Zirconium-Catalyzed Ethylmagnesiation of Imines − Scope and Mechanism

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The title reaction has been developed for a series of aldimines and ketimines. Most notably, ketimines – which are totally inert towards alkyl Grignard reagents in the absence of the zirconium catalyst – react smoothly when 10 mol % of Cp_2ZrCl_2 is added. The mechanism of the reaction has been studied. The intermediate azazirconacycle proved to react by two competing pathways involving mono- and dimagnesiated final products before hydrolysis.

Introduction

Asymmetric additions of organometallic reagents to the C=N functional group are of great interest for the preparation of chiral amines and derivatives.[1] Up to now, however, only a few catalytic enantioselective alkylation reactions have been reported. These reactions typically involve catalytic activation of organolithium or organozinc reagents with external chiral Lewis bases or activation of imines with chiral Lewis acids.[2] Transition metal catalyzed alkylation of imines is promising from the asymmetric synthesis point of view.[3] In this context, we noticed that imines, similarly to alkenes,[4] undergo Zr-catalyzed addition with ethylmagnesium reagents. During the final stages of our work there appeared a communication by Takahashi et al.[5] on a related zirconium-promoted reaction, which prompted us to report our work in this field. Our paper emphasizes the catalytic process and extends knowledge of this new reaction from both the synthetic and the mechanistic points of view.

Results and Discussion

The challenge of performing a catalyzed reaction rather than a non-catalyzed one was assisted by the poor electrophilicity of imines, which proved to be rather inert to alkyl Grignard reagents.[6] Thus, it was possible to form catalytically active alkylating species from a Grignard reagent *in the presence of the imine*. In fact, the Zr-catalyzed addition of EtMgCl to imines competed favorably with the non-catalyzed reaction. Table 1 compares the results for the treatment of several ketimines and aldimines with EtMgCl in the presence of 10 mol % of Cp_2ZrCl_2, and for the analogous reactions in the absence of any catalyst. Without Cp_2ZrCl_2, all the ketimines used (Entries 1−6), and also aldimine **17** (Entry 9), were inert to EtMgCl; only aldimines **13** and **15** (Entries 7 and 8) reacted to some extent under the conditions employed here (THF, room temp.). In contrast, when catalytic amounts of Cp_2ZrCl_2 were added, the reaction proceeded to afford the corresponding amines in moderate to good yields. Both aromatic and aliphatic ketimines and benzaldimines reacted with EtMgCl in the presence of Cp_2ZrCl_2. The reaction took place with the sterically crowded imines **5**, **11**, and **17** (Entries 3, 6, and 9) although long reaction times were required for **11** and **17**. In some cases, small amounts (up to 10%) of the reduction products were detected. However, no enolization of ketimines took place to any significant extent under these conditions. The reaction was also successful when a smaller quantity of Cp_2ZrCl_2 (5 mol %) was used, although yields were slightly lower. Finally, other ethylmagnesium reagents (EtMgBr and Et_2Mg) gave similar results.[7]

Zirconium-catalyzed carbomagnesiation of alkenes has been extensively studied, and zirconacycles have been demonstrated to act as intermediates in this reaction.[8] The mechanisms of the title reaction and of its counterpart involving alkenes might be similar, since imines and alkenes are isolobal. To clarify the mechanism, the stoichiometric reaction between the imine **1** and zirconocene ethylene (preformed from 1 equiv. of Cp_2ZrCl_2 and 2 equiv. of EtMgBr[9]) was carried out; it afforded the amine **2**, albeit in a lower yield (46%). When the stoichiometric reaction was quenched with D_2O/D_2SO_4 > 98% deuterium incorporation at the terminal carbon was observed [Scheme 1, Equation (a)].

Further deuterium-labeling experiments were performed (see Scheme 1). Firstly, treatment of **1** with 10 mol % Cp_2ZrCl_2, and 2 equiv. of EtMgBr and quenching with D_2O/D_2SO_4 produced a mixture of **2** and **2a** in a 1:1.5 ratio [Equation (b)]. Secondly, the Zr-catalyzed reaction between **1** and CD_3CH_2MgBr, quenching with water, gave a mixture of two dideuterated (**2b** and **2d**) and two trideuterated (**2c** and **2e**) compounds, in an approximate 6:6:1:1 ratio [Equation (c)]. Thirdly, when CD_3CH_2MgBr was used and the catalytic reaction was quenched with D_2O/D_2SO_4, **2c** and **2e** were formed in a 1:1 ratio [Equation (c)].

