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# HYDROMETALLATION OF 1-OCTENE WITH GRIGNARD REAGENTS, ALKYLMAGNESIUMS AND ALKYLMAGNESIUM HYDRIDES CATALYZED BY DICYCLOPENTADIENYLTITANIUM DICHLORIDE

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## Summary

The hydrometallation of 1-octene by a series of Grignard reagents (EtMgCl, EtMgBr, n-PrMgCl, i-PrMgCl, n-BuMgCl, sec-BuMgCl, iso-BuMgCl, iso-BuMgBr and iso-BuMgI), dialkylmagnesium compounds ($Me_2Mg$, $Et_2Mg$, n-$Pr_2Mg$, iso-$Pr_2Mg$, n-$Bu_2Mg$, sec-$Bu_2Mg$, iso-$Bu_2Mg$ and t-$Bu_2Mg$), alkylmagnesium hydrides (RMgH, where R = Me, Et, t-Bu, Cp and Ph) and magnesium hydrides ($MgH_2$, HMgCl and HMgBr) in the presence of 5 mol% dicyclopentadienyltitanium dichloride ($Cp_2TiCl_2$) in THF has been investigated. The percent yield of octane (produced on hydrolysis of the product) vs. time was plotted for several reactions in order to compare the effect of individual reagents. Most alkylmagnesium compounds with $\beta$ hydrogen atoms gave primarily the hydrometallation product, although t-$Bu_2Mg$ produced isomerized starting material. MeMgH gives the best yield of octane on hydrolysis of the reaction mixture. A mechanism is proposed which accounts for all observations.

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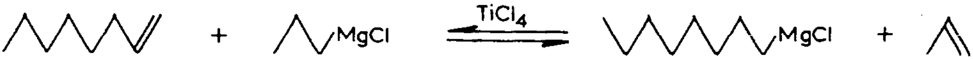
## Introduction

Titanium tetrachloride has been shown to catalyze the transfer of magnesium, from Grignard reagents with $\beta$ hydrogens to terminal olefins, resulting in the formation of a new organomagnesium compound [1].



Alkylmagnesium compounds prepared using this method are reported to be reactive toward many typical substrates [2] for example, a reaction involving 3-(*p*-methoxyphenyl)-1-propene) and a Grignard reagent was used by Horeau and co-workers as a key step of their estrone synthesis [3]. In addition Eisch has used ethyl-Grignard reagents with dicyclopentadienyltitanium dichloride ($Cp_2TiCl_2$) to hydrometallate alkenols [4]. More recently Grignard reagents and $Cp_2TiCl_2$ [5] have been used to reduce alkyl halides [6], ketones [7], and esters [8].

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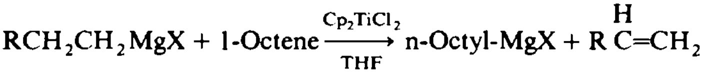
Initial studies from this laboratory have shown that $MgH_2$ is also an effective reagent for the hydrometallation of olefins in the presence of a catalytic amount of $Cp_2TiCl_2$ [9]. Since Grignard reagents are more readily available than $MgH_2$, we decided to study the hydromagnesiation reaction using a series of Grignard reagents, alkylmagnesiums and alkylmagnesium hydrides.

## Results and discussion

We have carried out a study of hydrometallation reactions using a series of magnesium compounds and a catalytic amount (5 mol%) of $Cp_2TiCl_2$ with l-octene as a typical olefin substrate. These reactions were carried out under identical reaction conditions with respect to the order of mixing, temperature and pressure.



$$RCH_2CH_2MgX + \text{1-Octene} \xrightarrow[THF]{Cp_2TiCl_2} \text{n-Octyl-MgX} + R\overset{H}{C}{=}CH_2 \qquad (1)$$

The concentrations of olefin (0.167 $M$), magnesium compound (0.200 $M$), and catalyst (0.00835 $M$) were held constant (1.0/1.2/0.05 ratio) so that comparisons of the change in product composition with time would give a good estimate of the relative rates of reaction and also indicate when the reactions have gone to completion. The solvent in each case was THF.

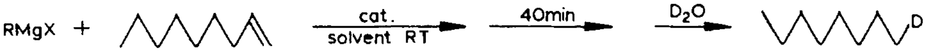
Table 1 shows the yields of octane and deuteroctane observed after 40 minutes reaction time, although the maximum yield of product was usually reached within 5 minutes. In general, we observed a gradual decrease in the yield of product after the maximum yield was attained. This is probably due to the reversible nature of the reaction as evidenced by the fact that the reaction of n-octylmagnesium bromide with $Cp_2TiCl_2$ in THF produced a 15% yield of a mixture of octenes. Therefore once the product is formed in the reaction mixture, it can undergo $\beta$ elimination to give starting olefin, which is known to undergo double bond isomerization under these conditions.

The yield of deuterium incorporation product formed by quenching an aliquot of the reaction mixture in $D_2O$ also decreased as the reaction proceeded. This conclusion was reached when several reactions were allowed to proceed for an extended period of time. Deuterium incorporation is important in these reactions because it indicates the presence of a reactive carbon–metal bond. The reaction of $MgH_2$ and $Cp_2TiCl_2$ in THF with 1-octene gave 90% deuterium incorporation when the reaction mixture was quenched after 1 h with $D_2O$, but after 24 h the yield of deuterium incorporation product had decreased to 50%.

