reduction of ethylenic aldehydes and ketones: Conant and Cutter showed that some carbonyl compounds could, in the presence of V(II), undergo a reductive duplication. Thus, benzalacetophenone is reduced to a mixture of two isomers of a diketone with a yield of 90%.[6]



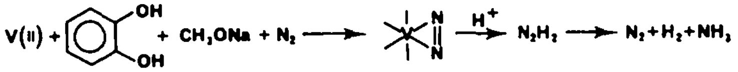
$$Ph{-}CH{=}CH{-}\underset{O}{\underset{\|}{C}}{-}Ph \xrightarrow{V(II)} \begin{matrix} Ph{-}CH{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}Ph \\ Ph{-}CH{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}Ph \end{matrix} \quad 90\%$$

In 1934, Rheinboldt and Schwenzer published a study on the reduction of various transition metal halides by magnesium in diethyl ether.[7] Interest in these reactions of reduction or duplication then waned and it was not until the 1960s that new results were found, mainly involving low valent titanium species. It appears that part of this element's reducing power may be due to the particular stability of the oxidization product, titanium dioxide. This enabled Van Tamelen to propose an efficient method for the coupling of allylic and benzylic alcohols into hydrocarbons:[8] the alcohol alkoxide treated by $TiCl_4$ leads to the dichlorotitaniumate complex reduced by potassium into a titanium(II) ester, which is heated to eliminate the titanium dioxide and isolate the hydrocarbon.

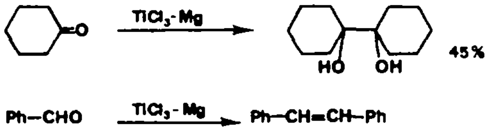


$$2\,RO^- + TiCl_3 \longrightarrow RO{-}\overset{Cl}{\underset{Cl}{Ti}}{-}OR \xrightarrow{K} RO{-}Ti{-}OR \xrightarrow{\Delta} R{-}R + TiO_2$$

Simultaneously, Volpin proposed a V(II) complex capable of reducing nitrogen into ammonia and hydrazine.[9] Recent works have shown that V(II), complexed by pyrocatechol, is one of the most powerful reducing agents (it reduces N_2, CO, C_2H_4, H^+...).[10]



But interest in the reductions promoted by low valent transition metal complexes considerably increased when Tyrlic and Wolochowicz[11] suggested using a Ti(II) species, they had obtained by reduction of $TiCl_3$ by Mg, as a reagent for reductive duplication of aldehydes or ketones.



At the same time, Mukaiyama proposed, independently, the use of $TiCl_4$–Zn to promote the same reactions,[12] and of $TiCl_4$–$LiAlH_4$ for the reduction of sulfides and vinyl or aromatic halides.[13]

A series of papers then followed; many of them written by McMurry *et al.* Reviews on titanium,[14–17] titanium and vanadium,[18] and chromium[19] are available; reviews on the reactivity, in organic chemistry, of low valent transition metal complexes of group IVB, VB and VIB[20] and lanthanides[21] are also available.

Table 1

Complex	Ref.	Complex	Ref.	Complex	Ref.
$TiCl_3$–Li	(34)	$TiCl_4$–Mg	(38)	$TiCl_3$ aqu.	(40)
$TiCl_3$–K	(35)	$TiCl_4$–Zn	(12)	$TiCl_4$–BuLi	(41)
$TiCl_3$–Zn(Cu)	(36)	$TiCl_4$–Mg(Hg)	(38)		
$TiCl_3$–$LiAlH_4$	(37)	$TiCl_4$–$NaBH_4$	(39)		
$TiCl_3$–Mg	(11)	$TiCl_4$–$LiAlH_4$	(13)		
		$TiCl_4$–BuLi	(41)		

1.2. *Examples of low valent transition metal and lanthanide complexes*

From the 1970s onwards, a number of reductive complexes have been proposed. Besides Ti, V and Cr complexes, which, because of their importance, will be discussed in greater detail later, reductive complexes involving the following metals have been proposed: Mn,[22] Fe,[23] Co,[24] Ni,[25] Nb,[26] Mo,[23] W,[27] Ce,[28] Sm[29] and Yb.[30] Because of its oxophilic character,[31] titanium is the most commonly used transition metal for the reductive duplication of carbonyl compounds; these reactions being the more interesting ones. Titanium can react under the following three valence degrees: O, II and III (the ways to obtain these complexes are indicated in Table 1).

In most cases, titanium complexes are prepared in THF, although DME has been successfully used.[32] It is worth noting that one can observe a slow insertion of magnesium when THF is heated to its boiling point for several hours in the presence of transition metal halides and magnesium.[33]

The Cr(II)[42] and V(II)[43] complexes are obtained by means of reducing Cr(III) and V(III) species by $LiAlH_4$.

2. REACTIVITY OF REDUCTIVE COMPLEXES

2.1. *Fixation and/or reduction of* N_2, CO, CO_2, C_2H_4 *and* C_2H_2

The reductive ability of transition metals has therefore, in part, been brought to light by their reactions with small molecules such as nitrogen, carbon monoxide or ethylene. In addition to the works of Volpin,[9] Schrauzer[10,44,45] and Van Tamelen,[46] Shilov's studies[47,48] also deserve to be mentioned.

$$CO + 4\,V^{2+} \xrightarrow{4H^+} CH_3OH + 4\,V^{3+}$$

$$CO + 2\,V^{2+} \xrightarrow{2H^+} CH_2O + 2\,V^{3+}$$

Sobota *et al.*, have shown that Ti(II)[49] and even Cr(II), Mo(II) and Fe(II)[23] complexes could fix N_2, CO_2 and H_2; more recently, they have conclusively shown the existence of a N—C bond in a Ti complex.[50] [For the nitrogen fixation on Ti(II) species[51]].

