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The Mechanism of the Zirconium Catalysed Ethyl- and 2-Magnesioethyl-magnesiation of Unactivated Alkenes.

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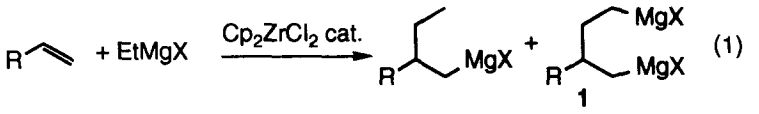
Abstract. Deuterium labelling experiments prove that the zirconocene dichloride catalysed ethylmagnesiation of alkenes occurs *via* a zirconocene η^2-ethylene complex and allow a deuterium isotope effect for a key β-hydride transfer to be estimated (k_H/k_D = 2.5). Transmetallation from zirconium to magnesium to form 1,4-dimagnesiated reagents is shown to be an intramolecular process. Kinetic studies show that the reaction between η^2-ethylene zirconocene and the alkene is rate limiting and that Lewis bases inhibit the reaction by decreasing the amount of η^2-ethylene zirconocene in equilibrium with the 'ate' complex $[Cp_2Zr(CH_2{=}CH_2)Et]^-.[MgX.Base]^+$.

INTRODUCTION

The zirconium catalysed ethylmagnesiation of terminal alkenes (**Eq. 1**) is a useful process which has been explored by several groups[1-8] following its initial discovery by Dzhemilev[9,10]. With certain substrates and conditions 2-magnesioethylation to give a 1,4-dimagnesiated species **1** is the major pathway[1].



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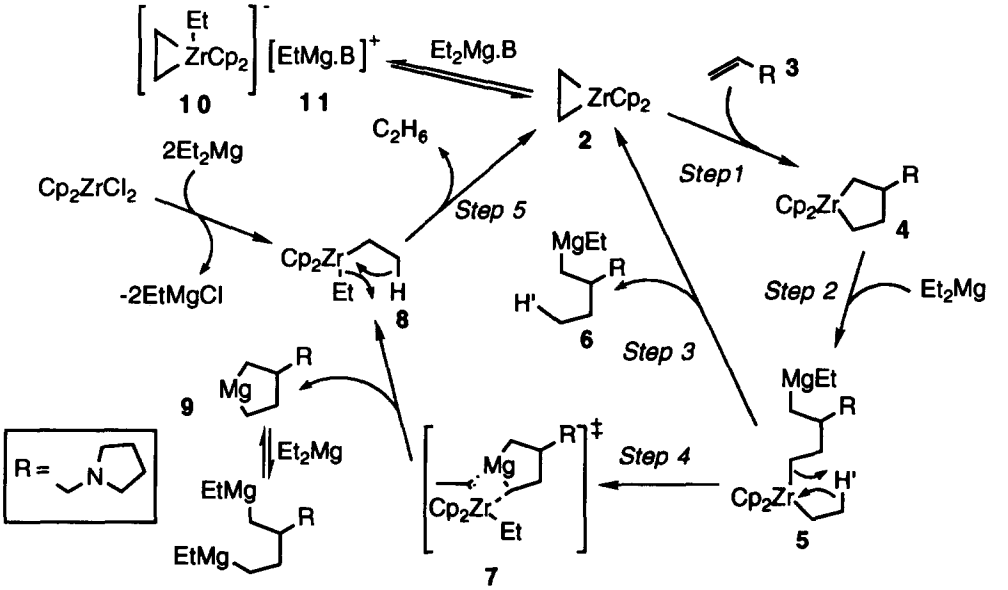
Related reactions catalysed by zirconocene include: the ethylation of conjugated diynes[11]; the formation of aluminocyclopentanes, and aluminocyclopentenes by the catalysed reaction between triethylaluminium and unactivated alkenes and alkynes[12,13]; the formation of magnesiocyclopentanes[14,15] and aluminocyclopentanes[16] by dimerisation of alkenes using dialkylmagnesiums and trialkylaluminiums as the source of the metal; the zirconium catalysed cyclomagnesiation of 1,n-dienes[17-19]; the zirconium catalysed addition / elimination of ethylmagnesium bromide to allylic ethers[20] including examples where the use of a homochiral ethylene-1,2-bis-(η^5-4,5,6,7-tetrahydro-indenyl)zirconium dichloride catalyst gives excellent chiral induction[21,22]; and the intramolecular cyclisation / elimination of alkenes to allylic ethers[23].

