

Aspects of the hydrozirconation-isomerisation reaction *

Ulf Annby, Jörgen Alvhäll, Salo Gronowitz and Anders Hallberg

Division of Organic Chemistry I, Chemical Center, University of Lund, P.O.B. 124, S-221 00 Lund (Sweden)

(Received May 30th, 1989)

Abstract

Aspects of the hydrozirconation-isomerization of nonfunctionalised olefins are discussed.

Cyclooctene and 1-methyl-1-cyclohexene were previously reported not to react with $\text{Cp}_2\text{Zr(H)Cl}$. In the present work after treatment of the former with $\text{Cp}_2\text{Zr(D)Cl}$, and subsequent hydrolysis, no cyclooctane could be detected. Although the olefin seemed not to have reacted, it was deduced that the corresponding cyclooctylzirconium was in fact formed, since the amount of deuterium incorporated in cyclooctene was roughly the same as the amount of zirconium deuteride used. Total scrambling of deuterium was observed. Cycloheptene and 2,2,11,11-tetramethyl-6-dodecene gave similar results. 1-Methyl-1-cyclohexene, on the other hand, was very unreactive. No evidence for deuterium incorporation in the recovered olefin (80–90%) was obtained.

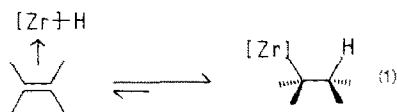
When *Z*-5-decene was used as substrate, zirconium migration towards the terminal carbon, and *cis*–*trans* isomerisation, were slower than expected. No internal alkylzirconium derivatives could be trapped. Competing hydrogenation of 1- and *Z*-5-decene is favoured when a deficiency of the zirconium hydride is used.

Introduction

At the beginning of the seventies, Schwartz and coworkers [2] discovered that $\text{Cp}_2\text{Zr(H)Cl}$ reacts with internal olefins to produce stable terminal σ -alkylzirconium complexes. The alkylzirconium compounds can be used in synthesis [2,3]. A mixture of positionally isomeric alkenes can thus be converted into a variety of terminally functionalised compounds. The migration is believed to proceed via initial π -complex formation and insertion of the olefin into the Zr–H bond, followed by rapid eliminations and readditions [2]. The metal in $\text{Cp}_2\text{Zr(H)Cl}$ formally has the d^0 -configuration, and thus the equilibrium (eq. 1) is shifted to the right by the energy

* Taken in part from the thesis by J. Alvhäll [1].

gained from formation of the new C–H bond [4]. The migration of zirconium from a secondary to a primary carbon is assumed to be caused by the steric requirements of the cyclopentadienyl ligands.



During the last ten years, we have been working on hydrozirconation [5]. After hydrozirconation of very long-chain internal *Z*-olefins a *cis*–*trans* isomerisation was often observed [5a,d,e]. The presence of positional isomers of the starting material, with the double bond only one or two carbons away from the original position, has been indicated by mass spectral analysis [5a], even after quite long reaction times. The zirconium migration is reported to be very fast [6], and the question arose of whether this is compatible with partial double bond isomerisation. We chose *Z*-5-decene as a model compound for a study of the process. ^{13}C NMR data of all internal decenes are available [7], and so the determination of the composition in the resulting isomer mixture presented no problem.

Results and discussion

1. Hydrozirconation of *Z*-5-decene

The results of the hydrozirconation of *Z*-5-decene (toluene, 40 °C, 4 h), with subsequent deuterolysis, are given in Table 1. As can be seen, a high proportion (60–85%) of isomeric olefins was observed [8*]. This is in contrast to what was previously reported by Hart and Schwartz [6], who observed only the starting olefin and the final 1-alkyl compound when the hydrozirconation of 4-octene was moni-

Table 1

Isomer distribution of decenes formed after hydrozirconation-deuterolysis of *Z*-5-decene ^a

Product	Composition (%) ^b	
	0.5 equiv. Cp ₂ Zr(H)Cl	1.5 equiv. Cp ₂ Zr(H)Cl
1- ² H-decane ^c	11	38
decane	4	2
1-decene	0	0
2-decene (<i>Z</i>)	4	4
2-decene (<i>E</i>)	5	4
3-decene (<i>Z</i>)	4	4
3-decene (<i>E</i>)	6	6
4-decene (<i>Z</i>)	13	8
4-decene (<i>E</i>)	18	15
5-decene (<i>Z</i>)	21	8
5-decene (<i>E</i>)	14	11

^a A solution of the olefin (1.0 g) and internal standard in 3 ml of toluene was added to a suspension of in situ generated Cp₂Zr(H)Cl in 20 ml of toluene. The mixture was stirred for 4 h at 40 °C and then quenched with deuterium oxide. The results are taken from reference [1]. ^b Determined by combinations of GLC, MS, ^2H and ^{13}C NMR [Cr(acac)₃] analyses. ^{13}C NMR data of all internal decenes are available in the literature [7]. ^c ^2H NMR: δ 0.91 (s, CH₂D).

