A comparative study of the McMurry reaction utilizing [HTiCl(THF)$_{\approx 0.5}$]$_x$, TiCl$_3$(DME)$_{1.5}$–Zn(Cu) and TiCl$_2$ · LiCl as coupling reagents *

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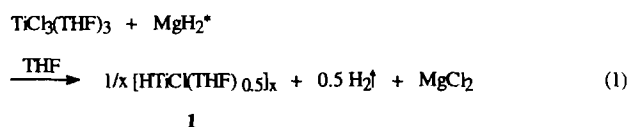*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany*

Abstract

An investigation of the reaction course and stoichiometry of the McMurry reaction of acetophenone utilizing [HTiCl(THF)$_{\approx 0.5}$]$_x$ (THF = tetrahydrofuran), TiCl$_3$(DME)$_{1.5}$–Zn(Cu) (DME = 1,2-dimethoxyethane) and TiCl$_2$ · LiCl as coupling reagents has been undertaken. The detection of 1-phenylethanol (3a) or dideutero-1-phenylethanol (3b) (Schemes 1 and 3) as hydrolysis or deuterolysis products in the early stage of reactions gave the first direct experimental evidence for the occurrence of the "side-on" bonded ketones 3 and 3″ as possible precursors of the pinacolates 4 and 7. This result supports the nucleophilic rather than the radical mechanism for the C–C coupling step of aromatic ketones. Contrary to the current opinion, upon refluxing TiCl$_3$(DME)$_{1.5}$–Zn(Cu) mixtures in DME, no reduction of Ti^{3+} to low valence Ti species could be detected. The reduction of Ti^{3+} by Zn (Scheme 2) only starts in the presence of the carbonyl substrate which is coordinated to the Ti (the "instant method"); both the ketone → pinacolate and the pinacolate → alkene steps (Scheme 2) apparently involve a transient reduction of Ti^{3+} to Ti^{2+} by Zn. This view is supported by experiments in which TiCl$_2$ · LiCl is used as a reagent and in which it behaves as a one-electron reductant (Scheme 3). On the basis of these results, the overall stoichiometry of the McMurry reaction utilizing TiCl$_3$(DME)$_{1.5}$–Zn(Cu) as a reagent can be represented by Eq. (4). High yields (95–97%) of the alkene 2 in acceptable reaction times can already be achieved with an acetophenone: TiCl$_3$(DME)$_{1.5}$: Zn(Cu) molar ratio of 1:2:2. A conclusion which can be drawn from the results is that the McMurry reaction when performed with two of the most commonly applied reagents, namely TiCl$_3$–LiAlH$_4$–THF (in fact HTiCl(THF)$_{0.5}$!) and TiCl$_3$(DME)$_{1.5}$–Zn(Cu)–DME, is mainly associated with changes in the (formal) oxidation state of titanium between Ti^{2+} and Ti^{3+}.

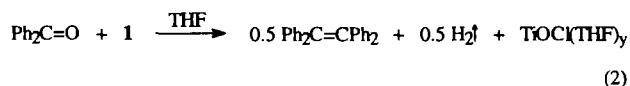*Keywords:* McMurry reaction; TiCl$_3$(1,2-dimethoxyethane); Low valent titanium-ketone complexes

1. Introduction

In a recent publication in this journal [1] we reported the synthesis of a highly reactive hydridotitanium chloride [HTiCl(THF)$_{\approx 0.5}$]$_x$ (1) (THF = tetrahydrofuran) from TiCl$_3$(THF)$_3$ and the catalytically prepared solid (MgH$_2^*$) [2] according to Eq. 1,

$$\text{TiCl}_3(\text{THF})_3 + \text{MgH}_2^*$$

$$\xrightarrow{\text{THF}} 1/x\,[\text{HTiCl(THF)}_{0.5}]_x + 0.5\,\text{H}_2\uparrow + \text{MgCl}_2 \qquad (1)$$

$$\mathbf{1}$$

or from dissolved magnesium hydride [3] in the molar ratio of 1:1 in THF [4]. We were able to demonstrate that 1, and not metallic Ti particles [5], is the active species of the well-known low valence titanium reagent obtained by reduction of TiCl$_3$ with LiAlH$_4$ and utilized in the McMurry reaction [5,6]. Possible structural models for 1 compatible with the extended X-ray absorption fine-structure (EXAFS) results have been proposed and a new interpretation of the mechanism for the McMurry reaction has been presented. Accordingly, the reductive coupling of benzophenone to give tetraphenylethene employing 1 as the reagent can be described by Eq. (2) [1].

$$\text{Ph}_2\text{C=O} + 1 \xrightarrow{\text{THF}} 0.5\,\text{Ph}_2\text{C=CPh}_2 + 0.5\,\text{H}_2\uparrow + \text{TiOCl(THF)}_y \qquad (2)$$

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* Dedicated to Professor H. Brunner on the occasion of his 60th birthday.

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The reduction of $TiCl_3$ (or $TiCl_4$) with magnesium in THF has also been shown not to produce metallic Ti particles but instead soluble complexes $[TiMgCl_2\text{-}(THF)_x]$ and $[Ti(MgCl)_2(THF)_y]$ [7].

In continuation of our studies about the nature of low valence titanium species prepared via different routes and their role in the McMurry and related reactions [1,4,7], in the first section of the present paper we report investigations concerning the reaction course for the McMurry coupling of acetophenone using 1 as a reagent. In this connection, the first direct experimental evidence for the postulated [8,9] "side-on" coordinated ketone as a reaction intermediate will be presented. In the subsequent sections, investigations will be described concerning the reaction course of the reductive coupling of the same substrate utilizing the $TiCl_3(DME)_{1.5}$–Zn(Cu) [10] and the $TiCl_2 \cdot LiCl$ [11] reagents in 1,2-dimethoxyethane (DME). Unexpectedly, it could be shown that the reduction of $TiCl_3$ by Zn(Cu), which triggers off the C–C coupling, can only take place if the ketone substrate is coordinated to the $TiCl_3$ center (the "instant method" [9b]). In conclusion, common features of the reaction course for the McMurry reaction utilizing these three reagents, will be discussed.

2. The reductive coupling of acetophenone induced by $[HTiCl(THF)_{\approx 0.5}]_x$

The reaction of acetophenone with 1 in the molar ratio of 1:2 in THF between −70 and +66°C takes place with evolution of about 0.5 mol of H_2 per mole of

Ti and gives 2,3-diphenyl-2-butene (2) with greater than 70% isolated yield:

$$+ \ TiOCl(THF)_y \qquad\qquad (3)$$
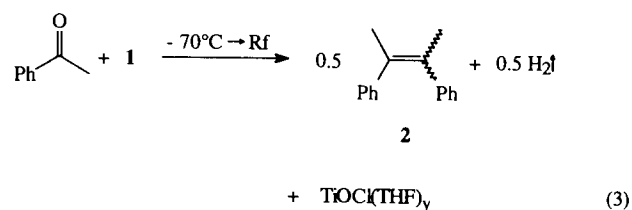
The course of the coupling reaction (Eq. (3)) was studied in the same manner as described for the benzophenone case [1], except that the reaction was started at −70°C. The reaction profile is presented in Fig. 1. As has already been shown for benzophenone [1], the reaction proceeds via the Ti–pinacolate intermediate (− − −). In addition to 2 and pinacol (4a), two further (hydrolysis) products of the reaction, 1-phenylethanol (3a) and 2,3-diphenyl-2-butanol (5) [12], were detected. Compound 3a amounts to 20–25% at the beginning and tends to zero in the further course of the reaction. It thus appears that 3a could be the hydrolysis product of the postulated [8,9] "dianion intermediate" 3 (Scheme 1). As indeed could be shown, deuterolysis of a sample of the reaction mixture at low temperature gave dideutero-1-phenylethanol (3b) with 98% deuteration in the 1-position. This result indicates the occurrence of a "side-on" coordinated ketone 3 as a precursor of the pinacolate 4 (Scheme 1). The existence of "dianions" of aromatic ketones has been demonstrated by us [13] and by others [14] via X-ray crystal structure determinations of dilithium benzophenone and of ytterbium benzophenone respectively. In both cases, the carbonyl group of
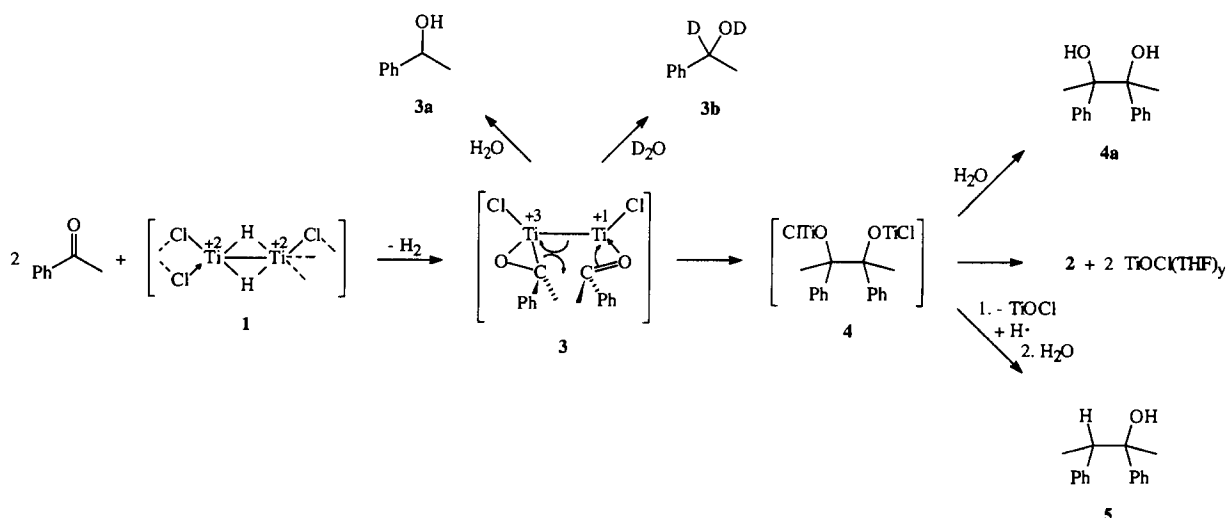
Scheme 1. The superscripts on titanium denote the formal oxidation state of the metal.
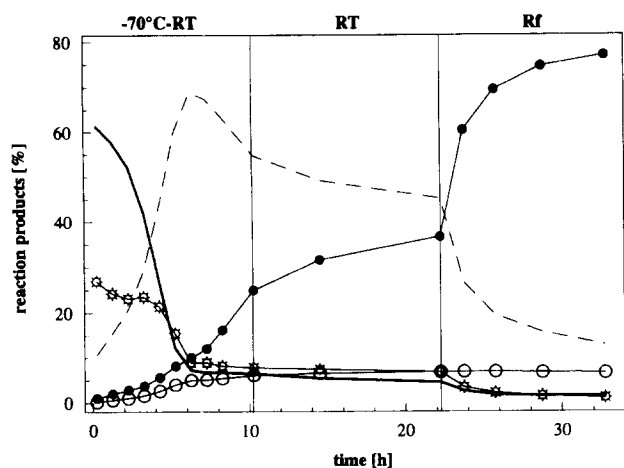
Fig. 1. The progression of the coupling reaction of acetophenone in THF utilizing [HTiCl(THF)$_{\approx 0.5}$]$_x$ (1) as the reagent; ———, acetophenone; ●, 2,3-diphenyl-2-butene (2); ✩, 1-phenylethanol (3a); - - - - -, 2,3-diphenyl-2,3-butanediol (4a); ⊖, 2,3,-diphenyl-2-butanol (5); RT, room temperature, Rf, reflux temperature.

the ketone ligand is "side on" attached to the metal. Complexes of Zr and Hf with "side-on" coordinated aldehydes have shown to be intermediates in C–C coupling reactions [15].

The interception of a "side-on" coordinated ketone as an intermediate in a McMurry reaction clearly points out the nucleophilic and not to the radical mechanism for the C–C coupling step of aromatic ketones [16]. According to the former mechanism and taking into account the structural models proposed for 1 on the basis of EXAFS [1], the C–C coupling can be envisaged to take place on the surface of [HTiCl(THF)$_{\approx 0.5}$]$_x$ particles, as represented in Scheme 1. As the hydride ligand in 1 is displaced by the ketone (evolution of hydrogen at the early stage of the reaction! [1]), the latter becomes "side on" coordinated to the titanium 3. Subsequent C–C bond formation affording pinacolate 4 occurs by a nucleophilic attack of the "side-on" coordinated ketone on the carbonyl group of an adjacent complexed (but not reduced) ketone. Alternatively, the C–C bond formation can take place by a nucleophilic attack of 3 on a free ketone molecule (not shown in Scheme 1).

3. The reductive coupling of acetophenone utilizing the TiCl$_3$(DME)$_{1.5}$-Zn(Cu) reagent

In 1989, McMurry et al. [10] proposed an optimized, now widely applied procedure [17] for carrying out the low-valence-titanium-induced carbonyl coupling reactions. The experimental procedure consits of heating the complex TiCl$_3$(DME)$_{1.5}$ with an excess of Cu-activated Zn (the so-called zinc–copper couple, denoted as Zn(Cu)) in DME for 2–4 h to reflux in order to form the active coupling reagent. It has been assumed that the active reagent is Ti(0) [5b]. The reagent and the carbonyl substrate are subsequently heated to reflux for several hours which affords high yields of alkenes [10].

Recently, however, Fürstner et al. [9b] put forward the so-called "instant method" for cyclizations of aromatic acylamido compounds to indoles [9a] in which they deliberately avoided the established two-step procedure commonly used for McMurry reactions [5b,10], but instead heated TiCl$_3$ with Zn dust in DME in the presence of substrates. Accordingly, the Lewis acidity of TiCl$_3$ is used to coordinate the substrate to titanium prior to reduction. It has been intuitively assumed that "upon treatment with, for example, Zn dust,...,the TiCl$_3$ will be reduced within the complex unit formed in situ". Using the instant method, excellent results in the synthesis of rather complicated indole ring containing natural products [9] or polynuclear systems [18] and also in coupling of simple aldehydes and ketones to alkenes [9b] have been achieved.

In view of a large number of synthetic applications and increasing significance of the TiCl$_3$(DME)$_{1.5}$-Zn-DME system, we wished to gain an insight into the nature of the active Ti species in this system, whether it be generated in the absence [10] or in the presence of carbonyl substrates [9b,c].

3.1. Attempted reduction of TiCl$_3$(DME)$_{1.5}$ by Zn in DME

Experiments aimed at the reduction of the TiCl$_3$(DME)$_{1.5}$ complex by Zn in DME were carried out using Zn(Cu) [10], Zn(Cu) in the presence of pyridine [19], and the active form of Zn prepared from

Table 1
Attempted reduction of TiCl$_3$(DME)$_{1.5}$ by Zn in DME (reflux temperature, 20 h)

Entry	Zn	Ti:Zn molar ratio [a]	Solid		Filtrate	
			Ti:Zn:Cl	Color	Ti:Zn:Cl	Color
1	Zn(Cu)	1:4.2	1:4.6:3.0	Grey	1:0.04:2.9	Green
2	Zn(Cu)–pyridine	1:2.1	1:2.6:3.1	Green	1:0.3:3.5 (2.9) [b]	Dark green
3	Zn*	1:3.6	1:4.4:3.4 (3.1) [c]	Greyish	1:0.2:3.4 (2.9) [b]	Brown

[a] Of the experiment.
[b] Corrected value under the assumption that Zn exists combined as ZnCl$_2$.
[c] Corrected value which takes into account that Zn* contains some Cl.

Table 2
Reaction of the solids and of the filtrates from the Table 1 with acetophenone in DME (molar ratio Ti:acetophenone, 1:1–2; reflux temperature, 20 h)

Entry	Zn	Reaction products [a] (%)					
		Solid			Filtrate		
		2	4a	5	2	4a	5
1	Zn(Cu)	79.8	14.4	5.6	0	0	0
2	Zn(Cu)–pyridine	77.7	14.6	7.2	0	0	0
3	Zn*	90.3	6.9	2.1	18.3	0.8	0.4

[a] The difference with respect to 100% gives the amount of acetophenone.

$ZnCl_2$ and magnesium anthracene · 3THF in THF(Zn*) [20]. The $TiCl_3(DME)_{1.5}$–Zn–DME suspension was heated to reflux for 20 h (cf. [10]) and filtered; the resulting solids and filtrates were analyzed separately. From the analyses (Table 1), it can be concluded that both solids and the filtrates contain Ti and Cl in approximately 1:3 atomic ratio and that the filtrates contain very low amounts of Zn. The results of the reactions of the solids and of the filtrates with acetophenone (Table 2) showed unequivocally that each of the solids behaved

as an active coupling reagent, while the filtrates only in the case of Zn* exhibited some (although very low) coupling activity.

