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SOME NOVELTIES IN OLEFIN CARBOMETALLATION ASSISTED BY ALKYL-MAGNESIUM AND -ALUMINIUM DERIVATIVES AND CATALYZED BY ZIRCONIUM AND TITANIUM COMPLEXES

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Summary

Carbometallation of α-olefins, as well as of those containing functional groups, and of norbornene derivatives has been investigated with alkyl-magnesium and -aluminium compounds and found to proceed under mild conditions in the presence of catalytic quantities of Zr and Ti complexes. The reactions have revealed their exclusively high regioselectivities.

Introduction

The addition of isoalkyl-, 2-alkenyl; and benzyl-magnesium derivatives to olefins with inactivated double bonds under rigid conditions according to Lehmkuhl [1] and the carbometallation of olefins, dienes, and acetylenes catalyzed by metal complexes under mild conditions by Grignard reagents [2–5] are considered to be the most available and well-known methods for constructing a carbon–carbon bond with organometallics. These reactions have been poorly employed due to their insufficient regioselectivities and low yields of target products.

We have recently reported the possibility of regioselective carbometallation of α-olefins with Et_2Mg catalyzed by Cp_2ZrCl_2 under mild conditions [6].

The Ti and Zr catalyzed carbometallation of linear and cyclic mono- and di-olefins, as well as of those containing functional substituents, by alkyl-magnesium and -aluminium derivatives has been investigated in order to expand further the sphere of application of the method and to develope some new effective and selective routes to the formation of a carbon–carbon bond by the available organometallics.

Results and discussion

The dependence of target product yields on the initial reagent ratio, catalyst concentration, reaction time, and temperature has been studied by the interactions

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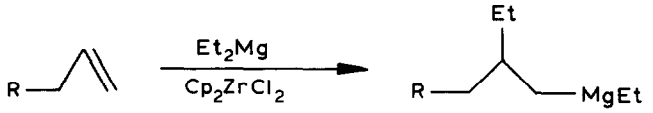
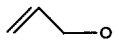
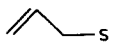
TABLE 1

THE EFFECT OF THE SUBSTITUENT NATURE OF THE ALLYL COMPOUND ON THE CARBOMAGNESATION PRODUCT YIELDS [a]

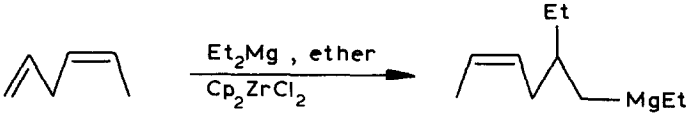


R	Yield (%)	Reaction time (h)
Et_2N	100	4
Me_3Si	96	4
n-BuO	90	30
	60	30
	4	25
PhO	–	90
HO	–	90

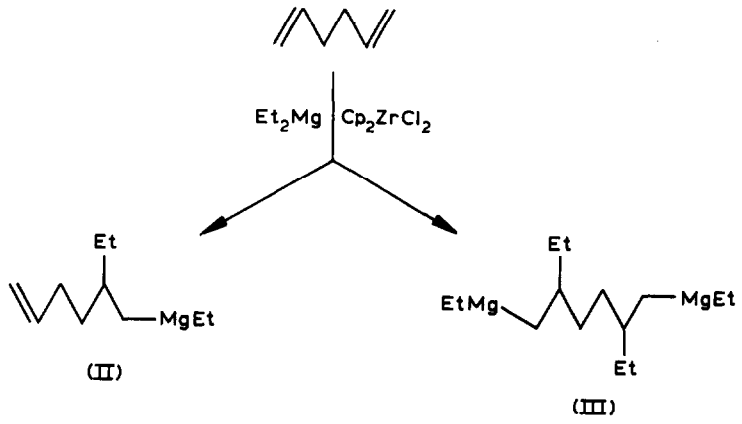
[a] Reaction conditions: $Et_2Mg/Cp_2ZrCl_2 = 100/1$; olefin/Mg = 1/1.5, 20°C, diethyl ether.

of Et_2Mg and EtMgBr and 1-hexene for proper selection of the optimal conditions of olefin carbometallation. The highest selectivities and yields of the addition of Et_2Mg and EtMgBr to olefins were reached at temperatures below 20–25°C in ether solvents (diethyl ether, di-n-propyl ether, THF, dioxane), the catalyst concentration being more than 1%, as related to an alkylating reagent and Et_2Mg/olefin 1.5/1, EtMgBr/olefin 2/1. The carbomagnesation reaction involves only one ethyl group of Et_2Mg or half of all the ethyl groups of EtMgBr, the latter reacting more slowly than Et_2Mg due to either the deactivating effect of $MgBr_2$ or the necessity of disproportionating Et_2MgBr into Et_2Mg and $MgBr_2$ to bring about the reaction. The highest catalytic activity was assigned to Cp_2ZrCl_2, selected from the whole scope of tested transition metal complexes to be employed as the catalyst in our subsequent experiments.

