Structure–Reactivity Correlations for the Formation of Zirconocene η^2-Imine Complexes from Amines

Nicholas Coles,† Michael C. J. Harris,† Richard J. Whitby,*,† and Julian Blagg‡

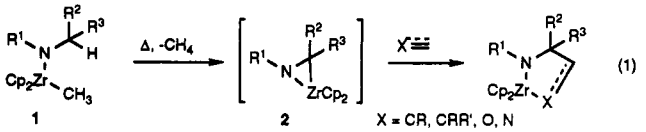
Department of Chemistry, Southampton University, Southampton, Hants SO9 5NH, England, and Pfizer Central Research, Sandwich, Kent CT13 9NJ, England

Received October 5, 1993®

The formation of η^2-imine–zirconocene complexes (zirconaziridines) ($Cp_2Zr(NR^1CR^2R^3)$) by elimination of R^4H from $Cp_2Zr(R^4)(NR^1CHR^2R^3)$ has been investigated with regard to the variation in R^1, R^2, R^3, and R^4, in particular by making use of Hammett type structure/rate correlations (R^1, R^2, R^4 = p-XC_6H_4, X = Me_2N, MeO, H, Cl, CO_2Me; R^1, ρ = 3.2; R^2, ρ = 0.5; R^4, ρ = −1.6). The elimination is first order in the zirconocene complex, has a deuterium isotope effect for the hydrogen eliminated of 8.2 at 20 °C, and kinetic studies on $Cp_2Zr(Me)(NPhCHMe_2)$ give the activation parameters $\Delta H^\ddagger$ = 100 kJ mol^{-1} and $\Delta S^\ddagger$ = −19 J K^{-1} mol^{-1} for the elimination of methane. A cyclometalation involving deprotonation α to nitrogen by $(R^4)^-$ best fits the data. The relationship between the rate of the reaction and the structure of the amine shows a marked dependency on both electronic and steric effects ranging between no reaction after 48 h at 110 °C for piperidine to below room temperature for silylamines and benzylanilines. For the first time η^2-imine complexes have been formed even from simple amines such as dibutylamine and trapped with an alkyne to form secondary allylic amines on workup. In the absence of a trap η^2-$(PhN{=}CMe_2)ZrCp_2$ rearranges *via* a rapidly reversible hydride shift to afford a η^3-azaallyl–zirconocene hydride.

Introduction

The formation of zirconocene η^2-imine complexes **2** *via* a C–H activation from methylzirconocene amides **1** and their trapping with alkenes, alkynes, allenes, and ketones



1 2 X = CR, CRR', O, N (1)

to give azazirconacycles which afford elaborate amines on protic workup have recently been reported.[1,2] This is a powerful synthetic transformation for organic chemistry since it accomplishes both a C–H activation and a carbometalation—reactions which are difficult using conventional reagents.

Zirconocene η^2-imine complexes have also been formed by rearrangement of iminoacyl complexes[3] and by ligand exchange between zirconocene butene and an imine.[4] Bis(pentamethylcyclopentadienyl)zirconium η^2-imine complexes have been formed by reaction between $Cp^*_2ZrH_2$ (Cp^* = Me_5C_5) and ArN≡C.[5] Bis(aryloxy)titanium η^2-imine complexes have been formed both by rearrangement of iminoacyl complexes[6] and by loss of ethene from 1,1-bis(aryloxy)-1-titana-2-azacyclopentanes[7] (effectively a ligand exchange since these are formed from the imine and diaryloxytitanium–ethene).

One limitation of the C–H activation method is that to date, the reaction **1** to **2** works well with just two classes of amines—*N*-arylamines and *N*-trimethylsilylamines, though dibenzylamine forms the corresponding trimethylphosphine stabilized η^2-imine complex under vigorous conditions.[2] The success of these two classes of amines has been explained by the reduced availability of the nitrogen lone pair for donation to the metal center due to conjugation with the aromatic π-system, or overlap with the silicon d orbitals (or Si–C σ^* orbitals).[1,2]

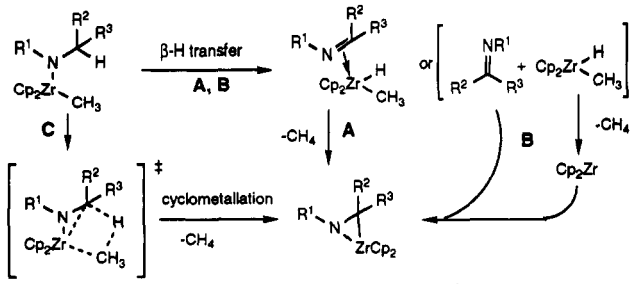
The mechanism of formation of **2** from **1** may be considered as either a β-hydride transfer followed by a reductive elimination (path A or B depending on whether the imine remains bound to the metal) or as a concerted cyclometalation *via* a four-member transition state (path C) in which the hydrogen moves with either protic or hydridic character (Scheme 1). The individual steps of A and B have some precedent in the formation of Cp_2ZrHCl by β-hydride transfer from $Cp_2Zr(Cl)(CRR'CHR''R''')$[8] and reductive elimination of RH from $Cp_2Zr(R)(H)$[9] (though $Cp_2Zr(H)(Me)$ is sufficiently stable to be isolated at room temperature[10]). Crossover experiments have ruled out a dissociative mechanism analogous to B for the

† University of Southampton.
‡ Pfizer Central Research.
® Abstract published in *Advance ACS Abstracts,* November 15, 1993.

(1) (a) Coles, N.; Whitby, R. J.; Blagg, J. *Synlett* **1990**, 271–272. (b) Idem. *Ibid.* **1992**, 143–145.
(2) Buchwald, S. L.; Wannamaker, M. W.; Watson, B. T. *J. Am. Chem. Soc.* **1989**, *111*, 776–777. Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *Ibid.* **1989**, 4486–4494. Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *Ibid.* **1991**, *113*, 2321–2322.
(3) Davis, J. M.; Whitby, R. J.; Jaxa-Chamiec, A. *Tetrahedron Lett.* **1992**, *33*, 5655–5658.
(4) Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1989**, *111*, 4495–4496. Ito, H.; Taguchi, T.; Hanzawa, Y. *Tetrahedron Lett.* **1992**, *33*, 4469–4472.
(5) Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450–6452.
(6) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75–80.
(7) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1775–1777.
(8) Negishi, E. I.; Miller, J. A.; Yoshida, T. *Tetrahedron Lett.* **1984**, *25*, 3407–3410. Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521–3531.
(9) Gell, K. I. Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846–1855.
(10) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687–2695 (but it has been suggested that elimination may be induced by donor ligands).

0276-7333/94/2313-0190$04.50/0

Scheme 1. Possible Mechanisms for the β-H Activation Route to Zirconocene η^2-Imine Complexes



formation of zirconocene alkene complexes from dialkylzirconocenes.[11] The closely related formation of zirconocene thioaldehyde complexes has been studied[12] and a mechanism analogous to path C with a small polarization in favor of the hydrogen moving with positive charge proposed. C–H activation by early transition metals has been reviewed,[13] as has the mechanism of intramolecular C–H activation.[14] The mechanism of the transformation 1 to 2, and the nature of the transition state is important both in the context of a general understanding of the many pathways available for C–H activation, and to assist extension of its application to organic synthesis.

We now report studies which define the electronic and steric effects which influence the success of the formation of zirconocene η^2-imine complexes 2 from zirconocene methyl amides 1, kinetic data which define the nature of the transition state, an improved method of carrying out the reaction on less reactive substrates, and the formation of a η^3-azaallyl zirconocene hydride by rearrangement of a zirconocene η^2-imine complex.

Results and Discussion

In order to delineate the factors which govern the ease with which zirconocene η^2-imine complexes can be formed by a C–H activation process from zirconocene methyl amides we undertook an NMR study of the rate of this reaction with a wide variety of substrates. An important additional aim was to extend the range of amines which undergo this β-hydrogen activation/alkyne insertion procedure beyond the *N*-aryl and *N*-trimethylsilyl cases previously reported.[1,2] The results are collected in Scheme 2 as are the yields of adducts obtained in preparative experiments trapping with 4-octyne.

Zirconocene methyl amides derived from benzylaniline, and *N*-trimethylsilylamines eliminate methane to form the corresponding zirconocene η^2-imine complexes too rapidly for convenient measurement—the reaction occurs below room temperature.[2] The cyclic amine piperidine readily formed the zirconocene methyl amide complex $Cp_2Zr(Me)(N(CH_2)_5)$ but this did not undergo elimination of methane to form an η^2-imine complex, being unchanged on heating at 110 °C for 48 h in the presence of 4-octyne. Thermolysis at 150 °C in a resealable Carius tube[15] was monitored by NMR and showed that the piperidine complex slowly decomposed (≈75% after 30 h) to a plethora of products, none of which indicated the intermediacy of the η^2-imine complex. On thermolysis at 110 °C in toluene in the presence of 4-octyne the zirconocene methyl amide formed from 1,2,3,4-tetrahydroisoquinoline gives only the zirconacyclopentadiene **9**[16] from dimerization of 4-octyne together with 3,4-dihydroisoquinoline. It is reasonable that the expected η^2-imine complex is formed initially, for which the rate can be estimated as -9.6×10^{-5} s^{-1} at 110 °C (extrapolated to $\approx 9.4 \times 10^{-7}$ s^{-1} at 60 °C, relative rate 0.0025 on the scale of Scheme 2).

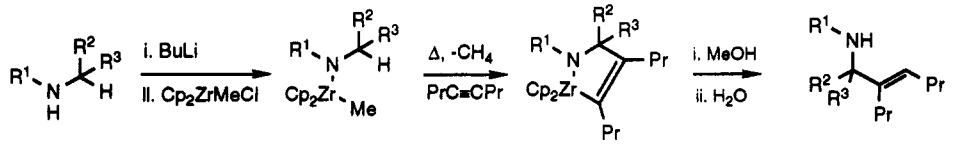
Four conclusions can be drawn from the data presented in Scheme 2: (i) Delocalization of the lone pair on nitrogen by conjugation with a phenyl ring dramatically increases the rate of reaction. Comparing Scheme 2 cases 1 and 9 suggests a 1000-fold increase in rate. (ii) Activating the hydrogen which is to be eliminated by making it benzylic increases the rate by a factor of around 100 (cf. cases 1 and 4, and 9 and benzylaniline[2]). (iii) The marked stereoelectronic requirement for the cyclometalation is shown in the comparison of piperidine and tetrahydroquinoline (case 7) with their acyclic analogues (cases 1 and 9). The effect can be quantified for aromatic amines by comparing cases 6 and 7 with 8 and 9, giving a rate drop factor of around 13 on constraining the system to a six-member ring. The effect is larger when the amine is not aromatic (piperidine cf. with dibutylamine and tetrahydroisoquinoline cf. with butylbenzylamine). (iv) There is a marked decrease in rate as the proton which is eliminated becomes more hindered (3-fold decrease in rate from methylene to methine proton, entries 6 vs 7 and 8 vs 9), though the rate decreases again for methyl protons (entry 9 vs 10), presumably reflecting the slightly higher C–H bond strength. These relative rates are quite different from those recently reported[17] for the formation of zirconocene η^2-alkene complexes by elimination of methane from $Cp_2Zr(Me)(CH_2CH_3)$, $Cp_2Zr(Me)(CH_2CH_2Me)$, and $Cp_2Zr(Me)(CH_2CHMe_2)$: $k \times 10^4$ at 20 °C = 8.72, 1.25, and 0.28 s^{-1}, respectively.

