

POLYMER-BOUND TITANIUM OLEFIN ISOMERIZATION CATALYSTS

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Summary

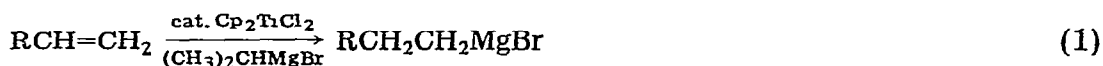
Polystyrene-bound bis(cyclopentadienyl)titanium dichloride has been shown to react with Grignard reagents to form a reactive alkene isomerization catalyst, which converts 1-alkenes primarily into *E*-2-alkenes at room temperature. The catalyst specificity seen for this polymer-bound catalyst is altered from that seen in an analogous homogeneous system. Hydrogenation of alkenes has also been accomplished when 1-alkenes are allowed to react with these same catalysts under hydrogen. Internal alkenes are unreactive toward these catalysts. The efficacy of organomagnesium versus organolithium reagents for preparation of these catalysts and the application of ^{13}C NMR to the study of polymer-supported catalytic systems is described.

Polymer-bound homogeneous catalysts have excited interest because of their potential for providing a way of combining the experimental simplicity of a heterogeneous catalyst with the selectivity and mild reaction conditions often associated with homogeneous catalysts [1]. More recently, the potential of polymer-bound catalysts to function as catalysts for reactions different than those catalyzed by their homogeneous analogs has been recognized [2]. Here we report our studies of the reactions of alkenes with reduced titanium species bound to polymers in which a significant alteration in the specificity of the catalyst is observed. In addition, our studies show that use of organomagnesium reagents instead of organolithium reagents in the catalyst preparation has a significant effect on activity of these reduced titanium catalysts.

The immobilization of bis(cyclopentadienyl)titanium dichloride on a polystyrene matrix was first described by Grubbs and Brubaker [3] who used this "immobilized" species to prepare an alkene hydrogenation catalyst whose activity was greater than its homogeneous analog. In this report we describe further examples of differences between catalysts derived from similar polystyrene-bound titanium species and their homogeneous analogs. In our studies we have shown that reduction of polystyrene-bound bis(cyclopentadienyl)-

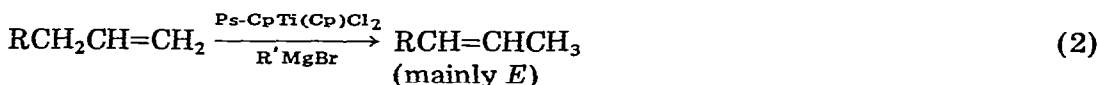
titanium(IV) dichloride (I) with alkylmagnesium halides in ethereal solutions produces an alkene isomerization catalyst. We have also studied alkene hydrogenations using organomagnesium-reduced I and its soluble analog as a further comparison to the organolithium-titanium(IV) systems. Although the exact nature of the catalytically active species could not be determined, ESR studies did establish that Ti^{III} was a component, although not an active catalytic species, of these catalyst mixtures.

Originally we hoped to prepare a polymeric version of the titanium hydrometalation catalyst first described by Finkbeiner and Cooper (eq. 1) [4,5].



Indeed, while our studies were in progress catalytic hydroalumination of alkenes using the same polymer-bound catalyst we employed was reported [6]. However, when we attempted reaction 1 with polystyrene-bound bis(cyclopentadienyl)titanium dichloride we saw mainly alkene isomerization and little or no hydrometalation. These alkene isomerization catalysts were prepared either using a 2% divinylbenzene-crosslinked polystyrene support or a 20% divinylbenzene-crosslinked polystyrene support*. Addition of excess alkylmagnesium bromide or chloride to either polymeric titanium complex suspended in ether resulted in a change in color from an initial red to black. The rate of the color change varied for different alkylmagnesium halides and corresponded roughly to the efficacy of the resulting isomerization catalyst (vide infra). Similar color changes were observed on addition of hydrocarbon solutions of *n*-butyllithium, *sec*-butyllithium, and *tert*-butyllithium. Grignard reagents without β -hydrogens (methyl, benzyl) also produced the same color change. The observed color changes were reversible in that work-up using dilute HCl regenerated the polymers I.

Addition of a terminal alkene to the catalyst prepared from I resulted in isomerization of the starting alkene (equation 2). This isomerization was success-



ful with 1-butene, 1-pentene, and 1-octene. Internal alkenes such as 2-octene apparently do not further react. Similar behavior was noted in hydrogenation reactions (vide infra). In long-term experiments in which fresh charges of Grignard reagent and starting alkene were periodically added, turnover numbers (total mmol isomerized/mmol Ti) as high as 1000 were achieved. Less than 15% of the starting alkene formed alkane in contrast to the homogeneous reaction which produced 70% octane (by protonation on aqueous HCl work-up of an intermediate *n*-octylmagnesium halide) when 1-octene was allowed to react with isopropylmagnesium bromide and bis(cyclopentadienyl)titanium dichloride under Finkbeiner and Cooper's conditions [4,5].