A plausible mechanism for the catalytic ethylmagnesiation of imines is presented in Scheme 2. In analogy to what had been proposed for the catalytic ethylmagnesiation

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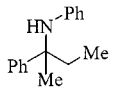
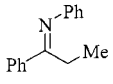
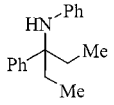
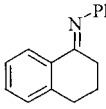
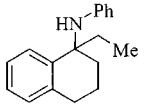
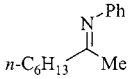
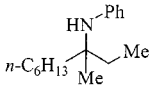
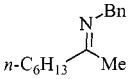
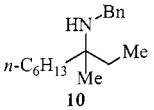
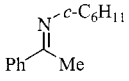
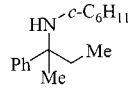
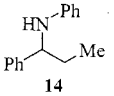
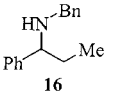
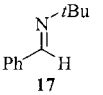
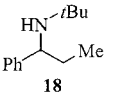
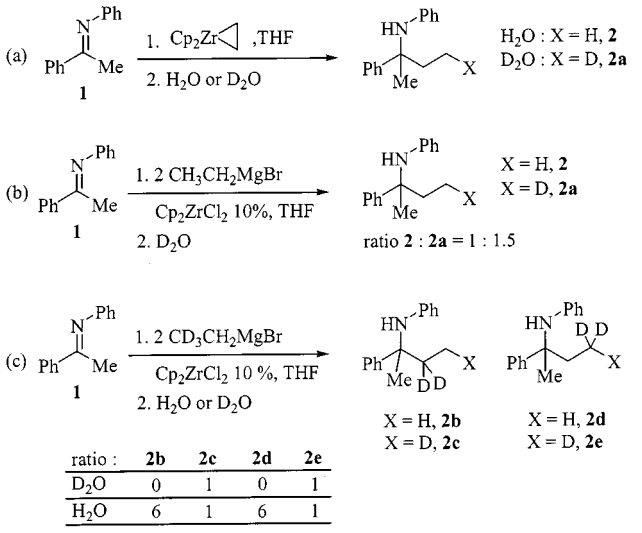
Table 1. Catalytic ethylmagnesiation of imines

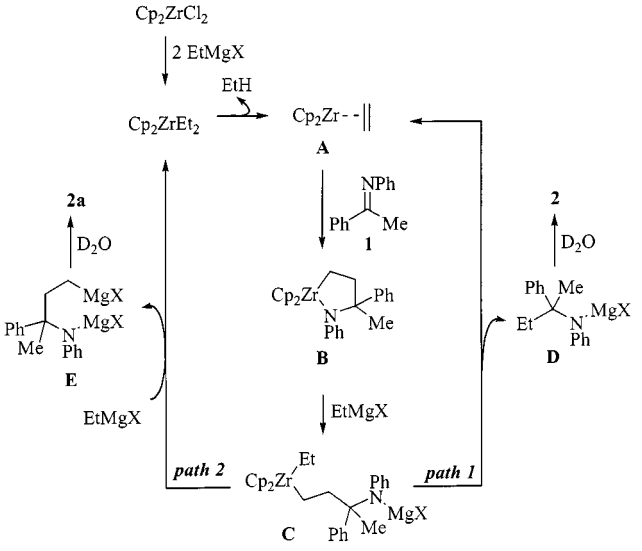
Entry[a]	Imine	Amine	Time [h]	Yield [%][b,c]
1	 **1**	 **2**	1.5	78 (0)
2	 **3**	 **4**	1.5	88 (0)
3	 **5**	 **6**	1.5	86 (0)
4	 **7**	 **8**	1.5	86 (0)
5	 **9**	 **10**	1.5	50 (0)
6	 **11**	 **12**	24	38[d] (0)
7	 **13**	 **14**	1.5	69 (16)
8	 **15**	 **16**	1.5 8	66 (< 5) 90 (12)
9	 **17**	 **18**	8 8	49 (0) 61[d] (0)

[a] Conditions: 2 equiv. of EtMgCl, 10 mol % of Cp_2ZrCl_2, 20 °C, THF. – [b] Yields refer to isolated compounds of >95% purity by GC and ^1H NMR. – [c] Yields for the reactions without Cp_2ZrCl_2 are given in parentheses. – [d] 4 equiv. of EtMgCl, 10 mol % of Cp_2ZrCl_2.