$$2\,TiCl_4.THF_2 + 6\,Mg + N_2 \xrightarrow[293\,°K]{THF} 2\,TiNMg_2Cl_2.THF + 2\,MgCl_2.THF_2$$

$$TiNMg_2Cl_2,\ THF + CO \longrightarrow TiCONMg_2Cl_2,\ THF$$

Lastly, we note that both the kinetic and the stoichiometry of the fixation reaction of N_2 on Ti(II) and V(II) complexes were established in 1972 by Keii *et al.*[52]

$$MCl_3(THF)_3 + 5/2\,Mg + 1/2\,N_2 \longrightarrow |MNMg_2Cl_2.THF| + 1/2\,MgCl_2(THF)_2$$

$$M = Ti,\ V$$

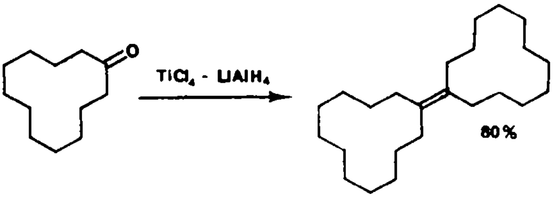
2.2. *Reductive duplication of aldehydes and ketones*

It is the reaction involving transition metal reductive complexes and complexes of titanium in particular, which has given rise to the greatest interest: reactivity, mechanism study and total synthesis applications. The reaction is either intra- or intermolecular (symmetrical or not), depending on conditions. It produces vicinal diols or alkenes (although there are examples where alcohols are formed).

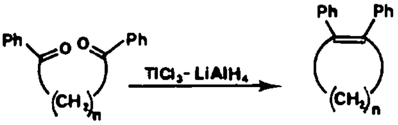
2.2.1. *Olefins obtained by an inter- or intramolecular reductive condensation.* This kind of reaction is characteristic of formally zero valent titanium complexes such as $TiCl_3$–Li, $TiCl_3$–K, $TiCl_3$–$LiAlH_4$ and $TiCl_3$–Zn(Cu).

$TiCl_3$–$LiAlH_4$ *and* $TiCl_4$–$LiAlH_4$

McMurry was the first to propose the reduction of $TiCl_3$ by $LiAlH_4$[37] and has lent his name to a reagent which is now commercially available.

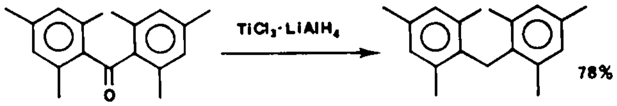


More recently, Baumstrack *et al.*, showed that the intramolecular reaction could be applied to phenyl substituted diketones leading to 3- to 12-membered rings.[53]



Since then, McMurry's reagent has helped organic chemists on many occasions[54–62] ($TiCl_4$–$LiAlH_4$).[63] It is also worth noting that Geise *et al.*, studied diarylketones[64,65] and that Bohrer was interested in the reactivity of cyclopropylketones.[66] We will refer to these results when evaluating the reaction mechanism.

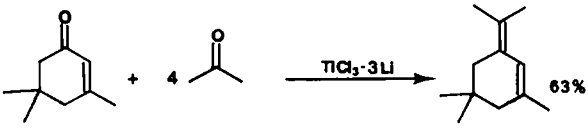
Moreover, Lenoir has shown that especially hindered aliphatic ketones yield the corresponding alcohols while hindered diarylketones yield the corresponding hydrocarbons (monomers).[67]



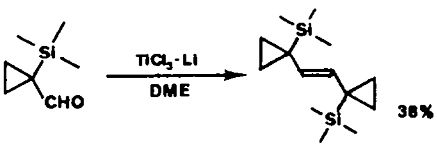
Lastly, Ashby reduced ethylenic ketones into saturated ones.[68]

$TiCl_3$–Li

McMurry *et al.*, were also the first to use lithium as a reducing agent for the preparation of a low valent Ti complex;[69] the best results being obtained using three equivalents of Li for one equivalent of $TiCl_3$. This reducing agent offers the possibility of dissymmetrical couplings.[34]



Later on, the same authors showed that DME could be used as the reaction solvent.[32] The $TiCl_3$–Li reagent was also used by Richardson[70] and Geise[64] in THF and Castedo,[71] Paquette[72] and Coe[73] in DME. One can illustrate these results with the coupling of two molecules of trimethylsilylcarboxaldehyde.[72]

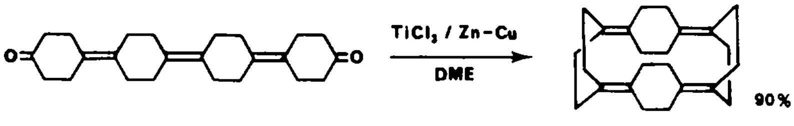


$TiCl_3$–K

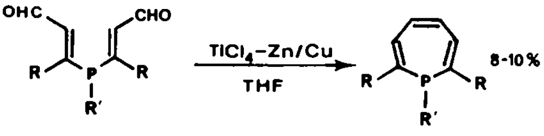
The use of potassium to reduce $TiCl_3$ was proposed by Nishida[35] and McMurry[74] in 1978, but the resulting complex seems to have been abandoned as it leads to too many by-products, especially with diarylketones.[64]

$TiCl_3$–Zn(Cu)

This complex, which is sometimes prepared in DME[36,75,76] is more commonly used for the cyclization of diketones, dialdehydes or ketoaldehydes. McMurry has employed it many times;[77–80] more recently to carry out the last step of his synthesis of the following tetraene:[81]



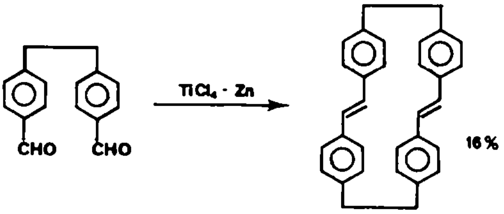
Preparations of phosphorus heterocycles were carried out by Markl[82] through an intramolecular coupling of dialdehydes.