Several advances are needed to make the zirconium catalysed carbomagnesiation reaction generally useful. These include optimising formation of the dimagnesiated species **1**, extending to organomagnesium species other than ethyl, and developing commercially viable asymmetric versions. A detailed knowledge of the catalytic cycle would provide a good basis from which to tackle these problems. Firm foundations for a catalytic cycle exist in the stoichiometric work of Negishi and Takahashi[24-27] particularly the remarkably regioselective first transmetallation[8] (*step 2*). During the course of the studies described herein mechanistic



Scheme 1. Proposed Catalytic Cycle for the Ethyl- and 2-Magnesioethyl-magnesiation

investigations have been reported[3]. A detailed mechanistic study of the closely related cyclomagnesiation of 1,n-dienes has also been described[17]. Particular questions to be answered include: to confirm that zirconocene ethylene **2** is an intermediate in the formation of both mono- and di-magnesium products; to investigate the factors which affect the relative proportions of the mono- and di-magnesiated products formed; and to determine what factors affect the rate of reaction, principally by identifying the 'rate determining step' (defined as that after the resting state of the catalyst). Elements of the catalytic cycle given in **Scheme 1** have been proposed by several authors[1,3,8,13]. We now present results which establish this catalytic cycle and identify the resting state of the catalyst. Allyl pyrrolidine **3** was chosen as our 'standard alkene' since it gives high levels of the dimagnesiated product **9** when the reaction is run with diethylmagnesium in diethyl ether[1].

RESULTS AND DISCUSSION

Detection of ethane evolution.

The catalytic cycle described in **Scheme 1** involves elimination of ethane from diethyl zirconocene **8** in the formation of zirconocene ethylene **2**. This should occur both during initial generation of the active catalyst from zirconocene dichloride, and to complete the part of the catalytic cycle (*steps 4* and *5*) which forms the dimagnesium reagent **9**. To detect and monitor ethane formation the gas space above a reaction was continuously bled into a mass spectrometer through a fine capillary[28]. Selected ion recording of the molecular ion region of ethane was employed. On addition of the diethylmagnesium (1M in THF) to a solution of zirconocene dichloride in THF a rapid evolution of ethane was observed presumably corresponding to formation of zirconocene ethylene (*step 5*). On addition of the alkene substrate (allyl pyrrolidine) a second evolution of ethane was observed (**Fig. 1**). The solubility of ethane in the solvent renders the quantitative results unreliable (the first evolution will be under

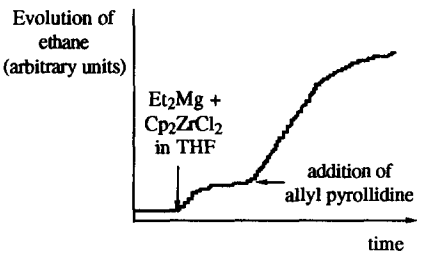
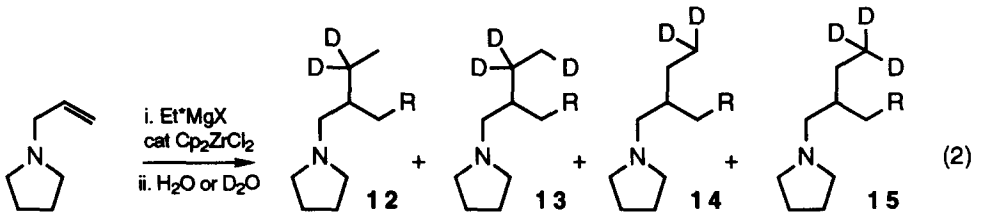


Fig. 1. Evolution of ethane

estimated) but if the first evolution corresponds to the 2% catalyst being formed, the second corresponds to approximately 8% of the substrate reacting *via* the dimagnesiation route - a reasonable agreement with that found through deuterium labelling experiments under these conditions.

Deuterium labelling studies.

In comparison with a possible 'direct ethylation' mechanism for the formation of the monomagnesium product **6**, the most direct proof of the presence of zirconocene ethylene **2** as the key intermediate in the catalytic cycle is by a labelling experiment since the CH_3 and CH_2 of Et_2Mg become equivalent on formation of **2**. Since completion of this work this experiment has been reported using 1,1-dideuterioethylmagnesium bromide for the ethylation of norbornenes[3] and allylic or homoallylic ethers and alcohols[6]. We chose to use 2,2,2-trideuterioethylmagnesium bromide together with the corresponding diethylmagnesium species in order to gain additional information about the supposed 'H-transfer' *step 3*. The zirconium catalysed ethylations of allyl pyrrolidine with CD_3CH_2MgBr in THF, and $(CD_3CH_2)_2Mg$ in diethylether were performed. These conditions were selected as with undeuterated organomagnesium species they give predominantly mono- and di-magnesium products respectively[1]. The reactions were quenched with both water, and D_2O (to allow the mono- and di-magnesium products to be distinguished) to give the results shown in **Eq. 2** and **Table 1**.



