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**Preliminary communication**

# Magnesium activation of dichlorodi-$\eta^5$-cyclopentadienyltitanium in the catalytic hydrogenation of olefins and acetylenes

**Frederick Scott, Helgard G. Raubenheimer, Gerard Pretorius and Augustine M. Hamese**

*Department of Chemistry and Biochemistry, Rand Afrikaans University, Johannesburg 2000 (Republic of South Africa)*

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## Abstract

Magnesium activation of dichlorodi-$\eta^5$-cyclopentadienyltitanium ($Cp_2TiCl_2$) in tetrahydrofuran (THF) under a dihydrogen atmosphere has been shown to produce a stable solution which effectively hydrogenates various types of olefins and acetylenes under ambient conditions. Addition of triphenylphosphine facilitated the hydrogenation of hex-1-yne and of the unsaturated ester methyl oleate.

Several groups have described the catalytic hydrogenation activity exhibited by reduced $Cp_2TiCl_2$; various reductants such as $LiAlH_x(OR)_y$ [1], $MgH_2$ [2], RMgX [3], RLi [4], Red-Al (sodium bis(2-methoxyethoxy)aluminium hydride) [5], and sodium or other alkali metal naphthalenide [6,7] used in the catalyst preparation, but some of the catalyst solutions had distinct disadvantages, such as instability [7,8], the need for high pressure or high temperature [2,8], and non-specificity, leading, for example, to hydrogenation as well as isomerization [7]. Furthermore, none of the hydrogenation studies mentioned involved more than a few simple alkenes.

The facile reduction of $Cp_2TiCl_2$ with magnesium in THF has found useful application in the preparation of di-$\eta^5$-cyclopentadienyltitanium complexes [9] as well as in stoichiometric organic synthesis [10,11], but this method has not been employed previously to activate $Cp_2TiCl_2$ for alkene hydrogenation reactions. As part of a systematic study on catalytic hydrogenation by low valent first row transition metal compounds, we have produced a very simple titanium-alkene (or -acetylene) hydrogenation catalyst system which is stable and which functions under mild conditions (room temperature; one atmosphere of $H_2$). Our preliminary results also show that the scope of the catalytic system may be extended to unsaturated esters when the hydrogenation is performed in the presence of triphenylphosphine.

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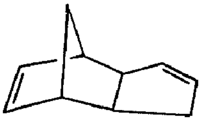
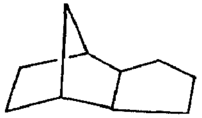
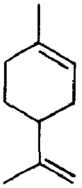
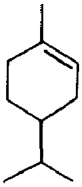
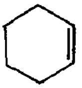
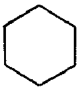
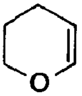
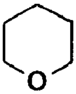
Table 1

Catalytic hydrogenation of unsaturated hydrocarbons with $Cp_2TiCl_2$ and magnesium in THF

| Run [a] | Olefin or acetylene | Product | Time (h) | Conversion [c] (%) |
|---|---|---|---|---|
| 1 | $C_6H_{13}CH{=}CH_2$ | $C_8H_{18}$ | 1.5 | > 98 |
| 2 |  |  | 2.0 | > 98 |
| 3 |  |  | 2.0 | > 98 |
| 4 |  |  | 2.25 | > 98 |
| 5 | PhC≡CPh | $PhCH_2CH_2Ph$ | 2.5 | > 98 |
| 6 | $C_3H_7CH{=}CHC_3H_7$ | $C_8H_{18}$ | 2.5 | > 98 |
| 7 |  |  | 2.5 | > 98 |
| 8 | $C_8H_{17}CH{=}CH\text{-}C_7H_{14}CO_2CH_3$ [b] | $C_{19}H_{38}O_2$ | 12 | ~ 80 |
| 9 |  | unchanged | 24 | 0 |

[a] 20.0 mmol substrate was added at room temperature to a stirred mixture of 0.5 mmol $Cp_2TiCl_2$ and 0.5 g (30 mmol) active magnesium in 15 $cm^3$ THF under dihydrogen at 1 atm. [b] 0.5 mmol of $PPh_3$ was added to the reaction mixture. [c] Determined by GLC peak heights (column: DB-1 15 m × 0.53 mm ID).