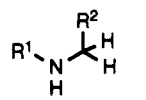
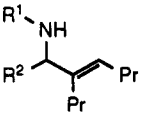
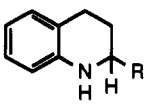
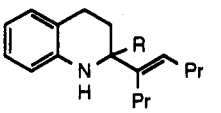
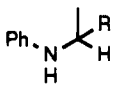
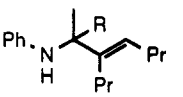
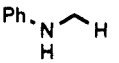
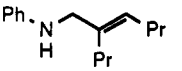
For application to organic synthesis the most important discovery is that benzylamines undergo the C–H activation/trapping procedure in good yield and even simple acyclic aliphatic amines such as dibutylamine (case 1; see below) and *N*-methyloctylamine (case 3) give moderate yields of adducts with 4-octyne. The latter reaction is notable in being highly regioselective, only the product shown due to methyl proton activation being isolated. This is somewhat surprising in light of the small rate difference measured for activation of the CH_3 and CH_2 protons in *N*-methyl and *N*-ethylaniline, respectively (Scheme 2, cases 9 and 10). In a similar observation *N*-isopropylbutylamine gives only the product of C–H activation on the "CH_2" side (case 2), the low yield being due to retroaddition and formation of the 4-octyne dimer **9**, as below.

Reversibility of the Insertion of 4-Octyne into η^2-(BuN=CHPr)$ZrCp_2$ and the Relative Rates of Ligand (Imine/Alkyne) Exchange and Cocyclization. The reaction temperature and duration for the formation and trapping of the zirconocene η^2-imine complex derived from

(11) Negishi, E.; Swanson, D. R.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1254–1255.
(12) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171–3175.
(13) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177–200.
(14) Raybov, A. D. *Chem. Rev.* **1990**, *90*, 403–424.
(15) Forrester, A. R.; Soutar, G. *Chem. Ind.* **1984**, 772–773.
(16) **9**: ^{1}H NMR (270 MHz, C_6D_6) δ 6.19 (s, 10 H), 2.57 (m, 4 H), 2.43 (m, 4 H), 1.60 (sextet, J = 7.3 Hz, 8 H), 1.21 (t, J = 7.3 Hz, 12 H); ^{13}C NMR (68 MHz, C_6D_6) δ 190.81 (s), 133.41 (s), 110.52 (d), 40.99 (t), 31.83 (t), 25.77 (t), 24.04 (t), 16.03 (q), 15.49 (q). The identity of **9** was confirmed by isolation of 5,6-dipropyl-(*E,E*)-deca-4,6-diene on protic workup.
(17) Negishi, E.; Nguyen, T.; Maye, J. P.; Choueiri, D.; Suzuki, N.; Takahashi, T. *Chem. Lett.* **1992**, 2367–2370.

Scheme 2. Rates of Formation of $Cp_2ZrNR^1CR^2R^3$ by Methane Loss from $Cp_2Zr(Me)(NR^1CHR^2R^3)$



Case	Amine	R¹	R²	- rate[a] x 10^4 s^{-1}	relative rates[b]	Product[c]	Yield %[d]
1		Bu	Pr	0.63 @ 100°C[e]	0.003		36%
2		^{i}Pr	Pr	-	-		16%
3		n-C_8H_{17}	H	-	-		46%
4		Bu	Ph	2.22 @ 70°C	0.21		55%
5		$PhCH_2$	Ph	2.04 @ 70°C	0.19		53%
		R					
6		Me		0.92 @ 70°C	0.087		75%
7		H		2.50 @ 70°C	0.24		85%
		R					
8		Me		3.76 @ 60°C	1		92%
9		H		12.9 @ 60°C	3.4		90%
10				9.45 @ 60°C 3.74 @ 50°C	2.5		80%

a. 1st order rate constant for the disappearance of $Cp_2Zr(Me)(NR^1CHR^2R^3)$ in the presence of 4-octyne. measured by n.m.r. in the heated probe of Brüker 360MHz spectrometer.

b. The rates were extrapolated to those expected at 60°C using the Arrhenius parameters calculated for **3**

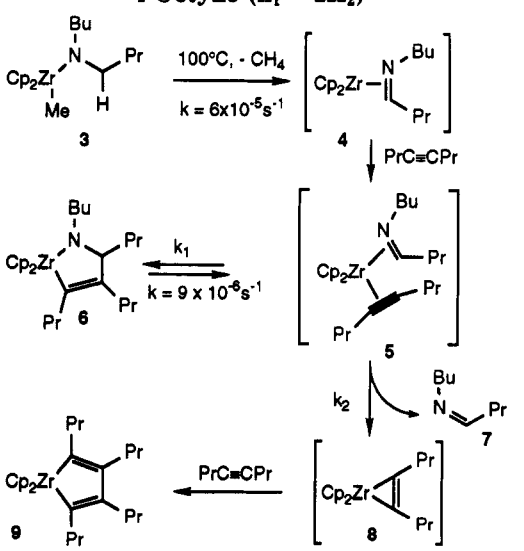
c. Product of 4-octyne trapping of the η^2-imine intermediate and protic work-up.

d. Isolated yield from preparative experiments.

e. An n.m.r. sample was heated at 100°C (steam) for various periods and monitored by n.m.r. at room temperature.

dibutylamine (Scheme 2, case 1) required careful control for maximum yield. On prolonged heating the azazirconacyclopentene **6** undergoes a "retroaddition" (C—C activation[18]) to form the imine **7**[19] together with 4-octyne–zirconocene **8** which adds another molecule of the alkyne to give the zirconacyclopentadiene **9** (Scheme 3). Monitoring the reaction by NMR showed that initially **9** is formed *concurrently* with **6** at about half the rate, independent of the concentration of 4-octyne, but on continued heating the ratio of **9** to **6** increases (Figure 1a). A plot of this data assuming first order kinetics (Figure 1b) allows the rate of "retroaddition" of **6** to be estimated as 9×10^{-6} s^{-1} (at 373 K) as well as providing a value for the rate of methane loss from **3** (6.3×10^{-5} s^{-1} at 373 K). The concurrent formation of **6** and **9** demonstrates that the rate of ring closure from the η^2-imine–η^2-alkyne–zirconocene complex **5** to give **6** is only twice the rate of extrusion of the imine **7**. An alternative explanation is that "free zirconocene", Cp_2Zr, is formed either by decomplexation of the imine from **4** or directly in the β-hydrogen activation process (Scheme 1, path B). This would be expected[20] to selectively complex to the alkyne, forming **8**. The high energy required to liberate Cp_2Zr

Scheme 3. Thermolysis of $Cp_2Zr(Me)(NBu_2)$ with 4-Octyne ($k_1 = 2K_2$)



and the mechanistic studies presented below render this explanation unlikely. With the zirconocene methyl amide derived from 1,2,3,4-tetrahydroisoquinoline, **9** is the only organometallic product though whether this results from unfavorable partition at a stage analogous to **5** or facile reversibility of the formation of the azazirconacycle analogous to **6** has not been determined.

Mechanistic Investigation on the C–H Activation Process. For a more detailed study of the C–H activation process which forms the zirconocene η^2-imine complexes we chose to study the methylzirconocene complex **10**[21] obtained from *N*-isopropylaniline. In the presence of

(18) Takahashi, T.; Fujimori, T.; Seki, T.; Saburi, M.; Uchida, Y.; Rousset, C. J.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1990**, 182–183. Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687–690.

(19) The identity of BuN=CHPr was confirmed by synthesis: ^{1}H NMR (360 MHz, C_7D_8) 7.52 (t, J = 4.5 Hz, 1 H), 3.40 (t, J = 6.8 Hz), 2.18 (m, 2 H), 1.4–1.7 (m, 6 H), 1.04 (t, J = 7 Hz, 3 H), 0.98 (t, J = 7 Hz, 3 H); ^{13}C NMR (90 MHz, C_7D_8) 162.72 (d), 61.56 (t), 38.03 (t), 33.65 (t), 2 0.85 (t), 19.60 (t), 14.10 (q), 13.94 (t).

(20) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336–3346.

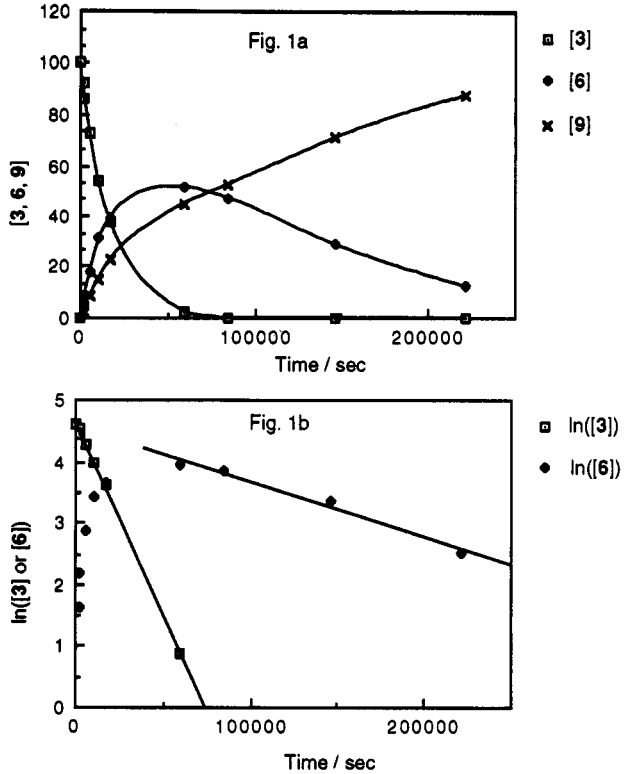
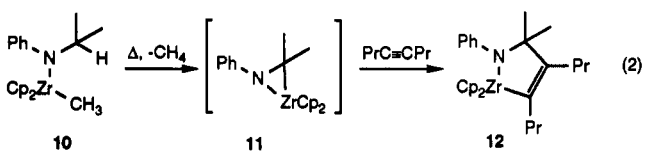
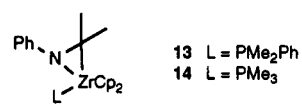


Figure 1. Course of the thermolysis of $Cp_2Zr(Me)(NBu_2)$ with 4-octyne.