Table 2

Hydrozirconation-deuterolysis of 1-decene ^a

Equiv. Cp ₂ Zr(H)Cl	Solvent	Reaction time (h)	Isotope composition (%) in decane ^b	
			d ₁	d ₀
0.5	dioxane	20	61	39
0.5	dioxane	40	42	58
0.5	toluene	20	0	100
1.5	dioxane	20	91	9
1.5	dioxane	40	84	16
1.5	toluene	20	92	8
1.5	toluene	60	73	27

^a Taken from reference [1]. The hydrozirconation was conducted at 40 °C. ^b Determined by mass spectrometry (15 eV). No significant amounts of by-products were detected.

tored by ¹H NMR spectroscopy. It was suggested that the rate of migration towards the terminal position is at least as fast as olefin insertion into the Zr–H bond [6]. In view of our results (Table 1), this idea must be questioned. The internal decenes are not formed from the 1-decylzirconium compound [9*]; the rearrangement to the terminal carbons seems to be quite slow, even at somewhat elevated temperature (40 °C).

The *Z/E* ratio of the 2-, 3- and 4-decenes was quite high (~ 3/4), especially when a deficiency (0.5 equiv.) of Cp₂Zr(H)Cl was used. The slow build-up of the *trans* isomers is a bit surprising. The *Z*-isomers must react faster [6,10*]. Deuterium was found only at the 1-position in decane, and no 1-decene could be detected. The most probable reason why deuterium was not found at internal carbons in decane is that only traces of secondary σ -alkylzirconiums are present in the reaction mixture when it is deuterolysed. At this stage, however, we could not exclude the possibility that the internal zirconium compounds were decomposed by deuterium oxide to give the isomeric decenes.

If this latter path is followed, it might be similar to a zirconium displacement, in which an alkene initially coordinates to the metal in a σ -alkylzirconium. The coordinated alkene would then be converted into a new σ -alkyl complex [11*,12*]. Such a process would account for the fact that more than 50% of *Z*-5-decene was consumed when only 0.5 equiv. of [Zr]–H was used. After treatment of preformed 1-decylchlorodi-(η^5 -cyclopentadienyl)zirconium with *Z*-5-decene (benzene, 40 °C, 4 h), the latter was recovered unchanged. If there is a displacement, the formation of isomeric decenes would be expected. Furthermore, attempts to generate an alkene from alkyl-ZrCp₂Cl by treatment with ethylene at high temperature and under high pressure, were unsuccessful [2]. Thus the displacement route can be ruled out. The reason why only 21% of *Z*-5-decene remains (0.5 equiv. of [Zr]–H) must be that the zirconium hydride leaves the hydrocarbon chain during rearrangement (cf. Section II), and attacks any alkene present in the mixture.

An excess olefin seems to promote competing hydrogenation, as deduced from the amount of unlabeled decane formed (Table 1). This was also observed when 1-decene was treated with 0.5 equiv. of [Zr]–H at 40 °C (Table 2). The hydrogenation

* Reference numbers with asterisks indicate notes in the list of references.

Table 3

Product composition: after hydrozirconation-deuterolysis of **1**^a

Entry	Equiv. Cp ₂ Zr(H)Cl	Solvent	Time (h)	Temp. (°C)	Composition (%) ^b		
					1	isomers of 1	2
1	0.5	dioxane	24	r.t.	16	82	2
2	1.5	dioxane	4	40	16	80	4
3	0.5	toluene	5	40	25 ^c	72 ^c	3
4	1.5	toluene	5	40	28 ^c	69 ^c	3
5	1.0–1.5 ^d	toluene	4–5	40	38	59	3