(2)

Table 1	% Composition			
Conditions	**12**	**13**	**14**	**15**
i. CD_3CH_2MgBr, THF, ii. H_2O, R = H	16	37	15	32
i. CD_3CH_2MgBr, THF, ii. D_2O, R = D	6	46	2	46
i. $(CD_3CH_2)_2Mg$, Et_2O, ii. H_2O, R = H	40	10	40	10
i. $(CD_3CH_2)_2Mg$, Et_2O, ii. D_2O, R = D	0	50	0	50

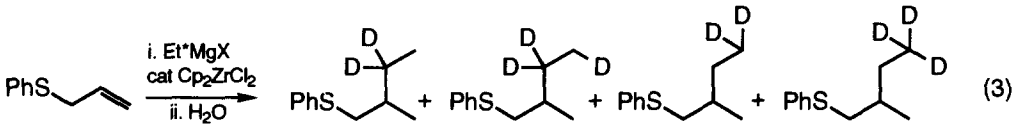
Table 2	% Comp.	
Conditions	**6**	**9**
CH_3CH_2MgBr, THF.	85	15
CD_3CH_2MgBr, THF.	69	31
$(CH_3CH_2)_2Mg$, Et_2O.	40	60
$(CD_3CH_2)_2Mg$, Et_2O.	20	80

Two conclusions can be drawn from these results. In the reactions quenched with water the 'CD_2' carbons are equally distributed over the two carbons originally part of the ethylmagnesium reagent demonstrating the intermediacy of **2**. Secondly the formation of **13** clearly demonstrates that a specific D transfer has occurred to the eliminated monomagnesium species **6** i.e. *step 3* in **Scheme 1**. **15** could arise from a simple ethylation, but given that the amount is equivalent to **13** it is far more likely that one of the deuteriums has been lost in the formation of **2**, and another transferred back in *step 3*.

Comparison of the results for quenching with water and D_2O allow us to estimate the ratio of mono- to di-magnesium reagents formed with the CD_3CH_2MgBr / THF and $(CD_3CH_2)_2Mg$ / Et_2O systems. These can be compared with the ratios formed using undeuterated organomagnesium species (**Table 2**). The difference is due to a primary kinetic isotope effect in the cyclometallation (*step 3*) which slows this step down, hence favouring the route giving the dimagnesium species (*step 4*), and can be estimated as $k_H/k_D = 2.5$. Values of $k_H/k_D = 7$ have been measured for related cyclometallations leading to zirconocene η^2-imine[29] and η^2-thioaldehyde[30] complexes. Secondary deuterium isotope effects have been neglected in this analysis but are known to be small in related processes[29]. The transmetallation *step 4* could also show a rate difference between CH_2CH_3 and CH_2CD_3 but the effect will be small.

So far we had only examined allyl pyrrolidine as a substrate - a somewhat special case as it gives a high selectivity for dimagnesium species formation in diethylether. Allyl phenyl thioether gives the monomagne-

siated species under all conditions[1] so this was examined for comparison. The results (**Eq. 3**) confirmed the scrambling of deuterium label, the selective transfer of a β-deuterium in *step 3*, and a deuterium isotope effect for this transfer. The amount of di-magnesium reagent formed was 10 and 19% (c.f. <5% for undeuterated species[1]) under the two reaction conditions. This suggests a somewhat higher value for the kinetic isotope effect than above, but the lack of 'D_2O quench' control experiments, and errors inherent in measuring low levels of deuterium incorporation by carbon-13 NMR render the absolute value unreliable.



	% composition			
CD_3CH_2MgBr, THF	4	44	6	46
$(CD_3CH_2)_2Mg$, Et_2O	9	42	10	39

Kinetic studies.

In investigating the kinetics of the reaction we concentrated on the use of diethylmagnesium since with Grignard reagents there is always a mixture of EtMgX, and Et_2Mg present through the Schlenk equilibria[31,32]. Allyl pyrrolidine was chosen as our standard alkene, and its disappearance and the formation of 2-methylbutyl pyrrolidine were monitored quantitatively by capillary gas chromatography.

Dilution experiment. We sought to confirm our initial hypothesis, that the bimolecular *step 1* was rate limiting, by carrying out the ethylmagnesiation of allyl pyrrolidine using the same quantities of all reagents, but at various dilutions (0.04 mmol Cp_2ZrCl_2, 4 mmol Et_2Mg, 2 mmol allyl pyrrolidine in ether with 1.3, 2, 4, 8 and 16 mL total volume). Much to our surprise we found that there was no significant change in either the rate of reaction or the ratio of mono- to di-magnesium products formed. The first point suggests that a bimolecular step is not rate limiting, and the second indicates that the transmetallation step which leads to the dimagnesium product (*step 4*) is intramolecular as shown in **Scheme 1** (i.e. *via* **7**). To attempt to identify the rate limiting step we next examined the effect of varying each component of the reaction independently.