4-octyne as a trap for the supposed η^2-imine complex a clean conversion of **10** into **12**[22] is observed (eq 2) with no





buildup of intermediates, demonstrating that it is the formation of **11** which is rate limiting. Other observations were in agreement with this hypothesis, for example the phenyldimethylphosphine stabilized η^2-imine complex **13** reacted with 4-octyne in 1–2 min[23] at room temperature to form **12**. The trimethylphosphine complex **14**[24] took 15 min[23] to form the same adduct, suggesting that in this case it is the dissociation of the phosphine ligand which is rate limiting. The rate of disappearance of **10** was independent of the concentration of 4-octyne and was identical in the absence of the trap.

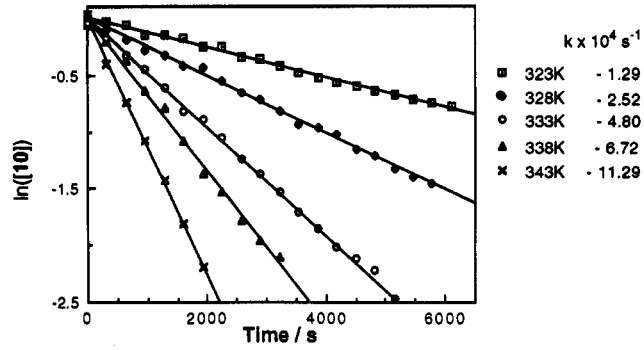


Figure 2. First order rate data for the thermolyis of **10**.

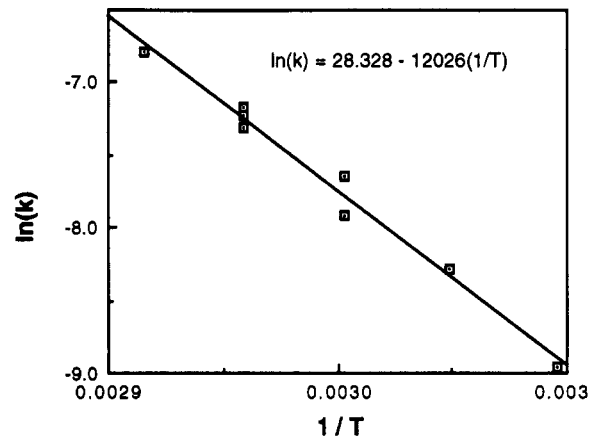


Figure 3. Arrhenius plot for the reaction of **10**.

The plot of ln [**10**] against time was linear over 4 half-lives (Figure 2), showing that the reaction is first order in the zirconocene complex. Carrying out the thermolysis at five different temperatures (Figure 2) allowed an Arrhenius plot to be constructed (Figure 3), from which the activation energy (E_a = 100 ± 5 kJ mol^{-1}) and A factor (ln(A) = 28.3 ± 1) can be calculated. Transition state theory[25] allows the enthalpy and entropy of activation of the reaction to be calculated ($\Delta H^{\ddagger}$ = 97 ± 5 kJ mol^{-1} (23 ± 1 kcal mol^{-1}); $\Delta S^{\ddagger}$ = −19 ± 8 J K^{-1} mol^{-1} (−4.5 ± 2 eu) at 333 K). The former is somewhat higher and the latter substantially smaller than that observed for the related formation of a zirconocene η^2-thioaldehyde complex ($\Delta H^{\ddagger}$ = 78.1 kJ mol^{-1} (18.6 kcal mol^{-1}), $\Delta S^{\ddagger}$ = −87.4 J K^{-1} mol^{-1} (−18.6 eu) at 80.4 °C).[12] Both differences can be accounted for by the shorter N–Zr and N–C bond lengths (cf. S–Zr and S–C), giving a more strained transition state but one involving less loss of entropy from the initial state. The small negative entropy of activation rules out the second step of paths A and B (Scheme 1) (dissociative) as rate limiting, since these would be expected to have large positive entropies of activation, and supports the highly ordered cyclic transition state in path C.

Kinetic Isotope Effects. A primary kinetic isotope effect for the cyclometalation was measured using the monodeuterated benzylaniline PhNH(CHDPh) obtained by $LiAlD_4$ reduction of PhN=CHPh. Reaction of the derived methylzirconocene amide **15** with 4-octyne at room temperature (293 K) followed by protic workup gave a product **16** (eq 3) in which the integral for the proton α

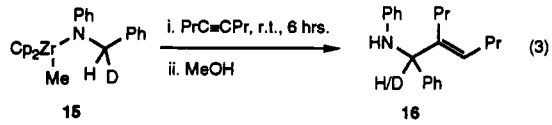
(21) **10**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20 (t, J = 7.4 Hz, 2 H), 7.03 (tt, J = 7.4, 1.1 Hz, 1 H), 6.7–6.75 (m, 2 H), 5.82 (s, 10 H), 3.90 (heptet, J = 6.6 Hz, 1 H), 0.86 (d, J = 6.5 Hz, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 153.53 (s), 129.72 (d), 127.46 (d), 116.04 (d), 109.89 (d), 52.77 (d), 22.08 (q), 20.48 (q).

(22) **12**: ^{1}H NMR (270 MHz, C_6D_6) δ 7.02 (t, J = 7.1 Hz, 2 H), 6.71 (t, J = 7.2 Hz, 1 H), 6.34 (d, J = 7.1 Hz, 2 H), 5.86 (s, 10 H), 2.15–2.23 (m, 2 H), 1.92–2.10 (m, 2 H), 1.4–1.7 (m, 4 H), 1.38 (s, 6 H), 1.02 (t, J = 6.8 Hz, 3 H), 1.00 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (67.6 MHz, C_6D_6) δ 184.58 (s), 151.42 (s), 147.21 (s), 129.23 (d), 128.12 (d), 120.58 (d), 112.57 (d), 70.43 (s), 40.48 (t), 33.38 (t), 26.66 (q), 24.96 (t), 24.60 (t), 16.47 (q), 16.28 (q).

(23) Addition of 4-octyne to an NMR sample of **13** gave a clear color change (very dark red/purple to light red/orange) in 1–2 min. The clean formation of **12** was confirmed by NMR after 7 min. The formation of **12** from **14** + 4-octyne was followed by NMR.

(24) **14**: ^{1}H NMR (270 MHz, C_6D_6) δ 7.73 (dd, J = 7.9, 7.2 Hz, 2 H), 7.29 (d, J = 7.3 Hz, 2 H), 7.10 (t, J = 7.2 Hz, 1 H), 5.61 (d, J_{PH} = 1.6 Hz, 10 H), 1.90 (d, J_{PH} = 1.6 Hz, 6 H), 1.06 (d, J_{PH} = 6 Hz, 9 H); ^{13}C NMR (68 MHz, C_6D_6) δ 157.22 (s, J_{CP} = 2.0 Hz), 129.91 (d), 115 .71 (d), 114.55 (d), 106.34 (d), 41.37 (s, J_{PC} = 18.6 Hz), 30.79 (q, J_{PC} = 2.0 Hz), 17.77 (q, J_{PC} = 16.6 Hz).

(25) Milton, J. M.; Wamser, C. C. *Fundamentals of Organic Reaction Mechanisms*; Wiley: Chichester, U.K., 1976; pp 106–109.



15 16

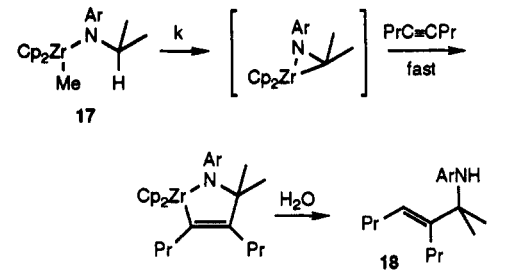
to nitrogen was only 10 ± 1% of that of the vinyl proton. This translates to a kinetic isotope effect k_H/k_D of 9 for the elimination of the hydrogen. Analysis by mass spectrometry gave the more accurate figure of k_H/k_D = 8.6. A similar competitive experiment for the formation of a zirconocene thioaldehyde complex (from $Cp_2Zr(Me)(SCHDPh)$) gave a primary kinetic isotope effect of 5.2 at 80 °C (extrapolates to ≈7 at 20 °C).[12] Both these experiments suffer from the presence of a secondary deuterium isotope effect when the C–H bond is broken, absent in the corresponding C–D breakage, which could distort the value given for the primary kinetic isotope effect by a factor of up to 1.5. To overcome this ambiguity, the rate of reaction of the deuterated complex $Cp_2Zr(Me)N(CDMe_2)Ph$ was measured directly as -7.48×10^{-5} s^{-1} at 333 K compared with the undeuterated complex **10** which gave a value of -4.80×10^{-4} s^{-1} under the same conditions. This yields a primary kinetic isotope effect k_H/k_D of 6.4 at 333 K which extrapolates to 8.2 at 293 K by assuming normal Arrhenius behavior, suggesting that the secondary kinetic isotope effect in the reaction of **15** is small and confirms the remarkably high value of k_H/k_D for this reaction. A similarly high kinetic isotope effect (9.7 at 25 °C) has been observed by Bercaw for the analogous formation of a tantalum η^2-imine complex.[26] Recently, it was concluded that these high values are characteristic of multicenter transition states[14] though the theoretical basis for this has not yet been established.

A small inverse deuterium isotope effect (k_H/k_D = 0.88(±0.05) with three deuteriums) was observed for the elimination of CD_3H from $Cp_2Zr(CD_3)(NPh^iPr)$ compared with CH_4 from **10** at 338 K. This is consistent with the methyl carbon bonding to both the zirconium and migrating H in the transition state (rehybridization decreases the strength of the C–D/H bonds).

Overall the best model for the formation of zirconocene η^2-imine complexes from zirconocene methyl amides is as a cyclometalation occurring *via* a four-member transition state as in path C (Scheme 1) above. The electronic nature of this transition state is investigated below.

Hammett Type Structure/Activity Relationships. As shown by the rate constants in Scheme 2, a phenyl or trimethylsilyl substituent on the nitrogen increases the rate of β-hydrogen activation by at least a factor of 1000. It is supposed that this is because the nitrogen lone pair is rendered less available for donation into the empty orbital on the zirconocene center by conjugation with the phenyl ring or by interaction with Si d orbitals (or C–Si σ* orbitals). This idea was examined in a more quantitative fashion by measuring the rate of formation of η^2-imine complexes from methylzirconocene amides **17** derived from para-substituted isopropylanilines (Scheme 4). We found a strong correlation between the rate of formation of the η^2-imine complex and the electron withdrawing/donating ability of the substituent on the aromatic ring. In particular the rate was greatly increased by electron withdrawing substituents (CO_2Me, Cl) and slowed by electron donating ones (OMe). The rates varied over such a wide range that the experiments could not all be done

Scheme 4. Rates of Reaction of $Cp_2Zr(CH_3)(N(Pr^i)(p\text{-}XC_6H_4))$



X	k x 10^4 / s	k_{rel}[a]	Yield of **18**	δ_H (Cp) in **17**
CO_2Me	6.43 at 30 °C	49.5	66%	5.62
Cl	5.45 at 55°C	2.16	69%	5.58
H	2.52 at 55°C	1	92%	5.64
OMe	5.31 at 80°C	0.165	78%	5.63

[a] Extrapolated to 55°C using Arrhenius parameters for **10**

at the same temperature—the relative rates quoted in Scheme 4 were obtained by extrapolating the observed rates to those expected at 55 °C using the activation parameters calculated for the parent complex **10** above. A rather poor correlation between these rates and the Hammett[27] substituent constants σ is found giving a reaction constant ρ of 3.2 (Figure 4, ArN)—the correlation with ρ^+ was worse. This is a high value and may indicate a substantial negative charge buildup on the nitrogen in the transition state. A more likely explanation is that in the transition state of the cyclometalation much of the electron density in the breaking C–H bond is accepted by the empty a_1 orbital on the metal (Figure 5) (agostic bonding). Competitive donation of the nitrogen lone pair into this orbital will destabilize the transition state, slowing the reaction, an effect which is reduced by electron withdrawing substituents. There is no systematic change in the chemical shift of the Cp rings in the complexes of the table in Scheme 4, which argues against a strong interaction between the nitrogen lone pair and the metal center in the ground state, and there is no NMR evidence for ground-state agostic bonding.