Surprisingly, however, a close investigation of the solids (Table 1) as the active coupling reagents has demonstrated that they were still mixtures of $TiCl_3(DME)_{1.5}$ with the zinc component, i.e. that, during the lengthy boiling period in DME, no reduction of $TiCl_3(DME)_{1.5}$ by zinc has taken place.

The methods of investigation and their results are summarized in the following:

(1) The X-ray diffraction pattern of the solids (Fig. 2), neglecting pyridine, can only be assigned to $TiCl_3(DME)_{1.5}$ and zinc.

(2) A combined transmission electron microscopy–energy dispersive X-ray inspection of the $TiCl_3$-$(DME)_{1.5}$–Zn(Cu) solid (Table 1, entry 1) has demonstrated a pronounced heterogeneous character of the sample; via energy-dispersive X-ray analyses of the particles, regions with high Zn content side by side of those with high Ti content were identified.

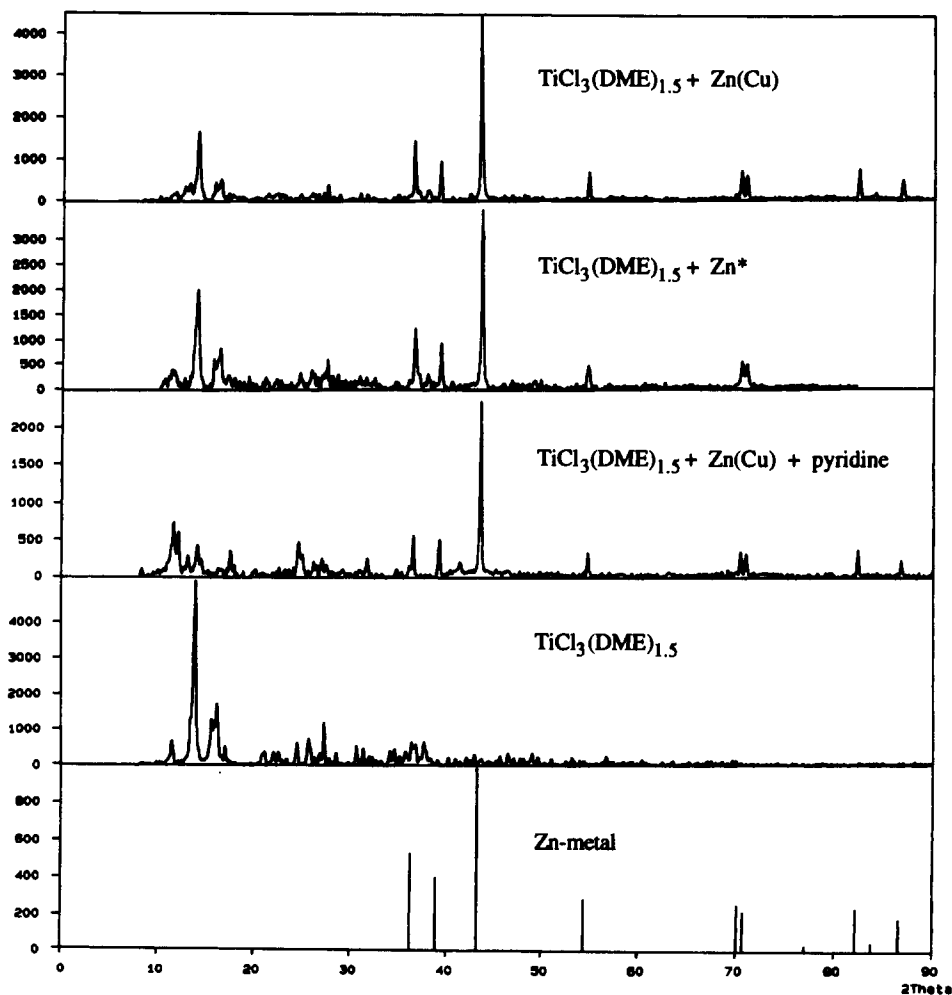(3) The IR-spectra of the samples (Table 1) in the region of absorption bands of coordinated DME have

Fig. 2. XRD patterns of the solids from Table 1 in comparison with that of $TiCl_3(DME)_{1.5}$ and Zn metal.

proved to be identical with that of TiCl$_3$(DME)$_{1.5}$. Formation of low valence Ti–Cl–DME complexes would be expected to cause a change in IR spectra in this region.

(4) The far IR (FIR) spectra of the samples (Fig. 3) have revealed no other Ti–Cl stretching frequencies except that of TiCl$_3$(DME)$_{1.5}$ at 342 cm^{-1}.

The filtrates (Table 1) proved to contain mainly dissolved TiCl$_3$(DME)$_{1.5}$ and small amounts of Zn. The changes in color observed during the boiling period of mixtures (Table 1) can be explained by partial DME cleavage by metallic Zn and/or exchange of DME in TiCl$_3$(DME)$_{1.5}$ by other electron donors. The slight coupling activity of the filtrate in the case of Zn* (Table 2) can be attributed to the dissolved TiCl$_3$(DME)$_{1.5}$ in combination with highly dispersed non-filterable Zn particles.

As the experiments described below will show, the reduction of Ti^{3+} by Zn only starts off in the presence of coordinated carbonyl substrate. The refluxing of the reaction mixture before addition of the latter can thus be omitted, i.e. the McMurry reaction using the TiCl$_3$(DME)$_{1.5}$–Zn–DME system, takes place in any case "according to the instant method" [9b].

3.2. Reaction course and stoichiometry of the reductive coupling of acetophenone utilizing the TiCl$_3$(DME)$_{1.5}$–Zn(Cu) reagent in DME

Since in the absence of a carbonyl substrate no reduction of TiCl$_3$(DME)$_{1.5}$ by Zn in boiling DME occurs (Section 3.1), the complexation of the carbonyl to TiCl$_3$ appears to be the essential prerequisite for the McMurry reaction using Zn as a reductant. The complexation of the acetophenone to TiCl$_3$ can indeed be demonstrated by the shift of the carbonyl stretching frequency from 1680 to 1620 cm^{-1} upon addition of acetophenone to a suspension of TiCl$_3$(DME)$_{1.5}$ in DME (Fig. 4).