Variation in alkene concentration. In a series of experiments in which the concentrations (and total amounts) of Et_2Mg and Cp_2ZrCl_2 were kept constant and the concentration of allyl pyrrolidine varied (0.01 mmol Cp_2ZrCl_2, 8 mmol Et_2Mg, 0.19, 0.38, 0.75, 1.5, & 3 mmol allylpyrrolidine, Et_2O, total volume of 8 mL) the rate of formation of product was clearly related to the starting alkene concentration confirming that under these conditions *step 1 is* rate limiting (**Fig. 2**). Since the concentration of the catalyst is not expected to

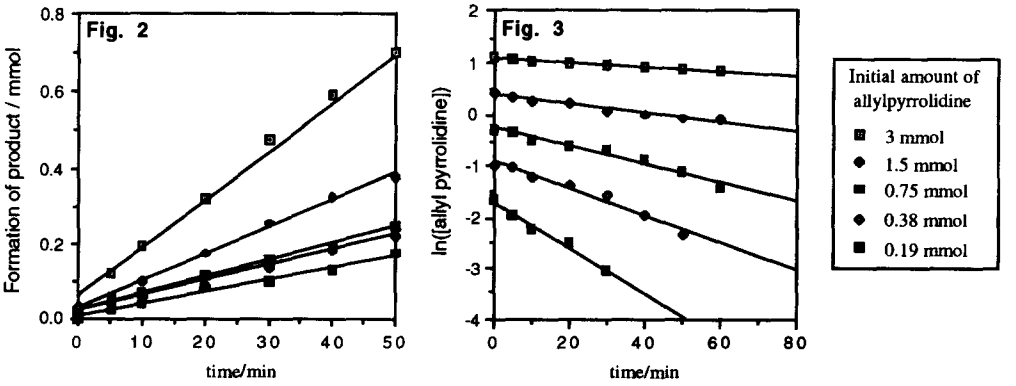


Fig. 2 and **3**. Effect of increasing starting concentration of allyl pyrrolidine.

change during the course of the reaction (we confirmed that catalysts decomposition was not significant) if *step 1* is rate limiting we would expect a first-order dependance of the rate on the concentration of alkene. Plots of ln([alkene]) *vs* time were indeed good straight lines (**Fig. 3**) but this simple model is clearly inadequate as with different starting concentration of alkene the lines are of different slope. A 1st order rate constant should be independent of the starting concentration of alkene.

Proposed Model. A model which explains the kinetic results given above is based on the notion that the amine functionality of our chosen substrate is having an inhibitory effect on the reaction. Negishi has observed that 1 equivalent of ethylmagnesium bromide converts zirconocene ethylene into an 'ate' complex like **10**[26]. The 'ate' complex **10** must be catalytically inactive (the metal has an 18 electron configuration) so the rate of the catalytic cycle is dependent on the small amount of zirconocene ethylene **2** in equilibrium with

The two equilibria which remove **2** as **10** are:

$$Et_2Mg.R_3N + \mathbf{2} \overset{K_1}{\rightleftharpoons} \mathbf{10}.\ (EtMg.R_3N)^+ \qquad K_1 = \frac{[\mathbf{10}.\ (EtMg.R_3N)^+]}{[Et_2Mg.R_3N][\mathbf{2}]}$$

$$Et_2Mg.Et_2O + \mathbf{2} \overset{K_2}{\rightleftharpoons} \mathbf{10}.(EtMg.Et_2O)^+ \qquad K_2 = \frac{[\mathbf{10}.(EtMg.Et_2O)^+]}{[Et_2Mg.Et_2O][\mathbf{2}]}$$

$[Et_2Mg.R_3N] = [R_3N]_0$ (the total [amine]) assuming that all of the amine is complexed to Et_2Mg.

And $[Et_2Mg.R_3N] + [Et_2Mg.Et_2O] = [Et_2Mg]_{tot}$

If **10** is the resting state of the catalyst then $[\mathbf{10}.(EtMg.R_3N)^+] + [\mathbf{10}.(EtMg.Et_2O)^+] \approx [Zr]_{tot}$

$$\therefore\ [Zr]_{tot} = K_1[R_3N]_0[\mathbf{2}] + K_2([Et_2Mg]_{tot} - [R_3N]_0)[\mathbf{2}] \quad \text{and} \quad [\mathbf{2}] = \frac{[Zr]_{tot}}{(K_1-K_2)[R_3N]_0 + K_2[Et_2Mg]_{tot}}$$

If *step 1* is rate limiting

$$\text{rate} = k[\mathbf{2}][\mathbf{3}] = \frac{k[Zr]_{tot}[\mathbf{3}]}{(K_1-K_2)[R_3N]_0 + K_2[Et_2Mg]_{tot}} = k_1[\mathbf{3}]$$

where k_1, the pseudo 1st order rate constant, does not alter on dilution.