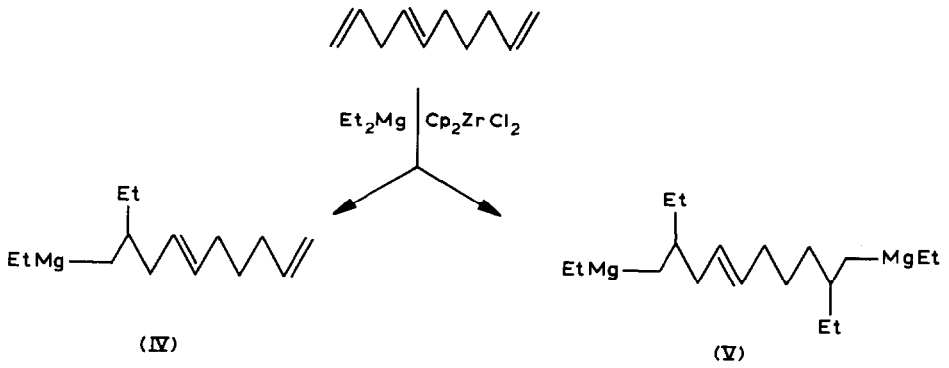
The interaction of 1,4*Z*-hexadiene and Et_2Mg in the presence of the catalyst mentioned above resulted in carbomagnesation of a vinyl group with the formation of an organomagnesium compound (I) (90% yield). A mixture of mono- and bis-organomagnesium compounds (II, III and IV, V; 90 and 95% yields, respectively) was produced from 1,5-hexadiene and 1,4*E*,9-decatriene with Et_2Mg under analogous conditions. An increase in the Et_2Mg concentration facilitated carbomagnesation in the direction of the formation of organomagnesium compounds (III and V, only).



(I)



(II) (III)

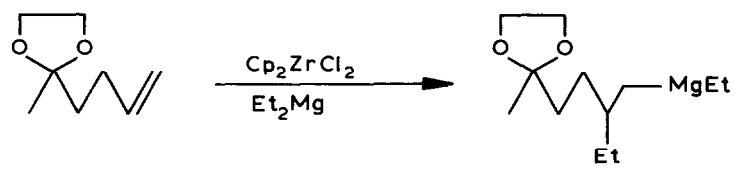


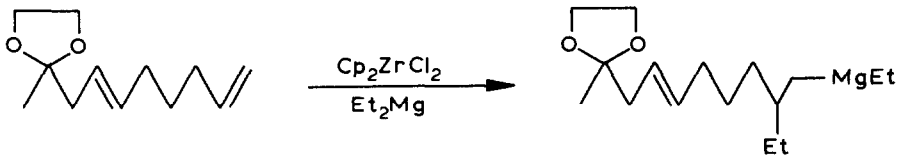
(IV) (V)

The internal disubstituted double bonds of various configurations are not affected in the course of carbomagnesation in either acyclic or cyclic hydrocarbons.

Carbomagnesation of allyl ethers, allyl alcohols, diethylallylamine, diallyl sulphide, and trimethylallylsilane (Table 1) was performed to prove the involvement of α-olefins with functional substituents. The experimental results confirmed the regioselectivity of carbomagnesation to be independent of the heteroatom nature of the allyl compound, whereas the product yields decreased with an increase in the electron-withdrawing property of the substituent.

Opposite results were obtained with 2,7-octadien-1-ol, methanol 2,7-octadienyl ethers, cyclohexanol, phenol, 2,7-octadienylpiperidine, 2-ethylene-dioxy-5-hexane, and 2-ethylene-dioxy-4*E*, 9-decadiene in their reactions with Et_2Mg. Here the carbomagnesation product yields were not influenced by the nature or structure of the initial diene substituent, values greater than 90% being obtained (Table 2).