Isomerized starting material (*cis*- and *trans*-2-octene) was formed to some extent under all of the reaction conditions employed. The yields ranged from about 30% with MeMgH to 75% with $t\text{-}Bu_2Mg$. The sum of the yields of octane, *cis*-2-octene, *trans*-2-octene and 1-octene starting material consistantly gave excellent mass balances, indicating that these are the only products formed. The relative rates of double bond isomerization and hydrometallation determine the product distribution. In the absence of alkylmagnesiums and hydrides, $Cp_2TiCl_2$, $Cp_2TiCl$ and $Cp_2TiMe_2$ all failed to isomerize 1-octene after 24 h reaction in tetrahydrofuran (THF) at room temperature. *trans*-2-Octene was recovered unchanged after 48 h reaction with $MgH_2$ and $Cp_2TiCl_2$ (5 mol%) in THF while *cis*-2-octene reacted under the same conditions to give 4% octane (after hydrolysis), 1% 1-octene and 4% *trans*-2-octene.

TABLE 1

REACTION OF ORGANOMAGNESIUM COMPOUNDS WITH 1-OCTENE[a] IN THE PRESENCE OF 5 mol% CATALYST IN THF AT ROOM TEMPERATURE



| R | X | Catalyst(5%) | Solvent | % octane | % D inc. |
|---|---|---|---|---|---|
| Me | Me | $Cp_2TiCl_2$ | THF | 0 | 0 |
| Et | Cl | $Cp_2TiCl_2$ | THF | 17 | 85 |
| Et | Br | $Cp_2TiCl_2$ | THF | 18 | 82 |
| Et | Et | $Cp_2TiCl_2$ | THF | 20[b] | 95 |
| n-Pr | Cl | $Cp_2TiCl_2$ | THF | 48 | 93 |
| n-Pr | n-Pr | $Cp_2TiCl_2$ | THF | 50 | 100 |
| n-Pr | n-Pr | $CpTiCl_3$ | THF | 24 | 100 |
| n-Pr | n-Pr | $TiCl_4$ | THF | 8 | – |
| n-Pr | n-Pr | $TiCl_4$ | $Et_2O$ | 8 | – |
| n-Pr | n-Pr | $Cp_2TiCl_2$ | $Et_2O$ | 27 | 91 |
| i-Pr | Cl | $Cp_2TiCl_2$ | THF | 37 | 90 |
| i-Pr | i-Pr | $Cp_2TiCl_2$ | THF | 29 | 92 |
| n-Bu | Cl | $Cp_2TiCl_2$ | THF | 56 | 92 |
| n-Bu | n-Bu | $Cp_2TiCl_2$ | THF | 58 | 98 |
| sec-Bu | sec-Bu | $Cp_2TiCl_2$ | THF | 53 | 85 |
| t-Bu | t-Bu | $C_{p_3}TiCl_2$ | THF | 5 | – |
| iso-Bu | Cl | $Cp_2TiCl_2$ | THF | 53 | 93 |
| iso-Bu | Br | $Cp_2TiCl_2$ | THF | 44 | 89 |
| iso-Bu | I | $Cp_2TiCl_2$ | THF | 40 | 87 |
| iso-Bu | iso-Bu | $Cp_2TiCl_2$ | THF | 65 | 100 |
| Cp | H | $Cp_2TiCl_2$ | THF | 56 | 81 |
| Me | H | $Cp_2TiCl_2$ | THF | 68 | 100 |
| Ph | H | $Cp_2TiCl_2$ | THF | 39 | 88 |
| t-Bu | H | $Cp_2TiCl_2$ | THF | 33 | 87 |
| Et | H | $Cp_2TiCl_2$ | THF | 28 | 91 |
| H | H | $Cp_2TiCl_2$ | THF | 45[c] | 90 |
| H | Cl | $Cp_2TiCl_2$ | THF | 52 | 87 |
| H | Br | $Cp_2TiCl_2$ | THF | 56 | 89 |

[a] Reactions carried out under identical conditions. [b] Yield increased to 60% after 24 h. [c] Yields varied from 45% to 65%.

The reaction of 1-octene with $Et_2Mg$ in THF with 5 mol% $Cp_2TiCl_2$ was slow compared to the other magnesium compounds studied (see Table 1). A yield of 20% of n-octane was observed after 40 minutes reaction which increased to a maximum yield of 60% after 24 h. All other magnesium compounds investigated reacted to give the maximum yield within 10 minutes. The competing isomerization reaction was also slower with ethylmagnesium compounds, otherwise the yields of octane would have been even lower due to the conversion of 1-octene to the less reactive 2-octenes. Hydrometallation with n-$Pr_2Mg$ is over in 5 minutes with yields of 48% octane, 47% 2-octenes and 5% starting material. Diisopropylmagnesium under the same reaction conditions gave lower yields of octane (37%) than n-$Pr_2Mg$ despite the presence of six $\beta$ hydrogens compared to two for the n-propyl group.