For constant [Zr] and $[Et_2Mg]$ the pseudo 1st order rate constant k_1 is

$$k_1 = \frac{k[Zr]}{(K_1-K_2)[R_3N]_0 + K_2[Et_2Mg]} \qquad \text{i.e.} \quad \frac{1}{k_1} = C_a[R_3N]_0 + C_b$$

Scheme 2. Kinetic analysis

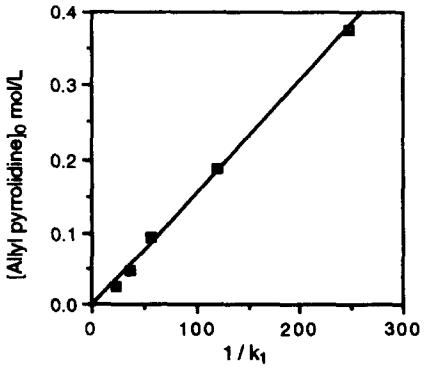


Fig. 4. Relation between initial [amine] and the 1st order rate constant.

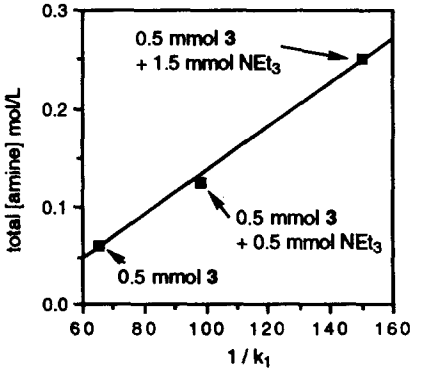


Fig. 5. Effect on 1st order rate constant of added triethylamine

10. In the formation of the 'ate' complex **10** the counterion ($EtMg^+$)must be stabilised by Lewis bases i.e. as **11**. Normally **B** is the etherial solvent but in our case the 'pyrrolidine' moiety should be more effective. A simplified analysis[33] based on these ideas (**Scheme 2**) correctly predicts the independence of reaction rate on dilution, and predicts a linear relationship between the concentration of amine, and the reciprocal of the 1st order rate constant of the reaction. Much to our delight this was indeed the case (**Fig 4**).

This model further predicts that any amine should have the same effect. This was demonstrated in two ways. In our standard allyl pyrrolidine system the addition of triethylamine did give an inhibition, and the reciprocal of the 1st order rate constant was proportional to the total amine concentration (**Fig. 5**). To avoid the complication of the substrate containing an amine we examined the inhibitory effect of added triethylamine on the carbomagnesiation of 1-octene. In general we found investigation of the kinetics of 1-octene reaction unrewarding since it is ≈ 10 times slower than allyl pyrrolidine and complicated by alkene isomerisation and catalyst decomposition. Despite this a good correlation between the concentration of added triethylamine and the reciprocal of the 1st order rate constant was observed (**Fig. 6**) lending strong support to our model. The much faster rate of reaction of allyl pyrrolidine compared to 1-octene, despite the 'inhibiting' amine function, is attributed to the strong electron withdrawing effect of $-N^+R_2.MgX$

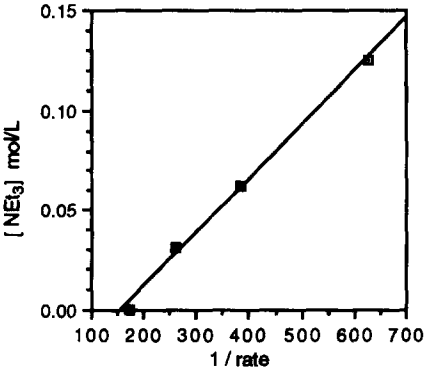
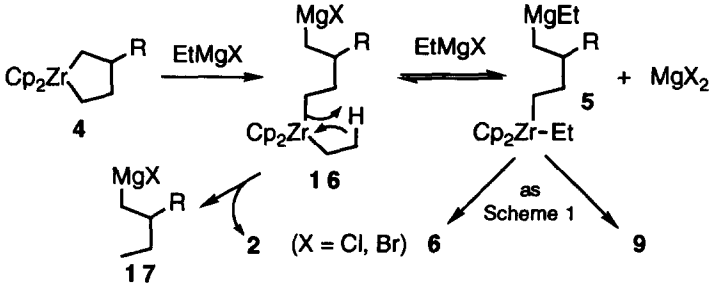


Fig. 6 Effect of added NEt_3 on the rate of carbomagnesiation of 1-octene

The conclusion of these studies is that *step 1* is rate limiting, but the rate is dramatically altered by Lewis bases which change the concentration of the active catalyst available.

Variation in diethylmagnesium concentration. The dilution result above strongly suggested that the transmetallation *step 4* must be intramolecular. To probe this under conditions where only one variable is changed we carried out a series of reactions where only the concentration of diethylmagnesium was altered (0.02 mmol Cp_2ZrCl_2, 2 mmol allyl pyrrolidine, 2, 4, 8, 16, and 32 mmol Et_2Mg in ether, total volume of 13.4 mL). The results were quite clear - the concentration of diethylmagnesium has no effect on either the rate of reaction (relative rates 1.8[34], 1.4, 1.3, 1.5, 1.2), or the ratio of mono- to di-magnesiated products (57 - 61% dimagnesiated product). The second point confirms that the transmetallation *step 4* is intramolecular as drawn in **Scheme 1**[35].