For use in synthetic organic chemistry an important observation from this work is that the aromatic ester group did not interfere with the reaction, indicating a useful functional group compatibility. The yields of allylic amines obtained in preparative experiments are also given in Scheme 4.

In order to further investigate the nature of the transition state, particularly whether the hydrogen is transferred as H^+ or H^-, we next probed the point from which this leaves by looking at a series of complexes $Cp_2Zr(Me)N(Bu)(CH_2\text{-}Ar)$ **19** (Scheme 5) with substituted aromatic rings at this position. Butylbenzylamines gave convenient rates to measure. As with the aryl substituent on nitrogen we found a significant increase in rate with electron withdrawing substituents, the ρ value of 0.5 (Figure 4) being similar to that of 0.3 observed by Buchwald in the analogous formation of zirconocene η^2-thioaldehyde complexes.[12] Together with the results from the substituted anilines above this shows that there is a movement of electrons toward the imine functionality in the transition state, implying that the hydrogen is moving as H^+ not the "hydride" implied by the term "β-hydride elimination". If paths A or B (Scheme 1) were followed, the first step would

(26) Mayer, J. M.; Curtis, C.J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651–2660.

(27) Johnson, C. D. *The Hammet Equation*; Cambridge University Press: Cambridge, U.K., 1973.

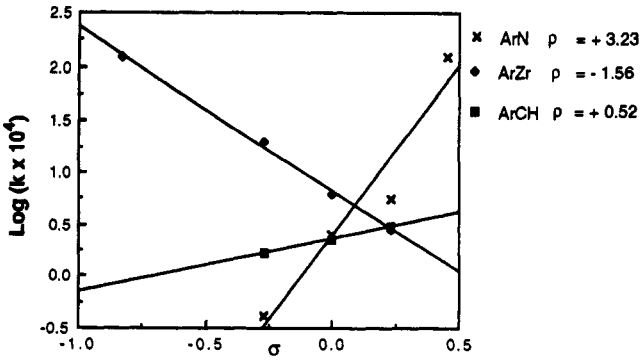


Figure 4. Hammett correlations for β-H activation.

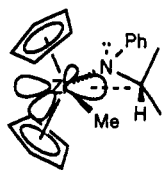
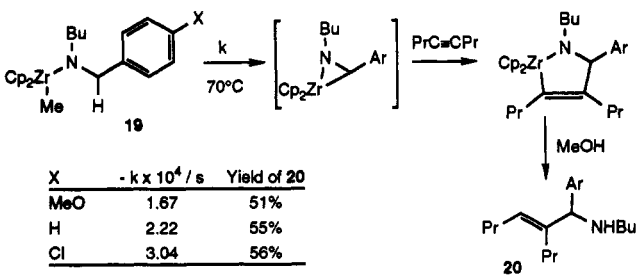


Figure 5.

Scheme 5. Rates of Reaction of p-$XC_6H_4CH_2N(Bu)(Cp_2Zr(Me))$ at 70 °C

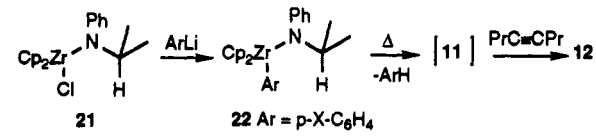


X	- k x 10⁴ / s	Yield of 20
MeO	1.67	51%
H	2.22	55%
Cl	3.04	56%

have to be viewed as a deprotonation α to nitrogen using the electrons in the Zr–N bond.

The final part of the transition state which we were able to probe was at the eliminated group. We have previously shown[1b] that the η^2-imine complexes may be generated by elimination of benzene from (phenyl)zirconocene amides as well as methane from (methyl)zirconocene amides, so we could directly investigate the effect of electron donor/acceptor with $Cp_2Zr(p\text{-}XC_6H_4)(NPh^iPr)$ **22**. The transition state **23** for the concerted cyclometalation with these precursors should resemble the "Wheland intermediate" in electrophilic aromatic substitution, so a pronounced accelerating effect of electron donors would be expected. The required precursors **22** were prepared from the crystalline zirconocene chloroamide **21** and the aryllithium, and the rate of reaction with 4-octyne was measured as before (Scheme 6). Much to our delight we found that the para substituent did have a dramatic effect on the rate of reaction and rather more surprisingly a very good correlation with the Hammett substituent constant σ, giving a reaction constant ρ of −1.56 (Figure 4). Synthetically important is that the use of p-(dimethylamino)phenyl as the eliminated group gives an 18-fold increase in rate compared to the elimination of methane. This result was extended to the less reactive amine benzyl butylamine in that the derived zirconocene amide $Cp_2Zr(p\text{-}Me_2NC_6H_4)(BuNCH_2Ph)$ eliminated p-(dimethylamino)benzene ($k = -1.42 \times 10^{-3}$ s^{-1} at 343 K) 6.4 times faster than methane (Scheme 2, case 4). In the hope of increasing the rather poor yield of the 4-octyne adduct obtained from **3** we also examined $Cp_2Zr(p\text{-}Me_2NC_6H_4)(NBu_2)$. This was prepared *in situ* from the corresponding chloride $Cp_2Zr(NBu_2)(Cl)$, in turn obtained from the remarkably clean

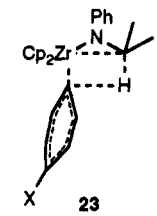
Scheme 6. Rates of Reaction of $Cp_2Zr(p\text{-}XC_6H_4)(N(^iPr)(Ph)$



21 **22** Ar = p-X-C$_6$H$_4$

X	k x 10⁴ / s	k_{rel}[a]	δ_H (Cp) in 21
Me_2N	24.2 at 50 °C	18.2	5.759
MeO	19.2 at 65°C	2.86	5.715
H	6.06 at 65°C	0.902	5.683
Cl	2.76 at 65°C	0.411	5.627

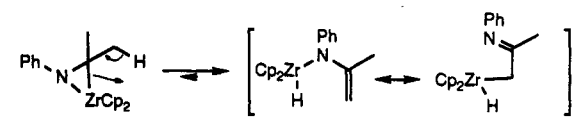
[a] rate relative to $Cp_2Zr(Me)NPh(iPr)$



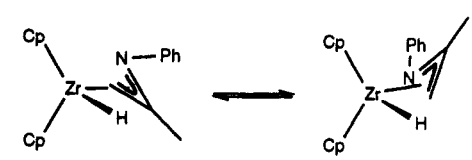
23

reaction between the magnesium amide and zirconocene dichloride (the lithium amide gave only an ≈20% yield in this reaction). The elimination of *N*,*N*-dimethylaniline and insertion of 4-octyne occurred at a convenient rate at 85 °C ($k = 3.16 \times 10^{-5}$ s^{-1} at 358 K for disappearance of starting material) but the concurrent formation of the 4-octyne dimer **9** at half the rate of the desired adduct **6** still limited the expected yield. One advantage is that the retroaddition of **6** (Scheme 3) is very slow at 85 °C making timing of the reaction less critical. A preparative experiment with aqueous workup gave *N*-((*E*)-1,2-dipropyl-2-hexenyl)butylamine in 53% isolated yield based on $Cp_2Zr(NBu_2)(Cl)$ together with 5,6-dipropyl-(*E*,*E*)-deca-4,6-diene (29%).

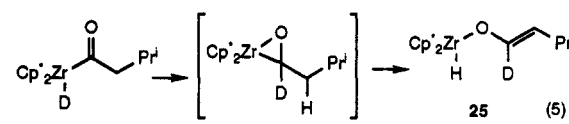
Formation of an (η^3-1-Azaallyl)zirconocene Hydride. Elimination of methane from **10** in the absence of a trap gave a new product shown by NMR (see below) to be the (vinylamido)zirconocene hydride **24**,[28] presumably formed by a β-hydride transfer to the metal from the unstabilized zirconocene η^2-imine complex **11** (eq 4). There



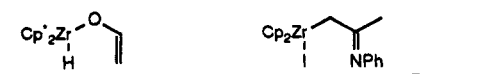
11 **24a** **24b** (4)



24c **24d**



25 (5)



26 **27**

is precedent for the transformation **11** to **24** in the β-hydride transfer from a bis(pentamethylcyclopentadienyl)zirconium

(28) **24**: ^{1}H NMR (360 MHz, C_7D_8, −30 °C) δ 7.32 (t, J = 8 Hz, 2 H), 6.95 (m, 3 H), 5.567 (s, 5 H), 5.287 (s, 5 H), 3.32 (s, 1 H), 3.08 (s, 1 H), 2.34 (s, 1 H), 1.40 (s, 3 H); ^{13}C NMR (90 MHz, C_7D_8, −30 °C) 151.15 (s), 139.73 (s), 128.90 (d), 121.88 (d), 120.38 (d), 103.73 (d, Cp), 101.64 (d, Cp), 57.35 (t), 18.67 (q).

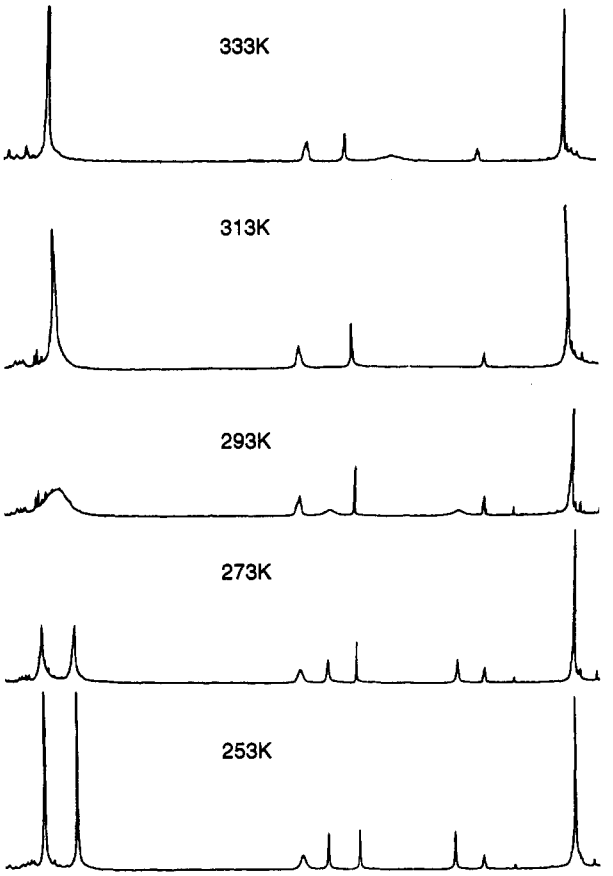


Figure 6. Variable temperature ^1H NMR of **24** (360 MHz, C_7D_8).