We have evidence that isomerization of 1-octene is caused by the intermediate,

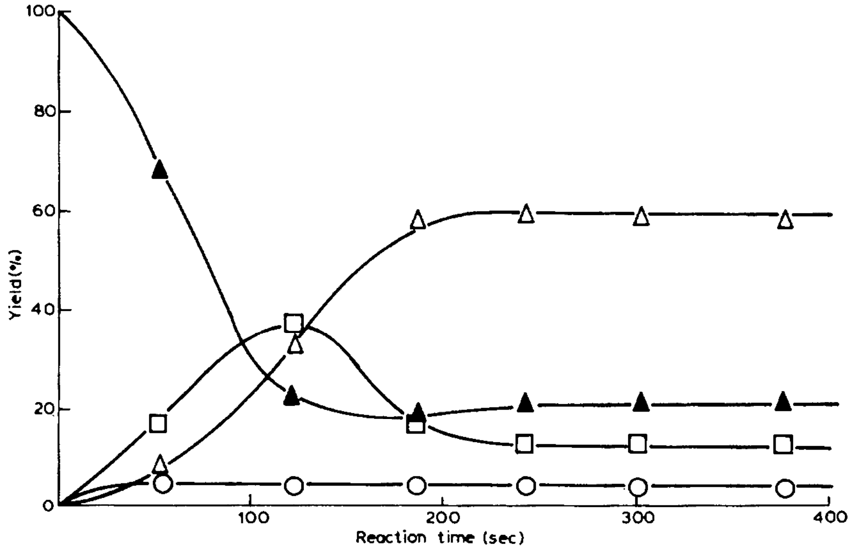


Fig. 1. Products from the $Cp_2TiCl_2$ catalyzed reaction of 1-octene (▲) with $t\text{-}Bu_2Mg$. *cis*-2-Octene (□), *trans*-2-octene (△) and octane (○).

$Cp_2TiR$. The reaction of $t\text{-}Bu_2Mg$ with 1-octene and catalyst gave a very low yield of octane (5%). After 3 days reaction the yield remained at 5%. Figure 1 shows the formation of products with time for this reaction. It is clear from these data that isomerization is occurring in the absence of hydrometallation during most of this reaction. The results indicate that isomerization is caused by a compound which is incapable of hydrometallation. The most reasonable explanation for this is that isomerization is caused by dicyclopentadienyl-t-butyltitanium ($Cp_2Ti\text{-}t\text{-}Bu$). This is the expected product from the reaction of $Cp_2TiCl$ with $t\text{-}Bu_2Mg$. Olefin isomerization in this and other reactions involving C–Mg compounds could proceed via a hydrido-$\pi$-allyl complex (see Scheme 1). It is interesting that initially *cis*-2-octene is formed which reisomerizes to the *trans* form. This could be due to base-catalyzed isomerization, which is known to give a large *cis*/*trans* ratio due to the greater stability of the *cis*-allyl anion [19] followed by isomerization of the *cis* to the more thermodynamically stable *trans* olefin.

Figure 2 shows the effect of increasing the chain length of the $R_2Mg$ compound on the rate of product formation for the hydrometallation of 1-octene by a series of dialkylmagnesium compounds. Dimethylmagnesium does not react at all, $Et_2Mg$ reacts very slowly while $n\text{-}Pr_2Mg$ and $n\text{-}Bu_2Mg$ show comparable reactivity. This can be attributed to the degree of substitution at the $\beta$ carbon. Both n-Bu and n-Pr groups have monoalkyl-substituted $\beta$ carbon atoms.

Figure 3 shows the yields of octane obtained on hydrolysis when isomeric dibutylmagnesium compounds were allowed to react with 1-octene and $Cp_2TiCl_2$ in THF. $n\text{-}Bu_2Mg$ and $s\text{-}Bu_2Mg$ gave comparable yields of 58 and 53%, respectively. $i\text{-}Bu_2Mg$ gave a yield of 65%, which was the highest yield next to MeMgH (68%). This suggests that olefin elimination is rapid from $Cp_2Ti(i\text{-}Bu)$. The butyl isomers show the following order of reactivity: i-Bu > n-Bu ~ s-Bu > t-Bu. This order is

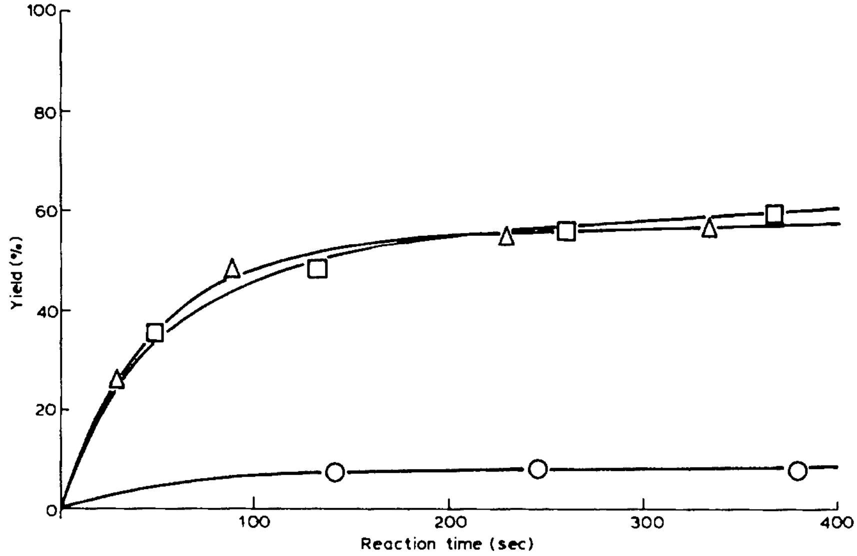


Fig. 2. Yields of octane from the $Cp_2TiCl_2$ catalyzed hydrometallation of 1-octene with $Et_2Mg$ (○), n-$Pr_2Mg$ (△) and n-$Bu_2Mg$ (□).

inversely related to the number of $\beta$ hydrogens present in the butyl group.