The relative efficacy of various Grignard reagents for promoting the isomer-

* Purchased from Strem Chemicals, Newburyport, MA.

ization was *tert*-butyl > isopropyl > *n*-butyl. Methylmagnesium bromide and benzylmagnesium chloride were ineffective at generating an alkene isomerization catalyst. Typical product mixtures from these isomerizations were: 1-octene; *E*-2-octene (84%), *Z*-2-octene (12%), *n*-octane (4%); 1-butene, *E*-2-butene (72%), *Z*-2-butene (28%); 1-pentene, *E*-2-pentene (85%), *Z*-2-pentene (15%). The starting 1-alkenes were typically completely consumed. Alkyl-lithium reagents were ineffective at producing this isomerization catalyst although they are known to form alkene hydrogenation catalysts [3].

Although we typically used gas chromatography to follow these reactions we also found ^{13}C NMR of sealed tubes containing substrate, alkene, a Grignard reagent, and polymeric catalyst could conveniently be used to follow these reactions. In these experiments the polymer and catalyst were not detectable because of the line broadening characteristic of solids. The substrate and product alkenes were, however, easily seen and their absorptions could be easily assigned. We believe this procedure could be generally useful in studying reactions involving polymer-bound catalysts so long as all substrates and reagents can be contained in an NMR tube and as long as the spectral analysis is simple.

Polymer-supported and homogeneous organomagnesium-reduced Cp_2TiCl_2 obviously differ in their efficacy as metalation catalysts. Since similar catalysts had been described previously as hydrogenation catalysts, we also chose to examine the activity of the isomerization and metalation catalysts described above as hydrogenation catalysts. The results of these studies described below reinforce the impression gained in isomerization reactions that the titanium catalysts we have prepared using Grignard reagents are complex entities which differ from titanium catalysts prepared from organolithium reagents. Specifically, marked differences in activity and specificity are also seen in hydrogenations catalyzed by these catalyst systems.

Table 1 contains a representative collection of data for hydrogenation reactions of alkenes catalyzed by either polystyrene-supported Cp_2TiCl_2 -Grignard reagent or homogeneous Cp_2TiCl_2 -Grignard reagent catalyst systems. For comparison purposes, data for hydrogenation catalysts prepared from these titanium catalyst precursors and alkyllithium reagents are included. Several significant things are apparent in these data. First, hydrogenation catalysts prepared using soluble Cp_2TiCl_2 and an alkylmagnesium reagent such as cyclohexylmagnesium bromide or *tert*-butylmagnesium chloride were the most active in terms of initial rates. However, both of these catalyst systems deactivate with time as noted before, albeit at differing rates. Hydrogenation occurs much faster than isomerization. Initial rates as high as 6000 ml H_2 /min/mmol Ti were observed in the Cp_2TiCl_2 -cyclohexylmagnesium bromide system with 10 mmol of 1-octene being consumed in ca. 4 min. Initial addition of excess 1-octene or styrene resulted in 1500 mmol of alkene being hydrogenated per mmol Ti before the catalyst activity decreased to an inconvenient level. Substitution of polystyrene-supported Cp_2TiCl_2 for soluble Cp_2TiCl_2 in these hydrogenation reactions led to much slower rates. For example, use of either a 2% or 20% DVB-crosslinked polystyrene as a support for Cp_2TiCl_2 led to a 1-octene hydrogenation catalyst (cyclohexylmagnesium bromide cofactor) which was initially twenty times slower than its homogeneous analog. Within 15 min a rather steady hydrogenation rate of 25 or 30 ml H_2 /min/mmol PS- Cp_2TiCl_2 was ob-

TABLE 1

ALKENE HYDROGENATION REACTIONS USING SOLUBLE AND POLYMER-BOUND $(Cp)_2TiCl_2$ REDUCED BY ORGANOMAGNESIUM AND ORGANOLITHIUM REAGENTS AS CATALYSTS ^a