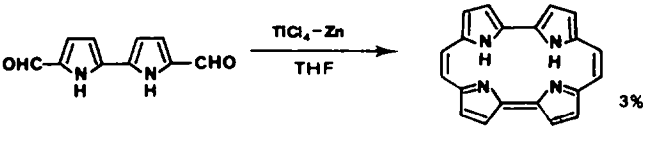
The literature contains other noteworthy examples of the use of $TiCl_3$–Zn(Cu).[83–87]

$TiCl_4$–Zn

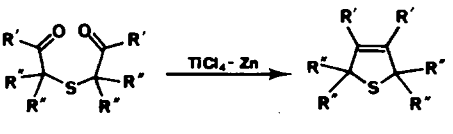
The use of this couple in order to obtain olefins by inter- or intramolecular reactions is less usual than those mentioned above; however, Tammer used it for the reductive dimerization of diketones or dialdehydes[88,89] and obtained, for example, the 2,2,4,4'-*trans*-stilbenophane.[90]



In a same way Vogel *et al.*, obtained 3% of porphycene, a novel porphin isomer.[91]



Lenoir prepared specially hindered hydrocarbons[92] such as indenylidene indenes[93] or fluorylidene fluorenes.[94] Among other examples of its use,[54,73,74,95–102] Nakayama's works are original[103–106] in that they lead to sulfur heterocycles, the 2,5-dihydrothiophenes.[104]

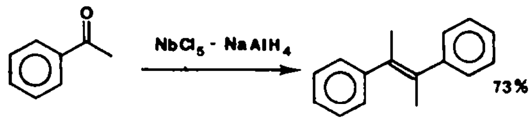


$Cp_2Ti(CO)_2$ *and* Cp_2TiCl_2–Na

Starting from various aldehydes and ketones, $Cp_2Ti(CO)_2$ can promote their reductive dimerization into olefins or their reduction into alcohols[107] and Cp_2TiCl_2–Na, their reduction into alkanes.[108]

Other metals

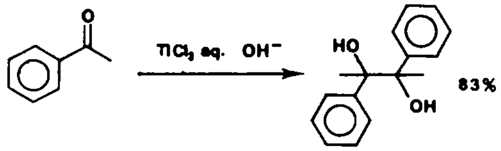
Likewise, in 1982, the synthesis of aromatic alkenes, from aldehydes or ketones using NbCl$_5$–NaAlH$_4$[26,109] and low valent tungsten[27,109–111] or molybdenum[109,110] species was proposed.



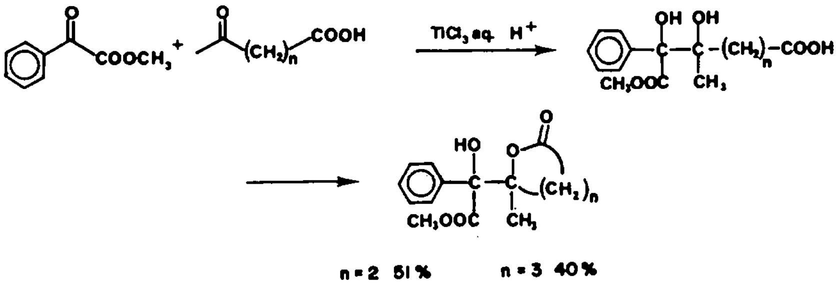
2.2.2. *Diols obtained by inter- or intramolecular reductive condensation.*

TiCl$_3$ *aqueous*

Clerici *et al.*, have brought to light that an acidic[40] or basic[112,113] aqueous solution of TiCl$_3$ can yield vicinal diols resulting from a reductive dimerization.

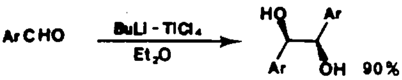


With ketoacids, the same authors have been able to show that the reaction yields lactones in one step.[40]

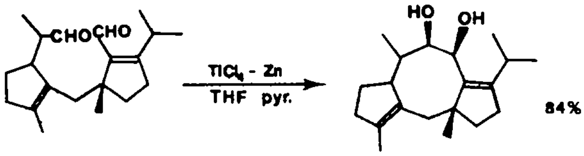


Other Ti *complex*

Using Ti(III), obtained by reduction of TiCl$_4$ by BuLi in diethylether, Seebach has obtained pinacols, with a high stereoselectivity, from aromatic aldehydes.[41]



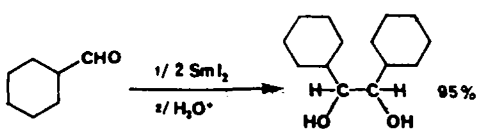
The following complexes, TiCl$_4$–Mg,[38,114,115] TiCl$_4$–Mg(Hg),[38,116–121] TiCl$_4$–Zn[38,122] and TiCl$_4$–Te(iBu)$_2$[123] have also been used to obtain pinacols by means of an inter- or intramolecular reaction. Takeshita has, then, employed TiCl$_4$–Zn, associated to pyridine, to synthesize variously substituted pinacols[124,125] as indicated.[126]



TiCl$_4$–LiAlH$_4$ has also been employed to prepare symmetrical diethoxy diphenyl ethane from diethylbenzaldehyde acetal.[127]