The hydrometallation reaction is little influenced by the presence of X in RMgX. Rate profile studies for a series of i-BuMgX compounds where X is Cl, Br, I, and i-Bu show comparable rates regardless of the nature of X. However i-$Bu_2Mg$ provides the highest yield of product (Fig. 4). Even when a 2/1 ratio of Grignard to dialkylmagnesium compound was employed (which gives equal concentrations of R

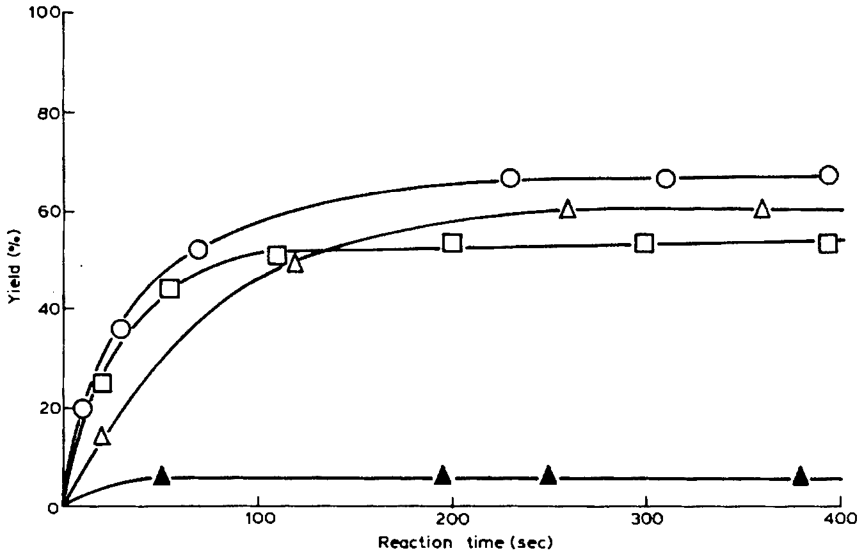


Fig. 3. Yields of octane from the $Cp_2TiCl_2$ catalyzed hydrometallation of 1-octene with n-$Bu_2Mg$ (□), s-$Bu_2Mg$ (△), i-$Bu_2Mg$ (○) and t-$Bu_2Mg$ (▲) after hydrolysis.

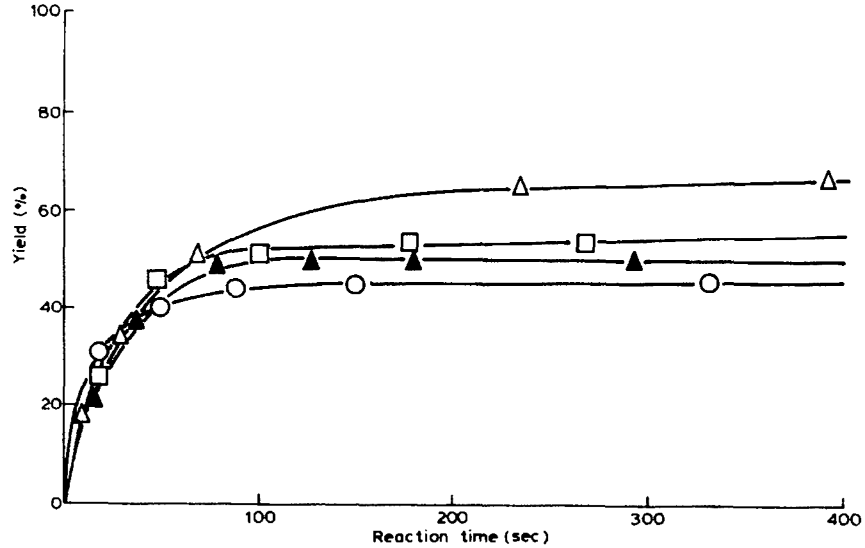


Fig. 4. Yields of octane from the $Cp_2TiCl_2$ catalyzed hydrometallation of 1-octene with i-$Bu_2Mg$ (△), i-BuMgCl (□), i-BuMgBr (▲) and i-BuMgI (○).

groups) the yields with the Grignard reagents are lower.

Figure 5 shows the rates of octane formation for the hydrometallation of 1-octene with $MgH_2$ and HMgX (where X is Cl, Br). These reactions were carried out using equal amounts of $MgH_2$ placed in two flasks. To one of the flasks was added $MgX_2$. The reactions were then carried out as usual. This procedure gave the same concentration of hydride in each raction, the only variable being the presence of