We have therefore to admit that the McMurry reaction of acetophenone using TiCl$_3$(DME)$_{1.5}$–Zn(Cu) as a reagent begins with a reduction of a TiCl$_3$–acetophenone complex (6) (Scheme 2) by Zn(Cu). It can be assumed that the coordination of acetophenone to Ti^{3+} causes a
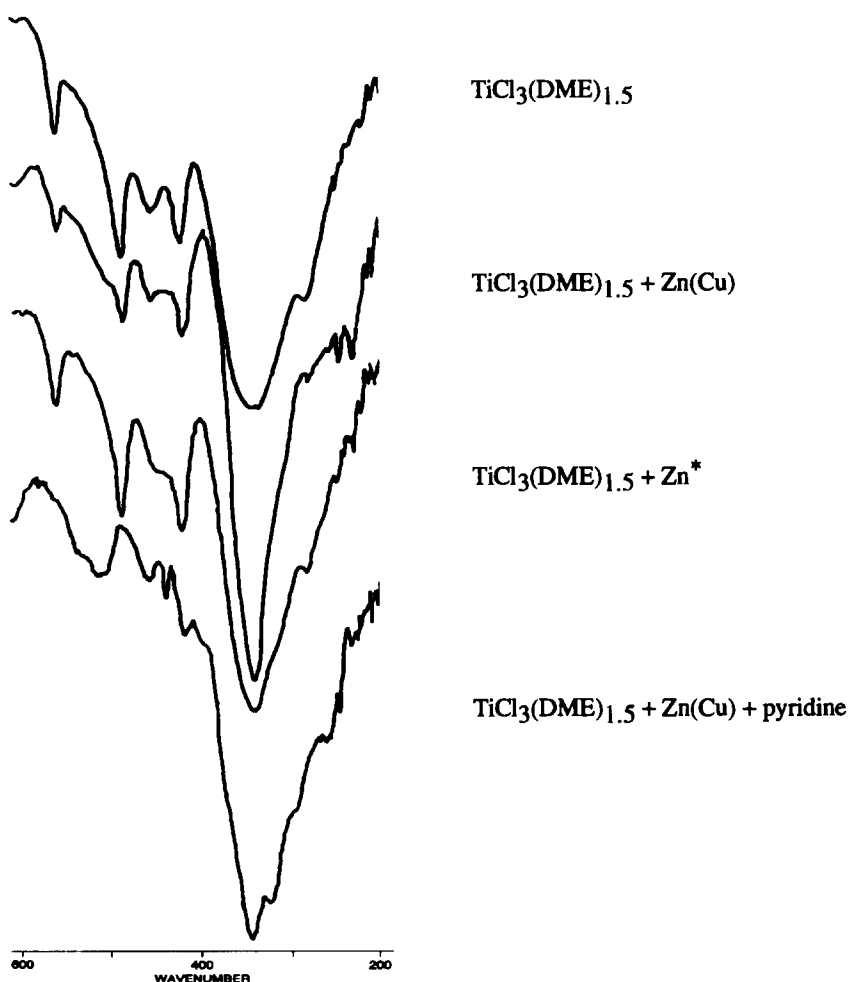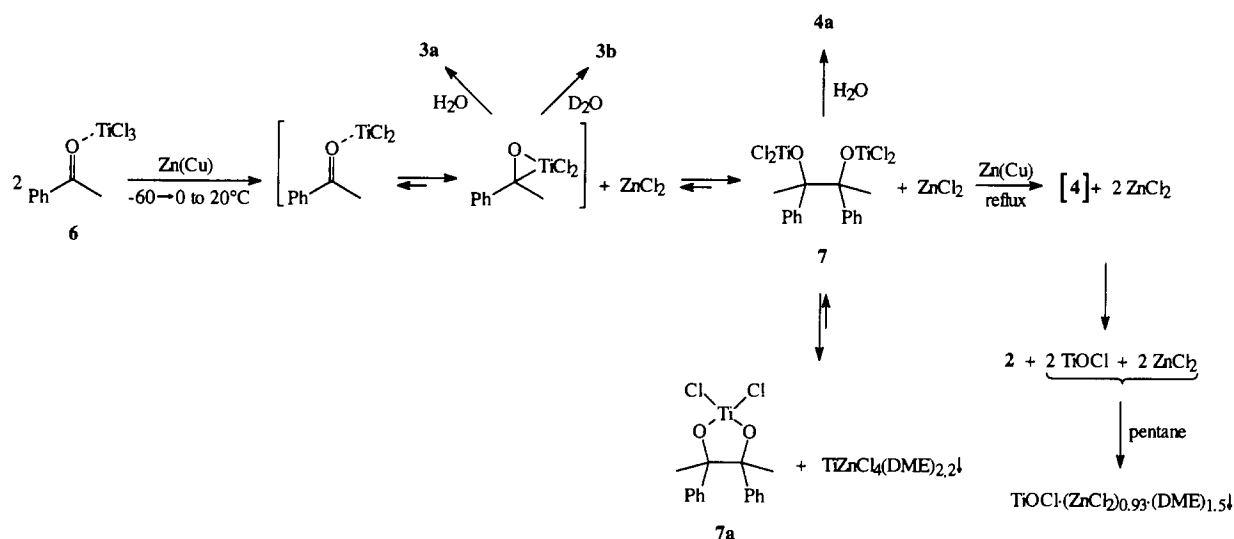

TiCl$_3$(DME)$_{1.5}$

TiCl$_3$(DME)$_{1.5}$ + Zn(Cu)

TiCl$_3$(DME)$_{1.5}$ + Zn*

TiCl$_3$(DME)$_{1.5}$ + Zn(Cu) + pyridine

WAVENUMBER

Fig. 3. FIR spectra of the solids from Table 1 in comparison with that of TiCl$_3$(DME)$_{1.5}$.

Scheme 2.

lowering of the reduction potential which renders possibly the reduction of 6 by Zn. This idea is supported by experiments showing that the McMurry reaction can be realized with reducing agents which are still weaker than Zn (see text at the end of this section).

The reaction profile of the McMurry reaction utilizing $TiCl_3(DME)_{1.5}$–Zn(Cu) as a reagent was determined in the same way as described in Section 2 and is represented in Fig. 5. A striking feature of the reaction profile (Fig. 5) is that from 0°C to room temperature the reaction can be completely stopped at the pinacolate stage; heating of the reaction mixture to reflux then leads to quantitative conversion of the pinacolate to the alkene 2. This gives, as shown in the following, the possibility to investigate separately the composition of

Fig. 4. Carbonyl region of the IR spectra of (a) neat acetophenone and (b) the solid $TiCl_3$·acetophenone (KBr).

the reaction mixture and the oxidation state of titanium in the pinacolate and in the final stage of the reaction and thus to establish the stoichiometry for both of these reaction steps.

Acetophenone, $TiCl_3(DME)_{1.5}$ and Zn(Cu) in the molar ratio of 1:1:2.3 were allowed to react in DME at a temperature ranging from −50 to 0°C and the unreacted Zn(Cu) then separated from the solution by filtration. After the solution was allowed to stay for 15 h at 0°C, a violet-colored solid of the composition $TiZnCl_4(DME)_{2.2}$ precipitated out of the solution. The composition of the solute in the remaining solution was found to correspond to $7a \cdot (ZnCl_2)_{0.3}(DME)_{1.0}$. The low solubility of the "$TiZnCl_4$–DME complex" apparently causes the initial pinacolate 7 to disproportionate, affording Ti^{2+} and Ti^{4+} complexes $TiZnCl_4$ and 7a (Scheme 2). Taking into account the compositions and the amounts of both the solid $TiZnCl_4(DME)_{2.2}$ and of the solute $7a \cdot (ZnCl_2)_{0.3}(DME)_{1.0}$, the composition of the reaction mixture in the pinacolate stage is calculated to correspond to $7 + ZnCl_2$ (Scheme 2). From these results it becomes evident that the reaction of the acetophenone–$TiCl_3$ complex 6 with Zn(Cu) up to the pinacolate stage of 7 requires the consumption of 1 mol of Zn(Cu) per mole of 7, i.e. abstraction of one Cl atom from each mole of 6. The oxidation state of Ti in 7 should thus be +3.

In a further experiment, acetophenone, $TiCl_3(DME)_{1.5}$ and Zn(Cu) in the molar ratio of 1:1:1 were heated to reflux in DME for 48 h (Table 3, entry 4) giving alkene 2 with an 84% isolated yield. Thereby it was found that the Zn(Cu) couple was completely consumed. Addition of pentane to the solution gave a 12–13% yield (with respect to Zn) of a grayish precipitate having the composition $TiOCl \cdot (ZnCl_2)_{0.9}(DME)_{1.5}$. Both the consumption of approximately 1 mol of Zn(Cu) per mole of
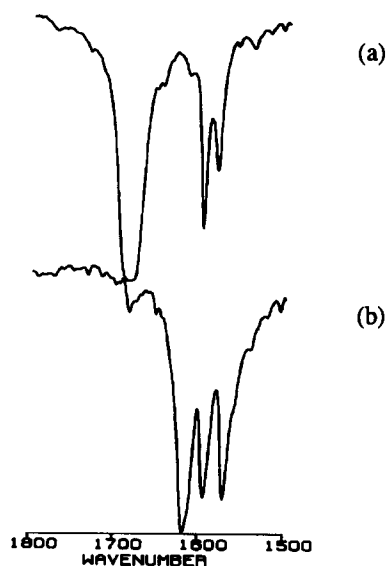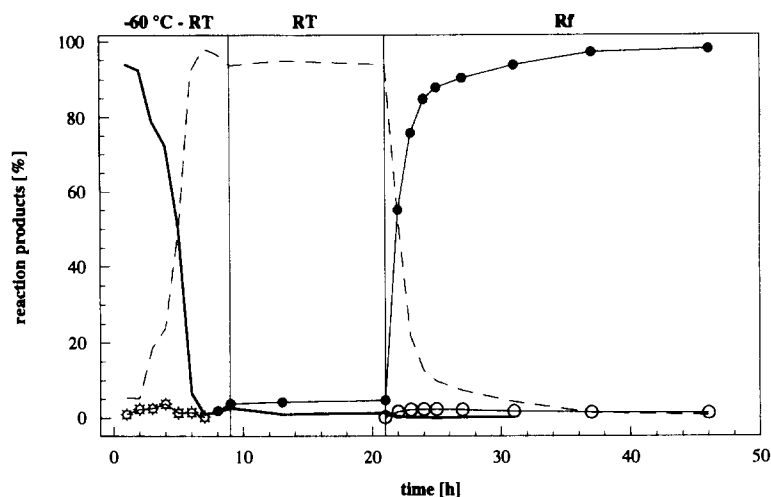
Fig. 5. The progression of the coupling reaction of acetophenone in DME using TiCl₃(DME)₁.₅–Zn(Cu) as the reagent (molar ratio, 1:4:16): ———, acetophenone; ●, 2,3-diphenyl-2-butene (2); ✡, 1-phenylethanol (3a); -----, 2,3-diphenyl-2,3-butanediol (4a); ⊖, 2,3,-diphenyl-2-butanol (5); RT, room temperature; Rf, reflux temperature.