An important consequence of the intramolecular transmetallation helps to explain why diethylmagnesium forms much more of the dimagnesiated product **9** (c.f. the monomagnesium species **6**) than ethylmagnesium bromide[1]. With ethylmagnesium bromide as the ethyl source, the first transmetallation (analogous to *step 2*) would give the zirconium species **16**. This is likely to undergo the cyclometallation (*step 3*) to regenerate zirconocene ethylene and the monomagnesium product **17** at a similar rate to **5**, but cannot undergo the intramolecular transmetallation (*via* **7**) to afford the dimagnesium species **9** until after a Schlenk equilibria to form **5** has occurred (**Scheme 3**).



Scheme 3

Effect of catalyst concentration. For the zirconium catalysed ethylmagnesiation of allylic ethers it has been suggested that the rate limiting step is second order in zirconium[6]. The carbomagnesiation of allyl pyrrolidine was carried out with various amounts of catalyst (0.25, 0.5, 1, and 2 mol% Cp_2ZrCl_2) and the rates measured. Assuming that rate = $k[Zr]^n$, a plot of ln (rate) *vs* ln([Zr]) gives n = 0.99 (**Fig 7**) showing that in the system we are studying the transition state for *step 1* contains only one zirconium atom. It may be significant that allylic ethers react around 10 times more slowly than allylic amines.

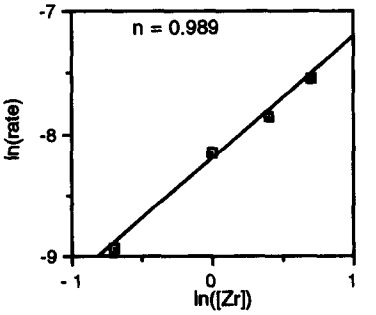


Fig. 7 The effect of catalyst concentration

CONCLUSIONS

The zirconocene catalysed ethyl- and 2-magnesioethyl-magnesiation of allyl pyrrolidine:

i. Occurs through the intermediacy of zirconocene ethylene generated initially through loss of ethane from diethylzirconocene, and regenerated either from diethylzirconocene in the formation of the dimagnesium species, or by elimination of the ethylated product through a specific H transfer which shows a deuterium kinetic isotope effect of 2.5.

ii. The resting state of the catalyst is as the catalytically inactive 'ate' complex $[Cp_2Zr(CH_2{=}CH_2)Et]^-.[MgEt.NR_3]^+$ and the rate limiting step of the catalytic cycle is the bimolecular reaction between zirconocene ethylene and allyl pyrrolidine. Lewis basic components alter the equilibrium between the 'ate' complex and the catalytically active species, zirconocene ethylene, favouring the former and hence slowing the reaction.

iii. The 2-magnesioethylated product is formed by an intramolecular transmetallation between EtMg- and Cp_2ZrEt-.

iv. A single zirconium atom is involved in the rate limiting step when allyl pyrrolidine is the substrate.

ACKNOWLEDGEMENTS

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EXPERIMENTAL SECTION

General

Diethyl ether and THF were freshly distilled from sodium/benzophenone. All reactions were carried out under a positive pressure of argon. Ethylmagnesium bromide was purchased as a 3 M solution in diethyl ether, or a 1 M solution in THF, from Aldrich and titrated by adding an aliquot of known volume to a measured excess of 0.1 M hydrochloric acid, which was then neutralised by the addition of 0.1 M sodium hydroxide, using phenolphthalein as the indicator[36]. Diethylmagnesium was prepared from ethylmagnesium bromide in ether by precipitation of the 1,4-dioxane complex of magnesium bromide (centrifuge) thus displacing the Schlenk equilibrium[37]. The ≈ 1-2 M ethereal solution of diethylmagnesium so formed was then titrated for total base content as above, and for Mg^{2+} content with ethylenediaminetetraacetic acid (EDTA) using Eriochrome Black T as the indicator[38]. CD_3CH_2MgBr and $(CD_3CH_2)_2Mg$ were prepared from CD_3CH_2OH (Aldrich) *via* the *p*-toluenesulphonate and bromide, and analysed as above.

^1H and ^{13}C n.m.r. spectra were recorded in Fourier transform mode on Jeol JNM-GX270, or Bruker AM360 spectrometers in $CDCl_3$ solution.

Typical carbomagnesiation procedure.