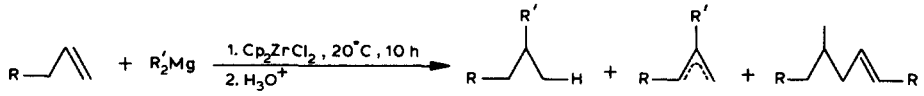




The results obtained confirm that the electron-withdrawing substituents at an allyl carbon atom cause a pronounced decrease in the double bond activity in the process of carbomagnesation with no effects on the regioselectivity. Those functional substituents which are further away from the reaction center do not have much influence on the reaction direction or the regioselectivity.

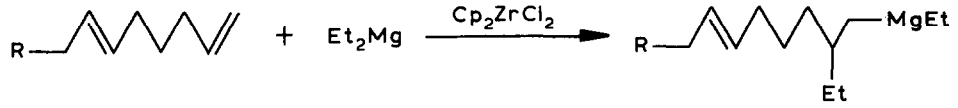
The carbomagnesation reactions of the olefins mentioned above work well with other analogues of the Grignard reagent, the activity of which, being evidently dependent on both steric and electronic factors, is inferior to that of diethylmagnesium and falls in the following series: $Et_2Mg = Et_3SiMgEt \gg CpMgEt > [Ph(Et)N]MgEt > ClMgEt > BrMgEt = C_5H_4NMgEt = (Et_2N)MgEt > IMgEt$ (Table 3). Such compounds as EtMgOR, EtMgSR, EtMgOC(=O)R, EtMgF, and EtMgC≡CR have demonstrated their total inactivity in carbomagnesation.

We further attempted to perform the carbometallation of α-olefins with higher dialkyls of magnesium. It appeared, however, that carbomagnesation of 1-hexene and 1-dodecene by di-n-propylmagnesium and di-n-butylmagnesium in the presence of catalytic quantities of Cp_2ZrCl_2 results in invariably high regioselectivities and is complicated by the formation of substantial amounts of the dehydromagnesation and dimer products, the mechanism of which remains vague.



(R = C_3H_7, C_9H_{19}; R = C_3H_7, C_4H_9)

TABLE 2. Cp_2ZrCl_2 CATALYZED CARBOMAGNESATION OF FUNCTIONALLY SUBSTITUTED 2,7-OCTADIENES ASSISTED BY Et_2Mg [a]



R	Yield (%)	Reaction time (h)
	98	4
$C_6H_{13}O$	95	4
MeO	95	4
PhO	95	4
HO	90	4

[a] Reaction conditions: $Et_2Mg/Cp_2ZrCl_2 = 100/1$, olefin/Mg = 1/1.5, ether.

As mentioned above, our attempts to carry out Cp_2ZrCl_2 catalyzed carbomagnesation of acyclic disubstituted (2*E*-hexene, 2*Z*-hexene) and monocyclic (cyclohexene, cyclooctene, cyclododecene) olefins by Et_2Mg failed. At the same time, such bicyclic hydrocarbons as [2,2,1]-bicycloheptene (V) and *endo*-tricyclo[5,2,1,$0^{2,6}$]3,8-decadiene (VI), which contain more active double bonds, react with an equimolar amount of Et_2Mg to yield (45–100%) the corresponding organomagnesium compounds (VII–IX), the hydrolysis of which converts them into *exo*-ethyl-bicyclo-[2,2,1]heptane (X) and into a mixture of *exo*-9-ethyl-*endo*-tricyclo[5,2,1,$0^{2,6}$]decen-3 (XI) and *exo*-9-ethyl-*endo*-tricyclo[5,2,1,$0^{2,6}$]decen-4 (XII). It should be noted that the carbomagnesation of bicyclic hydrocarbons proceeds more slowly than that of α-olefins.

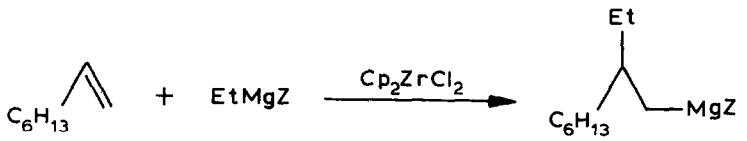
Of a different kind is the carbomagnesation of bicyclo[2,2,1]hepta-2,5-diene (XIII) to yield (~ 70%) the organomagnesium compound XIV, which is converted only into 3-ethylnortricyclene (XV). This phenomenon favours the process of intramolecular carbomagnesation to lead to XIV.

