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ansa-METALLOCENE DERIVATIVES

X *. HYDROGENOLYSIS OF THE ZIRCONIUM–ALKYL BOND IN BRIDGED AND UNBRIDGED ALKYL ZIRCONOCENE DERIVATIVES. EVIDENCE FOR DIRECT AND RING-MEDIATED HYDROGEN TRANSFER REACTIONS

FRANZ WOCHNER and HANS H. BRINTZINGER **

Fakultät für Chemie, Universität Konstanz, D-7750 Konstanz (Federal Republic of Germany)

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Summary

The rate of hydrogenolytic alkane liberation from permethylzirconocene neopentyl halide compounds, $(C_5(CH_3)_5)_2Zr(X)CH_2C(CH_3)_3$, X = F, Cl, Br), is greatly reduced if the ring ligands are interconnected by an ethylene bridge, as in $C_2H_4(C_5(CH_3)_4)_2Zr(X)CH_2C(CH_3)_3$. Hydrogenolysis of the corresponding permethylzirconocene neopentyl hydride compounds (X = H), on the other hand, is too fast for kinetic measurements at room temperature, even with the ethylene-bridged derivative. These observations, and the inverse kinetic isotope effect observed for reaction with D_2, are interpreted with the assumption that H_2-induced alkane liberation from permethylzirconocene alkyl halides proceeds via an indirect ring-mediated hydrogen transfer reaction which is feasible only with freely rotating ring ligands; hydrogenolysis of permethylzirconocene alkyl hydrides, on the other hand, apparently occurs without such limitation, by direct H_2-to-alkyl hydrogen transfer.

Introduction

Release of alkanes from alkylmetal compounds upon treatment with molecular hydrogen is of considerable practical interest. The hydrogenolysis of alkylzirconium(IV) derivatives, derived e.g. from olefins by hydrozirconation with $[(C_5H_5)_2Zr(H)Cl]_n$ or $[(C_5H_5)_2ZrH_2]_n$ [2,3] is an especially intriguing case, since the zirconium(IV) centre does not permit an oxidative addition of H_2. Several reaction mechanisms have been proposed for hydrogenolysis reactions of this type:

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* For Part IX see ref. 1.

** To whom correspondence should be addressed.

(i) A heterolytic cleavage of the H_2 molecule, with the Lewis-acidic zirconium(IV) centre extracting a hydride ion, while the H^+ moiety is taken up by the carbanionic alkyl ligand [4,5].

(ii) A "direct" conversion of H_2 into a Zr^{IV}–H and an alkyl–H moiety, induced by the back-donating properties of high-lying, occupied MOs of the $(C_5R_5)_2Zr^{IV}$-alkyl fragment [6].

(iii) Transfer of a hydride ligand from the Zr^{IV} centre to one of the ring ligands to generate an intermediate $(C_5R_5)(C_5R_5H)Zr^{II}$-alkyl, which would allow formation of the reaction products via oxidative addition of H_2 and subsequent reductive elimination of alkane [7].

In order to substantiate these mechanistic proposals we have tried to determine how the hydrogenolysis of alkyl zirconocene compounds responds (i) to changes of Lewis acidity and HOMO energies at the metal centre caused by the presence of different co-ligands, and (ii) to elimination of some of the otherwise possible transformations of the zirconocene framework by introduction of an interannular ethylene bridge. To avoid complications arising from the presence of dimeric and polymeric species in equilibrium with monomeric zirconocene hydride compounds [8,9], our present study utilizes mainly decamethylzirconocene derivatives, for which Bercaw and coworkers [7] have reported substantial reactivity data, and their ethylene-bridged counterparts recently prepared in our laboratory [10].

Experimental

The zirconocene derivatives $(C_5H_5)_2ZrCl_2$ [11], $(C_5(CH_3)_5)_2ZrCl_2$ [12] and $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$ [10] were prepared by published methods. $(C_5(CH_3)_5)_2ZrCl_2$ and $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$ were converted into their difluoride and dibromide analogues by methods reported for the corresponding permethyltitanocene dihalides [13]. The dihalide compounds were characterized by their mass spectra (parent ions with appropriate isotope distribution), by their ^1H NMR spectra (Table 1), and by elemental analysis: Found: C, 60.12; H, 7.69. $C_{20}H_{30}ZrF_2$ calcd.: C, 60.12; H, 7.52%. Found: C, 45.90; H, 5.85. $C_{20}H_{30}ZrBr_2$ calcd.: C, 46.07; H, 5.76%. Found: C, 59.70; H, 7.94. $C_{20}H_{28}ZrF_2$ calcd.: C, 60.41; H, 7.09%. Found: C, 46.08; H, 5.90. $C_{20}H_{28}ZrBr_2$ calcd.: C, 46.25; H, 5.43%.