Other metals

Though the use of Cr(II) salts as reductive duplication agents on ketones or aldehydes is uncommon, one can, nevertheless, mention Davies and Bigelow[128] who have dimerized benzaldehyde with a yield of 69%. V(II) has permitted the reductive duplication of pyruvic and phenylglyoxylic acids.[129] More recently, it has been proposed to reach pinacols by using low valent cerium;[28,130] the best results being obtained by using CeI$_3$–K and Ce–C$_6$H$_5$I in THF. Kagan *et al.*, have reported some excellent results using SmI$_2$.[29,131]



Lastly, it is worth noting that benzils can be reduced to benzoins when using V(II) or even Ti(II) species.[132]

2.3. *Alkylation of aldehydes and ketones*

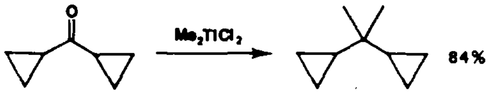
2.3.1. *With alkyltitanium complexes.* The alkylation examples of carbonyl compounds by titanium derivatives are numerous; in most cases, they are promoted by organotitanium species of various oxidation degrees. The reaction involves an alkylfunctional group transfer from the metal complex to the carbonyl [Seebach[133,134] and Reetz[135,136] are the two main authors in this field].

Then, the following aliphatic group transfers can be noticed:

Starting from Ti(O) derivatives: transfer of the 2-buten-2-yl moiety[137] (for other examples).[138]

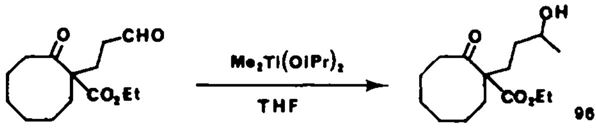
Starting from Ti(II) derivatives: direct geminal dimethylation of ketones is possible by using dichlorodimethyltitanium.[139] This complex can be prepared by an exchange between titanium tetrachloride and dimethylzinc.[140]

$$TiCl_4 + ZnMe_2 \xrightarrow{CH_2Cl_2} Me_2TiCl_2 \quad 90\%$$



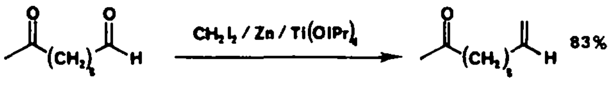
This reagent, which also allows geminal dimethylation of aromatic aldehydes,[141] has been used in a recent synthesis of modhephene.[142]

Moreover a very high chemoselectivity is reached with $Me_2Ti(OiPr)_2$.[143]

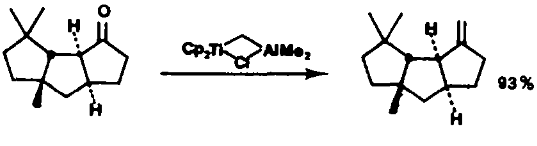


Starting from Ti(III) derivatives: the main complex is trichloromethyltitanium[144–146] (but alkyltriisopropoxytitanium also exists[147,148] which is obtained by an exchange between dimethylzinc (½ equi.) and titaniumtetrachloride (1 equi.). This reagent is particularly stereo- or chemoselective. Starting from Ti(IV) derivatives: one can mention the allyltitaniumate complexes which are prepared by addition of allylic anions on Ti(IV) derivatives (titanium triisopropoxychloride for instance); these complexes yield homoallylic alcohols after addition on aldehydes.[134,135,148,149]

Titanium derivatives are also involved in methylenation reactions. As it has been shown, these reagents result from the condensation between a carbonyl function and, an *in situ* formed complex system which involves a methylene halide, zinc and a Ti(IV) species;[150–153] one of which Takai has shown to be chemoselective.[154]



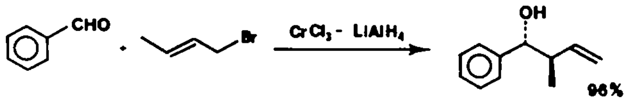
For the last few years, some other reagents which give rise to the same reaction have appeared in chemical literature.[155–157] This reaction, which can sometimes replace Wittig's[158] and Peterson's,[159] has received some interesting applications in organic synthesis;[160,161] for instance, Grubbs used Tebbe's reagent[162] to carry out the synthesis of $\Delta^{9,12}$-capnellene.[163]



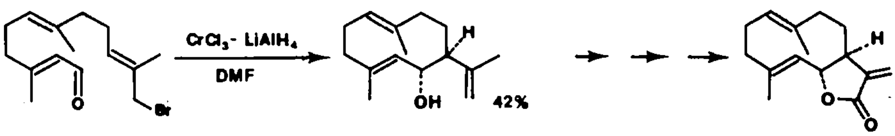
2.3.2. *With other reductive complexes.*

$CrCl_3$–$LiAlH_4$

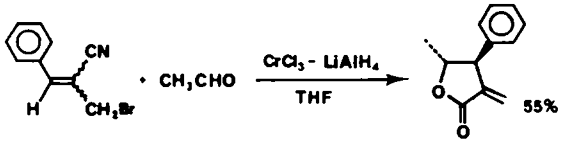
This couple (used either in THF or in DMF with a 2 : 1 ratio) is undoubtedly the more commonly used to provoke this reaction.[42,164] Thus, Nozaki and Hiyama have managed to obtain, with a yield of 96%, a single stereoisomer of this homoallylic alcohol.[165]



That reagent has also been used in the (±)-costunolide synthesis.[166]



In 1985, Nozaki[167] and Drewes[168] suggested the use of a β-carbetoxyallylic bromide (or a β-allylnitrile for Drewes) instead of an allylic halide and brought to light an easy synthesis of α-methylene γ-lactones.