ratio :	2b	2c	2d	2e
D_2O	0	1	0	1
H_2O	6	1	6	1

Scheme 1

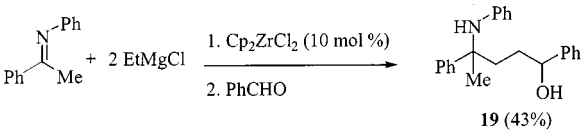


Scheme 2

of alkenes,[4b,8] zirconocene–ethylene (**A**), generated from EtMgBr and Cp_2ZrCl_2,[9] is suggested as the active alkylating agent. This is supported by the complete scrambling of deuterium between the two carbon atoms of the ethyl group in **2c** and **2e**, and also in **2b** and **2d** in Equation (c). Subsequent addition of **A** to the imine **1** gives the key intermediate azazirconacyclopentane **B**.[10] The intermediacy of **B** would account for the complete deuterium incorporation at the terminal carbon atom in the stoichiometric reaction [Equation (a)]. We also found that the rate of the catalytic reaction is first order in zirconium, indicating that the kinetically dominant catalyst is a single zirconium species. In addition, the azazirconacyclopentane corresponding to the imine **13** has been prepared independently,[11] and proved to be catalytically active in the reaction between **13** and EtMgBr.

In the next step, EtMgBr reacts with **B** to effect regioselective cleavage of the Zr–N bond, affording the ethylated complex **C**. Pathways 1 and 2 then follow. In pathway 1, **C** eliminates through β-H transfer to afford the monomagnesiated product **D** and to regenerate **A**. In pathway 2, transmetallation of the complex **C** with EtMgBr completes the catalytic cycle by forming the dimagnesiated product **E** and regenerating **A** through Cp_2ZrEt_2. The presence of the final product **E** accounts for the formation of **19** in the reaction with PhCHO (Scheme 3). The deuteration experiments in Scheme 1 support the proposition that pathways 1 and 2 coexist. In the absence of the direct alkylation process (Table 1), **2** would result from pathway 1 in Equation (b), and **2a** would result from pathway 2. Similarly, **2c** and **2e** (1:1) would result from pathway 1, while **2b** and **2d** (1:1) would result from pathway 2 [Equation (c), after addition

of H_2O].[12] Significantly, the equal distribution of only two products, **2c** and **2e**, after deuterolysis confirms this scenario. In addition, the detection of ca 0.6 mmol of ethane during the catalytic reaction of 1 mmol of **1** provides support for the formation of **A** from Cp_2ZrEt_2, completing the catalytic cycle in pathway 2. Finally, the possibility that an intermediate zirconate is involved in the catalytic process cannot be ruled out at present. In fact, zirconates have been postulated as intermediates in carbomagnesiation of alkenes.[7a,13]



Scheme 3

Conclusion

We have demonstrated that the title reaction works well not only with aldimines but also with various ketimines, which in the absence of the zirconium catalyst are totally inert towards ethylmagnesium reagents. Amines with a quaternary α-C atom may easily be prepared by this method. More importantly, the reaction opens up a new way to synthesize optically active amines with the aid of enantioselective catalysis using chiral zirconocenes. This is supported by the mechanism that we have proposed on the basis of deuteration experiments, the use of different ethylmagnesium reagents, kinetics, analysis of by-products and the catalytic activity of an independently prepared intermediate. A key azazirconacycle proved to react by two competing pathways, involving mono- and dimagnesiated final products before hydrolysis. The latter products, possessing C−Mg bonds, can be used for further transformations.

Experimental Section

General Remarks: All reactions and analytical investigations were conducted under dry argon using standard Schlenk techniques. Prior to use, tetrahydrofuran was distilled from sodium benzophenone ketyl. Cp_2ZrCl_2 (Strem) and Grignard reagents (Aldrich) were used as received. − Unless otherwise stated, ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a Bruker AC 250 or DRX 500 spectrometer. − Mass spectra were recorded with a ThermoQuest Trace MS spectrometer. − Gas chromatography was performed with a Hewlett−Packard model 6890 chromatograph using a flame ionization detector, a model 3395 integrator, and a DB-1 30-m column. − Elemental analyses were carried out with a Perkin−Elmer 2400 CHN elemental analyzer. − The starting imines were prepared according to literature procedures,[14] as were Et_2Mg[15] and CD_3CH_2MgBr.[8d] Deuterium incorporation was estimated from ^{13}C NMR spectra (gated decoupling pulse technique without NOE).