In the ^1H NMR spectra of the permethylzirconocene dihalides (Tab. 1) the methyl signals shift to lower fields on going from the difluoride to the dibromide, contrary to expectation based on electronegativity considerations *. The dihydride $(C_5(CH_3)_5)_2ZrH_2$ follows the same trend, its methyl signals appearing at even lower field. The mixed hydride halide compounds (cf. ref. 16), obtained in C_6D_6 solution by the hydrogenolysis reactions described below, have their CH_3 resonances about half-way between those of the dihydride and the corresponding dihalide compounds. The signal of the Zr-bound hydride could not be identified with certainty in the NMR spectra of these compounds.

In the case of the ethylene-bridged permethylzirconocene dihalides, the centre of both CH_3 signals again shifts downfield on going from the difluoride to the dibromide. In addition, the two CH_3 signals become increasingly separated in this series, the difference in chemical shift between the two resonance amounting to 0.04

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* For similar observations with $(C_5H_5)_2Ti$ dihalides see ref. 17, 18.

TABLE 1

^{1}H NMR SPECTRA OF $(C_5(CH_3)_5)_2Zr$ AND $C_2H_4(C_5(CH_3)_4)_2Zr$ COMPOUNDS (recorded at 250 MHz in C_6D_6 solution at room temperature; ^{1}H NMR shifts in ppm relative to δ 7.15 ppm for C_6D_5H.)

Compound	Assignment	Reference
$(C_5(CH_3)_5)_2ZrF_2$	$C_5(C\mathit{H}_3)_5$: 1.83(t) [a]	
$(C_5(CH_3)_5)_2ZrCl_2$	$C_5(C\mathit{H}_3)_5$: 1.84(s)	[12]
$(C_5(CH_3)_5)_2ZrBr_2$	$C_5(C\mathit{H}_3)_5$: 1.88(s)	
$(C_5(CH_3)_5)_2Zr(H)F$	$C_5(C\mathit{H}_3)_5$: 1.91(s)	
$(C_5(CH_3)_5)_2Zr(H)Cl$	$C_5(C\mathit{H}_3)_5$: 1.91(s)	
$(C_5(CH_3)_5)_2Zr(H)Br$	$C_5(C\mathit{H}_3)_5$: 1.93(s)	
$(C_5(CH_3)_5)_2ZrH_2$	$C_5(C\mathit{H}_3)_5$: 2.02(s, 30)	[14]
	$Zr\mathit{H}_2$: 7.46(s, 2)	[14]
$(C_5(CH_3)_5)_2Zr(F)CH_2C(CH_3)_3$	$Zr{-}C\mathit{H}_2$: 0.67(s, 2)	
	$C(C\mathit{H}_3)_3$: 1.29(s, 9)	
	$C_5(C\mathit{H}_3)_5$: 1.80(s, 30)	
$(C_5(CH_3)_5)_2Zr(Cl)CH_2C(CH_3)_3$	$Zr{-}C\mathit{H}_2$: 0.53(s, 2)	[15]
	$C(C\mathit{H}_3)_3$: 1.26(s, 9)	[15]
	$C_5(C\mathit{H}_3)_5$: 1.81(s, 30)	[15]
$(C_5(CH_3)_5)_2Zr(Br)CH_2C(CH_3)_3$	$Zr{-}C\mathit{H}_2$: 0.41(s, 2)	
	$C(C\mathit{H}_3)_3$: 1.26(s 9)	
	$C_5(C\mathit{H}_3)_5$: 1.83(s, 30)	
$(C_5(CH_3)_5)_2Zr(H)CH_2C(CH_3)_3$	$Zr{-}C\mathit{H}_2$: 0.04(s, 2)	
	$C(C\mathit{H}_3)_3$: 1.21(s, 9)	
	$C_5(C\mathit{H}_3)_5$: 1.93(s, 30)	
$C_2H_4(C_5(CH_3)_4)_2ZrF_2$	$C_5(C\mathit{H}_3)_4$: 1.84(s, 12)	
	1.88(s, 12) [b]	
	$C_2\mathit{H}_4$: 2.74(s, 4)	
$C_2H_4(C_5(CH_3)_4)_2ZrCl_2$	$C_5(C\mathit{H}_3)_4$: 1.73(s, 12)	[10]
	2.02(s, 12)	[10]
	$C_2\mathit{H}_4$: 2.64(s, 4)	[10]
$C_2H_4(C_5(CH_3)_4)_2ZrBr_2$	$C_5(C\mathit{H}_3)_4$: 1.70(s, 12)	
	2.15(s, 12)	
	$C_2\mathit{H}_4$: 2.61(s, 4)	
$C_2H_4(C_5(CH_3)_4)_2Zr(H)Cl$	$C_5(C\mathit{H}_3)_4$: 1.84(s, 6)	
	1.97(s, 6)	
	2.06(s, 6)	
	2.19(s, 6)	
	$C_2\mathit{H}_4$: 2.50(s, 4)	
$C_2H_4(C_5(CH_3)_4)_2Zr(F)CH_2C(CH_3)_3$	$Zr{-}C\mathit{H}_2$: 0.62(s, 2)	
	$C(C\mathit{H}_3)_3$: 1.21(s, 9)	
	$C_5(C\mathit{H}_3)_4$: 1.50(s, 6)	
	1.83(s, 6)	
	1.92(s, 6)	
	2.05(s, 6)	
	$C_2\mathit{H}_4$: 2.5–2.9(m, 4)	
$C_2H_4(C_5(CH_3)_4)_2Zr(Cl)CH_2C(CH_3)_3$	$Zr{-}C\mathit{H}_2$: 0.57(s, 2)	
	$C(C\mathit{H}_3)_3$: 1.20(s, 9)	
	$C_5(C\mathit{H}_3)_4$: 1.48(s, 6)	
	1.86(s, 6)	
	2.04(s, 6)	
	2.09(s, 6)	
	$C_2\mathit{H}_4$: 2.4–2.7(m, 4)	

continued

TABLE 1 (continued)