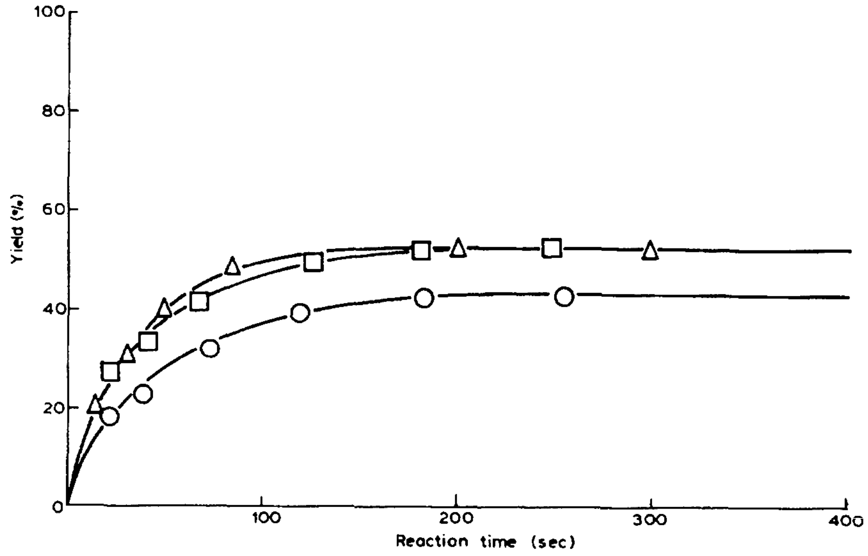


Fig. 5. Yields of octane from the $Cp_2TiCl_2$ catalyzed hydrometallation of 1-octene with HMgCl (△), HMgBr (□) and $MgH_2$(○).

$MgX_2$. While the presence of halide was shown to slow the reaction with alkylmagnesium compounds, it appeared to facilitate the reaction with $MgH_2$. The higher yields observed with the added $MgX_2$ is probably due to the formation of the THF soluble HMgX which is formed rapidly under these conditions. The lower yields observed with Grignard reagents compared from $R_2Mg$ compounds could be due to interference by halide on the metal hydride elimination process.

We compared the reactivity of $TiCl_4$ and $CpTiCl_3$ to that of $Cp_2TiCl_2$ as a catalyst towards hydrometallation in the reaction under study. $TiCl_4$ and $CpTiCl_3$ were substantially less effective than $Cp_2TiCl_2$ (Table 1). The order of reactivity for these catalysts increases as the number of cyclopentadiene rings increases due to either stabilization of the catalyst by the Cp rings or the increased solubility expected of the catalyst with more Cp rings. Purification of the catalyst was shown to be unnecessary. The yields of octane with respect to time for the hydrometallation of 1-octene by n-PrMgCl catalyzed by $Cp_2TiCl_2$ showed no difference in rate when the $Cp_2TiCl_2$ had been recrystallized from toluene, transferred as received in the dry box, or exposed to air for 1 h. Therefore, in these studies, all reactions involving $Cp_2TiCl_2$ were carried out using $Cp_2TiCl_2$ as received and handled in the dry box.

## Mechanism

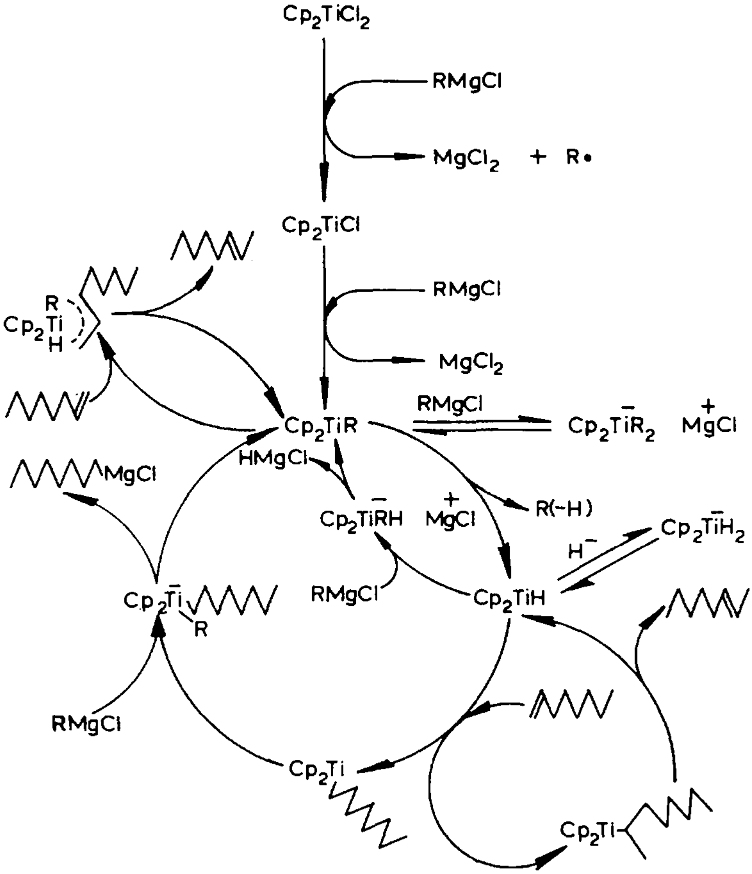
A possible mechanism consistent with all of the available data is outlined in Scheme 1. $Cp_2TiCl_2$ reduction to $Cp_2TiCl$ is known to occur under the conditions of the reactions under study [10,11]. Reactions of Grignard Reagents with $Cp_2TiCl$ gives $Cp_2TiR$, which can complex with olefin and cause isomerization, undergo olefin elimination [11], or react with alkylmagnesium to give the known compound, dicyclopentadienyldialkyltitanium anion ($Cp_2TiR_2^-$) [11]. $Cp_2TiR_2^-$ should be incapable of $\beta$ hydrogen elimination or olefin isomerization since either process would involve an intermediate with 19 valence electrons.

We would expect the equilibrium for the formation of $Cp_2TiR_2^-$ to lie futher to the right for small R groups due to steric interaction between the two R groups (eq. 2). The formation of $Cp_2TiEt_2^-$ would account for the observation that hydrometallation as well as olefin isomerization are much slower with ethylmagnesium compounds compared to other R groups with $\beta$ hydrogens. The other R groups have larger steric requirements which because of $\beta$ strain would tend to shift the equilibrium to the left.