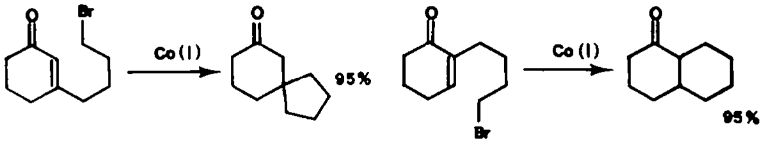
Various Cr(II) reagents have also been used by Heathcock,[169] Fuganti[170] and Takai.[171-173]

SmI_2

Kagan proposed the use of samarium diiodide[174] which can connect allylic or benzylic halides and aldehydes; Molander, using the same reagent, as well as ytterbium diodide, catalysed by Fe(III), has obtained bicyclic alcohols by means of an intramolecular reaction.[175,176]

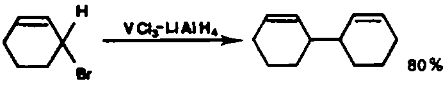
Other complexes

Mn(O)[22,177] and Co(I)[24] are also used; concerning the latter, vitamin B_{12} and vitamin B_{12} model compounds provide Michael addition by chemically catalyzed controlled potential electrolysis.



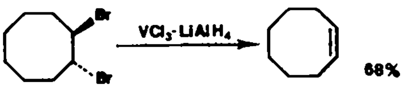
2.4. *Coupling and elimination of halo compounds*

2.4.1. *Coupling.* As early as 1961, reductive dimerisation of benzylic halides has been obtained when using a vanadium complex[178] or low valent compounds of Co, Cr, Fe, Cu and Mn.[179] However, this kind of reaction has only been developed in the last 20 years following the use of transition metal reductive complexes in organic synthesis. Thus, it has been shown that Cr(II),[171,180-182] V(II)[43,183] and Ti(II)[156,184] compounds make it possible to duplicate benzylic, allylic, alkyne or alkylhalides.

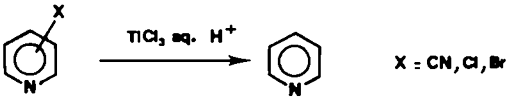


This reaction can also be obtained by using reductive complexes of Ni,[185] Zn–Cu–Hg,[186] Mo[187] or SmI_2[30] but examples are fewer.

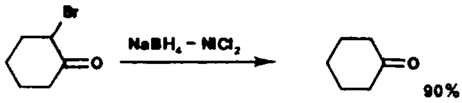
2.4.2. *Elimination.* The best documented reaction is the one yielding carbon–carbon double bonds starting from *vic*-dihalo compounds; the best results being obtained by using Ti(II),[184] V(II),[43] Ni(O)[25] or Cr(II)[188,189] complexes.



It must also be noted that the reduction of propargylic bromide with a Cr(II) complex yields allenes[190] (using a chiral reagent, Gore has obtained allenic derivatives with an optical activity;[191] the reduction of alkyl halides yields alkanes when Ce,[192] Cr(II)[19] or Ti(O)[193] complexes are used, while the reduction of halopyridines and cyanopyridines with $TiCl_3$ aqueous yields pyridine.[194]



2.4.3. *Reductive dehalogenation of α-haloketones.* The dehalogenation of α-haloketones is a reaction commonly used in organic synthesis. Alongside old methods such as using Zn–AcOH,[195] the use of transition metal reductive complexes is becoming more frequent; in 1983, Noyori published a review on the topic.[196] The reaction can be carried out using complexes of V(II),[197] Ti(III),[198] Mo(O),[199] Fe,[200–203] Ce(III)[204] or Cr(II)[205] among others. More recently, the $NaBH_4$–$NiCl_2$ couple has been successfully used by Sharma.[25]



Similar results are obtained with SmI_2[206] and SbR_3.[207]

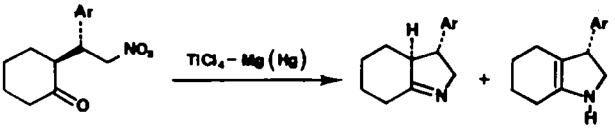
2.4.4. *Cyclization of halocompounds.* Crandall has shown that Cr(II) allows cyclization of alkyne halides.[208]

2.5. *Reduction of nitrogenous functional groups*

2.5.1. *Nitro, hydroxylamine, azide, nitrosamine and nitrile functions.* The first papers on this topic appeared as early as 1904 (reduction of nitroarene with Ti(III)),[209] but it has only recently been up-dated by McMurry[210] and Ho[211] who both used $TiCl_3$ aqueous; for other examples of the use of $TiCl_3$ aqueous.[212–214] For his part, Sobota studied the reduction of nitrobenzene—promoted by MCl_n–Mg/THF complexes with M = Ti, V, Cr, MoO, W and Fe—through the relative *ratio* of aniline and azobenzene, the two products of the reaction.[215]

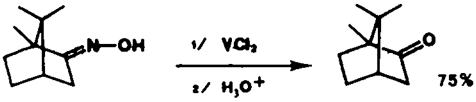
$$C_6H_5NO_2 \xrightarrow[THF]{MCl_n\text{-}Mg} C_6H_5NH_2 + C_6H_5N{=}NC_6H_5$$

$TiCl_4$–$NaBH_4$,[39] $TiCl_4$–$Te(iBu)_2$,[123] $TiCl_4$–Mg(Hg)[216] and $CrCl_2$[217] also allow the reduction of nitro functional groups into amines. Sometimes, this reduction is followed by a cyclization, as in the case of the synthesis of the 3-aryl hexahydroindoles.[218]