2 and the final inorganic product of the reaction, found to be TiOCl · (ZnCl₂)₀.₉(DME)₁.₅, prove that the pinacolate **7** → alkene **2** step of the reaction (Scheme 2) requires an additional mole of Zn(Cu) per mole of **2**, so that the pinacolate **4** (the same as in Scheme 1) as an intermediate is involved. The overall stoichiometry of

Table 3

Reductive coupling of acetophenone (AC) in DME utilizing TiCl₃(DME)₁.₅–Zn(Cu) as the reagents; effect of the reaction temperature and of the variation in the molar ratio of the reactants

Entry	AC : TiCl₃(DME)₁.₅ : Zn(Cu)	Reaction temperature [a] (°C)	Reaction time (h)	Reaction products [b] (%)		
				AC	4a	2
1	1:0.5:0.5	0	1.5	3.8	93.8	2.3
		RF	16.5	9.4	38.4	36.8
		RF	161.5	5.2	7.9	46.9
2	1:1:0.5	0	1.5	2.1	95.4	2.5
		RF	16.5	15.7	7.2	69.2
		RF	161.5	1.0	0.2	74.1
3	1:1:1	0	1.5	1.0	94.5	3.6
		RF	16.5	0.5	19.6	76.5
		RF	161.5	0	3.7	93.5
4	1:1:1	RF	48			84 [c]
5	1:2:1	0	1.5	2.2	96.2	1.6
		RF	16.5	0	3.3	93.7
		RF	161.5	0	1.7	93.9
6	1:2:2	0	1.5	0.7	97.5	1.9
		RF	16.5	0	3.3	94.9
		RF	40.5	0	1.6	97.0
7	1:2:2	RF	48			97 [c]
8	1:4:16	−60 → 0	7	1.0	98.0	0
		RF	46	0	0.7	98.0
9	1:4:18	RT	0.25	1.6	94.4	3.6
10	1:4:16	0	2		97 [c]	
11	1:4:15	RF	48			97 [c]

[a] RF, reflux temperature; RT, room temperature.

[b] After hydrolysis.

[c] Isolated yield.

Table 4

Reductive coupling of acetophenone (AC) in DME utilizing $TiCl_2 \cdot LiCl$ as the reagent; effect of the reaction temperature and of the variation of the molar ratio of the reactants

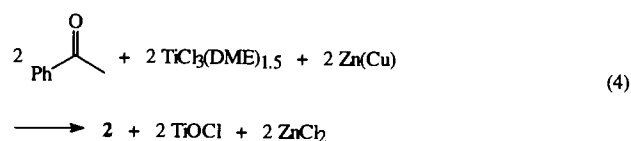| Entry	AC : TiCl$_2$ · LiCl	Reaction temperature [a] (°C)	Reaction time (h)	Reaction products [b] (%)		
				AC	4a	2
1	1 : 1	−70 → 20	9	4.1	91.4	1.1 [c]
		20	15			
		RF	93	28.5	16.2	46.0 [c]
2	1 : 2	20	0.5			
		RF	48			90 [d]
3	1 : 4	RF	48			91 [d]

[a] RF, reflux temperature.
[b] After hydrolysis.
[c] See Fig. 6.
[d] Isolated yield.

the McMurry reaction for the present case can thus be described by

$$2 \underset{Ph}{\overset{O}{\|}} + 2\,TiCl_3(DME)_{1.5} + 2\,Zn(Cu)$$

$$\longrightarrow 2 + 2\,TiOCl + 2\,ZnCl_2 \qquad (4)$$

The reaction course presented in Scheme 2 and the stoichiometry of reaction (Eq. (4)) were further supported by the experiments in which the acetophenone: $TiCl_3(DME)_{1.5}$:Zn(Cu) molar ratio was varied (Table 3). Using the 1:0.5:0.5 molar ratio of the components (entry 1) a yield of alkene 2 of maximally about 50% but a high yield of pinacol 4a (93.8%) can be achieved. The pinacol formation in this case can be envisaged to
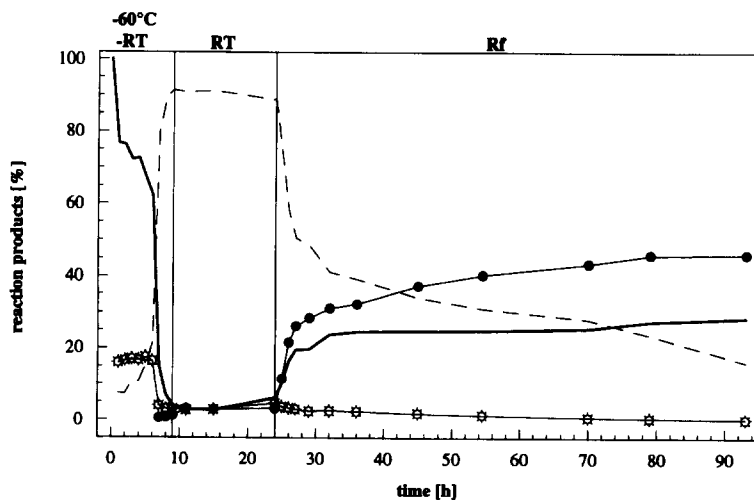
proceed via intermediate 3′ (related to 3, Scheme 1) and the pinacolate 7a:

$$2 \underset{Ph}{\overset{O}{\|}} \xrightarrow[- 0.5\,ZnCl_2]{\begin{array}{c}TiCl_3(DME)_{1.5},\\0.5\,Zn(Cu)\end{array}} \left[\begin{array}{c}Cl\;\;Cl\\Ti\cdots O\\O\cdots\\Ph\;\;Ph\end{array}\right]$$

$$\mathbf{3'}$$

$$\xrightarrow{} \begin{array}{c}Cl\;\;Cl\\Ti\\O\;\;O\\\\Ph\;\;Ph\end{array} \xrightarrow{H_2O} \mathbf{4a}$$

$$\mathbf{7a}$$

$$(5)$$

Fig. 6. The progression of the coupling reaction of acetophenone in DME with $TiCl_2 \cdot LiCl$ as the reagent (molar ratio, 1:1): ——, acetophenone; ●, 2,3-diphenyl-2-butene (2); ✡, 1-phenylethanol (3a); -----, 2,3-diphenyl-2,3-butanediol (4a); RT, room temperature; Rf, reflux temperature.

From the 1:1:1 molar ratio upwards (entries 3–8 and 11), in accordance with Eq. (4), in all cases high yields of alkene 2 can be attained. With increasing amounts of the Ti and Zn reagents, however, the pinacolate → alkene transformation becomes more rapid. Since already using the 1:2:2 molar ratio of the reactants (entries 6 and 7) 95% yield of the alkene after 16.5 h reflux time, or 97% isolated yield after 48 h reflux time, can be achieved, use of a large excess of the reagents (entries 8 and 11) is not necessary. With a 1:2:2 molar ratio of the reactants, high yields of the alkene 2 (90–92%) can also be reached when Fe or Sn powders in place of Zn powder are applied as reducing agents. On the basis of standard potentials for Fe and Sn ($E_0 = -0.44$ and -0.14 V respectively) the reduction of Ti^{3+} ($E_0 = -1.62$ V) by these reductants as well as by Zn ($E_0 = -0.76$ V) is highly improbable. Also, in these cases, the lowering of the reduction potential of the system by coordination of the ketone to the Ti^{3+} center appears to be the decisive factor for the reaction.

4. Reductive coupling of acetophenone using $TiCl_2$ · LiCl as a reagent

$TiCl_2$ in the presence of 2LiCl in THF has recently been applied by Eisch et al. [11] as a reagent, to effect among others the reductive coupling of aliphatic and aromatic aldehydes and ketones to a mixture of pinacols and/or alkenes in varying proportions. In the case of acetophenone, two equivalents of $TiCl_2$ to ketone gave an 83% yield of pinacol, while a 4:1 ratio of $TiCl_2$ to ketone produced 88% of alkene. It has been assumed that $TiCl_2$ can act as a two-electron donor and that the pinacol formation involves Ti^{4+} cyclic intermediates.