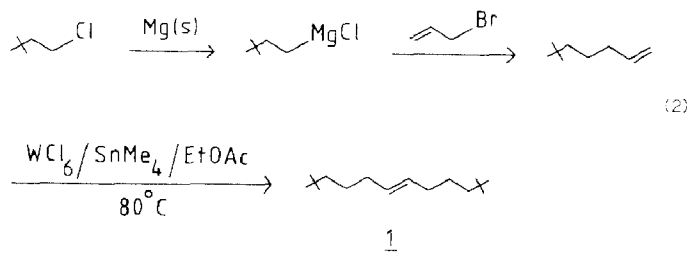
^a A solution of 0.3–0.4 g of olefin and internal standard in 2–3 ml of solvent was added to a suspension of the zirconium hydride in 7–9 ml of solvent. The mixture was stirred at the conditions indicated, before it was deuterolysed. ^b Determined by combinations of GLC, MS and ¹³C NMR [Cr(acac)₃] analyses. The presence of **2** was determined by GLC co-injection of authentic material (preparation described in the Experimental Section). ^c ¹³C NMR shifts in the vinylic region are: Entry 3: 132.71 (22%); 131.42 (6%); 131.04 (11%); 130.45 (26%, from **1**); 129.84 (10%); 127.19 (21%); 126.53 (4%). Entry 4: (21%); (6%); (11%); (27%); (11%); (19%); (5%). ^d Cp₂Zr(D)Cl was used. The reactions were quenched with water.

tion is more pronounced in toluene than in dioxane. The temperature and reaction time also influence this side reaction. We suspected that the remaining olefin acted as one hydrogen source, conceivably via coordination of excess alkene to the decylzirconium, followed by hydrogen transfer from the coordinated olefin to the decyl moiety to produce decane and an alkenylzirconium. Preliminary studies, however, indicated the absence of such alkenylzirconiums in the reaction mixture, and, so far, we have no evidence that the second hydrogen comes from the excess of olefin.

It seems unlikely that the solvent is the only hydrogen source (Table 2), and in a previous study in which hydrogenation was extensive, the solvent (dioxane) was found not to provide the extra hydrogen [5g]. This side reaction must be studied in more detail before definite conclusions can be drawn [13*].

II. Hydrozirconation of 2,2,11,11-tetramethyl-6-dodecene (**1**), cyclooctene (**3**), cycloheptene (**4**) and 1-methyl-1-cyclohexene (**5**)

In order to obtain information relevant to the failure to trap internal alkylzirconiums we decided to prepare and hydrozirconate compound **1**. Compound **1** was prepared by metathesis from 6,6-dimethyl-1-heptene (eq. 2). Of course, only secondary alkylmetals can be formed. The product compositions, after hydrozirconation-deuterolysis of **1**, are given in Table 3.



Not surprisingly, the formation of **2** is certainly not favoured, and does not depend on the conditions. The amount of **2** did not vary with the amount of olefin.

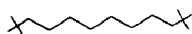
Table 4

Mass and ^2H NMR analyses of recovered olefins after deuteriozirconation-hydrolysis of compounds **1**, **3**, **4** and **5**^a

Entry	Compound	Amount recovered olefins (%) ^b	Isotope composition (%) ^c					^2H NMR (CHCl_3) ^d ppm (rel. integrals)
			d_0	d_1	d_2	d_3	d_4	
1	1	97	~ 80	~ 15	~ 5			δ 5.42 (2); 2.00 (4.3) 1.34 (3.9)
2	3	100	33	35	24	7	2	δ 5.70 (2); 2.16 (4); 1.53 (8)
3	4	> 90	34	36	21	8	2	δ 5.84 (2); 2.12 (4); 1.73 (2); 1.52 (4)
4	5	80–90	100					

^a The cycloolefins **3**, **4** and **5** (0.1–0.2 g) and internal standard were dissolved in 1–2 ml of dioxane. These solutions were added to a suspension of ~1 equiv. of $\text{Cp}_2\text{Zr(D)Cl}$ in 4–8 ml of dioxane. The mixtures were stirred for 22–23 h at 40 °C and then quenched with water. The experimental conditions for olefin **1** (entry 1) are given in Table 3. ^b According to GLC analysis. ^c Calculated from mass spectra. For the cycloolefins, the amount deuterium incorporated was roughly the same as the amount $\text{Cp}_2\text{Zr(D)Cl}$ used. ^d The ^2H NMR spectra were in accordance with ^1H NMR data of the starting materials, the only exception being the relative integrals in entry 1.