The active catalyst was generated in situ by stirring a catalytic amount of $Cp_2TiCl_2$ in THF with an excess of active magnesium [12*] and the olefin under one atmosphere of dihydrogen. The mixture became green and gradually turned dark as dihydrogen was taken up. Several alkenes were readily hydrogenated (Table 1) with this system.

No hydrogenation occurred under our conditions in the absence of a catalytic amount of $Cp_2TiCl_2$ [2]. The catalytic hydrogenation of the alkenes in Table 1 was usually complete within 1–3 hours, with terminal and strained ring alkenes being hydrogenated more rapidly than internal alkenes (entries 1, 2 and 3, Table 1). The hydrogenation of oct-1-ene gave octane, and no oct-2-ene formation was observed.

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* Reference number with asterisk indicates a note in the list of references.

The internal alkyne diphenylacetylene was readily hydrogenated (entry 5, Table 1), but the hydrogenation of hex-1-yne stopped after 20 min, yielding a mixture which consisted mainly of unchanged starting material and hexane but also contained low concentrations of hex-1-ene , hex-2-ene and a still unidentified aromatic product. The addition of one equivalent of triphenylphosphine resulted in a slower but more selective hydrogenation (14 h, 90% conversion) to give a mixture consisting of hexane and hex-1-ene in a ratio of 5/1. Previous workers [13] have shown that an alkynetitanium(II) complex selectively hydrogenates internal alkynes in the presence of trimethylphosphine. The possibility of catalyst poisoning by oxidative addition of terminal alkynes, which could be suppressed by selective phosphine addition, will receive our attention in future.

Trisubstituted alkenes were inert to hydrogenation with our catalytic system (entries 3 and 10, Table 1). The hydrogenation of dihydropyran to pyran occurred without any ring cleavage [14] (entry 7, Table 1). Kagan and coworkers have expressed the opinion that nitrile and carbonyl functionalised olefins are not hydrogenated with bis(cyclopentadienyl)titanium-based catalysts [5], but the catalytic hydrogenation of methyl oleate (entry 7, Table 1) proceeded satisfactorily on addition of one equivalent of triphenylphosphine per mole of catalyst.

Owing to the complexity of the titanium species produced on reduction of $Cp_2TiCl_2$ [6] and the difficulty of isolating pure intermediates, the exact nature of the magnesium-generated catalyst is still unclear. We found that the dark-coloured filtered THF solution obtained from $Cp_2TiCl_2$ and magnesium under argon retained its catalytic activity towards hydrogenation for several days when oxygen and air were rigorously excluded from the stored solution. This is in contrast with previous reports [6,15] that reduction of $Cp_2TiCl_2$ with alkali metals produces a stable "titanocene". The latter complex was subsequently fully identified by $^{13}C$ NMR spectroscopy as $\mu(\eta^5:\eta^5$-fulvalene)di-$\mu$-hydridodicyclopentadienyltitanium [16], and is inert as a hydrogenation catalyst for dec-1-ene. The stability of our system under argon is probably due to weak intermolecular catalyst-$MgX_2$ interactions. Intermolecular bonding is well known in titanium(III) complexes [17], and it is noteworthy that the thermal stability of the carbenoid (chloromethyl)lithium is greatly enhanced on coordination of the chlorine atom to a Lewis acid [18].

Our future studies on magnesium-generated homogeneous catalytic systems will focus on, inter alia, other metal precursors, other substrates including prochiral olefins, attempts to isolate, identify and characterize the active catalyst, and comparisons with existing catalysts. The work is relevant to current investigations [19] of enantioselective titanocene-based hydrogenation of alkenes.

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