Ethylmagnesiation Procedure: Cp_2ZrCl_2 (146 mg, 0.5 mmol) and the imine (5 mmol) were dissolved in THF (20 mL) under argon in a dry Schlenk flask. The ethyl Grignard reagent (1 M in THF, 2 equiv.) was added and the reaction mixture was stirred for 1.5 h. The reaction was carefully quenched with 15% NaOH (2 mL). After dilution with 15% NaOH, the phases were separated and the aqueous phase was extracted 3 times with ether. The combined organic layers were washed with a saturated solution of Na_2CO_3, dried with Na_2SO_4, and concentrated. Flash chromatography on silica provided amines of greater than 95% purity. Bubbling of gaseous HCl through ether solutions of these amines gave white crystals of the corresponding hydrochlorides on standing; these were collected by filtration and washed with ether. These solids were obtained in almost quantitative yields relative to the starting amine and gave suitable elemental analyses.

Ethylmagnesiation of 1: The imine **1** (977 mg, 5 mmol) was treated variously with EtMgCl, EtMgBr, and Et_2Mg, according to ethylmagnesiation procedure. After purification, compound **2** was isolated in the following yields: 78% (0.88 g) with EtMgCl, 76% (0.86 g) with Et_2Mg, and 59% (0.66 g) with EtMgBr. When EtMgCl and 5 mol % of Cp_2ZrCl_2 were used, ethylmagnesiation of **1** gave a 69% yield (0.78 g) of **2**.

(1-Methyl-1-phenylpropyl)phenylamine (2): Pale yellow oil. − ^1H NMR (250 MHz): δ = 0.85 (t, *J* = 7.6 Hz, 3 H), 1.65 (s, 3 H), 1.89 (dq, *J* = 13.7, 7.3 Hz, 1 H), 2.00 (dq, *J* = 13.4, 7.6 Hz, 1 H), 4.04 (br. s, N−H), 6.36 (d, *J* = 8.2 Hz, 2 H), 6.63 (t, *J* = 7.3 Hz, 1 H), 7.03 (t, *J* = 8.2 Hz, 2 H), 7.22−7.26 (m, 1 H), 7.36 (t, *J* = 7.3 Hz, 2 H), 7.51 (d, *J* = 8.4 Hz, 2 H). − ^{13}C NMR (62.5 MHz): δ = 8.2, 25.3, 36.4, 58.4, 115.1, 116.9, 126.2, 128.3, 128.6, 146.0, 146.6. − MS (70 eV, EI): *m*/*z* (%) = 225 (7) [$M^{+\cdot}$], 196 (28) [$M - C_2H_5]^+$, 117 (100), 93 (41) [$PhNH_2]^+$. − $C_{16}H_{19}N$·HCl (261.8): calcd. C 73.41, H 7.70, N 5.35; found C 73.05, H 7.57, N 5.19.

Ethylmagnesiation of Imines 3−17: These compounds were submitted to the ethylmagnesiation procedure using EtMgCl.

(1-Ethyl-1-phenylpropyl)phenylamine (4): Yield 1.05 g (88%), pale yellow oil. − ^1H NMR (250 MHz): δ = 0.77 (t, *J* = 7.3 Hz, 6 H), 1.93 (dq, *J* = 14.9, 7.3 Hz, 2 H), 2.08 (dq, *J* = 14.9, 7.2 Hz, 2 H), 3.99 (br. s, N−H), 6.34 (d, *J* = 8.0 Hz, 2 H), 6.61 (t, *J* = 7.3 Hz, 1 H), 7.00 (t, *J* = 7.8 Hz, 2 H), 7.20−7.29 (m, 1 H), 7.35 (t, *J* = 7.8 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H). − ^{13}C NMR (62.5 MHz): δ = 7.6, 29.3, 61.1, 115.0, 116.8, 126.2, 126.7, 128.2, 128.6, 145.6, 146.0. − MS (70 eV, EI): *m*/*z* (%) = 239 (5) [$M^{+\cdot}$], 210 (42) [$M - C_2H_5]^+$, 117 (100), 93 (65) [$PhNH_2]^+$. − $C_{17}H_{20}N$·HCl (275.8): calcd. C 74.03, H 8.04, N 5.08; found C 73.63, H 8.08, N 4.97.