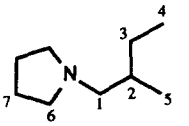
N-(2-methylbutyl)pyrrolidine. Diethylmagnesium (4 mL of a 1 M solution in diethyl ether, 4 mmol) was added to Cp_2ZrCl_2 (12 mg, 0.04 mmol) in ether (2 mL) under argon. *N*-Allylpyrrolidine **3** (0.22 g, 2 mmol) in ether (1 mL) was then added to give a transparent solution which was stirred at room temperature (20-25°C). The reaction was monitored by gas chromatography. When the reaction was considered to have reached completion* (usually 2-3 h) the reaction mixture was quenched by pouring into a saturated ammonium chloride solution (30 mL). The organic layer was then extracted with successive portions of ether (3 x 60 mL), the extracts combined, dried, and the solvent removed under reduced pressure. Column chromatography (silica column, eluant 75:20:5, petroleum ether:diethyl ether:triethylamine) and Kugelrohr distillation (12 mmHg, 37°C) furnished the *title compound* (0.24 g; 85%). δ_H (270 MHz; $CDCl_3$) 2.45 (4H, m), 2.36 (2H, dd, J = 4, 7 Hz), 1.76 (4H, m), 1.51 (2H, dq, J = 6, 8 Hz) 1.10 (1H, ttq, J = 7, 6, 7 Hz), 0.89 (3H, d, J = 7 Hz), 0.85 (3H, t, J = 8 Hz). δ_C (67.5 MHz; $CDCl_3$) 63.85 (t), 54.68 (t), 34.15 (d), 28.07 (t), 23.57 (t), 18.08 (q), 11.56 (q). IR (liq. film) ν_{max} 2962 (s), 2929 (s), 2875 (s), 2784 (s) cm^{-1}. m/z (EI, 70eV) 141 (M^+, 6%), 115 (5), 91 (31), 84 (100), 55 (14). HRMS: calc. for $C_9H_{19}N$ 141.1517; found 141.1510.

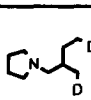
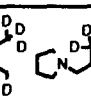
* For 'Deuterium quenched' reactions, at this point deuterium oxide (99.9 atom% D, *ex.* Aldrich, 0.5 mL) in THF (3 mL) was added and the mixture stirred at room temperature for 0.5 h, before pouring into ammonium chloride solution.

Reactions with 2,2,2-trideuterated ethylmagnesium bromide and diethylmangesium.

Allyl pyrrolidine. Reaction with CD_3CH_2MgBr / THF and $(CD_3CH_2)_2Mg$ / Ether was carried out by the procedure above. The composition of the deuterated products was established mainly by carbon-13 NMR (**Table 3**).

Table 3 Carbon-13 data for a range of deuteriated *N* - (2-methyl)-butyl pyrrolidines. δ_C (67.5 MHz, $CDCl_3$) / p.p.m.



C									
1	63.84 (t)	63.84 (t)	63.83 (t)	63.85 (t)	63.83 (t)	63.81 (t)	63.82 (t)	63.85 (t)	63.81 (t)
2	34.14 (d)	34.09 (d)	34.04 (d)	34.08 (d)	33.99 (d)	33.95 (d)	33.86 (d)	34.08 (d)	33.95(d)
3	28.06 (t)	28.05 (t)	27.93 (t)	28.81 (t)	27.79 (t)	*	*	27.89 (t)	*
4	11.55 (q)	11.56 (q)	11.25 (tt) (20.0 Hz)	*	*	11.02 (tt) (19.0 Hz)	11.04 (tt) (19.1 Hz)	*	11.31 (q)
5	18.07 (q)	17.77 (tt) (20.0 Hz)	17.77 (tt) (20.0 Hz)	18.08(q)	17.79 (tt) (19.1 Hz)	18.02 (t)	17.74 (tt) (20.0 Hz)	18.08(q)	18.02(q)
6	54.69 (t)	54.68 (t)	54.68 (t)	54.68 (t)	54.68 (t)	54.68 (t)	54.70 (t)	54.68 (t)	54.68 (t)
7	23.55 (t)	23.55(t)	23.55(t)	23.55 (t)	23.55(t)	23.55(t)	23.55(t)	23.55 (t)	23.55 (t)

* - Not observed. Where two multiplicities are give e.g. tt, the first is that due to diretly attached protons determined by DEPT experiments, and the second is due to carbon-deuterium coupling, and $J_{C\text{-}D}$ is given in brackets below.

Phenyl allyl thioether. Reaction with CD_3CH_2MgBr / THF and $(CD_3CH_2)_2Mg$ was carried out by the above procedure. The deuterated phenyl 2-methylbutylthioethers were analysed by carbon 13 NMR:

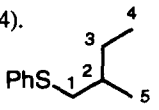
Phenyl 2-methylbutylthioether. δ_C (67.5 MHz, $CDCl_3$) / p.p.m. :

3,3,4-trideuterio 40.74 (t, C-1), 34.40 (d, C-2), 19.01 (q, C-5), 10.88 (tt, J_{CD} 19.6 Hz, C-4).

3,3-dideuterio- 40.74 (t, C-1), 34.40 (d, C-2), 19.01 (q, C-5), 11.17 (q, C-4).

4,4,4-trideuterio- 40.79 (t, C-1), 34.54 (d, C-2), 28.57 (t, C-3), 19.07 (q, C-5).