In order to lend support to the proposed reaction Scheme 2, we reacted acetophenone with $TiCl_2$ · LiCl [11] in DME using 1:1, 1:2 and 1:4 molar ratios of reactants (Table 4). Fig. 6 shows the profile of the 1:1 molar ratio reaction. From the figure it can be seen that the 1:1 molar ratio of the reactants causes the forma-

tion of the pinacolate 7 (Scheme 3) with a high yield at room temperature. At the reflux temperature and in the absence of a sufficient reductant, however, the alkene 2 reaches a maximum yield of only 46%. The formation of alkene is accompanied by a partial reversion to acetophenone (Fig. 6). This indicates the reversibility of the pinacolate formation process [21]. The reversal of the pinacolate formation process probably liberates (some) $TiCl_2$ required as a reducing agent for the pinacolate → alkene step (Scheme 3). This result suggests that in the present case $TiCl_2$ can act as a single- rather than as a two-electron donor. Accordingly, the application of 1:2 or 1:4 acetophenone to $TiCl_2$ reagent affords in both cases the alkene 2 with high yields (entries 2 and 3; 91% isolated yield).

Of interest again is the detection of the hydrolysis product 1-phenylethanol (3a) (Fig. 6) (yield, 15–18%) at the beginning of the reaction. A corresponding deuterolysis experiment also gave dideutero-1-phenylethanol (3b) (100% deuterium in 1-position) in this case (cf. Section 2). In the present case the "side-on" coordinated ketone complex could be a Ti^{3+} (3'', Scheme 3) as well as a Ti^{4+} species (Scheme 2).

5. Concluding remarks

The presented results concerning the stoichiometry and the reaction course of the reductive coupling of acetophenone using three different reagents permit a generalized look at the mechanism of the McMurry reaction. In the case of [HTiCl(THF)$_{\approx 0.5}$]$_x$ (1) as a reagent, during the course of the reaction (Scheme 1), titanium is oxidized from a formal valence state of 2 + (in the reagent and in the pinacolate intermediate 4) to +3 (in 3 and in TiOCl). However, as a result of the homolytic dissociation of the hydride ligand, an additional electron is left over for the reaction. Hence 1 behaves as a (strong) two-electron reducing agent, and the 1:1 ketone:1 molar ratio is sufficient in order to achieve a high yield of alkene 2. On the contrary, $TiCl_2$
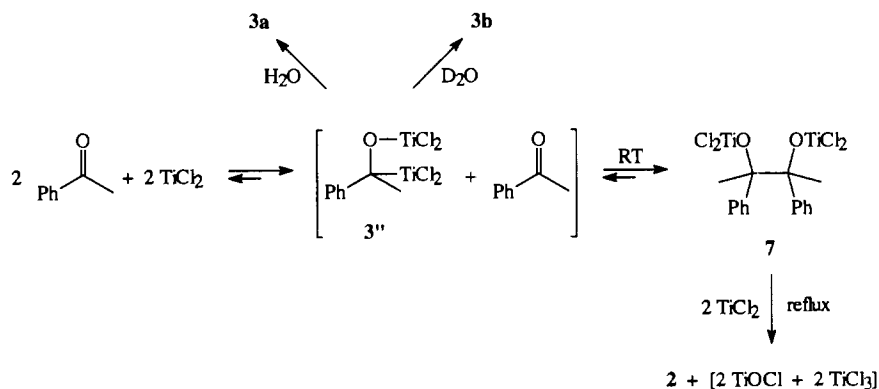
Scheme 3.

acts apparently (about 50% yield of alkene with a 1 : 1 ratio of reactants) as a single-electron donor, so that again during the reaction (Scheme 3) titanium is oxidized from 2 + to 3 + . The results concerning the coupling reaction when using $TiCl_3(DME)_{1.5}$–Zn(Cu) as a reagent (Scheme 2) demonstrate quite clearly that a one-electron reduction of Ti^{3+} by Zn is included in each of the two reaction steps. The reaction thus involves (transient) Ti^{2+} intermediates. The reduction Ti^{3+} by the weak reducing agent Zn is, however, only possible if the reduction potential of Ti^{3+} is lowered by coordination of the carbonyl substrate. The slow generation (and thus low stationary concentration of the reactive Ti^{2+} species over the course of the reaction in this case) may be one of the reasons for the high yields of alkenes achieved when this method is applied.

6. Experimental details

X-ray diffraction (XRD) spectra were measured at λ (Cu $K\alpha_1$) = 154.0598 nm. Elemental analyses were carried out by: Dornis & Kolbe, Mülheim an der Ruhr. Vacuum definitions are as follows: vacuum, 10^{-2} mbar; high vacuum, less than 10^{-3} mbar.

The starting material α-TiCl$_3$ (purity, 99%; Aldrich) was kept for 24 h in a high vacuum in order to remove TiCl$_4$. Acetophenone was dried over a molecular sieve (4 Å) and distilled. [HTiCl(THF)$_{\approx 0.5}$]$_x$ (1) was prepared according to literature data [1]. TiCl$_3$(DME)$_{1.5}$ and the Zn(Cu) were prepared according to published procedures [10]. The active zinc (Zn*) [20b] was obtained as follows: to a suspension of 107 mmol of magnesium anthracene in 500 ml of THF (prepared in situ from 2.61 g (107 mmol) of Mg powder (270 mesh) and 21.36 g (120 mmol) of anthracene [22] were added under stirring in small portions 14.63 g (107 mmol) of water-free ZnCl$_2$ which was dried in high vacuum for 24 h at 160°C. The suspension was stirred for 72 h at room temperature and filtered; the resulting Zn* thoroughly washed with THF and dried in a high vacuum. Zn* (7.26 g) was obtained as a grey powder with the following composition: Zn, 89.21; Mg, 1.04; Cl, 4.11; C, 3.12; H, 0.55%. To obtain TiCl$_2$ · LiCl [11], 140 ml of a 1.6 M solution of n-C$_4$H$_9$Li in hexane (224 mmol) were added dropwise over a period of 1.5 h to a suspension of 22.10 g (143 mmol) of α-TiCl$_3$ in 250 ml of pentane (slightly exothermic reaction!). The suspension was stirred for 1 h at room temperature and filtered; the solid on the frit washed with pentane and dried in vacuum. TiCl$_2$ · LiCl (21.48 g) was obtained as a green air-sensitive powder. Anal. Found: Ti, 29.28; Li, 4.36; Cl, 65.31; C, 0.44; H, 0.24. Calc.: Ti, 29.71; Li, 4.31; Cl, 65.99%. FIR (polyethylene): ν 260 cm^{-1}, broad shoulders in the 350–280 cm^{-1} region. XRD Cu $K\alpha$: 2θ (relative intensity): 14.5439 (32.2), 28.2477

(18.5), 29,5655 (42.8), 34.2576 (100), 45.0314 (11.2), 49.2664 (82.8), 61.3736 (23.0), 82.3934 (28.7).

THF was heated under reflux over magnesium anthracene [22] and distilled. DME was distilled over NaAlEt$_4$, pentane over Na–K alloy, and pyridine over LiAlH$_4$.

All reactions and operations with air-sensitive materials were performed under argon in air- and water-free solvents.

6.1. 2 from acetophenone and 1

1.44 g (12.0 mmol) of acetophenone were added at −70°C to a stirred suspension of 2.94 g (23.4 mmol of Ti content) of 1 in 50 ml of THF. The suspension was warmed over 5 h to room temperature and heated to reflux for 48 h. After the addition of 50 ml of pentane, the suspension was filtered over silica gel and the inorganic residue washed with pentane. Removal of the solvents afforded a yellow oil which was purified by flash chromatography (silica–pentane). 0.90 g (72%) of 2 were obtained as a colorless solid with a Z : E ratio of 2 : 1 (for analytical data see below).

6.2. Investigation of the reductive coupling of acetophenone using 1 (Fig. 1)

The starting materials were 1.06 g (8.4 mmol of Ti content) of 1 and 0.95 g and 0.95 g (7.9 mmol) of acetophenone in 25 ml of THF. The reaction was started at −70°C and the temperature raised to room temperature at 10°C h^{-1}. After stirring for 12 h at room temperature the reaction mixture was heated to reflux. At defined intervals, 0.4 ml samples were taken from the reaction mixture by means of a pre-cooled pipette, immediately quenched with 2.5 ml of H$_2$O and extracted with 2.5 ml of ether; the extracts dried over MgSO$_4$. The ether extracts were analyzed by gas chromatography (GC) or by GC–mass spectroscopy (MS) coupling analysis. One of the samples taken from the reaction at −40°C and quenched with D$_2$O contained 23.5% of deutero-1-phenylethanol (3b) with a deuteration grade in 1-position of 98%, according to the GC–MS analysis.