It is reasonable to assume that the formation of **2** would be favoured in hydrogenation when an excess of olefin **1** is used provided the concentration of internal σ -complexes is significant (cf. the competing hydrogenation of decenes in which terminal alkyls are formed; Section I). Neither the positions of the double bonds in the isomers of **1**, nor their configuration, could be determined. When **1** was treated with $\text{Cp}_2\text{Zr(D)Cl}$, deuterium was found at several carbons (^2H NMR) in the recovered olefins after hydrolysis (Table 4, entry 1).



2

The cycloolefins **3**, **4** and **5** were also deuteriozirconated. Cyclooctene **3** and 1-methyl-1-cyclohexene (**5**), in contrast to cyclopentene and cyclohexene, have been reported not to react with $\text{Cp}_2\text{Zr(H)Cl}$ [6]. For cyclooctene, the unreactivity towards the zirconium hydride was seemingly confirmed in another study [20]. After treatment of **3**, **4** and **5** with $\text{Cp}_2\text{Zr(D)Cl}$ and hydrolysis, no cyclooctane was observed and only small amounts of cycloheptane [21*] or methylcyclohexane were detected. However, mass spectrometry (Table 4, entries 2 and 3) showed that the recovered olefins **3** and **4** were deuterated. Total scrambling of the deuterium incorporated was observed (^2H NMR, Table 4), and the amount of deuterium was roughly the same as the amount of $\text{Cp}_2\text{Zr(D)Cl}$ used. 1-Methyl-1-cyclohexene (**5**), on the other hand, was very unreactive. No evidence for deuterium incorporation in the recovered olefin (80–90%) was obtained. The initial π -complex formation may be disfavoured with this substrate.



3



4



5

The isomerization of the double bond in **1** and the scrambling of deuterium in the recovered olefins (Table 4) show that $[\text{Zr}]-\text{D}$ ($[\text{Zr}]-\text{H}$) adds to the double bonds even if negligible or only very small amounts of the saturated analogues are found after hydrolysis (deuterolysis). The scrambling, together with the isotope composition of the cycloolefins **3** and **4** (mass spectrum, Table 4), indicates that $[\text{Zr}]-\text{H}$, which is eliminated (from the alkylzirconiums formed upon addition of $[\text{Zr}]-\text{D}$), dissociates from the olefins, and thus leaves them free to be attacked by another $\text{Cp}_2\text{Zr}(\text{D})\text{Cl}$ species. This is however contradicted by the isotope composition of **1** and its isomers (Table 4, entry 1), only a minor part of the deuterium from the reagent being found in the olefins. The conditions (40°C , toluene, 4–5 h) were the same as those used for the hydrozirconation of *Z*-5-decene.

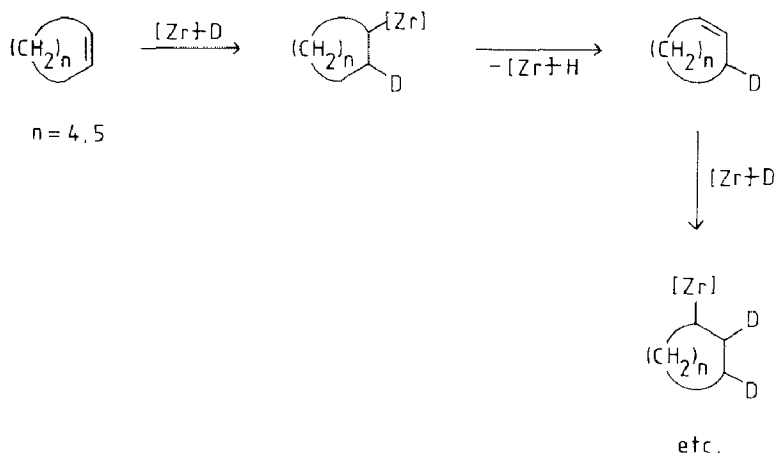
In cases where no positional isomers of the starting olefins can be formed, it is obvious that it cannot be unambiguously decided that they do not react with $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ merely because no σ -alkylzirconiums can be trapped. The cyclopentyl- and cyclohexyl-zirconiums [14,23], in contrast to the cyclooctyl and cycloheptyl analogues, are obviously thermodynamically stable.

We conclude that if secondary σ -alkylzirconiums, although formed, cannot be trapped, this is, as expected, due to the absence of observable amounts in the reaction mixtures [24*,25*].