(1-Ethyl-1,2,3,4-tetrahydronaphth-1-yl)phenylamine Hydrochloride (6·HCl): This compound was obtained pure by bubbling gaseous HCl into an ether solution of the crude mixture without prior flash chromatography. Yield 1.24 g (86%), white solid. − ^1H NMR (500 MHz): δ = 0.55 (t, *J* = 7.3 Hz, 3 H), 1.02−1.14 (m, 1 H), 1.47−1.54 (m, 1 H), 2.02−2.12 (m, 1 H), 2.34−2.52 (m, 4 H), 2.54−2.64 (m, 1 H), 6.98 (d, *J* = 7.5 Hz, 1 H), 7.08−7.15 (m, 2 H), 7.17−7.22 (m, 4 H), 7.25−7.31 (m, 1 H), 8.13 (d, *J* = 7.9 Hz, 1 H), 11.28 (br. s, NH_2). − ^{13}C NMR (125 MHz): δ = 8.5, 19.3, 29.5, 30.5, 33.0, 69.1, 126.2, 126.8, 128.5, 128.6, 128.8, 128.9, 129.2, 131.1, 132.6, 140.2. − $C_{18}H_{21}N$·HCl (287.8): calcd. C 75.11, H 7.70, N 4.87; found C 74.98, H 7.79, N 4.77.

(1-Ethyl-1-methylheptyl)phenylamine (8): Yield 1.00 g (86%), pale yellow oil. − ^1H NMR (500 MHz): δ = 0.88 (t, *J* = 7.5 Hz, 3 H), 0.89 (t, *J* = 7.0 Hz, 3 H), 1.24 (s, 3 H), 1.20−1.40 (m, 8 H),

1.53−1.75 (m, 4 H), 6.65−6.75 (m, 3 H), 7.15 (t, J = 8.4 Hz, 2 H). − ^{13}C NMR (62.5 MHz): δ = 8.0, 14.1, 22.6, 23.5, 25.6, 29.8, 31.8, 31.9, 39.4, 56.2, 116.1, 117.3, 128.9, 147.0. − MS (70 eV, EI): *m/z* (%) = 233 (5) [$M^{+\cdot}$], 204 (48) [$M - C_2H_5$]$^+$, 148 (100) [$M - C_6H_{13}$]$^+$, 93 (47) [$PhNH_2$]$^+$. − $C_{16}H_{27}N$·HCl (269.9): calcd. C 71.21, H 10.46, N 5.19; found C 71.12, H 10.73, N 5.52.

Benzyl(1-ethyl-1-methylheptyl)amine (10): Yield 0.62 g (50%), pale yellow oil. − ^{1}H NMR (250 MHz): δ = 0.82−0.95 (m, 6 H), 1.06 (s, 3 H), 1.20−1.55 (m, 12 H), 3.65 (s, 2 H), 7.20−7.40 (m, 5 H). − ^{13}C NMR (62.5 MHz): δ = 7.8, 14.1, 22.7, 23.4, 24.4, 30.0, 30.8, 31.9, 38.3, 46.1, 54.6, 126.6, 128.2, 128.3, 141.6. − MS [70 eV, CI(NH_3)]: *m/z* (%) = 248 (72) [M + 1]$^+$, 106 (46) [$PhCH_2NH$]$^+$, 108 (100) [$PhCH_2NH_2$ + 1]$^+$. − $C_{17}H_{29}N$·HCl (283.9): calcd. C 71.93, H 10.65, N 4.93; found C 71.81, H 10.55, N 5.07.

Cyclohexyl(1-methyl-1-phenylpropyl)amine (12): With 4 equiv. of EtMgCl and a reaction time of 24 h, the yield was 0.44 g (38%, pale yellow oil). − ^{1}H NMR (500 MHz): δ = 0.67 (t, J = 7.4 Hz, 3 H), 0.83−1.18 (m, 7 H), 1.45 (s, 3 H), 1.46−1.80 (m, 5 H), 2.20−2.30 (m, 1 H), 7.19 (t, J = 7.3 Hz, 1 H), 7.29 (t, J = 7.6 Hz, 2 H), 7.41 (d, J = 8.0 Hz, 2 H). − ^{13}C NMR (62.5 MHz): δ = 8.6, 24.7, 25.5, 25.6, 25.7, 36.0, 36.6, 36.9, 51.6, 59.2, 125.9, 126.5, 127.7, 147.4. − MS [70 eV, CI(NH_3)]: *m/z* (%) = 232 (7) [M + 1]$^+$, 133 (28) [$PhC(CH_3)(C_2H_5)$]$^+$, 100 (100) [$C_6H_{11}NH_2$ + 1]$^+$. − $C_{16}H_{25}N$·HCl (267.8): C 71.75, H 9.78, N 5.23; found C 71.86, H 10.13, N 5.10.