Attention should be paid to the fact that the reactivity of EtMgBr is much lower than that of Et_2Mg in carbomagnesating bicyclic olefins. Thus, for instance, the employment of even a four-fold excess of EtMgBr, as related to an unsaturated substrate, results in carbomagnesation product yields of only 3–35%, while a two-fold excess of Et_2Mg leads to an increase in the conversion of bicyclenes, (V, VI), with yields up to 95%.

The carbomagnesation of olefins by magnesium dialkylates and Grignard reagents that are insoluble in hydrocarbons may be performed in ether solvents only, thus limiting the synthetic application of this method. In view of such limitations, some novel modified carbomagnesating reactants based on R_2Mg and Grignard

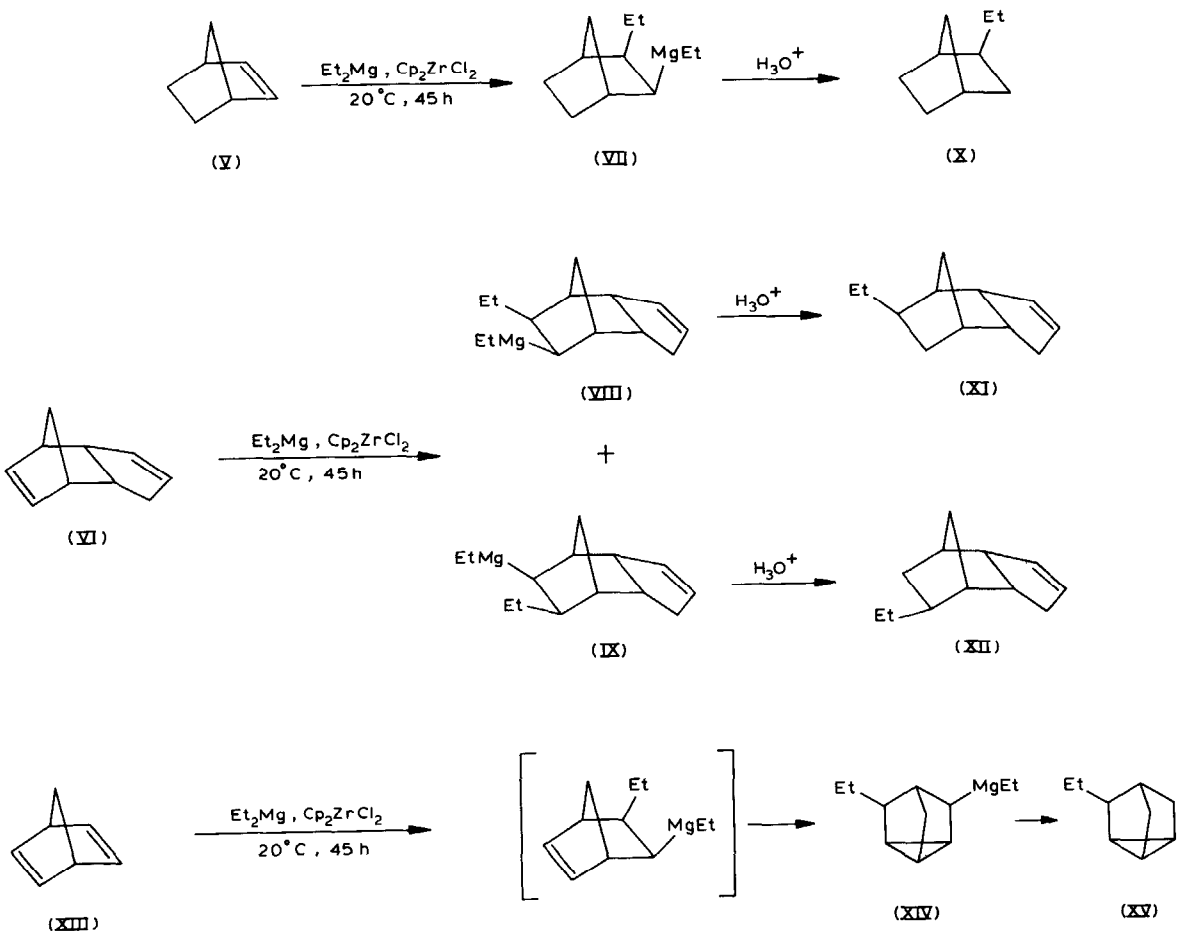
TABLE 3

RELATIVE CARBOMAGNESATION RATES OF 1-OCTENE WITH VARIOUS GRIGNARD REAGENT ANALOGUES [a]



