indicated by the upper limit of 0.24.

Acknowledgment. We thank Dr. Tak Wai Leung, Dr. S.-C. H. Su, and Mr. Michael T. Goode for synthesis of compounds. We are indebted to Mr. E. Ray for maintenance of electronic equipment. Mr. E. C. Alsmeyer of U. S. Industrial Chemicals Co. was kind enough to provide us with the ethanol. This work was supported by the Department of Energy under Contract DE-AC02-76ER01763.A005 (L.M.D.), by the National Science Foundation, Grant CHE-7911882 (A.W.), and by the Natural Sciences and Engineering Research Council of Canada (W.L.W.).

Registry No. $Re(CO)_5\cdot$, 15684-00-1; $Re_2(CO)_{10}$, 14285-68-8; $ReMn(CO)_{10}$, 14693-30-2; $Re(CO)_5Br$, 14220-21-4; $Re(CO)_5Cl$, 14099-01-5; $Re(CO)_5I$, 13821-00-6; $Re(CO)_5SO_2CH_3$, 37988-72-0; $Mn(CO)_5\cdot$, 15651-51-1; CCl_4, 56-23-5.

Hydrogenation of Alkylzirconium(IV) Complexes: Heterolytic Activation of Hydrogen by a "Homogeneous" Metal Alkyl

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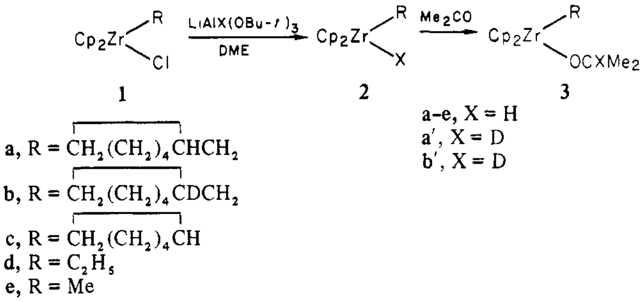
Abstract: Bis(η^2-cyclopentadienyl)zirconium(IV) alkyl chlorides and hydrides have been prepared and characterized. Hydrogenation of these species yields the corresponding alkane and zirconium hydride complexes, Cp_2ZrHCl and Cp_2ZrH_2, respectively. Deuterium labeling experiments suggest that these d^0 complexes activate H_2 by heterolytic attack on that molecule. Qualitative rates for hydrogenation of a series of complexes were $Cp_2Zr(R)H > Cp_2Zr(R)Cl \simeq Cp_2ZrR_2 > [(Cp_2ZrCl)_2(\mu\text{-OCHR})] > Cp_2Zr(COR)Cl$. This rate trend is the same as that for carbonylation and suggests a conceptual link between mechanisms for hydrogenation and carbonylation of these unsaturated complexes. A possible relationship is noted between heterolytic activation and oxidative addition of H_2 to transition-metal species.

The development of novel systems for activation of hydrogen continues to be an active area of research:[1,2] an understanding of elementary processes effecting this transformation may ultimately allow the design of catalysts for the selective reduction of "difficult" substrates such as carbon monoxide. One interesting approach to the design of such systems would be to utilize a transition-metal complex which can react directly with H_2 to give "hydridic" hydride ligands (where "hydridic" is defined as the ability of that ligand to reduce a carbonyl group to give the corresponding metal alkoxide).[3] Whereas most transition-metal hydrides are neutral or weakly acidic,[4] group 4a metal hydrides have reactivity patterns which are similar to those of boron or aluminum hydrides.[3,5] Perhaps because of this property, CO is stoichiometrically reduced to methane by $Cp_2Ti(CO)_2$ under H_2,[6] to methanol precursors by systems based on Zr(IV),[7-9] and to a mixture of precursors of linear aliphatic alcohols, promoted by $Cp_2ZrCl_2\cdot3(i\text{-}Bu)_2AlH$.[8] Although simple CO reduction systems based on group 4A metals are unlikely to be catalytic because of the strength of the metal–oxygen bond,[10] stoichiometric processes based on them are instructive examples which can suggest directions for further investigation: a knowledge of mechanisms for H_2 activation by group 4 transition-metal complexes is important to a general understanding of stoichiometric reductions using hydrides of this class.