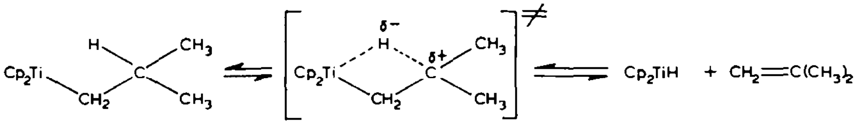
$$Cp_2TiR + RMgX \leftrightharpoons Cp_2TiR_2^- + MgX^+ \qquad (2)$$

The order of reactivity for hydrometallation by a series of dibutylmagnesium compounds appear to correlate with the degree of alkyl substitution at the $\beta$ carbon. The isobutyl group has two methyl groups on the $\beta$ carbon, n-butyl has an ethyl substituted $\beta$ carbon, the s-butyl group has one unsubstituted $\beta$ carbon and a methyl substituted $\beta$ carbon, and the t-butyl group has three unsubstituted $\beta$ carbons. The alkyl groups on the $\beta$ carbon appear to facilitate the olefin elimination step. If the $\beta$ hydrogen transfer involves the migration of hydrogen from carbon to metal, the $\beta$ carbon would become electron deficient as hydrogen departs with a pair of electrons (eq. 3). Electron donation by the alkyl groups on the $\beta$ carbon lowers the energy barrier in the transition state and allows the olefin elimination to proceed more readily. The reverse reaction (hydrometallation) proceeds via the same transition state. Markovnikov addition to olefin by $Cp_2TiH$ results from initial donor–acceptor

SCHEME 1



complexation of the olefin at the titanium center, which acts as a Lewis acid to give the more highly substituted cationic intermediate followed by rapid hydride transfer.



(3)

$Cp_2Ti$(i-Bu) rapidly eliminates isobutylene to give $Cp_2TiH$ due to the stabilizing effect of the two methyl groups on the $\beta$ carbon. Isomerization caused by $Cp_2Ti$(i-Bu) is minimal because it has a short lifetime. On the other hand, $Cp_2Ti$(t-Bu) is very slow to undergo $\beta$ elimination because the $\beta$ carbons are primary so that more time is available to complex with olefin and cause isomerization.

The active compound in the $Cp_2TiCl_2$ catalyzed hydrometallation reaction appears to be $Cp_2TiH$ [6,7,12]. This reactive intermediate is stabilized by complex formation with donors in solution. The odd electron in the $\psi_z$ orbital might accelerate complex formation by mixing with electron pairs of olefins and other donors. Brintzinger has allowed $Cp_2TiCl_2$ to react with ethyl and propyl Grignard Reagents in THF and recorded the low temperature esr spectra [11]. The signal developed more rapidly with propyl Grignard than with ethyl Grignard due to a faster rate of olefin elimination by $Cp_2Ti(Pr)$ than $Cp_2Ti(Et)$. Both reaction mixtures gave a triplet which was attributed to the formation of $Cp_2TiH_2^-$. We mixed $Cp_2TiCl_2$ with excess $MgH_2$ in THF and recorded the ESR spectrum of this mixture at room temperature (see experimental section). The blue solution gave a triplet which correlates well with the spectrum of $Cp_2TiH_2^-$, although the hyperfine splitting was lost at room temperature. When $Cp_2TiCl_2$ was mixed with excess $t\text{-}Bu_2Mg$ in THF, no signal was observed within one hour at room temperature, however after 24 h, the brown reaction mixture gave the same triplet. This indicates that metal hydride elimination by $Cp_2Ti(t\text{-}Bu)$ is very slow. We had hoped to observe a resonance due to $Cp_2Ti(t\text{-}Bu)$ but apparently splitting by t-Bu hydrogens causes the signal to broaden and decrease in intensity. $Cp_2TiH_2^-$ should be less reactive than $Cp_2TiH$ because of the filled coordination site as well as the negative charge on titanium.

Isomerization is observed when the catalyst is reduced with $MgH_2$. This reaction gives $Cp_2TiH$ directly so that the olefin elimination step is avoided. $Cp_2TiH$ could cause isomerization in the same manner as $Cp_2TiR$ or by a process of addition to 1-octene to give dicyclopentadienyl-2-octyltitanium followed by $\beta$ elimination to give 2-octene [6]. Another possibility is that the $Cp_2Ti(n\text{-}octyl)$ formed from addition of $Cp_2TiH$ to 1-octene catalyzes the isomerization of the remaining olefin before the reaction has time to go to completion. Figure 6 shows the percent yield of products with time for the reaction of 1-octene with $MgH_2$ in THF with $Cp_2TiCl_2$ at room temperature. Both isomerization and hydrometallation occur rapidly early in the reaction and slow down as the reaction subsides in roughly first order fashion. It is disconcerting that the yield in the reaction of $MgH_2$ with l-octene varied from 45–65%, however previous experience with $MgH_2$ and its subsequent heterogeneous reactions teaches us that there are significant differences in reactivity among different preparations of $MgH_2$. The reasons for this are not clear to us.