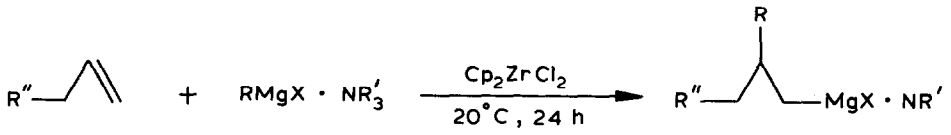
Z	Yield (%)	Reaction time (h)
Et	65	0.5
Et_3Si	60	0.5
Cp	48	1.0
Ph(Et)N	28	1.0
Cl	18	1.0
Br	13	1.0
	10	1.0
Et_2N	5	1.0
I	3	1.0

[a] Reaction conditions: Mg/olefin/Zr = 100/100/1, 20°C, ether. [EtMgZ] concentration 1.1 mmol/ml.


Et
MgEt
Et_2Mg , Cp_2ZrCl_2
20°C , 45h
H_3O^+
(V)
(VII)
(X)
Et
EtMg
(VIII)
(XI)
(VI)
+
EtMg
Et
(IX)
(XII)
(XIII)
(XIV)
(XV)

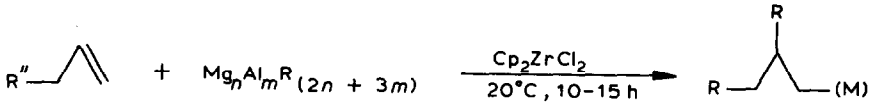
reagents that are soluble in aliphatic and aromatic hydrocarbons have been suggested.

The stoichiometric molecular complexes of Et_2Mg and RMgX with tertiary amines (Et_3N, Ph_3N, Et_2NPh) carbomagnesate α-olefins (1-hexene, 1-dodecene) in the presence of Cp_2ZrCl_2 in aromatic or aliphatic solvents. The activity of thus modified organomagnesium alkylating reagents is inferior to none of the ether solvents of the related magnesium dialkylates or alkylmagnesium halides.



(R" = C_3H_7, C_9H_{19}; R = Et; R' = Et, Ph)

Mixed organoaluminium compounds of the $Mg_nAl_m \cdot R_{(2n+3m)}$ type [7], where $n/m = 1/1 \div 20$, also carbomagnesate the above-mentioned α-olefins in aliphatic and aromatic solvents.

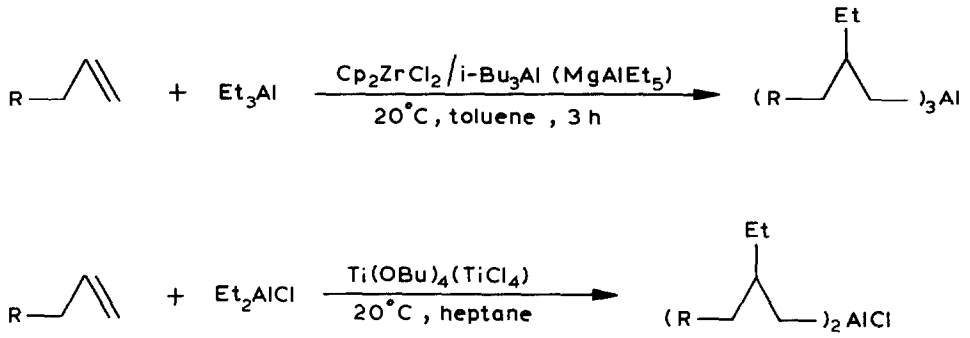


(R = C_2H_5; R" = C_3H_7, C_9H_{19}; (M) = Mg, Al)

The interactions of α-olefins with $AlEt_3$ and Et_2AlCl in the presence of Cp_2ZrCl_2 were investigated to compare the reactivity of Mg and Al alkylates in the course of catalyzed carbomagnesation.