Experimental

Analyses

^1H NMR spectra were recorded on a Varian T-60 NMR spectrometer, or a Varian XL-300 MHz instrument at 299.943 MHz. For ^2H (46.004 MHz) and ^{13}C NMR (75.429) spectra, the Varian XL-300 MHz spectrometer was again used. The ^1H and ^{13}C NMR shifts are given relative to TMS (CDCl_3). ^{13}C NMR spectra were recorded with chromium(III) acetylacetonate (0.04 *M*) present in the samples and this, with long pulse intervals (6–15 s), allowed quantitative analyses. The ^2H NMR (CHCl_3) shifts are given relative to TMS- d_{12} . Mass spectra were obtained using a Finnigan 4021 (Data System Incos 2100) spectrometer. The degree of deuteration



after hydrozirconation-deuterolysis (deuterozirconation-hydrolysis) was calculated from mass spectra (15–20 eV) by use of non-deuterated compounds as standards. Gas chromatographic analyses were performed on a Varian 3700 gas chromatograph equipped with a 30 m Supelcowax 10 capillary column; peak areas were determined with a Varian 4270 integrator. Elemental analyses were made at Dornis und Kolbe, Mikroanalytisches Laboratorium (Mühlheim a.d. Ruhr, West Germany) and at the Department of Analytical Chemistry, University of Lund (Sweden).

Materials

1,4-Dioxane and toluene were dried by refluxing over sodium wire, and were distilled under nitrogen prior to use. Benzene was dried by slow percolation under argon through a column containing activated molecular sieves.

Vitride [$\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$; Hexcel] was diluted with anhydrous toluene and stored under argon. *Z*-Cyclooctene (Aldrich) and 1-methyl-1-cyclohexene (Janssen Chimica) were distilled and stored over activated molecular sieves. Deuterium oxide (99.8% D; Norsk Hydro) was stored under argon. Cycloheptene (Janssen Chimica), WCl_6 (Ventron), SnMe_4 (Alfa Products), Cp_2ZrCl_2 (Aldrich), chromium(III) acetylacetonate (Merck), palladium on charcoal (10%; Kebo), 1-decene (Fluka), and other materials from commercial sources were used as received. 5-Decyne [26], *E*-5-decene [27], 6,6-dimethyl-1-heptene [28], $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ [29] and $\text{Cp}_2\text{Zr}(\text{D})\text{Cl}$ [30] were synthesised by published procedures.

Thoroughly dried glassware was used for the solvents, reagents, and olefins, which were stored under an inert atmosphere or over molecular sieves.

Z-5-Decene

This compound was prepared from 5-decyne by catalytic hydrogenation [27]. Lindlar catalyst and a small amount of quinoline were used. The reaction was carried out in hexane (degassed). After work-up [27], the colourless liquid was found to consist of only one component (GLC and ^{13}C NMR [7]).

2,2,11,11-Tetramethyl-6-dodecene (I)

This compound was made by the procedure for the metathesis of α -olefins described by Gibson and Tulich [31]. A dry, three-necked 250 ml flask, fitted with a reflux condenser (drying tube) and a septum, was flushed with argon. The flask was charged with 9.0 g (71 mmol) of 6,6-dimethyl-1-heptene, stoppered, and heated in an oil bath (80 °C). Then 2.8 g (7.1 mmol) WCl_6 , 1.9 ml (14.0 mmol) SnMe_4 and 2.8 ml (28.6 mmol) ethyl acetate were quickly added as a strong flow of argon was passed through the flask. The mixture was kept under argon and stirred for about 20 h at 80 °C. After cooling, the mixture was diluted with pentane, filtered (silica) and concentrated in vacuo. The residue was then distilled. The fractions boiling at 84–86 °C (0.65 mmHg) gave a 23% yield of the title compound, sufficiently pure to be used in the hydrozirconations.

^1H NMR: δ 5.40 (m, 2H, vinyl); 1.95 (b q, 4H, allyl); 1.38–1.13 (multiplets, 8H); 0.88 (s, 18H, ^tBu). ^{13}C NMR [32]: δ 130.47 (vinyl.); 43.81 (C H_2 - ^tBu); 33.49 (allyl.); 30.28 (^tBu , quarternary carbons); 29.48 (^tBu , methyl carbons); 24.69 (C H_2 - ^tBu). Mass (70 eV): m/e (rel. int.) 224 (0.031) M^+ ; 168 (0.026) M^+ – isobutylene; 57 (0.942) ^tBu . Anal. Found: C, 85.11; H, 14.72. $\text{C}_{16}\text{H}_{32}$ (224.42) calcd.: C, 85.63; H, 14.37%.