η^2-aldehyde complex to form the hydride-enolate complex **25** reported by Bercaw[29] (eq 5). The benzene solution of **24** was remarkably stable, little change being observed after heating at 80 °C for 16 h. Addition of 4-octyne or trimethylphosphine to NMR samples of **24** gave immediate reactions to afford the products **12** and **14** which would be expected from **11**. This indicates that the hydride shift is fast and reversible and provides a possible explanation for the rapid racemization of certain zirconocene η^2-imine complexes which has been noted.[1b]

The 360-MHz ^1H NMR spectrum of **24** at room temperature included a very broad Cp resonance at δ_H 5.4 ppm, broad 1 H singlets at δ_H 3.3 and 2.3, and sharp singlets at δ_H 3.1 (1 H) and 1.43 (3 H) ppm. The carbon-13 spectrum showed a broad Cp signal at δ_C 103 ppm together with signals at δ_C 151.2 (C), 57.54 (CH_2), and 18.63 (CH_3) ppm (phenyl signals excluded). The broadening of some of these signals was shown to be due to fluxional effects by variable temperature NMR studies (Figure 6). At low temperatures (−20 °C) two Cp resonances are observed in both carbon and proton NMR (δ_H 5.556 and 5.300 ppm, coalescence 293 K; δ_C 103.71 and 101.63 ppm). At increased temperatures the broad 1 H singlets at δ_H 2.3 and 3.3 coalesce (coalescence 323 K) to give a signal at δ_H 2.8 ppm. C–H correlation spectroscopy at −40 °C proved that these protons were attached to the carbon at δ_C 57.54 ppm, and that the proton at δ_H 3.1 ppm was not attached to a carbon.

The variable temperature NMR is best explained by the η^3-1-azaallyl[30] structure **24c/d** rather than by the various interconversion available to the forms **24a** and **24b**. Rapid flipping between the two (degenerate) conformers **24c** and **24d** of this representation swaps the environments of the Cp rings and that of the terminal CH_2 hydrogens without affecting any other signals. Similar fluxional behavior has been observed with zirconocene azadiene complexes.[31] The coalescence temperatures and frequency differences of the proton signals for the exchange of Cp and CH_2 environments correspond to free energies of activation for the exchange processes of 57 kJ mol^{-1} at 293 K and 59.5 kJ mol^{-1} at 323 K, respectively.[32] This is consistent with both deriving from the same process. The high value of this activation energy provides strong evidence for the η^3-azaallyl bonding mode with significant bonding between the central carbon of the azaallyl group and the metal center. In the oxygen analogue **26** of **24** (formed by hydrogenation of an η^2-ketene complex[33]) the terminal vinyl protons do not exchange on an NMR time scale. The orientation of the bound azaallyl group in **24c/d** relative to the hydride was established to be as shown by a nuclear Overhauser experiment carried out at −40 °C. Irradiation of the terminal CH_2 proton at δ_H 2.3 ppm gave a 9.5% enhancement in the Zr–H signal at δ_H 3.1 ppm and irradiating the latter gave a 4.5% enhancement of the former.

Further evidence for the identity of **24** came from the reaction with methyl iodide which gave an immediate evolution of a gas, presumably methane, and the formation of the nonfluxional zirconocene iodide **27**.[34] Heating the initial methylzirconocene amide **3** with methyl iodide (80 °C, benzene, 2 h) gave **27** cleanly. NMR chemical shifts and IR do not conclusively distinguish between the nitrogen and carbon bound (enamine/imine) forms of **27**, but the sharp singlet observed for the CH_2 group in several solvents and at low temperature (−60 °C) are conclusive. The overall transformation accomplishes a γ-hydrogen activation of the amine.

Conclusion

The formation of zirconocene η^2-imine complexes by loss of R^4H from $Cp_2Zr(R^4)(NR^1CHR^2R^3)$ has been shown, at least when R^1 = Ph, to be a concerted cyclometalation *via* a four-member transition state where the hydrogen moves as H^+. The reaction rate substantially increases when using an electron rich aromatic for R^4. Under appropriate conditions this reaction works even for simple aliphatic amines such as dibutylamine which suggests that it will find much wider use in synthesis than so-far realized even though the stereoelectronic requirements of the transition state inhibit the reaction for cyclic amines. In the absence of a trap the η^2-imine complex η^2-(PhN=CMe_2)$ZrCp_2$ undergoes a rapidly reversible hydride shift to afford a novel fluxional η^3-azaallylzirconium hydride.

(29) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724. Roddick, D. M.; Bercaw, J. E. *Chem. Ber.* **1989**, *122*, 1579–1587.

(30) The only well characterized early transition metal species showing η^3-azaallyl coordination is a vanadium complex: de With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1993**, *12*, 1493–1496. This bonding mode has also been suggested for a cationic zirconocene pyridyl complex: Guram, A. S.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1992**, *114*, 8991–8996.

(31) Davis, J. M.; Whitby, R. J.; JaxaChamiec, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1743–1745.

(32) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

(33) Moore, E. J.; Straus, D. A.; Armantrout, J.; Sabtarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068–2070.

(34) **27**: ^1H NMR (270 MHz, C_7D_8) δ 7.18 (t, J = 8 Hz, 2 H), 6.92 (t, J = 8 Hz, 1 H), 6.56 (d, J = 8 Hz, 2 H), 5.79 (s, 10 H), 3.84 (s, 2 H), 1.41 (s, 3 H); ^{13}C NMR (90 MHz, C_7D_8) δ 151.50 (q), 150.87 (q), 137.50 (2 × d), 122.38 (2 × d), 122.03 (d), 110.97 (d, Cp), 77.79 (tq, J_{CH} = 1 59, 4 4 Hz) 18.82 (qt, J_{CH} = 128.5, 4.4 Hz); IR (CCl_4 solution) 1664 cm^{-1}.

Experimental Section

Unless otherwise indicated materials were obtained from commercial suppliers and used without further purification. Ether, tetrahydrofuran, benzene, and toluene were distilled from sodium/benzophenone. Hexane was stirred with concentrated sulfuric acid to remove alkene impurities, washed with sodium bicarbonate solution and water, dried, distilled from CaH_2, and then distilled under nitrogen from sodium/benzophenone/tetraglyme. Amines were distilled from calcium hydride. Petroleum ether refers to the petroleum fraction bp 40–60 °C and was distilled before use. Ether refers to diethyl ether.

The para-substituted *N*-isopropylaniline derivatives (4-$XC_6H_4NH^iPr$; X = CO_2Me, H,[35a] Cl,[35b] OMe[35b]) were prepared by reductive amination of acetone with the commercially available anilines using $NaBH(OAc)_3$/AcOH in dichloroethane.[36] The para-substituted *N*-butylbenzylamines (4-$XC_6H_4CH_2NHBu$; X = Cl,[37] OMe[37]) were prepared by reductive amination of the commercially available benzaldehydes using $NaBH_4$ and butylamine.[38]

$Cp_2ZrMeCl$ was prepared by the method of Wailes[39] and recrystallized from toluene/hexane to provide material >96% pure by NMR (Cp_2ZrCl_2 and $(Cp_2ZrCl)_2O$ are impurities). This was dissolved in THF to give a solution of known concentration (usually around 1 M) which was stored at 4 °C. NMR of aliquots confirmed that this solution was stable for at least 2 months when kept in this way. Butyllithium (Aldrich) was titrated against 1,3-diphenylacetone *p*-tosylhydrazone.[40] All reactions involving organozirconium intermediates were carried out under argon using standard Schlenk and syringe techniques. Chromatography was carried out on 230–400-mesh silica gel under a slight positive pressure.

NMR spectra were recorded on Brüker EM360 (360 MHz proton, 90 MHz carbon) or JEOL GX270 (270 MHz proton, 68 MHz carbon) spectrometers. Carbon-13 spectra were proton decoupled and signals are reported as s, d, t, and q depending on the number of directly attached protons (0–3, respectively) this usually being determined by DEPT experiments.

Variable temperature and kinetic NMR studies were carried out in a Brüker 360-MHz spectrometer using the built in temperature regulating and measuring systems. The accuracy of these was checked using an ethylene glycol sample.

Mass spectra, including accurate masses were recorded on a VG-250-SE double focusing mass spectrometer and were obtained using electron impact ionization (70 eV) unless otherwise indicated. Chemical ionization (CI) used ammonia as the reagent gas and poly(ethylene glycol)s as the calibration compounds for accurate mass measurement.[41] HRMS were recorded on distilled compounds ≥95% pure by high field ^1H and ^{13}C NMR spectroscopy. IR spectra are for liquid films between sodium chloride plates unless otherwise stated.

Kinetic NMR Experiments—Sample Preparation and Analysis. The amine (1 mmol) was dissolved in THF (5 mL) and cooled to −40 °C, and ^{n}BuLi (1 mmol, 0.4 mL of a 2.5 M solution in hexanes) was added. The mixture was stirred for 15 minutes at this temperature and then added to a solution of $Cp_2Zr(Me)Cl$ (1 mmol, 1 mL of a 1 M solution in THF) in THF (4 mL) at −40 °C. The mixture was stirred while warming to 0 °C and for a further 10 min at this temperature before removal of solvents *in vacuo*. The residue was dissolved in toluene (5 mL), and either the precipitate was allowed to settle and a 1-mL aliquot of the supernatent transferred to another flask or the mixture was filtered through a No. 3 sinter. The toluene was removed *in vacuo*, the residue dissolved in toluene-d_8 or benzene-d_6 and if required 4-octyne added (to give a final concentration 2–3 times that of the zirconocene amide complex), and then the solution was transferred by syringe into an NMR tube. This was sealed with a tight fitting plastic cap and labfilm. When necessary the sample was filtered into the NMR tube through a plug of dry cotton wool.

In some cases care was taken to keep the temperature of the sample below 0 °C during these manipulations to minimize premature reaction [$Cp_2Zr(Me)(PhNMe)$, $Cp_2Zr(Me)(PhNEt)$, $Cp_2Zr(Me)(p\text{-}ClC_6H_4N^iPr)$, $Cp_2Zr(Me)(p\text{-}MeO_2CC_6H_6N^iPr)$].