Compound	Assignment	Reference
$C_2H_4(C_5(CH_3)_4)_2Zr(Br)CH_2C(CH_3)_3$	Zr-CH_2: 0.51(s, 2)	
	$C(CH_3)_3$: 1.21(s, 9)	
	$C_5(CH_3)_4$: 1.46(s, 6)	
	1.85(s, 6)	
	2.04(s, 6)	
	2.23(s, 6)	
	C_2H_4: 2.4–2.7(m, 4)	
$C_2H_4(C_5(CH_3)_4)_2Zr(H)CH_2C(CH_3)_3$	Zr-CH_2: 0.19(s, 2)	
	$C(CH_3)_3$: 1.13(s, 9)	
	$C_5(CH_3)_4$: 1.61(s, 6)	
	1.93(s, 6)	
	2.18(s, 6)	
	2.36(s, 6)	
	C_2H_4: 2.3–2.5(m, 4)	

[a] Partially resolved triplet with $^3J(^1H-^{19}F)$ 0.8 Hz; for a similar $^1H-^{19}F$ coupling of $^3J(^1H-^{19}F)$ 1.7 Hz in $(C_5H_5)_2TiF_2$, cf. ref. 18. [b] Broadened relative to signal at 1.836 ppm, probably due to unresolved $^1H-^{19}F$ coupling.

ppm for the difluoride, to 0.29 ppm for the dichloride, and 0.45 ppm for the dibromide derivative.

Mono-neopentyl mono-halide derivatives were prepared in situ from neopentyllithium [15]: A 10 mm O.D. NMR tube containing 0.05 mmol of the respective dihalide was attached to a vacuum manifold by means of an O-ring connection, filled with Ar, and cooled to 0°C in an ice–water bath. A syringe was used to introduce 2.5 ml of a freshly prepared 0.02 M solution of neopentyllithium in dry deaerated C_6D_6, and this was followed by 0.05 ml of cyclohexane as an internal integration standard. The NMR tube was then closed with a ground stopper, detached from the vacuum line, and shaken overnight. The bright yellow solutions thus obtained, from which LiCl later separated as a solid, gave ^1H NMR spectra in which the mononeopentyl monohalide derivatives were the predominant species; residual dihalide signals as well as signals assignable to the respective dineopentyl derivatives accounted for less than 5% of the total signal intensity *.

In the ^1H NMR spectra of the unbridged $(C_5(CH_3)_5)_2Zr$ neopentyl halides (Table 1), the ring-substituent and the neopentyl CH_3 signals appear within the rather narrow ranges of 1.80–1.83 and 1.26–1.29 ppm, respectively. The Zr-bound neopentyl CH_2 group is shifted to somewhat higher field on going from the fluoride (0.66 ppm) to the bromide (0.41 ppm), in accord with expectation based on electronegativity considerations. Because of their unsymmetric ligand environments the ethylene-bridged $C_2H_4(C_5(CH_3)_4)_2Zr$ neopentyl halides give rise, to four ring-CH_3 signals; the difference between the highest and the lowest resonance increases from 0.55 ppm for the fluoride to 0.61 ppm for the chloride and to 0.77 ppm for the bromide. This four-line pattern makes these mixed alkyl halide derivatives clearly distinguishable from their symmetric dihalide precursors. The

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* Other, sterically less demanding alkyllithium reagents yield higher proportions of the respective dialkylzirconocene compounds.

chemical shifts of the Zr-bound neopentyl CH_2 group in the three neopentyl halide derivatives follow closely the pattern observed for their unbridged counterparts.

In order to initiate the reactions of these compounds with H_2, the Ar atmosphere was replaced by H_2 by cooling the NMR tube, attached to a vacuum line, to $-5°C$, pumping to 0.01 mbar, and warming to 25°C in a water bath under H_2 at 1 atm. At 25°C the vapour pressure of benzene is 128 mbar; the partial pressure of H_2 thus amounts to 885 mbar. The gas volume of about 10 ml, containing ca. 0.4 mmol H_2, represents a ca. 8-fold excess of H_2 over the zirconocene alkyl halide *.

The tightly stoppered NMR tubes were then shaken at a controlled ambient temperature of 23°C in a near-horizontal fashion to allow for optimal H_2 exchange between gas and solution phases, while decay of the neopentyl halide and growth of the corresponding halide hydride ^1H NMR signals were periodically monitored on a 250 MHz spectrometer.