Alkene	Catalyst ^b	Organometallic Cofactor	Initial Rate ^c (ml H ₂ /min/mmol Ti)	Subsequent Rate ^d (ml H ₂ /min/mmol Ti)
Styrene	A	(CH ₃) ₃ CMgCl	5669	f
Styrene	B	(CH ₃) ₃ CMgCl	369	234
Styrene	C	(CH ₃) ₃ CMgCl	117	112
Styrene	A	c-C ₆ H ₁₁ MgBr	6211	f
Styrene	B	c-C ₆ H ₁₁ MgBr	291	185
Styrene	C	c-C ₆ H ₁₁ MgBr	341	197
Styrene	A	CH ₃ CH ₂ CH ₂ CH ₂ MgBr	99	21
Styrene	B	CH ₃ CH ₂ CH ₂ CH ₂ MgBr	39	15
Styrene	C	CH ₃ CH ₂ CH ₂ CH ₂ MgBr	103	23
Styrene	A	(CH ₃) ₂ CHMgBr	280	139
Styrene	B	(CH ₃) ₂ CHMgBr	308	162
Styrene	C	(CH ₃) ₂ CHMgBr	219	113
Styrene	A	CH ₃ CH ₂ CH ₂ CH ₂ Li	57	23
Styrene	B	CH ₃ CH ₂ CH ₂ CH ₂ Li	38	6
Styrene	C	CH ₃ CH ₂ CH ₂ CH ₂ Li	58	36
Styrene	C ^e	CH ₃ CH ₂ CH ₂ CH ₂ Li	243	—
Styrene	A	(CH ₃) ₃ CLi	335	41
Styrene	B	(CH ₃) ₃ CLi	33	23
Styrene	C	(CH ₃) ₃ CLi	20	27
1-octene	A	(CH ₃) ₃ CMgCl	8619	f
1-octene	B	(CH ₃) ₃ CMgCl	315	187
1-octene	C	(CH ₃) ₃ CMgCl	523	206
1-octene	A	c-C ₆ H ₁₁ MgBr	7342	f
1-octene	B	c-C ₆ H ₁₁ MgBr	312	94
1-octene	C	c-C ₆ H ₁₁ MgBr	303	114

^a Hydrogenation reactions were run at 25°C and atmosphere pressure using 2 mmol of alkene, 10 ml of solvent (ether for RMgX reactions, hexanes for RLi reactions), and 2 mmol of the indicated organometallic cofactor. ^b A is soluble bis(cyclopentadienyl)titanium dichloride; B is Cp₂TiCl₂ attached to a 2% DVB-crosslinked polystyrene; C is Cp₂TiCl₂ attached to a 20% DVB-crosslinked polystyrene. ^c The rate after 1 min of reaction. ^d The rate after 10 min of reaction. ^e Data from ref. 3. ^f Complete before 10 min elapsed.

tained for these two catalysts, respectively. Grinding these polymers markedly increases their eventual catalytic activity as noted earlier by Grubbs and Brubaker [3], but the polymer-bound catalysts were always less active than their homogeneous analogs. A minimum turnover number of ca. 100 mmol alkene hydrogenated per mmol of titanium was measured for these polymer-supported catalyst systems using 1-octene. Long-term turnover number experiments were not carried out. Nevertheless, these polymer-supported hydrogenation catalysts were clearly not as useful as their homogeneous analogs in view of their slower hydrogenation rates.

There were some similarities between the hydrogenation and isomerization experiments. The failure of the Grignard-reduced titanium catalysts to hydrogenate cyclohexene corresponds to the failure of these same catalysts to isomerize internal alkenes. An unusual observation was the low yield (5%) of benzene resulting from the attempted hydrogenation of cyclohexene by the tert-butylmagnesium chloride-Cp₂TiCl₂ system with either soluble or polymer-bound titanium. Formation of this dehydrogenated product is plausibly related

to the isomerization reaction mechanism (*vide infra*).

The organolithium-reduced titanium catalysts' activity paralleled that reported earlier although the reaction rates we measured were not as high as reported previously. In general, polystyrene-supported hydrogenation catalysts prepared using organolithium reagents were less reactive than those prepared using Grignard reagents and I. However, the combination of soluble Cp_2TiCl_2 and Grignard reagents clearly gave the most active alkene hydrogenation catalyst systems.

In order to study the possible reasons for the differences in these catalyst systems we have tried to find out what differences, if any, there were between homogeneous or heterogeneous lithium and magnesium systems. Although our studies have not successfully identified the actual catalyst species, we have successfully carried out ESR studies which demonstrate that the initial titanium(IV) species are in all cases reduced, at least partly, to some titanium(III) species. The titanium(III) species formed gave rise to different ESR spectra, depending on the reducing agent used. For example, the active isomerization and hydrogenation catalyst suspensions prepared from cyclohexylmagnesium bromide and 20% DVB-crosslinked polystyrene-supported Cp_2TiCl_2 gave a broad singlet by ESR. Catalyst suspensions prepared from the same titanium precursor and methylmagnesium bromide, benzylmagnesium chloride and *n*-butyllithium produced different spectra. In each case several different ESR peaks were seen which overlapped to give a multiplet. The titanium(III) species are not active catalysts. The ESR spectra did not change with time with any of the above systems. Thus, the ESR-active species are not likely to be the catalytically active species (catalytic activity did change with time). Titanium(II) or titanium(0) are likely alternatives to titanium(III) and have been postulated as catalyst intermediates in similar systems.