The complexes $Cp_2ZrAr(RNR')$ were prepared from the chlorozirconocene amides: To a solution of the aryl bromide (1 mmol) in ether at −40 °C was added BuLi (1 mmol as a solution in hexanes) and the mixture allowed to warm to −20 °C. To the so-formed solution of the aryllithium was added $Cp_2Zr(PhN^iPr)(Cl)$, **21** (1 mmol), in THF (4 mL) at −50 °C and the mixture stirred while warming to 0 °C and for a further 10 min at this temperature. The rest of sample preparation was as described above. For $Cp_2Zr(p\text{-}Me_2NC_6H_4)(PhN^iPr)$ and $Cp_2Zr(p\text{-}MeOC_6H_4)(PhN^iPr)$ care was taken to keep the temperature below 0 °C during these manipulations. $Cp_2Zr(CD_3)(PhN^iPr)$ was prepared from CD_3MgI and **21**. $Cp_2Zr(p\text{-}Me_2NC_6H_4)(PhCH_2NBu)$ and $Cp_2Zr(p\text{-}Me_2NC_6H_4)(NBu_2)$ were prepared in a similar fashion from $Cp_2Zr(Cl)(PhCH_2NBu)$ or $Cp_2Zr(Cl)(NBu_2)$, and $p\text{-}Me_2NC_6H_4Li$.

The NMR sample tube was preheated in water of the appropriate temperature to aid in thermal equilibrium with the NMR probe and placed in the NMR spectrometer, and after 2–4 minutes to allow thermal equilibration and shimming a series of spectra were recorded using an auto program (usually every 5 min for 100 min or until the amount of starting complex was negligible).

The spectra were processed in "absolute integral" mode whereby the integral of the appropriate Cp peaks could be used directly as a measure of the amount of that component remaining (through the series). The validity of this was confirmed by also comparing the integrals to those of internal standards included in some of the reactions, or by comparing to the total integral of the "Cp" region. Where possible, signals elsewhere in the spectrum were used to confirm the results from the "Cp" region but were generally less satisfactory.

The rate constants were evaluated (from effectively a ln(integral of starting material Cp peak) vs time plot) using a least-squares fitting routine, and all showed excellent linearity. The small variation between repeat experiments is thought to result from a variation in the probe temperature of $<\pm 0.5$ deg with changes in air flow rates. The temperature could only be set in 1 deg increments but calibration with an ethylene glycol sample showed that with a fixed air flow these were held very accurately.

***N*-((*E*)-1,1-Dimethyl-2-propyl-2-hexenyl)-aniline.** *N*-isopropylaniline (0.135 g, 1 mmol) in THF (5 mL) was cooled to −40 °C and ^{n}BuLi (1 mmol, 0.4 mL of a 2.5 M solution in hexanes) added. The mixture was stirred for 15 min at this temperature and then added by syringe to a solution of $Cp_2Zr(Me)Cl$ (1 mmol, 1 mL of a 1 M solution in THF) in THF (4 mL) at −40 °C. The mixture was warmed to 0 °C and 4-octyne (1.2 mmol, 0.13 g) added. The mixture was heated at reflux (67 °C) for 6 h to give a bright red solution and cooled to room temperature and methanol (1 mL) added. The color rapidly discharged to give a pale yellow solution. After 10 min of stirring at room temperature the mixture was poured into water (50 mL) and the organic products were extracted into ether (3 × 30 mL). The combined extracts were dried ($MgSO_4$), concentrated *in vacuo*, and purified by chromatography on silica (5% ether in petroleum ether as eluent). Kugelrohr distillation (60 °C, 1 mmHg) gave the title allylic amine as a pale yellow oil (0.225 g, 92%): ^1H NMR (270 MHz, $CDCl_3$) δ 7.09 (dd, J_1 = 9.1 Hz, J_2 = 7.9 Hz, 2 H), 6.6–6.7 (m, 3 H), 5.51 (t, J = 7.2 Hz, 1 H), 3.7 (br s, 1 H), 2.03–2.13 (m, 4 H), 1.41 (s, 6 H), 1.40–1.45 (m, 4 H), 0.95 (t, J = 7.5 Hz, 3 H), 0.92 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 147.27 (s), 144.41 (s), 128.68 (d), 125.74 (d), 116.80 (d), 115.29 (d), 57.24 (s), 30.63 (t), 30.43 (t), 28.84 (q), 23.78 (t), 23.16 (t), 15.17 (q), 14.16 (q); MS *m/z* 245 (M^+, 36%), 230 (17), 202 (42), 153 (20), 134 (50),

(35) (a) Schellenberg, K. A. *J. Org. Chem.* **1963**, *28*, 3259–3260. (b) Greenfield, H.; Dovel, F. S. *J. Org. Chem.* **1967**, *32*, 3670–3671.
(36) Abdelmagid, A. F.; Maryanoff, C. A. *Synlett* **1990**, *9*, 537–539.
(37) Schoenenberger, H.; Thies, H.; Rappl, A. *Arch. Pharm.* **1967**, *300*, 483–491.
(38) Billman, J. H.; Diesing, A. C. *J. Org. Chem.* **1957**, *22*, 1068–1070.
(39) Wailes, P. C.; Weigolg, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *33*, 181.
(40) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155–158.
(41) Langley, G. *J. Org. Mass. Spectrom.* **1990**, *25*, 429–431.

97 (55), 93 (100), 83 (30), 69 (47), 55 (40); IR 3395, 1595, 1493, 1460, 1260, 1050, 760, 700 cm^{-1}. Anal. Calc for $C_{17}H_{27}N$: C, 83.2; H, 11.1; N, 5.7. Found: C, 83.1; H, 11.4; N, 5.7.

By similar procedures, modified as indicated for the time, temperature, and solvent of reaction, and purification method, the following allylic amines were prepared.

***N*-((*E*)-1,2-Dipropyl-2-hexenyl)butylamine.** The reaction mixture was heated at 100 °C in toluene for 14 h. The crude product was purified by column chromatography (petroleum ether then 1:1 ether:petroleum ether) followed by Kugelrohr distillation (80 °C, 0.9 mmHg) to afford the title amine as a pale yellow oil (36%): ^1H NMR (360 MHz, $CDCl_3$) δ 5.21 (t, J = 7.2 Hz, 1 H), 2.89 (t, J = 6.8 Hz, 1 H), 2.48 (ddd, J = 6.4, 8.1, 11.3 Hz, 1 H), 2.38 (ddd, J = 6, 7.9, 11.3 Hz, 1 H), 2.01 (q, J = 7.3 Hz, 1 H), 1.90 (m, 2 H), 1.6 (m, 16 H), 0.9 (m, 12 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 140.32 (s), 127.78 (d), 65.90 (d), 47.30 (t), 37.45 (t), 32.61 (t), 29.93 (t), 29.83 (t), 23.38 (t), 23.28 (t), 20.76 (t), 19.91 (t), 15.00 (t), 14.29 (t), 14.19 (t), 14.01 (t); IR 1716, 1688, 1462, 1377, 1262, 1126, 910, 735 cm^{-1}; MS (CI) m/z 240 ((M + H)$^+$, 100%), 216 (18), 196 (38), 128 (10), 95 (20); HRMS (CI) calc for $C_{16}H_{34}N$ (M + H) m/z 240.269, found 240.271.

***N*-((*E*)-1,2-Dipropyl-2-hexenyl)isopropylamine.** The reaction mixture was heated at reflux in toluene for 48 h. The crude product was purified by column chromatography (4:1 petroleum ether:ether) followed by Kugelrohr distillation (70 °C, 0.9 mmHg) to afford the title amine as a colorless oil (16%): ^1H NMR (360 MHz, $CDCl_3$) δ 5.2 (t, J = 7.2 Hz, 1 H), 3.04 (t, J = 6.8 Hz, 1 H), 2.68 (septet, J = 6.4 Hz, 1 H), 2.00 (q, J = 7.2 Hz, 2 H), 1.90 (m, 1 H), 1.13 (m, 10 H), 0.95 (m, 15 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 140.00 (s), 128.04 (d), 62.6 9 (d), 45.08 (d), 37.59 (t), 29.99 (t), 29.57 (t), 24.40 (q), 23.53 (t), 23.31 (t), 22.03 (q), 19.97 (t), 15.11 (q), 14.28 (q), 14.05 (q); IR 1463 (m), 1377 (m), 1174 (m), 1115 (m) cm^{-1}; MS (CI) m/z 226 ((M + H)$^+$, 100%), 182 (21), 167 (10); HRMS (CI) calc for $C_{15}H_{32}N$ (M + H) m/z 226.2535, found 226.2535.

The 4-octyne dimer (*E,E*)-5,6-dipropyldeca-4,6-diene was also isolated in 44% yield based on the zirconium amide complex: ^1H NMR (270 MHz, $CDCl_3$) δ 5.37 (t, J = 7.1 Hz, 2 H), 2.15 (t, J = 7.6 Hz, 4 H), 2.06 (q, J = 7.2 Hz, 4 H), 1.43 (quintet, J = 7.5 Hz, 4 H), 1.33 (quintet, J = 7.7 Hz, 4 H), 0.93 (t, J = 7.3 Hz, 6 H), 0.89 (t, J = 7.4 Hz, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 141.46 (s), 126.20 (d), 30.51 (t), 30.26 (t), 23.41 (t), 22.26 (t), 14.29 (t), 14.19 (q), 14.12 (q); IR 1375 (m), 1260 (m), 1063 (m), 1107 (m), 888 (m), 805 (m) cm^{-1}; MS m/z 222 (m$^+$, 73%), 193 (42), 179 (100), 109 (32); HRMS calc for $C_{16}H_{30}$ m/z 222.2343, found 222.2347.

***N*-((*E*)-2-Propyl-2-hexenyl)octylamine.** The reaction mixture was heated at reflux in toluene for 15 h. The crude product was purified by column chromatography (2:1 petroleum ether: ether) and by Kugelrohr distillation under reduced pressure (75 °C, 0.3 mmHg) to afford the title amine as a colorless oil (46%): ^1H NMR (360 MHz, $CDCl_3$) δ 5.25 (t, J = 7.2 Hz, 1 H), 3.07 (d, J = 1.1 Hz, 2 H), 2.50 (t, J = 7.3 Hz, 2 H), 1.95 (m, 4 H), 1.30 (m, 17 H), 0.85 (t, J = 7.3 Hz, 9 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 137.76 (s), 126.26 (d), 55.50 (t), 49.37 (t), 31.89 (t), 31.44 (t), 31.10 (t), 30.18 (t), 29.75 (t), 29.60 (t), 29.50 (t), 29.32 (t), 27.48 (t), 23.10 (t), 22.69 (t), 22.27 (t), 21.79 (t), 20.76 (t), 14.17 (t), 14.07 (t), 13.69 (t); IR 2895 (s), 1457 (s), 1377 (m), 1110 (m), 893 (w), 739 (w) cm^{-1}; MS m/z 253 (M$^+$, 34%), 210 (80), 154 (100), 130 (55), 96 (61); HRMS calc for $C_{17}H_{35}N$ (M$^+$ m/z 253.2769, found 253.2762.