6.3. Attempted reduction of TiCl$_3$(DME)$_{1.5}$ by Zn in DME (Tables 1 and 2)

The general procedure was as follows. TiCl$_3$(DME)$_{1.5}$ and Zn(Cu) or Zn* were suspended in DME and heated to reflux over 20 h. The cooled suspensions were filtered and the solids washed with DME and dried in vacuum. The solids (suspended in DME) and the filtrates were separately reacted with acetophenone (reflux temperature; 20 h). 0.4 ml of the respective mixtures was quenched with 2.5 ml of H$_2$O and shaken with 2.5

ml of ether. The ether extracts were dried over $MgSO_4$ and analyzed by GC or GC–MS coupling analysis.

For Tables 1 and 2, entry 1, 10.8 mmol of $TiCl_3(DME)_{1.5}$ and 45.2 mmol of Zn(Cu) in 60 ml of DME were used. The solid (5.95 g) contained 9.5 mmol of Ti, 43.8 mmol of Zn and 29.0 mmol of Cl IR (KBr): ν 2940, 1460, 1445, 1283, 1248, 1185, 1075, 1025, 895, 855, 790 cm^{-1}. FIR (polyethylene): ν 342 cm^{-1}. XRD: $TiCl_3(DME)_{1.5}$ and Zn metal. 0.97 g (1.64 mmol Ti) of the solid were reacted with 0.13 g (1.1 mmol) of acetophenone in 10 ml of DME. GC: 5.6% 5; 14.5% 4a; 64.8% Z-2; 14.4% E-2. The filtrate (62.8 ml) contained 1.26 mmol of Ti, 0.06 mmol of Zn and 3.61 mmol of Cl. 20 ml of the filtrate were reacted with 30 mg (0.25 mmol) of acetophenone. GC: 100% acetophenone.

For Tables 1 and 2, entry 2, 12.4 mmol of $TiCl_3(DME)_{1.5}$, 26.5 mmol of Zn(Cu) and 1.0 ml of pyridine in 50 ml of DME were used. The solid (4.74 g) contained 9.2 mmol of Ti, 23.9 mmol of Zn and 28.1 mmol of Cl, IR (KBr): ν(Py · HCl?) 3065, 2945, 1635, 1605, 1485, 1330, 900, 745, 675; ν(complexed Py) 1445, 1215, 705; ν(complexed DME) 1940, 1460, 1445, 1283, 1248, 1185, 1075, 1025, 895, 855 cm^{-1}. FIR (polyethylene): ν 342 cm^{-1}. XRD: 2θ 11.4889, 11.9970, 13.9728, 24.3972 and Zn-metal. 1.11 g (2.14 mmol Ti) of the solid were reacted with 0.23 (1.93 mmol) of acetophenone in 10 ml of DME. GC: 7.2% 5; 14.6% 4a; 66.5% Z-2; 11.2% E-2. The filtrate (52 ml) contained 3.04 mmol of Ti, 0.88 mmol of Zn and 10.6 mmol of Cl. 30 ml of the filtrate were reacted with 130 mg (1.1 mmol) of acetophenone. GC: 100% acetophenone.

For Tables 1 and 2, entry 3, 13.0 mmol of $TiCl_3(DME)_{1.5}$ and 46.6 mmol of Zn* in 50 ml of DME were used. The solid (6.17 g) contained 9.8 mmol of Ti, 43.4 mmol of Zn and 33.2 mmol of Cl. IR (KBr): ν 2940, 1460, 1445, 1283, 1248, 1185, 1075, 1025, 895, 855, 790 cm^{-1}. FIR (polyethylene): 342 cm^{-1}. XRD: TiCl3(DME)$_{1.5}$ and Zn metal. 1.07 g (1.71 mmol Ti) of the solid were reacted with 0.18 g (1.50 mmol) of acetophenone in 10 ml of DME. GC: 2.1% 5; 6.9% 4a; 72.5% Z-2; 17.8% E-2. The filtrate (55 ml) contained 3.14 mmol of Ti, 0.67 mmol of Zn and 10.65 mmol of Cl. 25 ml of the filtrate were reacted with 146 mg (1.21 mmol) of acetophenone. GC: 80.5% acetophenone; 0.4% 5; 0.8% 4a; 17.2% Z-2; 1.1% E-2.

6.4. Complex formation between $TiCl_3(DME)_{1.5}$ and acetophenone (Fig. 4)

0.55 g (4.6 mmol) of acetophenone were added to a suspension of 1.30 g (4.6 mmol Ti content) of $TiCl_3(DME)_{1.5}$ in 10 ml of DME, whereby the color of the suspension turned violet. After stirring for 1 h the suspension was filtered and the solid dried in vacuum. The solid exhibited in the IR spectrum (KBr) a strong

absorption band at 1620 cm^{-1} of the complexed acetophenone, while the filtrate showed in an IR spectrum the presence of free acetophenone (1680 cm^{-1}). After evaporating the solvent (from the filtrate) in vacuum, violet-colored crystals were obtained which also exhibited the band at 1620 cm^{-1} in the IR spectrum (KBr).

6.5. Investigation of the reductive coupling of acetophenone using $TiCl_3(DME)_{1.5}$–Zn(Cu) (Fig. 5)

The starting materials were 5.86 g (19.9 mmol of Ti content) of $TiCl_3(DME)_{1.5}$, 0.60 g (5.0 mmol) of acetophenone and 5.78 g (82.2 mmol of Zn content) of Zn(Cu) in 50 ml of DME. The experiment was conducted in the same way as described for the experiment using 1 as a coupling reagent. A sample taken from the reaction at $-40°C$ and quenched with D_2O contained 2.5% of deutero-1-phenylethanol (3b) with 92% deuteration in the 1-position, according to the GC–MS analysis.

6.6. $TiZnCl_4(DME)_{2.2}$ and 7a · $(ZnCl_2)_{0.3}(DME)_{1.0}$ from acetophenone, $TiCl_3(DME)_{1.5}$ and Zn(Cu)

1.48 g (21.4 mmol Zn content) of Zn(Cu) was added at $-50°C$ to a stirred suspension of 2.68 g (9.4 mmol of Ti content) of $TiCl_3(DME)_{1.5}$ and 1.14 g (9.4 mmol) of acetophenone in 75 ml of DME. The stirred reaction mixture was warmed to 0°C over a period of 3 h and then stirred at 0°C for a further 2 h. The reaction mixture was filtered (P-4 frit) at 0°C to give 1.82 g of a grey solid with the composition $TiCl_2 · ZnCl_2(DME)_{2.0}$ · $Zn_{7.67}$ · $Cu_{0.37}$. Anal Found: C, 9.83, H, 1.92; Ti, 5.34; Zn, 63.20; Cl, 13.57; Cu, 2.63. Calc.: C, 10.01; H, 2.10; Ti, 4.99; Zn, 59.03; Cl, 14.77; Cu, 2.45%. IR(KBr): ν(complexed DME) 2955, 1455, 1070, 1020, 850, 795 cm^{-1}. FIR (polyethylene): ν 435, 357, 315, 300 cm^{-1}.

The brown-colored filtrate was allowed to stand for 15 h at 0°C during which time a solid precipitated from the solution. A further filtration at 0°C, washing of the solid with pentane and drying in a high vacuum yielded 0.91 g of a violet-colored powder with the composition $TiCl_2 · ZnCl_2(DME)_{2.2}$. Anal Found: C, 23.62; H, 4.71; Ti, 10.77; Zn, 14.91; Cl, 31.84; O, 14.15 (difference). Calc.: C, 23.32; H, 4.89; Ti, 10.56; Zn, 14.42; Cl, 31.28; O, 15.53%. IR (KBR): ν(complexed DME) 2955, 1455, 1070, 1020, 850, 795 cm^{-1}. FIR (polyethylene): ν 435, 357, 315, 300 cm^{-1}.