2,2,11,11-Tetramethyldodecane (2)

Palladium on charcoal (0.1 g) was added to a solution of 0.2 g of **1** in about 10 ml of ethanol. The mixture was hydrogenated (~ 50 psi) overnight at room temperature. The mixture was diluted with ether and the solution was filtered and concentrated under reduced pressure.

¹H NMR (60 MHz): δ 1.26 (b s, 16H); 0.89 (s, 18H). Anal. Found: C, 84.8; H, 15.1. C₁₆H₃₄ (226.44) calcd.: C, 84.86; H, 15.14%.

Hydro- and deuteriozirconations

All hydrozirconations were carried out under argon in dried glassware. Solid transfers were performed under nitrogen in a drybox. Liquid transfers were performed by a syringe or under argon pressure by the septum technique. For the hydrozirconations of 1-decene, *Z*- and *E*-5-decene, the reagent (Cp₂Zr(H)Cl) was generated in situ from Cp₂ZrCl₂ and Vitride® (1.5 M in toluene). In all other cases isolated Cp₂Zr(H)Cl or Cp₂Zr(D)Cl was used. For quantitative GLC analyses the following conditions and internal standards were used: *Z*-Cyclooctene, *Z*- and *E*-5-decene; 40°C isotherm, dodecane. Cycloheptene and 1-methyl-1-cyclohexene; 30°C isotherm., dodecane. Compound **1**; 50–200°C (5°C/min), octadecane.

The olefin and internal standard were dissolved in anhydrous solvent. The solution was added to a suspension of Cp₂Zr(H)Cl (Cp₂Zr(D)Cl). The suspension was then stirred under the conditions given in Tables 1–4. The mixtures were quenched with deuterium oxide (water) and small samples were analysed by GLC and MS. The mixtures were extracted with pentane and the extracts were filtered (alumina), dried (MgSO₄), concentrated, and, if necessary (*Z*- and *E*-5-decene) chromatographed on neutral alumina (ether/hexane). The products were then analysed by ²H and ¹³C NMR. For further experimental and analytical details, see Tables 1–4.

Treatment of 1-decylchloro-η⁵-cyclopentadienylzirconium with Z-5-decene

1-Decene was hydrozirconated to completion (as judged by GLC) in 25 ml of anhydrous benzene with isolated Cp₂Zr(H)Cl. The mixture was filtered by the Schlenk technique under argon. To the clear yellow filtrate was added ~ 1 equivalent of *Z*-5-decene. After 4 h at 40°C the mixture was quenched (D₂O). According to GLC (30°C; isotherm.) analysis and ¹³C NMR spectroscopy the recovered material consisted only of *Z*-5-decene (>97% unchanged) and decane (terminally deuterated).

Acknowledgement

Grants from the Board of Technical Development and from the Swedish Natural Research Council to S.G. and A.H. are gratefully acknowledged. We also thank Karlshamns AB for financial support.

References and Notes

- 1 Taken in part from: J. Alvhäll, Hydrozirconation of Some Unsaturated Fatty Acid Derivatives, Thesis, 1988, University of Lund, Sweden.
- 2 J. Schwartz and J.A. Labinger, *Angew. Chem.* 88 (1976) 402 and ref. cited therein.