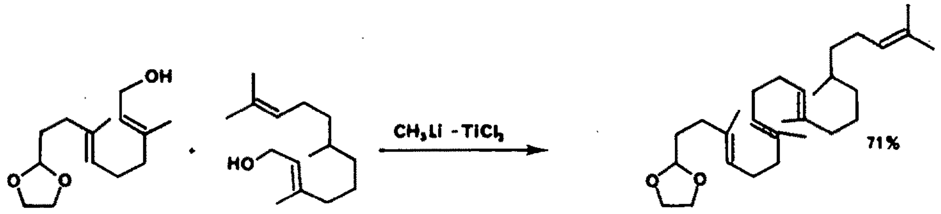
Moreover, it is possible to transform *N*,*N*-disubstituted hydroxylamines into imines or amines (depending on the reaction conditions),[219] nitro into amine[220] or to reduce the nitrosamine group, using either low valent titanium[221–223] or nickel[223] species. V(II) and Cr(II) reduce nitroamine(NH_2NO_2) into nitrogen (and ammonia with Cr(II))[224] and V(II) leads to primary amines starting from arylazides.[225]

2.5.2. *Hydrazones and oximes.* Many transition metals (for example: Ti(II) and Ti(III),[39,226–228] V(II)[229,230] and Cr(II))[231,232] have been used to reduce, and sometimes hydrolyse in mild conditions, hydrazones and oximes.



2.6. *Elimination and coupling of alcohols*

The first results in this area were published by Van Tamelen (see Introduction); using the coupling of allylic alcohols promoted by Ti(II) species, 1,5-dienes are obtained.[233]



The mechanism of that reaction has also been studied.[234]

This reaction can also be carried out with McMurry's reagent ($TiCl_3$–$LiAlH_4$) in an inter-[235,236] or intramolecular way.[237,238] Moreover, $NbCl_5$–$NaAlH_4$ allows the formation of hydrocarbons with yields of up to 90%.[26]

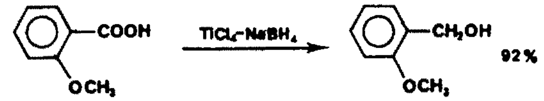
McMurry's reagent has also been used to obtain 1,3-dienes starting from 2-ene-1,4-diols and even 1,1,4,4-tetraphenyl-1,2,3-butatriene starting from 1,1,4,4-tetraphenyl-2-butyne-1,4-diol with a yield of 83%.[239]

The reduction, promoted by low valent titanium species, of vicinal diols into alkenes has been studied in the course of experiments on the mechanism of reductive duplication of aldehydes and ketones;[34] such a result can also be achieved by using WCl_6–BuLi.[240]

Lastly, McMurry's reagent allows the reduction of bromohydrins to olefins[241] and $TiCl_4$–Zn, the reduction of α-keto-alcohols to ketones.[235]

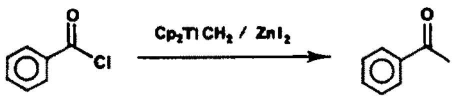
2.7. *Action on carboxylic acids, esters and acyl chlorides and cyanides*

2.7.1. *Carboxylic acids.* The reduction of carboxylic acids with reductive complexes leads to a range of products: primary alcohols ($TiCl_4$–$NaBH_4$),[39] symmetrical diols and methylketones ($TiCl_3$–5MeLi)[242] or furanic derivatives ($TiCl_3$–$LiAlH_4$).[243]

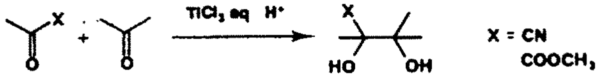


Moreover, hydrogenation of unsaturated dicarboxylic acids can be attained by using $Cp_2Ti(CO)_2$[244] or $TiCl_3$ aqueous;[245] the latter also reduces 2-ene-1,4-diones into saturated diketones.

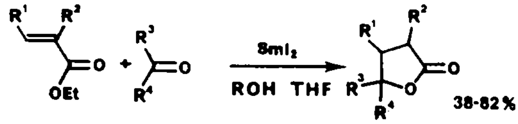
2.7.2. *Acyl chlorides.* In this type of reaction chlorides react not unlike the corresponding acids; some products can be obtained either from the acid or from the acyl chloride.[39,243] Moreover, SmI_2 allows the preparation of symmetrical α-diketones,[246] aldehydes and α-hydroxyketones (when acyl chloride and ketone are mixed coupled.[247] Lastly, symmetrical ketones or methylketones can be obtained by using, respectively, reductive complexes of Fe, Ni[248] or Ti.[156]



2.7.3. *Esters and acyl cyanides.* Clerici and Porta have reported that, in the presence of $TiCl_3$ aqueous, acyl cyanides can undergo a dimerization leading to symmetrical diols; these cyanides can also condense on aldehydes and on saturated or α,β-unsaturated ketones leading to dissymmetrical diols,[249–251] which can at times be allylic.



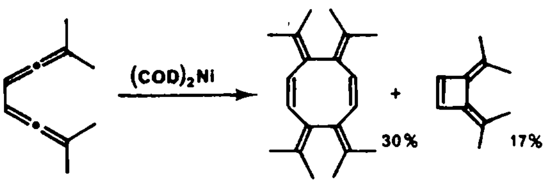
On the other hand, Fukusawa has proposed a reaction using SmI_2 which, from ketones and unsaturated esters, yields γ-lactones.[252]



Lastly, from the esters, alkanes[108] or vinyl ethers[253] can be directly reached using, respectively, Cp_2TiCl_2–Na or Tebbe's reagent.[162]

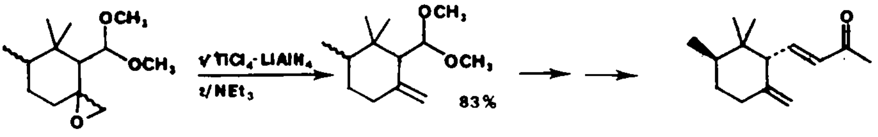
2.8. *Other uses of low valent transition metal complexes*