The filtrate was evaporated in a vacuum and the solid residue dried in a high vacuum affording 2.38 g of a brown-colored powder with the composition corresponding to 7a · $(ZnCl_2)_{0.33}(DME)_{1.0}$. Anal. Found: C, 47.38, H, 5.38; Ti, 10.17; Zn, 4.61; Cl, 18.47; O, 13.99 (difference). Calc.: C, 48.61; H, 5.30; Ti, 9.69; Zn, 4.37; Cl, 19.08; O, 12.95%. IR (KBr): ν(complexed DME) 2990, 2940, 1445, 1370, 1125, 1070, 1030, 940,

850, 800; $\delta_{sym(CH_3)}$ 1370; ν(phenyl) 3030, 1600, 1495, 875, 700; $\nu_{(Ti-O-C)}$. 565 w cm^{-1}. FIR (polyethylene): ν 415, 357, 345, 315, 298, 262 cm^{-1}.

From the amount of Ti found in the solids TiCl$_2$ · ZnCl$_2$(DME)$_{2.0}$ · Zn$_{7.67}$ · Cu$_{0.37}$ and TiCl$_2$ · ZnCl$_2$-(DME)$_{2.2}$ (4.07 mmol) and in the remaining solution (5.05 mmol), it can be calculated that 53.7% of Ti are contained in **7a** (Scheme 2) after the reaction. The disproportionation from **7** to **7a** thus occurs quantitatively. The amount of ZnCl$_2$ contained in the solid TiCl$_2$ · ZnCl$_2$(DME)$_{2.0}$ · Zn$_{7.67}$ · Cu$_{0.37}$ can be calculated from the difference between the total amount of Cl found in the solid (6.97 mmol) and the Cl combined as TiCl$_2$ (4.06 mmol): (6.97 − 4.06)/2 = 1.45 mmol of ZnCl$_2$. The total amount of ZnCl$_2$ formed during the reaction amounts to 1.45 + 2.06 (from the solid TiCl$_2$ · ZnCl$_2$(DME)$_{2.2}$ + 1.68 (from the solute) = 5.19 mmol of ZnCl$_2$ (0.55 mol ZnCl$_2$ (mol acetophenone)$^{-1}$).

6.7. TiOCl · (ZnCl$_2$)$_{0.9}$(DME)$_{1.5}$ and 2 from acetophenone, TiCl$_3$(DME)$_{1.5}$ and Zn(Cu) (molar ratio, 1:1:1) (Table 3, entry 4)

Acetophenone (1.02 g, 8.5 mmol) was added at −60°C to a stirred suspension of 2.44 g (8.6 mmol of Ti content) of TiCl$_3$(DME)$_{1.5}$ and 0.60 g (8.6 mmol) of Zn(Cu) in 50 ml of DME. The stirred reaction mixture was warmed to room temperature and then heated to reflux for 48 h, whereby the suspension turned to a greyish color. After the addition of 30 ml of pentane, the reaction mixture was filtered, and the solid collected on the frit washed with pentane and dried in vacuum. A greyish powder (3.88 g) was thus obtained which according to an XRD analysis was free of metallic Zn, namely TiOCl(ZnCl$_2$)$_{0.93}$(DME)$_{1.5}$ · Cu$_{0.03}$. Anal. Found: C, 20.57; H, 4.01; Ti, 14.03; Zn, 17.80; Cl, 28.63; Cu, 0.61; O, 14.90 (difference). Calc.: C, 20.76; H, 4.36; Ti, 13.79; Zn, 17.51; Cl, 29.21; Cu, 0.55; O, 13.80%. IR (KBr): ν(complexed DME) 2960, 1455, 1070, 1040, 1020, 855, 800 cm^{-1}. FIR (polyethylene): ν 430, 350, 342, 314, 300 cm^{-1}.

The filtrate was evaporated to dryness in a rotary evaporator vacuum and the residual yellow oil purified by means of flash chromatography (silica gel–pentane). 0.744 g (84%) of **2** were obtained as a colorless solid with a $Z:E$ ratio of 9:1 (GC analysis). The compound was identified by IR and NMR spectroscopy [23] and MS analysis [24] (cf. experiment in the molar ratio of 1:2:2.)

6.8. 2 from acetophenone, TiCl$_3$(DME)$_{1.5}$ and Zn(Cu) (molar ratio, 1:2:2) (Table 3, entry 7)

0.934 g (7.8 mmol) of acetophenone was added dropwise to a stirred suspension of 4.34 g (15.2 mmol) of TiCl$_3$(DME)$_{1.5}$ and 1.13 g (16.3 mmol of Zn content)

of Zn(Cu) in 50 ml of DME. The suspension was heated to reflux for 48 h. After the addition of 50 ml of pentane, the suspension was filtered over silica and the inorganic solid thoroughly washed with pentane. After removal of the solvent the residual solid was purified by flash chromatography (silica, pentane) yielding 792 mg (97%) of **2** as a colorless solid. **2** was 96% pure and had a $Z:E$ ratio of 91:9, according to GC analysis. The stereoisomers were separated by preparative GC and identified by ^{1}H [23] and ^{13}C NMR spectroscopy and MS analysis [24]. ^{1}H NMR (CDCl$_3$): *E*-2, δ 1.796 (6 H, s), 7.090–7.315 (10 H, m); *Z*-2, δ 2.187 (6 H, s), 6.949–7.139 (10 H, m) ppm.

6.9. 2 from acetophenone, TiCl$_3$(DME)$_{1.5}$ and Zn(Cu) (molar ratio, 1:4:15) (Table 3, entry 11)

The starting materials were 0.436 g (3.63 mmol) of acetophenone, 4.28 g (14.5 mmol Ti) of TiCl$_3$(DME)$_{1.5}$ and 3.41 g (54.4 mmol of Zn) of Zn(Cu) in 50 ml of DME. The reaction was conducted and the reaction products were analyzed in the same way as described for the experiment with a molar ratio of 1:2:2.

6.10. 4a from acetophenone, TiCl$_3$(DME)$_{1.5}$ and Zn(Cu) (molar ratio, 1:4:16) (Table 3, entry 10)

0.980 g (8.16 mmol) of acetophenone was added dropwise at −20°C to a stirred suspension of 9.91 g (31.3 mmol of Ti content) of TiCl$_3$(DME)$_{1.5}$ and 9.83 g (141.8 mmol of Zn content) of Zn(Cu) in 75 ml of DME. The suspension was stirred for 2 h at 0°C. 20 g of ice were added to the suspension which was then shaken with ether (5 × 30 ml). The combined ether extracts were dried over MgSO$_4$. Removal of the solvent from the filtered extracts in vacuum afforded 0.960 g (97%) of **4a** as a colorless solid. The *rac*:*meso* ratio of **4a** was determined by GC analysis to be 74:26. **4a** was identified by IR, ^{1}H [25] and ^{13}C NMR spectroscopy and MS analysis [24].

The remaining experiments of Table 3 (5–20 mmol of acetophenone scale and 30–40 ml of the DME solvent) were started at 0°C and then were reacted and analyzed in the same way as described for the experiment using **1** as a coupling reagent.

6.11. Investigation of the reductive coupling of acetophenone using TiCl$_2$ · Li (Fig. 6 and Table 4, entry 1)

0.415 g (2.54 mmol Ti content) of TiCl$_2$ · LiCl were added at −60°C to a stirred suspension of 0.29 g (2.4 mmol) of acetophenone in 25 ml of DME. The temperature of the reaction mixture was raised at 10°C h from −60°C to room temperature, kept at room temperature for 15 h and finally heated to reflux. The samples were taken from the reaction mixture and analyzed in the

same way as described for the experiment using **1** as a coupling reagent.

6.12. 2 from acetophenone and $TiCl_2 \cdot LiCl$ with a molar ratio of 1 : 2 (Table 4, entry 2)

1.55 g (12.9 mmol) of acetophenone were added to a stirred suspension of 4.25 g (26.0 mmol of Ti content) of $TiCl_2 \cdot LiCl$ in 50 ml of DME. After stirring at room temperature for 30 min the reaction mixture was heated to reflux for 48 h. **2** (1.21 g (90%); $Z : E = 7 : 3$) was isolated and analyzed in the same way as described for the experiment utilizing **1** as a coupling reagent.

6.13. 2 from acetophenone and $TiCl_2 \cdot LiCl$ with a molar ratio of 1 : 4 (Table 4, entry 3)

The starting materials were 1.16 g (9.7 mmol) of acetophenone and 6.17 g (37.7 mmol of Ti) of $TiCl_2 \cdot$ LiCl in 50 ml of DME. The experiment was conducted the same way as the experiment using the molar ratio of 1 : 2.

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