The ethylene-bridged zirconocene chloro hydride compound, which could not be efficiently obtained in this manner, was prepared in C_6D_6 solution by reduction of the dichloride derivative with excess sodium amalgam under 1 atm of H_2 at room temperature for 36 h. The ^1H NMR spectrum of this unsymmetric complex (Table 1) shows the expected four-line pattern for its ring CH_3 substituents.

The hydrido alkyl derivatives were obtained, again in C_6D_6 solution, by addition under Ar of one equivalent * of neopentyllithium solution to a solution of the corresponding zirconocene chloro hydride followed by shaking at room temperature overnight. In the ^1H NMR spectra of these compounds, the ring-substituent and neopentyl CH_3 signals follow the pattern observed for their halide analogues; the signals of their neopentyl CH_2 groups lie significantly above those of their neopentyl halide analogues, in accord with electronegativity considerations. Reactions of these compounds with H_2 were monitored the way described for the alkyl halide compounds.

The kinetics of these and analogous reactions under D_2 were analyzed by a least-squares fitting programme. In all cases a pseudo-first order rate law was obeyed with reasonable precision up to 90% conversion. The pseudo-first order rate constants k_{obs}, derived from the increase in the signals from the halo hydride species and from the decrease in those from the neopentyl halide compound were generally reproducible within ca. 5%. Second order rate constants can be derived by dividing these values by the concentration of H_2 in the solutions ($2.48*10^{-3}$ M in benzene at 885 mbar H_2 and 23°C [19]); the mean values from several runs are listed in Table 3.

In some cases, hydrogenolysis rates were determined in the presence of an H_2/Ar mixture containing 12.5 vol − % H_2. These runs, which involved hydrogen and zirconocene derivative in approximately equivalent concentrations, followed a second-order rate law and, when H_2 solubility data from ref. 19 were used, yielded second order rate constants in acceptable agreement with those obtained from runs under 1 atm of H_2.

The relative abundance of neopentane-d_1 in the hydrogenolysis products obtained with D_2 or H_2/D_2 mixtures was determined by mass spectroscopy. The mass

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* In these kinetic experiments care was taken to avoid any excess of neopentyllithium; the presence of some residual fraction of dihalide signals in the NMR spectrum was used to ensure this.

TABLE 2

RELATIVE INTENSITIES OF MASS PEAKS FOR C_4H_{7-9} FRAGMENT IONS IN THE MASS SPECTRA OF UNDEUTERATED, MONODEUTERATED AND PARTIALLY MONODEUTERATED NEOPENTANE

	m/e				
	55	56	57	58	59
$C(CH_3)_4$ (obsvd. [a])	11.8	8.7	72.9	5.6	0.2
$C(CH_3)_3CH_2D$ (calcd. [b])	4.5	11.0	24.0	56.1	4.2
$C(CH_3)_3CH_2D$ (calcd. [c])	7.4	19.6	42.8	100.0	7.5
$C(CH_3)_3CH_2D$ (obsvd. [d])		10.4	42.3	100.0	4.5
$C(CH_3)_4+C(CH_3)_3CH_2D$ [e]	2.4	5.8	100.0	73.4	1.3

[a] From hydrolysis of $C(CH_3)_3CH_2Li$ with H_2O, normalised to $\Sigma I=100$. [b] Normalised to $\Sigma I=100$. [c] Relative to $I(58)=100$. [d] From reaction of $(C_5(CH_3)_5)_2Zr(Cl)CH_2C(CH_3)_3$ with D_2. [e] From reaction of $(C_5(CH_3)_5)_2Zr(Cl)CH_2C(CH_3)_3$ with H_2/D_2 mixture.

spectrum of neopentane is dominated by the fragment ions $C_4H_{7-9}^+$; their peaks at $m/e=55$ to 59 yield, at IE 70 eV, the normalised intensities shown in Table 2. From these values, one can calculate normalised intensities for the corresponding peaks arising from pure neopentane-d_1 (cf. ref. 20). Experimentally obtained relative intensities for the mass peaks at *m/e* 57 and 58 were used to determine relative abundancies of undeuterated and monodeuterated neopentane in the hydrogenolysis products, following essentially the procedure outlined in ref. 20.

Results and discussion

Under the experimental conditions specified above (C_6D_6 solution at 23°C, 885 mbar H_2), the unbridged $(C_5(CH_3)_5)_2Zr$ neopentyl fluoride, chloride and bromide derivatives react with H_2 with half-lives of about 1/2 to 2 hours. The chloride and bromide derivatives give rather similar rate constants of 3.2 and 2.9 $l\ mol^{-1}\ min^{-1}$) while the fluoro derivative reacts about 2–3 times as rapidly (Table 3).

TABLE 3

KINETIC DATA FOR THE HYDROGENOLYSIS OF $(C_5(CH_3)_5)_2Zr$ AND $C_2H_4(C_5(CH_3)_4)_2Zr$ NEOPENTYL DERIVATIVES IN 0.02 *M* BENZENE-d_6 SOLUTION AT 23°C AND 1 atm GAS PRESSURE (Second-order rate constants k in $l\ mol^{-1}\ min^{-1}$, based on $c(H_2)$ 2.48×10^{-3} *M* in C_6H_6 at $P(H_2)$ 885 mbar and 23°C [19].)