4,4-dideuterio- 40.79 (t, C-1), 34.54 (d, C-2), 28.65 (t, C-3), 19.07 (q, C-5).



Monitoring of ethane evolution using mass spectrometry

A solution of zirconocene dichloride (0.02 mmol) in tetrahydrofuran (5 mL) was prepared in a Schlenk flask, under argon, and containing a magnetic follower. Tetrahydrofuran was used as the reaction solvent, rather than diethyl ether, because fragment ions of the latter are isobaric with the molecular ion region of ethane, hence less "interference" from the solvent ions was observed. Using a modified continuous flow FAB probe[28] inserted *via* the EI direct insertion vacuum lock on a VG Analytical 70-250-SE double focusing mass spectrometer the gas above the stirred reaction mixture was introduced into the ion source volume through a fine fused silica capillary (10 μm i.d.). Selected ion recording (SIR) of the molecular ion region of ethane was employed. The molecular ion of argon was also monitored and used as an internal standard.

Diethylmagnesium (2 ml of a 1 M solution in THF, 2 mmol) was added and the system allowed to equilibrate (no further ethane evolution). *N*-Allylpyrrolidine (0.11 g; 1 mmol) in THF (5 ml) was then added and monitoring continued until the concentration of ethane became constant. A reaction in which a placebo second addition (*i.e.* an addition of THF containing no allylpyrrolidine) was made, was also performed. In this case no increase in the concentration of ethane above the reaction mixture was observed.

Kinetic Studies.

Typical Experiment: The effect of allylpyrrolidine concentration. To each of five Schlenk tubes fitted with rubber septa and containing a magnetic follower was added, under an inert atmosphere, zirconocene dichloride (0.1 mL of a 0.1 M solution in THF, 0.01 mmol). The solvent was removed *in vacuo*, and diethylmagnesium (3.6 mL of a 2.2 M solution in diethyl ether, 8 mmol) added by syringe to each flask. A specific amount (to give 0.19, 0.38, 0.75, 1.5, & 3 mmol allylpyrrolidine) of a standard solution containing allylpyrrolidine and a mixture of alkanes (C9-C12, acting as internal standards) in diethyl ether was then added to the stirring solution , together with an appropriate amount of diethyl ether to ensure that the total volume of each reaction mixture was 8 mL. Aliquots of each reaction were removed at appropriate intervals by syringe, quenched with water, diethyl ether added, and the ethereal extract analysed by capillary g.c.

Similar procedures were use to examine the other variables discussed. All reactions carried out to test a particular variable were run in parallel, and the set of experiments repeated two or three times to ensure reproducibility.

Gas Chromatographic Studies.

Aliquots of the reaction mixture to be monitored (which had been 'doped' with inert materials, usually C9-C12 alkanes, to act as internal standards) were removed at appropriate intervals by syringe under a positive argon pressure, quenched with water, diethyl ether added, and the composition of the ethereal extract analysed by capillary gas chromatograph (OV101, 24 m column in a Perkin Elmer 8320 Capillary g.c. interfaced to a P.E. GP100 Graphics Printer). The output from the auto-integrator, was then analysed by computer spreadsheet packages, using the internal standards as calibrants, and appropriate graphs drawn. The linearity of the response of the flame ionisation detector for each component of the reaction mixture was determined by analysing solutions of known concentration, and constructing calibration curves. In all cases a linear response was obtained.

The auto-integrator did not always give satisfactory results. In these cases two other techniques were

used to estimate peak areas. One was to use the peak height times the peak width at half height[39]. This value gives 94% of the total area of the Gaussian peak, which would be found by integration. This technique fails for unsymmetrical (*i.e.* non Gaussian) peaks and for very sharp, or very small peaks where width at half height cannot be measured with the desired accuracy. As an alternative the g.c. peaks were photoexpanded, cut out and weighed, the ratio of their weights being proportional to their peak areas. In most cases, the two techniques employed bore favourable comparison with the results generated by the auto-integrator.

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33. Many assumptions as to the state of aggregation of the various components have been made, and many alternatives are possible. It is even conceivable that the amine directly coordinates to the zirconocene ethylene. The essential feature however seems secure - the amine is favouring the formation of an inert 'resting state' of the zirconocene ethylene. Most of the other possible analysis lead to the same prediction of a linear relationship between the [amine] and (1/rate), although not the observed independence of the rate on dilution. In the data obtained (figs. 4, 5, and 6) there is a not the linear relationship between the rate and (1/[amine]) which is predicted by models which ignore the solvent contribution.
34. The slight increase in rate at the lowest concentration of diethylmagnesium may be significant, and is explained by a small shift in the equilibrium between **2** and **10** in favour of the former at lower [Et_2Mg].
35. An intramolecular transfer from a diethylmagnesium bound to the amine is another possible explanation, but we consider it unlikely. One reason is that 1-decene, and allyl silane give similar rations of mono-to di-magnesium products without this coordinating group[1].
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