- 3 (a) References cited in D.J. Cardin, M.F. Lappert and C.L. Raston, *Chemistry of Organo-Zirconium and -Hafnium Compounds*, Ch. 20, Ellis Horwood Limited, Chichester (1986); (b) S.L. Buchwald and S.J. La Maire, *Tetrahedron Lett.*, 28 (1987) 295; (c) E. Negishi, D.R. Swanson and S.R. Miller, *ibid.*, 29 (1988) 1631. (d) M.D. Fryzuk, G.S. Bates and C. Stone, *ibid.*, 27 (1986) 1537; (e) V.G. Kumar Das and O. Ghee Chee, *J. Organomet. Chem.*, 321 (1987) 335; (f) B. Gautheron, G. Tainturier and Ph. Meunier, *ibid.*, 209 (1981) C49; (g) Ph. Meunier, B. Gautheron and A. Mazouz, *J. Chem. Soc., Chem. Commun.*, (1986) 424; (h) S. Pouly, G. Tainturier and B. Gautheron, *J. Organomet. Chem.*, 232 (1982) C65; (i) M.D. Fryzuk, G.S. Bates and C. Stone, *J. Org. Chem.* 52 (1987) 2334; (j) P.J. Fagan and W.A. Nugent, *J. Am. Chem. Soc.*, 110 (1988) 2310; (k) M.D. Fryzuk, C. Stone and R.F. Alex, *Tetrahedron Lett.*, 29 (1988) 3915; (l) M.D. Fryzuk, G.S. Bates and C. Stone, *J. Org. Chem.*, 53 (1988) 4425.
- 4 J.W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 98 (1976) 1729.
- 5 (a) R. Svenson and S. Gronowitz, *Chemica Scripta*, 19 (1982) 149; (b) J. Alvhäll, S. Gronowitz, A. Hallberg and R. Svenson, *ibid.*, 24 (1984) 170; (c) J. Alvhäll, S. Gronowitz and A. Hallberg, *ibid.*, 25 (1985) 393; (d) U. Annby, S. Gronowitz and A. Hallberg, *ibid.*, 27 (1987) 445; (e) S. Karlsson, A. Hallberg and S. Gronowitz, *ibid.*, 28 (1988) 185; (f) J. Alvhäll, S. Gronowitz and A. Hallberg, *ibid.*, 28 (1988) 285; (g) U. Annby, S. Gronowitz and A. Hallberg, *J. Organomet. Chem.*, 365 (1989) 233; (h) U. Annby, S. Gronowitz and A. Hallberg *ibid.*, 368 (1989) 295; (i) S. Karlsson, A. Hallberg and S. Gronowitz, *J. Am. Oil Chem. Soc.*, accepted for publication.
- 6 D.W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, 96 (1974) 8115.
- 7 J.W. de Haan and L.J.M. van de Ven, *Org. Magn. Reson.*, 5 (1973) 147.
- 8 Shortly after these results were obtained, a paper by Gibson appeared in which it was stated (in a note) that hydrozirconation of long-chain internal olefins gave variable amounts of positional isomers, with the double bonds completely randomised along the hydrocarbon chain (T. Gibson *Organometallics*, 6 (1987) 918).
- 9 If this were the case, the terminal zirconium alkyl, formed from 10-hendecenoic acid oxazoline and $\text{Cp}_2\text{Zr(H)Cl}$, would rearrange to the 2- and 3-zirconium analogues [5a,b,c]. This does not occur [1].
- 10 After hydrozirconation-deuterolysis it was found from the rate of decane formation (GLC) that Z-5-decene reacted about twice as fast as the *E*-isomer.
- 11 It has been proposed that 1-octylchlorodi- η^5 -cyclopentadienylzirconium may be formed from $^t\text{BuZrCp}_2\text{Cl}$ and 1-octene in such a displacement, with concomitant liberation of isobutene: E. Negishi, J.A. Miller and T. Yoshida, *Tetrahedron Lett.*, 25 (1984) 3407.
- 12 A similar reaction in related titanium systems has been suggested. (a) G. Henrici-Olivé and S. Olivé, *J. Polym. Sci., Polym. Lett. Ed.*, 12 (1974) 39; (b) O. Novaro, S. Chow and P. Magnouat, *ibid.*, 13 (1975) 761.
- 13 With some substrates the hydrogenation becomes the main reaction [5b,g], and in certain cases the hydrogen source is $\text{Cp}_2\text{Zr(H)Cl}$ [5g]. In most of our studies, however, the hydrogen source and the reduction mechanism(s) are not known. Several possibilities exist: Small amounts of Cp_2ZrH_2 (A) are usually present in the reagent. A may form $\text{Cp}_2\text{Zr(H)R}$ (B) or Cp_2ZrR_2 (C) with an olefin. B may then decompose to "zirconocene" and R-H [14]. It should be mentioned that alkynes and ethylene induce R-H elimination from B [15]. Compound B can probably also be formed from $\text{Cp}_2\text{Zr(Cl)R}$ [14,16]. There is evidence for the formation of R-H and $\text{Cp}_2\text{ZrR}_{-1\text{H}}$ from C [17,18], but this process usually requires fairly vigorous conditions, except in the case of $\text{Cp}_2\text{Zr}(n\text{-Bu})_2$ [19]. There is also proof for the participation of cyclopentadienyl hydrogens in the elimination of R-H during thermolysis of C [18], and $\text{Cp}_2\text{Zr(Cl)R}$ might undergo a similar process. In all our cases, where the hydrogenation is the main reaction, temperatures were below 50 °C.
- 14 K.I. Gell, B. Posin, J. Schwartz and G.M. Williams, *J. Am. Chem. Soc.*, 104 (1982) 1846.
- 15 (a) M. Yoshifuji, K.I. Gell and J. Schwartz, *J. Organomet. Chem.*, 153 (1978) C15; (b) D.R. McAlister, D.K. Erwin and J.E. Bercaw, *J. Am. Chem. Soc.*, 100 (1978) 5966.
- 16 G. Erker, K. Kropp, J.L. Atwood and W.E. Hunter, *Organometallics*, 2 (1983) 1555.
- 17 S.L. Buchwald and R.B. Nielsen, *Chem. Rev.*, 88 (1988) 1047 and ref. cited therein.
- 18 G.A. Razuave, V.P. Mar'in and Yu.A. Andrionov, *J. Organomet. Chem.*, 174 (1979) 67.
- 19 (a) S.L. Buchwald, B.T. Watson and J.C. Huffman, *J. Am. Chem. Soc.*, 109 (1987) 2544; (b) E. Negishi, F.E. Cederbaum and T. Takahashi, *Tetrahedron Lett.*, 27 (1986) 2829.
- 20 T. Gibson, *Tetrahedron Lett.*, 23 (1982) 157.
- 21 According to ref. [22], cycloheptene is converted into cycloheptane via hydrozirconation in benzene at room temperature, with subsequent hydrolysis. In dioxane, at 40 °C (Table 4), the conversion was < 10%. We were unable to obtain more than ~ 30% (GLC) cycloheptane (toluene, 25 °C, 20.5 h).