Reaction	$t_{1/2}$	k
$(C_5(CH_3)_5)_2Zr(F)CH_2C(CH_3)_3+H_2$	36 min	8.3
$(C_5(CH_3)_5)_2Zr(Cl)CH_2C(CH_3)_3+H_2$	87 min	3.2
$(C_5(CH_3)_5)_2Zr(Cl)CH_2C(CH_3)_3+D_2$	68 min	4.1
$(C_5(CH_3)_5)_2Zr(Br)CH_2C(CH_3)_3+H_2$	95 min	2.9
$(C_5(CH_3)_5)_2Zr(Cl)CH_2C(CH_3)_3+H_2/Ar$ (1/7)	820 min	3.9
$(C_5(CH_3)_5)_2Zr(H)CH_2C(CH_3)_3+H_2/Ar$ (1/7)	< 5 min	> 300
$C_2H_4(C_5(CH_3)_4)_2Zr(F)CH_2C(CH_3)_3+H_2$	> 6000 min	< 0.05
$C_2H_4(C_5(CH_3)_4)_2Zr(Cl)CH_2C(CH_3)_3+H_2$	> 6000 min	< 0.05
$C_2H_4(C_5(CH_3)_4)_2Zr(Br)CH_2C(CH_3)_3+H_2$	> 6000 min	< 0.05
$C_2H_4(C_5(CH_3)_4)_2Zr(H)CH_2C(CH_3)_3+H_2/Ar$ (1/7)	< 5 min	> 300

Reaction of the chloro derivative with D_2 instead of H_2 leads to an increase in rate by a factor of ca. 1.3. This inverse kinetic isotope effect, $k_H/k_D = 0.78$, was confirmed by competition experiments. We observed that whereas hydrogenolysis with pure D_2 yielded exclusively monodeutero-neopentane *, reaction with a large excess of a gas mixture containing H_2 and D_2 in a mol ratio of 1/1.07 gave a mixture of neopentane-d_0 and -d_1 in a mol ratio of 1/1.25 ± 0.05, corresponding to a value of $k_H/k_D = 0.85 \pm 0.05$, in reasonable agreement with the rate data in Table 3.

Reaction of the $(C_5(CH_3)_5)_2Zr$ neopentyl hydride with H_2 was faster by at least two orders of ten than that of its halide analogues. In this case, only a lower limit could be determined for the rate of conversion of the neopentyl hydride to the dihydride compound. The reaction is so fast, even with a 1/7 H_2/Ar gas mixture, that it is probably limited by the rate of H_2 dissolution in the benzene phase.

In examining the hydrogenolysis of ethylene-bridged permethylzirconocene neopentyl halides we observed an unexpected absence of reactivity. In the presence of H_2 the breakdown of these compounds requires several days; first-order kinetics are observed, with half-lives of > 100 hours. The ethylene-bridged permethylzirconocene alkyl halides thus react with H_2 at least 100 times as slowly as their unbridged analogues **.

With the ethylene-bridged zirconocene neopentyl hydride derivative $C_2H_4(C_5(CH_3)_4)_2Zr(H)CH_2C(CH_3)_3$, on the other hand, we observe the same very fast reaction with H_2 as with its unbridged analogue, the hydrogenolysis products being formed at a rate comparable to that of gas exchange.

The reaction of H_2 with unmethylated $(C_5H_5)_2Zr(Cl)CH_2C(CH_3)_3$ proceeds quite slowly, with a half-life of more than 24 h. Similarly lower hydrogenolysis rates for unmethylated zirconocene alkyl halide derivatives have been noted previously by Schwartz and coworkers [5].

The much lower rates of hydrogenolysis of ethylene-bridged compared with those for unbridged permethylzirconocene neopentyl halides indicate that an essential step in the reaction sequence is blocked by the presence of an interannular bridge, and may thus yield some useful information concerning this sequence. The initial step in the sequence is most likely an attack of H_2 at one of the coordination sites of the potentially pentacoordinate metal centre [6]; this follows from the stability of the neopentyl halide reactants in the absence of H_2, and from the improbability of any alternative mechanism involving metal-to-ring transfer of a halide ligand.

The accessibility of the metal centre could thus be a crucial factor for the rate of hydrogenolysis. From crystal structures of the analogous Ti compounds $(C_5(CH_3)_5)_2TiCl_2$ [21] and $C_2H_4(C_5(CH_3)_4)_2TiCl_2$ [10], it is clear, however, that there is less crowding between the ligands in the ethylene-bridged complex than in its unbridged analogue; the C_2H_4-bridged permethylzirconocene derivatives should thus be at least as accessible to an initial H_2 attack as their unbridged counterparts.