The carboalumination of α-olefins may also be catalyzed by Cp_2ZrCl_2 and may proceed under mild conditions to reveal its high regioselectivity. The Zr catalyst should be activated beforehand by the addition of i-Bu_3Al or $MgAlEt_5$. In contrast to $AlEt_3$, Et_2AlCl does not react with α-olefins in the presence of Zr catalysts. The selective carboalumination of α-olefins by diethylaluminium chloride takes place only if effected by the catalytic quantities of titanium(IV) complexes [$Ti(OBu)_4$, TiCl]. Each experiment resulted in carboalumination product yields of over 95%. In this case, all the ethyl groups in the organoaluminium compound participate in the reaction with olefins.

The developed catalytic methods of regioselective olefin carbometallation assisted by Mg and Al alkylates in the presence of Zr and Ti complexes have proved to be highly favorable for employment in enantio-selective, regio- and stereo-specific syntheses of natural compounds. Besides, the suggested methods allow us to obtain higher Mg and Al organic compounds which were practically inaccessible earlier proceeding from the available organometallics and olefins.



Experimental

All experiments were carried out in an argon atmosphere. The hydrocarbons were distilled over $LiAlH_4$ before use, their purities being more than 98%. OMC (organomagnesium compound) yields were determined by their hydrolysis products calculated with respect to the initial olefin. The hydrocarbon mixtures were analyzed by a Chrom-5 chromatograph equipped with a flame-ionizing detector, 3.7 × 3 mm column packed with 15% of PEG-600 on Chromosorb N-AW.

Et_2Mg was produced by disproportionating EtMgBr with dioxane [8], EtMgF, according to ref. 9 and, the mixed Mg-Al complexes, according to ref. 7. The other Grignard reagent analogues used were obtained by the interactions of Et_2Mg ether solutions with stoichiometric quantities of the appropriate compounds containing an active hydrogen atom according to the following reaction:

$$Et_2Mg + HZ \rightarrow EtMgZ + EtH$$

Olefin carbomagnesation in ether solvents

Cp_2ZrCl_2 (0.15 mmol) and α-olefin (10 mmol) or norbornene, norbornadiene, dicyclopentadiene (7.5 mmol) were added in sequence to the organomagnesium compound (15 mmol) in ether solution (15 mmol) to give a transparent solution, which was stirred at 20–25°C for a definite period of time (see Tables). The reaction mixture was cooled to 0°C and hydrolyzed with saturated NH_4Cl; the organic layer was separated, dried over $MgSO_4$ and analyzed by GLC. The hydrocarbons were isolated by vacuum distillation and were identified either by their spectral assignments or by comparison with known samples.

α-Olefin carbomagnesation in aromatic and aliphatic solvents

A diethylmagnesium suspension (10 mmol) in benzene, toluene or petroleum ether solvent (5 ml) was mixed, by a magnetic stirrer, with a tertiary amine (10 mmol), i.e. triethylamine, *N,N*-diethylamine, triphenylamine, at room temperature to form a transparent solution (~ 1 h). The solution obtained was stirred with Cp_2ZrCl_2 (10 mmol) and α-olefin (10 mmol), added in sequence at room temperature, for 2 h and was analyzed as described above.

α-Olefin carbometallation by mixed Al-Mg reagents

Cp_2ZrCl_2 (0.6 mmol) and octen-1 (70 mmol) were added to a solution of

Mg_2AlEt_7 (10 mmol) in heptane (100 mmol). The mixture was stirred at 20°C for 10 h and treated in the usual way. The conversion of octene was estimated to be 65% by GLC.

α-Olefin carboalumination by Et_3Al

Cp_2ZrCl_2 (0.1 mmol) was dissolved in toluene (20 ml) containing i-Bu_3Al (0.6 mmol). $AlEt_3$ (50 mmol) and α-olefin (150 mmol) were gradually added to the obtained catalyst at 0°C. The mixture was warmed to 20°C and stirred for 3 h. The reaction mixture was cooled by CO_2 and hydrolyzed with 5% HCl; the organic layer was separated, dried over $MgSO_4$, and analyzed.

α-Olefin carboalumination by Et_2AlCl

Et_2AlCl (50 mmol) and α-olefin (100 mmol) were gradually added to a solution of $TiCl_4$ or $Ti(OBu)_4$ (1 mmol) in heptane (20 ml) cooled to 0°C. The mixture was warmed to 20°C, stirred for 3 h, and treated as described above.

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