- 22 D.W. Hart, *Transition Metal Hydrides in Organic Synthesis*, Thesis, 1975., Princeton University, Xerox University Microfilms, Ann Arbor, Michigan 48106.
- 23 P.C. Wailes, H. Weigold and A.P. Bell, *J. Organomet. Chem.*, 43 (1972) C32.
- 24 Gibson [20] did not observe any cyclooctyl alcohol after hydrozirconation of cyclooctene, followed by treatment with ¹BuOOH. Attempted CO insertion, after hydrozirconation of **1**, failed.
- 25 Secondary alkylchlorodi- η^5 -cyclopentadienylzirconium compounds are apparently stabilised when Zr is situated at either (a) the 1 position in ethers: S.L. Buchwald, R.B. Nielsen and J.C. Dewan, *Organometallics*, 7 (1988) 2324; (b) the 3 position in zirconium alcoholates [5i]; (c) benzylic positions (see for example [5g] and [8*]). (After hydrozirconation-deuterolysis of 1-arylhexenes [5g], $\leq 5\%$ of the incorporated deuterium was found at positions other than the benzylic or terminal ones); (d) the 1 and 2 positions in tertiary amines: ref. [5d]. (In some cases deuterium was indicated at other secondary positions (always $< 10\%$ of the total amount of incorporated deuterium)); (e) the 2 and 3 positions in oxazolines [5c]. After a very short reaction time (30 min), 40% of the incorporated deuterium was present at other secondary carbons upon hydrozirconation-deuterolysis of a long-chain oxazoline. The degree of deuteration was very low in this case. After 5 h, only the 2-, 3- and ω -carbons were deuterated.
- 26 E.A. Bried and G.F. Hennion, *J. Am. Chem. Soc.*, 59 (1937) 1310.
- 27 K.N. Campbell and L.T. Eby, *J. Am. Chem. Soc.*, 63 (1941) 216.
- 28 J.W.H. Faber, J. van den Berghe and K.R. Dunham, Patent, Fr. 1,423,429, 1966; *Chem. Abstr.*, 66 (1967) 29360r.
- 29 D.B. Carr and J. Schwartz, *J. Am. Chem. Soc.*, 101 (1979) 3521.
- 30 S.L. Buchwald, S.J. La Maire, R.B. Nielsen, B.T. Watson and S.M. King, *Tetrahedron Lett.*, 28 (1987) 3895.
- 31 T. Gibson and L. Tulich, *J. Org. Chem.* 46 (1981) 1821.
- 32 A 2-D HETCOR NMR (¹H-¹³C) spectrum was in accordance with the assignments.