***N*-((*E*)-1-Phenyl-2-propyl-2-hexenyl)butylamine.** The reaction mixture was heated at reflux in toluene for 15 h. The crude amine was purified by column chromatography (4:1 petroleum ether:ether) followed by Kugelrohr distillation (100 °C, 1 mmHg) to afford the title amine as a colorless oil (55%): ^1H NMR (360 MHz, $CDCl_3$) δ 7.3 (m, 1 H), 5.63 (t, J = 7.5 Hz, 1 H), 4.1 (s, 1 H), 2.57 (dt, J = 7.1, 11.4 Hz, 1 H), 2.47 (dt, J = 7.1, 11.4 Hz, 1 H), 2.06 (q, J = 7.3 Hz, 1 H), 1.97 (ddd, J = 5.6, 10, 13.4 Hz, 1 H), 1.75 (ddd, J = 6.4, 10.2, 13 .5 Hz, 1 H), 1.3 (m, 8 H), 0.95 (t, J = 7.3 Hz, 3 H), 0.91 (t, J = 7.3 Hz, 3 H), 0.82 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 143.72 (s), 140.89 (s), 128.15 (d), 127.69 (d), 126.81 (d), 126.06 (d), 68.73 (d), 47.85 (t), 32.64 (t), 31.03 (t), 29.92 (t), 23.24 (t), 22.64 (t), 20.66 (t), 14.58 (q), 14.15 (q), 14.07 (q); IR 3333, 1707, 1601, 1491, 1452, 1377, 1261, 1123, 1029, 899, 737, 700 cm^{-1}; MS (CI) m/z 274 ((M + H)$^+$, 100%), 201 (17), 162 (21); HRMS (CI) calc for $C_{19}H_{32}N$ (M + H) m/z 274.2534, found 274.2529. Anal. Calc for $C_{19}H_{31}N$: C, 83.5; H, 11.4; N, 5.1. Found: C, 83.5; H, 11.3; N, 5.2%.

***N*-((*E*)-1-Phenyl-2-propyl-2-hexenyl)benzylamine.** The reaction mixture was heated at reflux in toluene for 15 h. The crude product was purified by column chromatography (4:1 petroleum ether:ether) and by Kugelrohr distillation (120 °C, 1 mmHG) to afford the title amine as a colorless oil 53%): ^1H NMR (360 MHz, $CDCl_3$) δ 5.72 (t, J = 7.2 Hz, 1 H), 4.24 (s, 1 H), 3.75 (d, J = 12.4 Hz, 2 H), 2.10 (q, J = 7.4 Hz, 2 H), 2.05 (ddd, J = 6.2, 10.1, 13.4 Hz, 1 H), 1.85 (ddd, J = 5.5, 10.2, 13.4 Hz, 1 H), 1.7 (s, 1 H), 1.5 (sextet, J = 7.3 Hz, 2 H), 1.25 (m, 2 H), 1.0 (t, J = 7.3 Hz, 3 H), 0.87 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) 143.37 (s), 141.01 (s), 140.64 (s), 128.41 (d), 128.23 (d), 127.75 (d), 126.93 (d), 126.88 (d), 126.94 (d), 67.87 (d), 51.85 (t), 30.94 (t), 29.97 (t), 23.26 (t), 22.69 (t), 14.60 (t), 14.10 (t); IR 3323 (w), 1493 (m), 1452 (m), 735 (m), 698 (s) cm^{-1}; MS (CI) m/z 308 ((M + H)$^+$, 100%), 200 (23), 196 (23), 91 (9); HRMS (CI) calc for $C_{22}H_{30}N$ (M + H) m/z 308.2378, found 308.2368.

2-Methyl-2-((*E*)-4-octen-4-yl)-1,2,3,4-tetrahydroquinoline. The reaction mixture was heated at reflux in THF for 14 h. The crude amine was purified by column chromatography (ether:petroleum ether 1:5) and Kugelrohr distillation (100 °C, 1 mmHg) to afford a colorless oil (75%): ^1H NMR (360 MHz, $CDCl_3$) δ 7.00 (td, J = 6.9, 1.4 Hz, 1 H), 6.95 (dd, J = 6.2, 1.2 Hz, 1 H), 6.59 (td, J = 7.4, 1.3 Hz, 1 H), 6.51 (dd, J = 8.0, 1.2 Hz, 1 H), 5.40 (t, J = 7.2 Hz, 1 H), 3.8 (br s, 1 H), 2.58–2.62 (m, 2 H), 2.10 (t, J = 7.6 Hz, 2 H), 2.06 (dt, J_1 = 8.1, J_2 = 7.6 Hz, 2 H), 1.95–1.98 (m, 1 H), 1.64 (ddd, J = 13.0, 8.8, 6.8 Hz, 1 H), 1.43 (sextet, J = 7.4 Hz, 2 H), 1.33 (s, 3 H), 0.97 (t, J = 7.3 Hz, 3 H), 0.85 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 144.24 (s), 143.76 (s), 129.04 (d), 126.62 (d), 126.02 (s), 120.43 9s), 116.13 (d), 113.23 (d), 56.93 (s), 31.88 (t), 30.52 (t), 30.35 (t), 28.33 (t), 24.58 (t), 24.32 (t), 23.20 (d), 15.09 (q), 13.90 (q); IR 3406, 2800–3100, 1651, 1607, 1588, 1483, 1424, 1373, 1313, 1261, 743 cm^{-1}; MS m/z 257 (M$^+$, 9%), 242 (16.6), 146 (100); HRMS calc for $C_{18}H_{27}N$ (M$^+$) m/z 257.407, found 257.410.

2-((*E*)-4-Octen-4-yl)-1,2,3,4-tetrahydroquinoline. The reaction mixture was heated at reflux in THF for 16 h. The crude amine was purified by column chromatography (ether:petroleum ether 1:5) and Kugelrohr distillation (100 °C, 1 mmHg) to afford a colorless oil (85%): ^1H NMR (360 Mhz, $CDCl_3$) δ 6.9–7.04 (m, 2 H), 6.65 (td, J = 7.4, 1.2 Hz, 1 H), 6.52 (dd, j = 7.8, 1.1 Hz, 1 H), 5.50 (t, J = 7.2 Hz, 1 H), 3.77 (dd, J = 9.5, 3.0 Hz, 1 H), 3.72 (br s, 1 H), 2.85 (ddd, J = 16.2, 11.0, 5.3 Hz, 1 H), 2.74 (dt, J = 16.1, 4.7 Hz, 1 H), 2.17 (ddd, J = 13.4, 9.7, 6.7 Hz, 1 H), 2.08 (q, J = 7.7 Hz, 2 H), 1.95–2.05 (m, 1 H), 1.80 (dddd, J = 12.8, 10.9, 9.6, 5.2 Hz, 1 H), 1.37–1.55 (m, 4 H), 1.03 (t, J = 7.3 Hz, 3 H), 1.01 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 145.13 (s), 141.80 (s), 129.18 (d), 126.80 (d), 126.51 (d), 120.99 (s), 117.71 (d), 113.85 (d), 57.70 (d), 30.62 (t), 29.86 (t), 28.03 (t), 26.73 (t), 23.24 (t), 23.13 (t), 14.60 (q), 13.99 (q); IR 3410, 1607, 1586, 1483, 1470, 743 cm^{-1}; MS m/z 244 (M$^+$, 7.3%), 243 (45), 214 (10), 200 (24), 158 (5), 132 (100), 106 (19); HRMS calc for $C_{17}H_{25}N$ (M$^+$) m/z 243.377, found 243.377.

***N*-((*E*)-1-Methyl-2-propyl-2-hexenyl)aniline.** The reaction mixture was left for 16 h at room temperature in THF. The crude amine was purified by chromatography (3% ether in petroleum ether) and Kugelrohr distillation (60 °C, 1 mmHg) to afford a pale yellow oil (90%): ^1H NMR (270 MHz, $CDCl_3$) δ 7.17 (dd, J = 7.4, 1.1 Hz), 6.72–6.78 (m, 3 H), 5.14 (t, J = 7.4 Hz, 1 H), 3.9 (s, 1 H), 3.52 (q, J = 6.8 Hz, 1 H), 1.95–2.02 (m, 4 H), 1.40 (sextet, J = 7.4 Hz, 2 H), 1.32 (sextet, J = 7.3 Hz, 2 H), 1.09 (d, J = 6.8 Hz, 3 H), 0.94 (t, J = 7.3 Hz, 3 H), 0.93 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 145.30 (s), 144.72 (s), 128.26 (d), 125.98 (d), 116.65 (d), 115.03 (d), 53.71 (d), 30.62 (t), 30.28 (t), 23.77 (t), 23.21 (t), 18.21 (q), 15.20 (q), 14.19 (q); IR 3415, 1605, 1504, 1462, 1313, 1250, 845, 791 cm^{-1}; MS m/z 231 (M$^+$, 75%), 216 (95), 188 (48), 120 (100), 93 (95); HRMS calc for $C_{16}H_{25}N$

m/z 231.1987, found 231.1987. Anal. Calc for $C_{16}H_{25}N$: C, 83.1; H, 10.8; N, 6.1 Found: C, 82.9; H, 10.6; N, 6.3.

***N*-((*E*)-2-Propyl-2-hexenyl)aniline.** The reaction mixture was left for 16 h at room temperature in THF. The crude amine was purified by chromatography (3% ether in petroleum ether) and Kugelrohr distillation (60 °C, 1 mmHg) to afford the title compound as a pale yellow oil (80%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.15 (t, J = 7.5 Hz, 2 H), 6.71–6.75 (m, 3 H), 5.16 (t, J = 7.5 Hz, 1 H), 3.7 (s, 1 H), 3.41 (s, 2 H), 1.98–2.11 (m, 4 H), 1.42 (sextet, J = 7.3 Hz, 2 H), 1.28 (sextet, J = 7.3 Hz, 2 H), 0.97 (t, J = 7.2 Hz, 3 H), 0.95 (t, J = 7.33 Hz, 3 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 146.70 (s), 145.07 (s), 127.80 (d), 126.04 (d), 116.70 (d), 115.05 (d), 54.72 (t), 30.612 (t), 30.30 (t), 23.97 (t), 23.10 (t), 15.20 (q), 14.19 (q); IR 3423, 1603, 1505, 1464, 1313, 1252, 847, 791 cm^{-1}; MS m/z 217 (M^+, 68%), 188 (10), 174 (58), 106 (55), 93 (100); HRMS calc for $C_{15}H_{23}N$ (M^+) m/z 217.337, found, 217.340.