2.8.1. *On unsaturated hydrocarbons.* Berthelot's works (see Introduction) on alkenes reduction excepted, it is worth noting the works involving V(II),[254] Cr(II)[255] and Ti(O);[256] the latter also allowing reduction of alkynes into alkenes. Ni(O) leads to the reductive dimerization of the 2,7-dimethyl-2,3,5,6-octatetraene.[257]



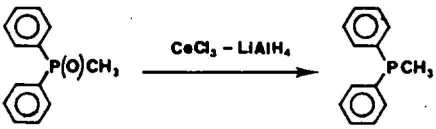
Lastly, VCl_2 enables the dimerisation of tropylium cation.[258]

2.8.2 *On epoxides.* One can observe a deoxygenation, and the formation of an olefin, when an epoxide is treated by McMurry's reagent,[235] $NbCl_5$–$NaAlH_4$,[26] WCl_6–BuLi,[27] WCl_6–$LiAlH_4$,[110] Cr(II),[188,189] Mn(II)[259] or SmI_2.[30] The first has been used by Tochtermann[260] and Takazawa has employed $TiCl_4$–$LiAlH_4$ in the course of his *trans* γ-irone synthesis.[261]



One can also notice that Cp_2TiCl_2–Na in benzene leads to the corresponding alkane.[108]

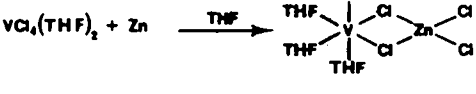
2.8.3. *On sulfoxides, phosphine oxides and enol phosphates.* Low valent titanium species promote the reduction of sulfoxides into sulfides [$TiCl_3$,[262,263] $TiCl_4$–$NaBH_4$,[39] $TiCl_4$–Te(iBu)$_2$[123] and $TiCl_4$–Zn][264,265] and arsine oxides into arsines;[266] a reaction that is also possible using Mo and V(II) complexes[267] or SmI_2.[30] The $TiCl_3$–3K couple reduces enol phosphates into alkenes[268,269] and the $CeCl_3$–$LiAlH_4$ couple reduces phosphine oxides into phosphines.[152]



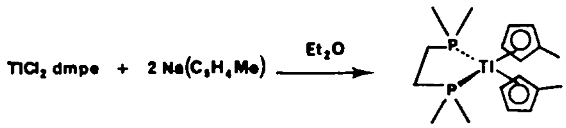
3. MECHANISMS OF ALDEHYDE AND KETONE REDUCTION PROMOTED BY LOW VALENT TITANIUM COMPLEXES

3.1. *Structures of* Ti *and* V *low valent complexes*

Although the X-ray diffraction structures of some low valent complexes of Ti and V are known, none of them, Vohwinkel's expected,[270] which has been successfully used by Corey,[38] has been employed as a reagent in a reductive coupling reaction. Among the examples of low valent vanadium complexes,[271–275] one can mention the complex Caulton *et al.*, obtained $VCl_4(THF)_2$ and Zn in refluxing THF.[275]



We will illustrate the titanium complexes,[276-281] with the one prepared by Wilkinson *et al.*[282]

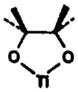


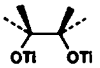
On the other hand, ESR has often been used to study low valent titanium complexes.[283-288]

3.2. *Mechanisms of the duplicative reduction*

There are few texts on the mechanism of this reaction; most authors have postulated a radical mechanism (except in the case of crossed coupling involving diarylketones where the mechanism appears to be an anionic one), but the lack of knowledge concerning the structure of the involved complexes does not make a modelization of these mechanisms any easier.

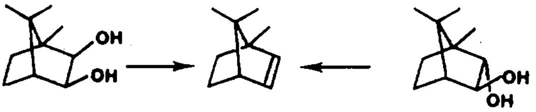
3.2.1. *Coupling of molecules with analogous reduction potentials.* This interesting case has been the subject of much study. As early as the mid seventies, McMurry proposed two possible mechanisms: one involving an acyclic intermediate with two titanium atoms and the other involving a 5-membered cyclic intermediate.[74]



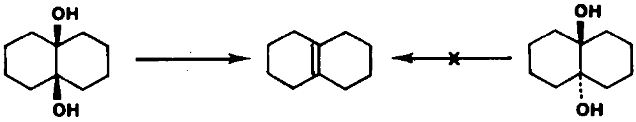


But in 1978, he was to propose a third mechanism.[34] As a matter of fact, neither of the first two proposed intermediates could explain the following results; this study having been carried out after the formation of vicinal diols was proved to be a step in the reaction:

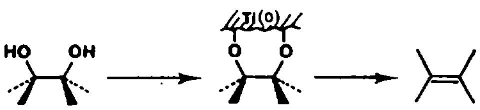
The two isomers of the camphordiol are reduced at a similar rate. This is not consistent with the 5-membered cyclic intermediate; indeed, during the oxidation of the same molecules by $Pb(OAc)_4$ (a reaction in which the existence of a cyclic intermediate is accepted) the *cis*-isomer reacts 10^6 faster than the *trans* isomer.[289]



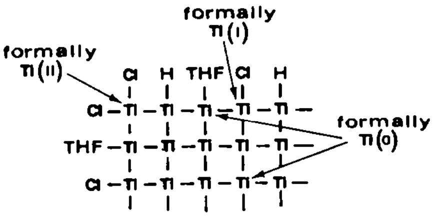
Only the *cis*-isomer of that decalinediol is reduced. The acyclic intermediate fails to explain that selectivity.



So the mechanism that McMurry proposed, which is consistent with these two results and all others, requires that Ti(O) particles are the reactive species in the reaction.

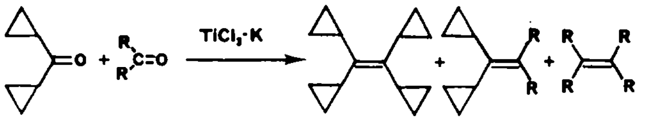


This has been confirmed by the works of Geise,[64] who observed that McMurry's reagent is not crystallised but made of solvated metal particles. He then proposed a model of 'active' titanium.