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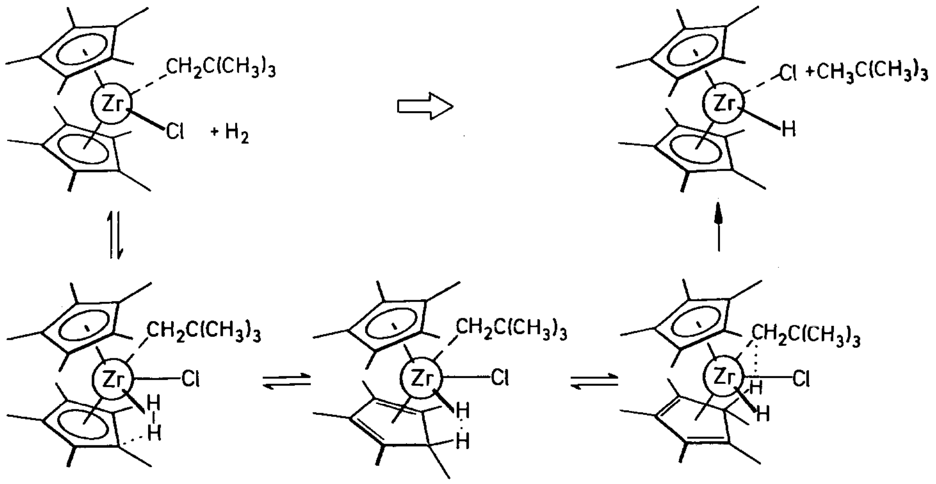
* Analogous observations have been reported for reactions of D_2 with $(C_5H_5)_2Zr(H)CH_2C_6H_{11}$ and $(C_5(CH_3)_5)_2Zr(H)CH_2CH(CH_3)_2$ [5,7].

** The ^1H NMR signals of the expected halide hydride product were not detectable in the reaction mixtures. Since controlled-atmosphere experiments cannot be conducted in sealed NMR tubes, leakage of grease or O_2 from the ground joint closures is difficult to exclude over the extended reaction times and may contribute to the decay rate.



SCHEME 1

However, a subsequent reaction step of the hydrogenolysis sequence could be blocked by the presence of the C_2H_4 bridge and the consequent restriction of ring ligand mobility, as follows. For the pentacoordinate intermediate formed by coordination of H_2 at the tetracoordinate d^0 metal centre, three isomers are possible, depending upon the site of H_2 coordination: (a) H_2 in the central site: i.e. between halide and neopentyl group; (b) H_2 in a lateral site, adjacent to a central neopentyl group; and (c) H_2 in the opposite lateral site, adjacent to a central halide ligand. Of these three isomers only (c), with H_2 in a lateral site adjacent to the centrally located halide ligand, appears to be accessible as a reaction intermediate. From space-filling models it is apparent that both the other sites, which are adjacent to the alkyl ligand, are totally blocked by the bulky t-butyl group *. Furthermore steric and electronic factors appear to favour coordination of H_2 pendicular to (rather than coplanar with) the plane of the equatorial ligand set. From an H_2 adduct with this topology the hydrogenolysis reaction can proceed only in such a manner that one of the cyclopentadienyl C atom acts as an intermediary hydrogen atom acceptor (see Scheme 1). If the cyclopentadiene ligand in this 16-electron Zr^{IV} intermediate can rotate with moderate activation energy **, this rotation will carry the H-bearing ring-C atom close to the alkyl group so as to make a ring-to-alkyl H-atom transfer a rather likely event.

For ethylene-bridged zirconocene derivatives, on the other hand, such a route would be unavailable, since the ring ligands cannot rotate by more than a few degrees, and so hydrogen transfer between the ring ligands and the alkyl group would be impossible. It is possible that H_2-uptake gives an intermediate with a

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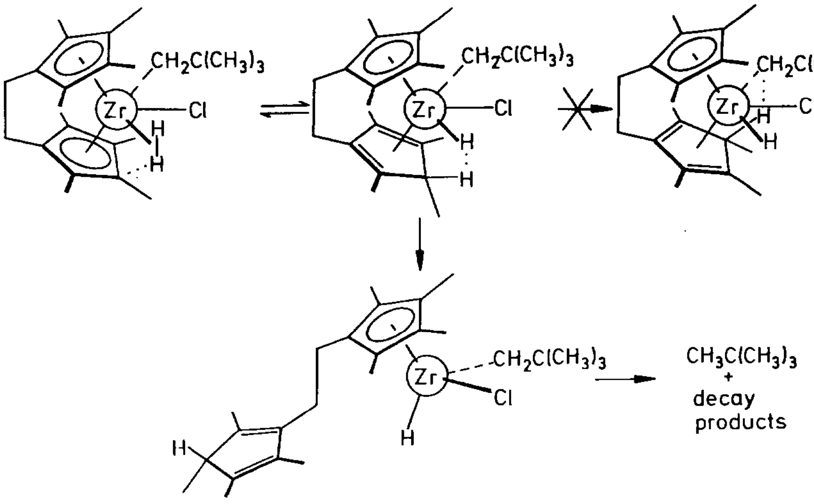
* Preliminary results of an EHMO study indicate that coordination of H_2 in the lateral site adjacent to the central halide ligand is preferred for electronic reasons also [22].