***N*-((*E*)-1,1-Dimethyl-2-propyl-2-hexenyl)-4-carbomethoxyaniline.** The reaction mixture was left for 6 h at room temperature in THF. The crude amine was purified by chromatography (30% ether in petroleum ether) to afford the title compound as a pale yellow oil (66%) which decomposed on attempted Kugelrohr distillation. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.76 (d, J = 8.7 Hz, 2 H), 6.58 (d, J = 8.7 Hz, 2 H), 5.50 (t, J = 7.1 Hz, 1 H), 4.20 (br s, 1 H), 3.83 (s, 3 H), 1.98–2.09 (m, 4 H), 1.13 (s, 6 H), 1.25–1.50 (m, 4 H), 0.93 (t, J = 7.3 Hz, 3 H), 0.88 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.59 (s), 151.22 (s), 143.35 (s), 131.00 (d), 126.41 (d), 117.62 (s), 113.70 (d), 57.56 (s), 51.56 (q), 30.59 (t), 30.41 (t), 28.66 (q), 23.68 (t), 23. 68 (t), 23.11 (t), 15.10 (q), 14.15 (q); IR 3378, 1695, 1605, 1522, 1434, 1274, 1174, 1108, 841, 772 cm^{-1}; MS m/z 303 (M^+, 50%), 288 (20), 272 (15), 260 (55), 192 (67), 163 (77), 151 (98), 120 (35), 111 (42), 97 (100), 83 (60), 69 (86); HRMS calc for $C_{19}H_{29}NO_2$ (M^+) m/z 303.2198, found 303.2186.

***N*-((*E*)-1,1-Dimethyl-2-propyl-2-hexenyl)-4-chloroaniline.** The reaction mixture was left for 6 h at room temperature in THF. The crude amine was purified by chromatography (5% ether in petroleum ether) to afford the title compound as a pale yellow oil (69%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.03 (d, J = 9.1 Hz, 2 H), 6.57 (d, J = 9.0 Hz, 2 H), 5.50 (t, J = 7.2 Hz, 1 H), 3.7 (br s, 1 H), 2.0–2.2 (m, 4 H), 1.41 (quintet, J = 7.2 Hz, 4 H), 1.40 (s, 6 H), 0.95 (t, J = 7.2 Hz, 3 H), 0.93 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (68 MHz, $CDCl_2$) δ 145.81 (s), 144.02 (s) , 128.54 (d), 126.14 (d), 121.43 (s), 116.29 (d), 57.37 (s), 30.64 (t), 30.43 (t), 28.71 (q), 23.77 (t), 23.16 (t), 15.16 (q), 14.18 (q); IR 3419, 1598, 1496, 1456, 1382, 1316, 1294, 1255, 1177, 1093, 817 cm^{-1}; MS m/z 279 (M^+, 49%)*, 264 (11)*, 236 (37)*, 168 (45)*, 153 (65), 127 (97)*, 111 (45), 97 (100) (* = Cl isotope pattern, only ^{35}Cl signals reported); HRMS calc for $C_{17}H_{26}N^{35}Cl$ m/z 279.1738, found 279.1747.

***N*-((*E*)-1,1-Dimethyl-2-propyl-2-hexenyl)-4-methoxyaniline.** The reaction mixture was heated at reflux in THF for 16 h. The crude amine was purified by column chromatography (30% ether in petroleum ether) to afford the title compound as a pale yellow oil (78%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.72 (d, J = 9.1 Hz, 2 H), 6.63 (d, J = 9.1 Hz, 2 H), 5.49 (t, J = 7.1 Hz, 1 H), 3.75 (s, 3 H), 3.4 (br s, 1 H), 2.05–2.20 (m, 4 H), 1.38 (s, 6 H), 1.40–1.50 (m, 4 H), 0.96 (t, J = 7.3 Hz, 3 H), 0.95 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 152.06 (s), 144.80 (s), 141.26 (s), 125.72 (d), 117.37 (d), 114.25 (d), 57.53 (s), 55.73 (q), 30.65 (t), 30.52 (t), 28.82 (q), 23.87 (t), 23.18 (t), 15.19 (q), 14.19 (q); IR 3402, 1616, 1510, 1464, 1380, 1237, 1180, 1041, 821 cm^{-1}; MS m/z 275 (M^+, 33%), 260 (7), 232 (23), 164 (18), 123 (100); HRMS calc for $C_{18}H_{29}NO$ (M^+) m/z 275.2249, found 275.2254.

***N*-((*E*)-1-(4-Chlorophenyl)-2-propyl-2-hexenyl)butylamine.** The reaction mixture was heated at reflux in THF for 12 h. The crude product was purified by column chromatography (3:1 petroleum ether:ether) and by Kugelrohr distillation (110 °C, 0.9 mmHg)) to afford the title amine as a colorless oil (56%): ^{1}H NMR (360 MHz, $CDCl_3$) 7.29 (m, 4 H), 5.59 (t, J = 7.2 Hz, 1 H), 4.08 (s, 1 H), 2.55 (dt, J = 12.1, 7.2 Hz, 1 H), 2.42 (dt, J = 11.5, 7.1 Hz, 1 H), 2.05 (q, J = 7.3 Hz, 2 H), 1.95 (ddd, J = 13.5, 10.4, 6.1 Hz, 1 H), 1.72 (ddd, J = 13.5, 10.1 , 5.6 Hz, 1 H), 1.3 (m, 9 H?), 0.92 (t, J = 7.3 Hz, 3 H), 0.90 (t, J = 7.3 Hz, 3 H), 0.82 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 142.32 (s), 140.74 (s), 132.38 (s), 129.02 (d), 128.28 (d), 126.59 (d), 68.21 (d), 47.8 (t), 32.51 (t), 30.92 (t), 29.89 (t), 23.18 (t), 22.67 (t), 20.63 (t), 14.55 (q), 14.13 (q), 14.04 (q); IR 1732 (m), 1487 (m), 1090 (m), 1014 (m) cm^{-1}; MS (CI) m/z 308 ($M + H)^+$, 100%), 235 (25), 196 (25); HRMS (CI) calc for $C_{19}H_{31}N^{35}Cl$ ($M + H$) m/z 308.2145, found 308.2137. Anal. Calc for $C_{19}H_{30}NCl$: C, 74.3; H, 9.8; N, 4.6. Found: C, 74.6; H, 9.5; N, 4.6.

***N*-((*E*)-1-(4-Methoxyphenyl)-2-propyl-2-hexenyl)butylamine.** The reaction mixture was heated at reflux in THF for 15 h. The crude product was purified by column chromatography (3:1 petroleum ether:ether) followed by Kugelrohr distillation (105 °C, 0.9 mmHg) to afford the title amine as a colorless oil (51%): ^{1}H NMR (360 MHz, $CDCl_3$) 7.25 (d, J = 8.5 Hz, 2 H), 6.82 (d, J = 8.5 Hz, 2 H), 5.59 (t, J = 7.5 Hz, 1 H), 4.05 (s, 1 H), 3.80 (s, 3 H), 2.55 (dt, J = 11.3, 7.1 Hz, 1 H), 2.45 (dt, J = 11.3, 7.1 Hz, 1 H), 2.05 (q, J = 7.4 Hz, 2 H), 1.95 (ddd , J = 13.4, 10.1, 6.7 Hz, 1 H), 1.71 (ddd, J = 13.3, 9.5, 6.1 Hz, 1 H), 1.45 (m, 4 H), 1.33 (m, 3 H), 1.20 (m, 2 H), 0.94 (t, J = 7.4 Hz, 3 H), 0.90 (t, J = 7.3 Hz, 3 H), 0.82 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) 158.55 (q), 141.03 (q), 135.85 (q), 128.67 (d), 125.57 (d), 113.53 (d), 67.98 (d), 55.29 (OCH_3), 47.82 (t), 32.53 (t), 31.10 (t), 29.91 (t), 23.26 (t), 22.61 (t), 20.66 (t), 14.58 (t), 14.14 (t), 14.07 (t); IR 1609 (s), 1508 (s), 1464 (s), 1248 (s), 1039 (m), 827 (m) cm^{-1}; MS (CI), m/z 304 ((M + H)$^+$, 38%), 231 (100), 192 (27); HRMS (CI) calc for $C_{20}H_{34}NO$ (M + H) 304.2640, found 304.2622.

***α*-Deuterio-*N*-phenylbenzylamine.** Benzylideneaniline (0.91 g, 5 mmol) was dissolved in ether (5 mL). This was added to a suspension of lithium aluminum deuteride (0.21 g, 5 mmol) in ether (5 mL) and stirred at room temperature for 1 h. The mixture was poured into water (20 mL), and the organic products were extracted into ether (3 × 25 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was Kugelrohr distilled to yield a colorless oil (title), which solidified on standing (0.846 g, 92%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20–7.35 (m, 5 H), 7.15 (dd, J = 8.5, 7.3 Hz, 2 H), 6.70 (tt, J = 7.3, 1.0 Hz, 1 H), 6.60 (m, 2 H), 4.27 (t, J_{HD} = 2.1 Hz, 1 H), 4.0 (br s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.27 (s), 139.52 (s), 129.39 (d), 127.64 (d), 127.35 (d), 117.66 (d), 112.95 (d), 48.07 (d) (J_{CD} = 22.5 Hz); IR 3418, 1602, 1505, 1450, 1428, 1315, 1286, 749, 719, 691, 668 cm^{-1}; MS 136 (M^+, 13%), 121 (25), 106 (12), 92 (100). Comparison with the mass spectrum of the undeuterated compound showed the title amine to be >99% monodeuterated.

Bis(cyclopentadienyl)chloro(*N*-isopropylanilido)zirconium, 21. *N*-isopropylaniline (2.19 g, 15 mmol) was dissolved in THF (20 mL) and cooled to −30 °C, ^{n}BuLi (6 mL of 2.5 M solution in hexanes, 15 mmol) was added and the mixture warmed to room temperature and stirred 10 min. This was added to a solution of zirconocene dichloride (3.2 g, 11 mmol) in THF (20 mL) at −50 °C, and the mixture was warmed to room temperature and stirred for 1 h. Solvents were removed *in vacuo*, and the residue was dissolved in toluene and passed through a no. 3 sinter. Toluene was removed *in vacuo* and the residue washed with hexane (2 × 10 mL). The yellow solid was dissolved in the minimum volume of toluene and hexane layered onto the solution. Cooling to 0 °C induced formation of bright yellow needles (title) which were washed with hexane (2 × 10 mL) (3.78 g, 88%); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.27 (t, J = 7.3 Hz, 2 H), 7.1 (tt, J = 7.3, 1.2 Hz, 1 H), 6.8 (dd, J = 7.0, 1.3 Hz, 2 H), 6.10 (s, 10 H), 4.32 (heptet, J = 6.4 Hz, 1 H), 0.94 (d, J = 6.4 Hz, 6 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 154.07 (s), 123.93 (d), 112.92 (d), 55.21 (d), 21.00 (q).

Acknowledgment. We thank Pfizer Central Research, Sandwich, England, and the Science and Engineering Research Council (U.K.) for generous support of this work. We also thank Mrs. Joan Street for help in the NMR studies.

OM930687E