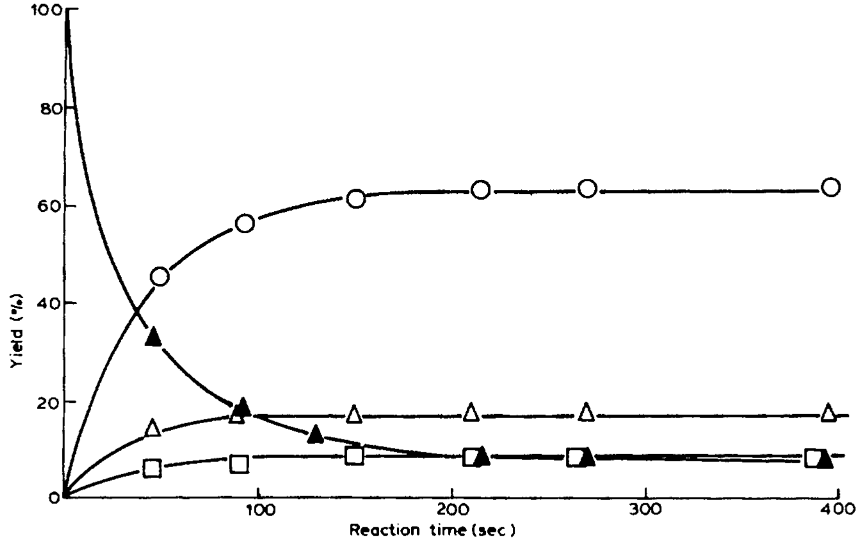


Fig. 6. Products found after hydrolysis from the $Cp_2TiCl_2$ catalyzed hydrometallation of 1-octene (▲) with $MgH_2$. Octane (○), *trans*-2-octene (△) and *cis*-2-octene (□).

## Conclusions

The most effective reagent found for the hydrometallation of olefins is MeMgH. Hydrometallation of 1-octene with MeMgH gave the highest yield of octane (68%) and quantitative deuterium incorporation after 40 minutes at room temperature. The best Grignard reagent found for this reaction is i-BuMgCl, which gave a 53% yield of octane after hydrolysis. The Grignard solution should be free from alkyl halide since this can react with the titanium catalyst [6]. The yield can be increased by about 10% by precipitating $MgCl_2$ with dioxane to give i-$Bu_2Mg$, which is probably the best reagent overall considering product yield and ease of preparation.

Olefin isomerization is a major drawback to this method. Even under the most favorable conditions we observed about 30% conversion of 1-octene to 2-octene. $Cp_2Ti$(t-Bu) was shown to cause double bond isomerization. Other $Cp_2TiR$ compounds should also be capable of isomerizing olefin by a similar mechanism. It is probably impossible to completely stop isomerization since $Cp_2Ti$(n-octyl) is an intermediate in all of the reactions.

Another problem is the effect of the titanium catalyst on the reactivity of the product which is then used to react with various organic substrates. Although the usual reaction of n-octylmagnesium chloride with organic substrates is alkylation, the preferred reaction in the presence of $Cp_2TiCl_2$ with ketones [7], esters [8], and alkyl halides [6] is reduction. The reducing agent probably involves $Cp_2TiH$. We have tried to remove the catalyst from the hydrometallation mixture by stirring with mercury, magnesium amalgam, and activated charcoal, however these attempts were unsuccessful.

Olefin elimination from $Cp_2TiR$ involves transfer of hydride from the $\beta$ carbon to titanium, which results in electron deficiency at the $\beta$ carbon. This conclusion is based on relative rate data which seems to indicate that alkyl groups on the $\beta$ carbon facilitate olefin elimination.

## Experimental

Proton NMR were recorded on a Varian T-60. All chemical shifts are expressed in $\delta$ (TMS). IR spectra were recorded on a Perkin–Elmer 621 spectrometer. ESR spectra were recorded on a Varian E-109. Mass spectra were obtained on a Varian MAT 1125 GC-MS system. Octane was analyzed by GLC using a 20′ × 1/4 column packed with 10% TCEP on Chromosorb P. Alkyl halides were analyzed on a 15′ × 1/4″ column packed with 10% Apiezon L on Chromosorb P. Magnesium was analyzed by titration with EDTA at pH 10 using Eriochrome Black T as the indicator. Titanium was determined gravimetrically as $TiO_2$ by pyrolysis of the cupferron complex. Hydrides were analyzed by hydrolyzing with water and measuring the evolved gas with a Toepler pump. Halogen was determined by a modified Volhard procedure. Alkyl groups bound to magnesium were analyzed by NMR integration of the $\alpha$ hydrogens using mesitylene as the internal standard [13].

All reactions were carried out in dry glassware under argon. Diethyl ether was distilled from $LiAlH_4$. THF was distilled from $NaAlH_4$ using triphenylmethane as the indicator. Toluene and dioxane were distilled from sodium benzophenone ketyl. 1-Octene (Aldrich) was distilled from calcium hydride (b.p. 120°C) at atmospheric pressure and the purity was determined to be > 98% by GLC. Deuterium oxide

(Aldrich) was used as received. $Cp_2TiCl_2$ (Alfa) was kept in a dry box and used as received. $TiCl_4$ (Baker) was distilled prior to use (b.p. 135°C). Ethyl bromide (b.p. 38°C), 1-chloropropane (b.p. 46°C) and 1-chlorobutane (b.p. 78°C) were prepared by known procedures [14] and distilled from $CaH_2$. 2-Chloropropane (b.p. 35°C), 2-chlorobutane (b.p. 68°C), isobutyl iodide (b.p. 120°C) and t-butyl chloride (b.p. 51°C) were obtained from Aldrich and distilled from $CaH_2$.