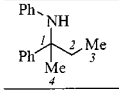
Phenyl(1-phenylpropyl)amine (14):[16] Yield 0.73 g (69%), pale yellow oil. − ^{1}H NMR (250 MHz): δ = 0.97 (t, J = 7.4 Hz, 3 H), 1.84 (quint d, J = 7.4, 2.0 Hz, 1 H), 4.09 (br. s, N−H), 4.24 (t, J = 6.7 Hz, 1 H), 6.52 (d, J = 7.8 Hz, 2 H), 6.64 (t, J = 7.3 Hz, 1 H), 7.09 (t, J = 7.8 Hz, 2 H), 7.19−7.40 (m, 7 H). − ^{13}C NMR (62.5 MHz): δ = 10.8, 31.6, 59.7, 113.2, 117.1, 126.4, 126.8, 128.5, 129.0, 143.9, 147.5.

Benzyl(1-phenylpropyl)amine (16): With a reaction time of 6 h, the yield was 1.01 g (90%, pale yellow oil). − ^{1}H NMR (250 MHz): δ = 0.95 (t, J = 7.4 Hz, 3 H), 1.95−1.67 (m, 2 H), 3.63 (dd, J = 7.5, 5.9 Hz, 1 H), 3.64 (d, J = 13.2 Hz, 1 H), 3.77 (d, J = 13.2 Hz, 1 H), 7.28−7.50 (m, 5 H). − ^{13}C NMR (62.5 MHz): δ = 10.7, 31.0, 51.4, 64.1, 126.7, 126.8, 127.4, 128.0, 128.2, 140.6, 143.9. − MS [70 eV, CI(NH_3)]: *m/z* (%) = 226 (98) [M + 1]$^+$, 196 (23) [$M - C_2H_5$]$^+$, 108 (100) [$PhCH_2NH_2$ + 1]$^+$, 106 (72) [$PhCH_2NH$]$^+$. − $C_{16}H_{19}N$·HCl (261.8): calcd. C 73.41, H 7.70, N 5.35, found C 72.81, H 7.74, N 5.17.

***tert*-Butyl(1-phenylpropyl)amine (18):** With 4 equiv. of EtMgCl and a reaction time of 8 h, the yield was 0.58 g (61%, pale yellow oil). − ^{1}H NMR (250 MHz): δ = 0.79 (t, J = 7.4 Hz, 3 H), 1.00 (s, 9 H), 1.62 (quint, J = 7.3 Hz, 2 H), 3.62 (t, J = 7.0 Hz, 1 H), 7.15−7.38 (m, 5 H). − ^{13}C NMR (62.5 MHz): δ = 11.2, 30.1, 33.3, 51.3, 59.2, 126.3, 127.1, 128.0, 147.7. − MS [70 eV, CI(NH_3)]: *m/z* (%) = 192 (100), [M + 1]$^+$. − $C_{13}H_{21}N$ (191.3): calcd. C 81.61, H 11.06, N 7.32; found C 81.76, H 11.31, N 7.51.

Reaction between Cp_2Zr(ethylene) and Imines: We have previously reported a new methodology for the insertion of carbonyl compounds into Cp_2Zr(ethylene).[17] This was applied to the imine **1**. The reaction mixture was quenched with 30% D_2SO_4 in D_2O. KOH pellets were added to make the mixture strongly basic before extraction. The amine **2a** was purified as described above (46% yield). Significant ^{13}C NMR chemical shifts for **2a** are listed in Table 2.