** C_5H_5 and $C_5(CH_3)_5$ ring ligands rotate with minimal activation energies [23,24]; a moderate barrier of 52 kJ/mol has been reported for the rotation of the C_5H_6 ligand in $(C_5H_6)Re(P(C_6H_5)_3)_2H_3$ [25].



SCHEME 2

different topology which is formed at a greatly reduced rate. Alternatively, prolonged existence of the cyclopentadiene Zr^{IV} intermediate might lead to loss of the cyclopentadiene ligand and subsequent formation of breakdown products, from which the initial C_2H_4-bridged permethylzirconocene structure is not regenerated in significant quantity.

A reaction sequence as in Scheme 1 would certainly lead to the observed product labelling in the presence of D_2. As for the observed, inverse kinetic isotope effect, several possible contributions have to be considered. While a direct hydrogen transfer from H_2 to an alkyl ligand would be associated with a significant normal kinetic isotope effect *, an inverse kinetic isotope effect can arise either from a preequilibrium favouring the reactive species in its deuterated form **, or from a steric isotope effect, i.e. from the reduced steric hindrance by an X–D as compared to an X–H group ***.

A ring-mediated hydrogen transfer sequence, such as that depicted in Scheme 1, could thus very well give rise to an inverse kinetic isotope effect. Uptake of H_2, especially into a rather crowded intermediate, as well as steric restriction of cyclopentadiene rotation by the extra *endo*-positioned H atom might contribute to the observed value of k_H/k_D of 0.85. In any case, the inverse kinetic isotope effect appears to rule out a direct H-atom transfer from H_2 to the alkyl group.

The much lower rate of hydrogenolysis of the neopentyl chloride of $(C_5H_5)_2Zr$, in comparison to its permethyl analogue, is in line with the reaction sequence of

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* A closely related example is the hydrogenolysis of n-octyllithium, for which Vitale and San Fillippo [26] have recently reported k_H/k_D values of 1.642 (at 50°C) to 1.392 (at 80°C).

** Inverse kinetic isotope effects of $k_H/k_D = 0.7–0.9$ have been reported for olefin hydrogenation reactions catalyzed by rhodium phosphine complexes, which involve H_2-uptake preequilibria [27,28], but have been contested in a more recent communication [29].

*** Steric isotope effects of about $k_H/k_D = 0.85$ have been observed e.g. for the sterically hindered racemisation of 1,1′-biphenyl compounds deuterated in the 6- and 6′-positions [30].

Scheme 1, since the reduced basicity of the unsubstituted cyclopentadienyl ligand (C_5H_6: $pK_a = 18$ [31]; $C_5(CH_3)_5H$: $pK_a = 26$ [32]) and the decreased electron density at the Zr centre would certainly disfavour the H_2 uptake intermediate.

The rates of hydrogenolysis for the various $(C_5(CH_3)_5)_2Zr$ neopentyl halide are too close to each other to allow an assessment of the relative contributions of Lewis acidity and HOMO energies at the Zr centre to the overall rate of the proposed reaction sequence.

The high rates of hydrogenolysis of both bridged and unbridged permethylzirconocene neopentyl hydrides, on the other hand, indicate that hydrogen transfer from H_2 to the alkyl ligand is not mediated by a cyclopentadiene ligand in these compounds. Apparently, the hydride ligand is small enough to accomodate coordination of the H_2 molecule at a site adjacent to the neopentyl ligand *, i.e. within the distance appropriate to a direct H_2-to-alkyl hydrogen transfer. Such an arrangement would obviate the necessity for the circuitous (or, in case of ring-bridged zirconocenes, inoperable) ring-mediated hydrogen transfer route.

The crucial intermediate in Scheme 1, which contains a cyclopentadiene ligand as a hydrogen carrier, is formally analogous to that proposed by Bercaw et al. [7] for the hydrogenolysis of permethylzirconocene alkyl hydride compounds. Our results would indicate, however, that such an intermediate is required for the hydrogenolysis of zirconocene alkyl halides only, and that it is formed without changing the oxidation state of the metal centre. Apparently the cyclopentadienyl ligands of these and other metallocenes [33–36] can play an unexpectedly active role in various types ** of hydrogen transfer reactions.

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References

1 H. Schwemlein, W. Tritschler, H. Kiesele and H.H. Brintzinger, J. Organomet. Chem., 293 (1985) 353.
2 P.C. Wailes, H. Weigold and A.P. Bell, J. Organomet. Chem., 43 (1972) C32.
3 J. Schwartz in D. Seyferth (Ed.), New Applications of Organometallic Reagents in Organic Synthesis, Elsevier, Amsterdam, 1976, p. 41.
4 K.I. Gell and J. Schwartz, J. Am. Chem. Soc., 100 (1978) 3246.
5 K.I. Gell, B. Posin, J. Schwartz and G.M. Williams, J. Am. Chem. Soc., 104 (1982) 1846.
6 H.H. Brintzinger, J. Organomet. Chem., 171 (1979) 337.