Mercuric halides were supplied by Fisher Scientific and dried under vacuum prior to use. Diphenyl- and dimethyl-mercury were obtained from Organometallics, Inc. and used as received. Cyclopentadiene (b.p. 41°C) was obtained by thermolysis of dicyclopentadiene (Aldrich).

Magnesium halides were prepared from the corresponding mercuric halides and excess magnesium chips (Alfa) in ether or THF [15]. Grignard reagents were prepared by the addition of alkyl halide in ether or THF to excess magnesium. Isobutyl Grignard reagents were prepared by mixing diisobutylmagnesium and magnesium halide. Dimethylmagnesium was prepared from dimethylmercury and excess magnesium at room temperature. Diphenylmagnesium was prepared from diphenylmercury and magnesium at 140°C [16]. Other dialkylmagnesium compounds were prepared by the dioxane precipitation method. The ether solutions were filtered through celite, solvent removed in vacuo, and redissolved in THF. All $R_2Mg$ compounds gave alkyl/Mg ratios close to 2 with less than 3% halogen. $Cp_2Mg$ was prepared by adding 2 equivalents of freshly distilled cyclopentadiene to $Me_2Mg$ in THF at 0°C. The reaction was monitored by NMR. After 60 h, the reaction was 98% complete.

Magnesium hydride was prepared as follows [17]. 100 ml of 0.25 *M* $Et_2Mg/Et_2O$ was placed in a 500 ml flask with magnetic stirrer and dropping funnel, which contained 35 ml of 0.36 *M* $LiAlH_4/Et_2O$. The $LiAlH_4$ solution was added dropwise with stirring. A white precipitate formed and stirring was continued for 1/2 h. The slurry was cannulated into a 100 ml round bottom flask equipped with a magnetic stirring bar and serum cap. Insoluble $MgH_2$ was separated by centrifuging, then was washed twice with 80 ml $Et_2O$, then once with 80 ml THF and suspended in 30 ml THF. The stirred slurry was analyzed. Calcd.: Mg/H/Al = 1.00/2.00/0. Found: 1.00/2.10/0.01. RMgH compounds were prepared by mixing equimolar amounts of $R_2Mg$ and $MgH_2$ in THF [16]. The resulting clear solutions were subjected to elemental analysis, IR, and NMR spectroscopy. HMgX (X = Cl, Br) were prepared by mixing $MgH_2$ and $MgX_2$ in THF. The following procedure was used to prepare $CpTiCl_3$ [18]. To 5.7 g $Cp_2TiCl_2$ in a 500 ml flask with condenser was added 100 ml of toluene followed by 7 ml $TiCl_4$. The mixture was then refluxed for 2 days followed by cooling to yield a yellow solid. Toluene was decanted and 200 ml freshly distilled toluene added. The mixture was then heated to give a homogeneous solution. The flask was stoppered and stored at −10°C for four days. Yellow crystals were collected by filtration, washed with cold toluene and dried under vacuum. M.p. 185°C. Anal. Calcd. for $CpTiCl_3$: Ti, 21.8%; Cl, 48.5%. Found: Ti, 22.3%; Cl 46.8%. NMR ($CDCl_3$) $\delta$ 7.03 ppm.

### *Hydrometallation of 1-octene*

To a tared 100 ml flask equipped with a magnetic stirring bar was added 200 mg $Cp_2TiCl_2$. 13.6 ml THF was then added and the catalyst dissolved. 2.50 ml of 1-octene was then added to the stirred solution resulting in a solution 1.00 *M* in 1-octene and 0.050 *M* in catalyst.

To a 250 ml flask, equipped with a stirring bar and dried under Argon was added 14 ml of 0.90 *M* n-$Pr_2Mg$/THF (12.5 nmol), 36 ml THF and an internal standard. The olefin/catalyst solution (10 ml) was then added with stirring and a timer started. The reaction mixture, which immediately turned dark brown, was 0.167 *M* in 1-octene with 5 mol% catalyst and excess magnesium compound. Pressure in the flask was maintained at 1 atm. by venting through a bubbler. Three ml samples were removed with a syringe and quenched by adding to test tubes containing dilute $H_2SO_4$ or $D_2O$. The exact time of quenching was noted. Typically 6 quenches were made during the first 500 seconds of reaction. In all experiments a $D_2O$ quench was made after 40 minutes. The hydrolyzed samples were worked up and extracted into pentane for GLC analysis. All reactions were carried out under identical conditions and the resulting rates charted by plotting the percent yield of octane vs. time.

All of these reactions were carried out at room temperature.

### *ESR spectra*

$Cp_2TiCl_2$ was allowed to react with excess $MgH_2$ in THF at room temperature. The resulting dark blue solution was diluted to $10^{-4}$ *M* concentration and the ESR spectrum recorded. A triplet was observed ($g = 1.9935$, $a = 7.7$ gauss) which is in good agreement with the reported low temperature ESR spectrum of $Cp_2TiH_2^-$ [11].

$Cp_2TiCl_2$ and excess t-$Bu_2Mg$ gave a brown solution in THF. No ESR signal was observed within 1 h after mixing, however after 24 h a triplet ($g = 1.9938$, $a = 7.9$ gauss) was observed which can be attributed to $Cp_2TiH_2^-$. This observation indicates that olefin elimination is very slow for $Cp_2Ti$(t-Bu).

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