Table 2. Selected ^{13}C NMR chemical shifts for compounds **2**, **2a−e**

	C-1	C-2	C-3	C-4
2	58.41	36.36	8.16	25.31
2a	58.40	36.28	7.88 (t) $J_{C,D}$ = 19.1	25.30
2b	58.25	35.47 (quint) $J_{C,D}$ = 19.0	7.91	25.29
2c	58.27	35.36 (quint) $J_{C,D}$ = 19.6	7.68 (t) $J_{C,D}$ = 19.2	25.33
2d	58.37	36.17	7.58 (quint) $J_{C,D}$ = 19.0	25.29
2e	58.38	36.10	7.34 (sept) $J_{C,D}$ = 19.0	25.33

Monitoring and Identification of the Released Gas: Treatment of **1** (195 mg, 1 mmol) with EtMgBr and Cp_2ZrCl_2 was conducted according to the ethylmagnesiation procedure, in a Schlenk tube connected to a graduated gas-collecting burette. After completion, a volume of 13 mL was measured. A quantity of [D_6]benzene (0.5 mL) was saturated with this gas. The ^{1}H NMR spectrum of this solution was identical to one obtained with a saturated [D_6]benzene solution of pure ethane.[18] − ^{1}H NMR (250 MHz): δ = 0.79 (s).

Deuterium-Labeling Experiments with CD_3CH_2MgBr: Compound **1** was treated with 2 equiv. of CD_3CH_2MgBr (1 M in THF) and 10 mol% of Cp_2ZrCl_2 according to the ethylmagnesiation procedure. In the first experiment, the reaction mixture was quenched with 30% D_2SO_4 in D_2O, after which KOH pellets were added to make the mixture strongly basic before extraction. After purification, the ^{13}C NMR spectrum revealed a 1:1 mixture of **2c** and **2e**. In the second experiment, the reaction mixture was quenched with 15% NaOH. Signals of the compounds **2b**, **2c**, **2d**, and **2e** were observed in the ^{13}C NMR spectrum in 6:6:1:1 ratio. Significant chemical shifts are listed in Table 2.

4-Anilino-1,4-diphenyl-1-butanol (19): Compound **1** (0.98 g, 5 mmol) was treated with EtMgCl (2 equiv.) according to the ethylmagnesiation procedure. Benzaldehyde (1.06 g, 10 mmol) was then added dropwise at 0 °C. After 3 h at room temperature, the reaction was quenched with 15% NaOH (2 mL) and treated as above. Two isomers were obtained. Yield 0.68 g (43%, brown oil). − ^{1}H NMR (250 MHz): δ = 1.64 (s, 3 H), 1.65−2.15 (m, 4 H), 4.54 (q, J = 5.7 Hz, 1 H), 4.69 (s, 1 H), 6.28−6.36 (m, 2 H), 5.59−6.66 (m, 1 H), 6.95−7.26 (m, 2 H), 7.18−7.45 (m, 10 H). − ^{13}C NMR (62.5 MHz): δ = 25.6, 26.4, 32.8, 33.0, 39.5, 40.0, 74.4, 74.6, 115.2, 117.0, 125.8, 126.1, 126.3, 126.9, 127.6, 128.4, 128.5, 128.6, 140.8, 144.1, 144.2, 145.8, 146.1, 146.2. − MS (70 eV, EI): *m/z* (%) = 331 (5) [$M^{+\cdot}$], 196 (100) [$PhCH(NHPh)CH_3$]$^+$.

GC Kinetics: In a series of experiments, the imine **1** (200 mmol/L) was treated at 25±1 °C with EtMgBr (2 equiv.) and a catalytic amount of Cp_2ZrCl_2 (10, 20, 30, 40 mmol/L) according to the ethylmagnesiation procedure. A 0.2-mL aliquot was removed by cannula every 30 s for the first 5 min, then every minute. These were immediately poured into water. Each aliquot was extracted with ether and analyzed directly by GC. During the reaction the appearance of **2** relative to the amount of cyclododecane internal standard was monitored. Yields were calculated by conversion of the observed **2**/cyclododecane ratio into a molar concentration of **2**, using a calibration curve constructed with known mixtures of

pure **2** and cyclododecane. Initial rates (1.87, 3.64, 5.81, 7.53 min^{-1}) were obtained for the first 10% of the reaction from the linear plots of GC yields vs. time. A plot of ln(rate) vs. ln of initial concentration of Cp_2ZrCl_2 gave a straight line slope of 1.016 ($y = 1.016 \cdot x - 1.723$; $R^2 = 0.999$). The rate of the reaction is thus first order in zirconium.

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