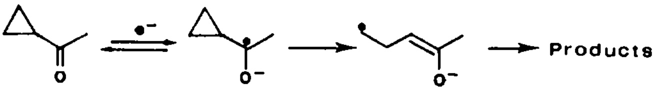
The advantage of this model is that Ti(O), Ti(I) and Ti(II) species coexist. In addition to McMurry's reagent, Geise has also studied the $TiCl_3$–Li and $TiCl_3$–Mg couples.

Meanwhile, it is worth noting that the results found by Nishida (using $TiCl_3$–K)[35] and by some other authors[34,72,80,102,119,290] are not consistent with a radical mechanism.

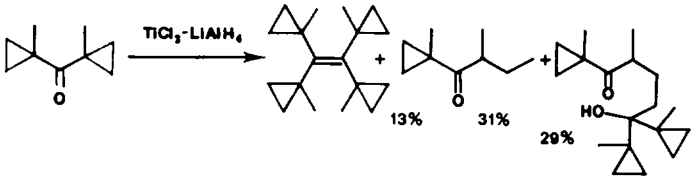


R = $CH(CH_3)_2$	29 %	(	25 %	60 %	15 %)
R = CH_2CH_3	31 %	(	10 %	65 %	25 %)

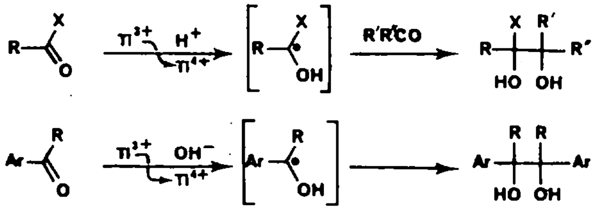
It is well known that the cyclopropylcarbinyl radical anion irreversibly isomerises itself (with a rate constant of $10^8\ s^{-1}$ at 25°C approximatively) into a homoallylic radical anion.[291-294]



As far as we know, only one work[66] reports the formation of products, that could involve a cyclopropylcarbinyl radical, but duplicative alkene is also formed. One can notice that the obtained ketol could result from an homoconjugated addition of an anion.[295]



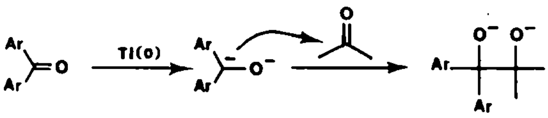
On the other hand, Clerici and Porta have shown that both the symmetrical and dissymmetrical couplings they obtained—in acidic or basic media, under the action of $TiCl_3$ aqueous—involve a radical mechanism.



With $TiCl_3$ aqueous such a mechanism can be correct even when the reaction is carried out with molecules of different reduction potential values; indeed, in an aqueous solution, any dianion would, at once, be protoned and such a phenomenon has not been observed.[296]

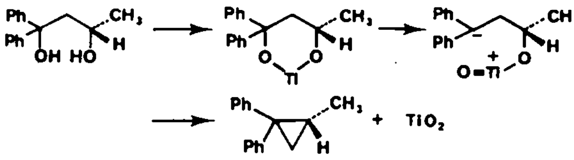
In general, enones lead to the corresponding allylic diols[115] but some of them with particular structures are reduced into ε-diketones.[57,297,298]

3.2.2. *Coupling of molecules with different reduction potentials.* The difference between the reduction potential values of diarylketones and aliphatic ketones has lead McMurry to propose an ionic mechanism. It involves a bielectronic transfer from the complex to the diaryl ketone and then, an attack by the resultant dianion on the aliphatic ketone.[69]



When the reductive dimerization is performed by dihalodicyclopentadienyltitanium species, it has been possible to observe, by X-ray diffraction, the complex which results from the association of the reagent with the diarylketones; it has been noted that the reductive coupling is reversible.[299]

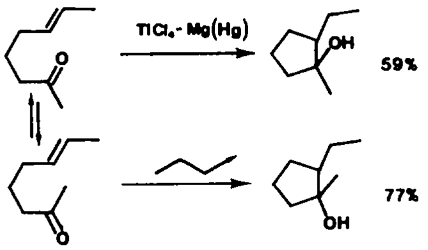
Various works have brought some confirmation of this mechanism;[238,300] Walborsky, in particular, has shown that 1,3-diols cyclize into cyclopropanes with a configuration inversion of one of the carbon atoms, if the other is substituted by two phenyl groups.[238]



The author's explanation is that a diphenylcarbinyl anion attacks the secondary hydroxyl group.

3.3. *δ-Enone cyclization*

The cyclization of a δ-enone promoted by the $TiCl_4$–Mg(Hg) complex leads to the *trans* isomer of the corresponding cyclopentanol (transition state with an overlapping of the double bonds) while the electrolysis of the same molecule leads to the *cis* isomer.[301] This difference in stereoselectivity does not seem to be consistent with an identical mechanism, involving a cetyl radical, in both cases.



4. CONCLUSIONS

All the work done in the last two decades shows that low valent transition metal complexes are reagents that can provoke coupling reductive reactions. These reactions are a good way of creating carbon–carbon bonds, as some syntheses have shown. But surprisingly, all this work has not given rise to a clear mechanism concerning these electronic transfer reactions. This is undoubtedly due to the complicated and often unknown structure of the various reagents used. The complexes of known structure are difficult to prepare so that most organic chemists choose more readily available reagents of unknown structure. The majority of contemporary experiments deal with reductive duplication but there has been mounting evidence of a widening of the field of application of low valent transition metal complexes to other reactions such as carbonyl compounds alkylation and nitrogen derivatives reduction.

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