The mechanism of alkene isomerization was not studied explicitly. However, a mechanism involving oxidative addition of an allylic C-H bond to titanium may be involved. This process is likely to be occurring to a very limited extent for cyclohexene to give the small amount of benzene observed in attempted cyclohexene hydrogenations. Similar processes have been described for other metals [7,8]. The alternative process involving "Ti-H" addition and β elimination may also occur. A similar hydride addition-elimination seems likely to be occurring in the metalation reactions employing soluble Cp_2TiCl_2 , isopropylmagnesium bromide and alkenes [4,5].

Heterogeneous species such as the polymer-supported catalysts described above are not readily characterized except by analogy to homogeneous systems. Thus, we have been unable to further define the actual catalyst. Nevertheless, our studies show that immobilization of homogeneous catalysts can achieve not only activation and experimental simplicity but also modified catalyst selectivity.

Experimental section

All reactions of organometallic compounds were carried out in oven-dried glassware under nitrogen or argon using unexceptional procedures [9]. Tetrahydrofuran and other ethereal solvents were distilled from solutions of

disodium benzophenone dianion prior to use. Styrene, cyclohexene, and 1-octene were treated before use by shaking with alumina and filtering. Subsequent to this treatment these alkenes were stored at 0°C. 1-Butene and 1-pentene were used as supplied by Matheson and Tridom Chemical, respectively. Bis(cyclopentadienyl)titanium dichloride was purchased from Strem Chemicals as was a sample of polymer-bound bis(cyclopentadienyl)titanium dichloride on 20% DVB-crosslinked polystyrene. Grignard reagents were prepared by standard procedures [10] from reagent halides purchased from Aldrich Chem. Co. Organolithium reagents were also purchased from Aldrich. Organolithium and Grignard reagents were titrated before use [11] and discarded if they contained more than 15% residual base. Bis(cyclopentadienyl)titanium dichloride on 2% DVB-crosslinked polystyrene was prepared from Merrifield resin (Sigma Chem.) according to a literature procedure [12]. The polymeric catalysts were analyzed by Galbraith Labs. ¹³C NMR spectra were recorded on a JEOL FT-100 spectrometer in sealed tubes using external CDCl₃/Me₄Si as a lock signal and reference. GC analyses were carried out on a Hewlett Packard 5830 GC using an n-octane/Porasil C column for analysis of isomeric alkenes.

Typical procedure for alkene isomerization

To a flame-dried 40 ml flask under nitrogen was added 0.100 g of I (0.032 mmol Ti). The flask was flushed with nitrogen and 10.0 ml of ether was added. After adding 1.0 ml of 1-octene (6.4 mmol) using a syringe, the active catalyst was prepared in situ by addition of 2 ml of 1 N cyclohexylmagnesium bromide (2 mequiv.). n-Nonane (50 μl, 0.28 mmol) was added as an internal standard for subsequent analysis. The resulting black suspension was shaken for 1 week. At intervals of 2, 8, 24, 72, and 168 hours (1 week) the flask was removed from the shaker and the heterogeneous contents allowed to settle. From the clear supernatant were withdrawn aliquots which were quenched with aqueous HCl, neutralized with NaHCO₃, dried over magnesium sulfate and analyzed using a 1/8 in × 12 ft n-octane/Porasil C column. Generally, 1-octene was completely isomerized in 1 day in this scale experiment.

In ¹³C NMR experiments, the catalyst, the substrate alkene, the Grignard reagent cofactor and solvent were added to an 8 mm o.d. tube which was then sealed under reduced pressure. The tube was agitated using a shaker and the reaction progress was monitored by periodically placing the reaction tube inside of a 10 mm o.d. NMR tube containing CDCl₃ (lock) and Me₄Si and observing the ¹³C NMR spectrum of the alkene region.

Typical procedure for alkene hydrogenation

To a flame-dried 2-necked flask equipped with a magnetic stir bar was added 0.048 g of I (0.015 mmol Ti). The flask was attached to the hydrogenation apparatus via one neck and reagents were added through a septum capped stop-cock in the other neck. The reaction flask was evacuated and flushed with hydrogen a total of 4 times. Then 10 ml of dry ether was added followed by 1.5 ml of 1 N cyclohexylmagnesium bromide (1.5 mequiv). The suspension was stirred under a hydrogen atmosphere for 1 hour while the polymer blackened. Then 0.31 ml (2 mmol) of 1-octene was injected and hydrogen uptake was followed as a function of time using a gas buret.

Acknowledgement

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