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* Judging from space-filling models, the t-butyl group of a centrally located neopentyl ligand can be accomodated without steric strain on the side of the more compact hydride ligand; this geometry would leave the adjacent, lateral coordination site accessible for H_2 coordination.

** For previous reports on intermolecular hydride transfer via exo and *endo* positions of a C_5H_6 ligand group cf. ref. 37–40, for interference of an interannular bridge with H_2 release from zirconocene hydride compounds, cf. ref. 41.

7 D.R. McAlister, D.K. Erwin and J.E. Bercaw, J. Am. Chem. Soc., 100 (1978) 5966.
8 P.C. Wailes and H. Weigold, J. Organomet. Chem., 24 (1970) 405.
9 S.B. Jones and J.L. Petersen, Inorg. Chem., 20 (1981) 2889.
10 F. Wochner, L. Zsolnai, G. Huttner and H.H. Brintzinger, J. Organomet. Chem., 288 (1985) 69.
11 A.F. Reid, J.S. Shannon, J.M. Swan and P.C. Wailes, Austr. J. Chem., 18 (1965) 173.
12 J.M. Manriquez, D.R. McAlister, E. Rosenberg, A.M. Shiller, K.L. Williamson, S.I. Chan and J.E. Bercaw, J. Am. Chem. Soc., 100 (1978) 3078.
13 P.G. Gassman, W.H. Campbell and D.W. Macomber, Organometallics, 3 (1984) 385.
14 J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, J. Am. Chem. Soc., 100 (1978) 2716.
15 E.J. Moore, D.A. Straus, J. Armantrout, B.D. Santarsiero, R.H. Grubbs and J.E. Bercaw, J. Am. Chem. Soc., 105 (1983) 2068; Dissertation E.J. Moore, Pasadena, 1983.
16 P.T. Barger and J.E. Bercaw, Organometallics, 3 (1984) 278.
17 H.C. Beachell and S.A. Butter, Inorg. Chem., 4 (1965) 1133.
18 P.M. Druce, B.M. Kingston, M.F. Lappert, T.R. Spalding and R.C. Srivastava, J. Chem. Soc., (1969) 2106.
19 M.W. Cook, D.N. Hanson and B.J. Alder, J. Chem. Phys., 26 (1957) 748.
20 R.R. Schrock and J.D. Fellman, J. Am. Chem. Soc., 100 (1978) 3359.
21 T.C. McKenzie, R.D. Sanner and J.E. Bercaw, J. Organomet. Chem., 102 (1975) 457.
22 H. Berke and H.H. Brintzinger, in preparation.
23 W.D. Luke and A. Streitwieser, Jr., J. Am. Chem. Soc., 103 (1981) 3241.
24 D.F.R. Gilson, G. Gomez, J. Organomet. Chem., 240 (1982) 41.
25 W.D. Jones and J.A. Maguire, Organometallics, 4 (1985) 951.
26 A.A. Vitale and J. San Filippo, Jr., J. Am. Chem. Soc., 104 (1982) 7341.
27 F.H. Jardine, J.A. Osborn and G. Wilkinson, J. Chem. Soc., (1967), 1574.
28 H. Simon and O. Berngruber, Tetrahedron, 26 (1970) 1401.
29 S. Siegel and D.W. Ohrt, Chem. Comm., (1971) 1529.
30 L. Melander and W.H. Saunders, Jr., Reaction Rates of Isotopic Molecules, New York, 1980, p. 189.
31 A. Streitwieser, Jr. and L.L. Nebenzahl, J. Am. Chem. Soc., 98 (1976) 2188.
32 F.G. Bordwell, G.E. Drucker and H.E. Fried, J. Org. Chem., 46 (1981) 632; F.G. Bordwell and M.J. Bausch, J. Am. Chem. Soc., 105 (1983) 6188.
33 P.J. Fagan, J.M. Manriquez, E.A. Maata, A.M. Seyam and T.J. Marks, J. Am. Chem. Soc., 103 (1981) 6650.
34 W.J. Evans, J.H. Meadows, A.L. Wayda, W.E. Hunter and J.L. Atwood, J. Am. Chem. Soc., 104 (1982) 2008.
35 H. Mauermann, P.N. Swepston and T.J. Marks, Organometallics, 4 (1985) 200.
36 P.L. Watson and G.W. Parshall, Accounts Chem. Res., 18 (1985) 51.
37 S.G. Davies, H. Felkin and O. Watts, J. Chem. Soc., Chem. Comm., (1980) 159.
38 D.L. Reger, K.A. Belmore, J.L. Atwood and W.E. Hunter, J. Am. Chem. Soc. 105 (1983) 5710.
39 B.M.R. Bandara and A.J. Birch, J. Organomet. Chem., 265 (1984) C6.
40 R.M. Bullock, C.E.L. Headford, S.E. Kegley and J.R. Norton, J. Am. Chem. Soc., 107 (1985) 727.
41 C.S. Bajgur, S.B. Jones and J.L. Petersen, Organometallics, 4 (1985) 1929.