Scheme I



Catalytic hydrogenation of olefins using Zr(IV) (d^0) species Cp_2ZrH_2,[11] $Cp_2Zr(H)Cl$,[11] and $Cp_2ZrCl_2\cdot(i\text{-}Bu)_3Al$[12] has been demonstrated. In these reactions intermediary low-oxidation-state complexes of Zr have been assumed to be responsible for H_2 activation. Indeed, complexes of Zr(II)[7a–c,13] are known to oxidatively add H_2 to generate the corresponding Zr(IV) dihydrides. To better define mechanisms by which Zr(IV) complexes react with H_2, we have studied hydrogenation of alkylbis(η^5-cyclopentadienyl)zirconium(IV) complexes which are likely intermediates in the Cp_2ZrHX-catalyzed (X = Cl or H) hydrogenation of olefins. Our results suggest that mechanisms for hydrogenation and carbonylation of alkylzirconium(IV) hydrides are related and imply that a pathway previously unacknowledged in the hydrogenation chemistry of transition-metal alkyls (one other than

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Table I. Composition of Deuterated Methylcyclohexanes Formed in Mixed-Label Hydrogenations

reaction	% RH, (time, h)	composition of MCH, %,[a] d_0	$d_1{}^0$	$d_1{}'$	d_2	% MCH containing atmos. label at Me	% MCH atmos. incorporation at 1-posn
(i) **2b**′ + H_2	80 (6)	6	7	83	4	89 ($d_0 + d_1{}'$)	13 ($d_0 + d_1{}^0$)
(ii) **2a**′ + H_2	80 (10)	82	3	14	1	96 ($d_0 + d_1{}'$)	*b*
(iii) **2a** + D_2	65 (5)[c]	19	61	3	17	78 ($d_1{}^0 + d_2$)	20 ($d_1{}' + d_2$)

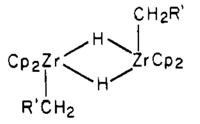
[a] MCH = methylcyclohexane. [b] The original label at the β position of the cyclohexylmethyl group is the same as the atmosphere. [c] Reaction not run to completion.

conventional activation of H_2 by oxidative addition) accounts for hydrogenolysis of these d^0 species.

Results

Preparation and Characterization of Alkylbis(η^5-cyclopentadienyl)hydridozirconium(IV) Complexes. Alkylbis(η^5-cyclopentadienyl)hydridozirconium(IV) complexes, $Cp_2Zr(R)H$ (**2**), are prepared by reduction of the corresponding Zr(IV) alkyl chloride complex, **1**, with lithium tri-*tert*-butoxyaluminum hydride (Scheme I) in DME, from which they precipitate as white air- and moisture-sensitive solids. Most of the model reactions in this study have been performed with (cyclohexyl)methyl complexes **1a** and **2a**. Although complexes **2d** and **2e** are more readily prepared and have clear advantages for the interpretation of NMR spectral data, they are less reactive than **2a**, presumably because of their low solubility. The deuterated analogues (**2a**′, **2b**′) of **2a** are readily accessible by regiospecific synthesis,[14] and the composition of mixtures of deuterated methylcyclohexanes which result from many of the reactions in this study can be determined accurately by mass spectrometry.

Complex **2a** is dimeric in benzene;[15] low molecular weights are obtained, which suggests that some dissociation occurs in solution. ^1H NMR and IR spectra show that **2a** contains bridging hydride ligands.



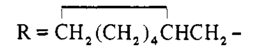
$2a_2$, $R' = CH_2(CH_2)_4CH$-

The chemical shift of the hydride ligand (δ −2, $\nu_{1/2}$ = 45 Hz, absent for **2a**′) is typical for hydrides bridging Zr(IV) centers;[16] terminal hydrides on Zr(IV) have chemical shifts downfield of δ 4.[7,16] In the IR of **2a** a broad strong absorption at 1380 cm^{-1} (which shifts to 990 cm^{-1} in the spectrum of the deuteride **2a**′) is assigned to a vibration of the bridging hydride ligands[16,17] (in monomeric Zr(IV) complexes containing terminal hydrides, ν_{Zr-H} is approximately 1550 cm^{-1} [7,16]).

Hydrolysis of **2a** produces methylcyclohexane and H_2. In a reaction typical of transition-metal hydrides,[18] **2a** reduces a variety of organic halides to the corresponding alkane. The "hydridic" character of the hydride ligand in **2** is indicated by the reaction with acetone, which gives the corresponding Zr(IV) alkyl isopropoxide, **3** (Scheme I). This reaction is a convenient means of assaying the less soluble members of the series.

Scheme II

$$Cp_2Zr(R)H + H_2 \rightarrow Cp_2ZrH_2 + RH$$



$$R = CH_2(CH_2)_4CHCH_2-$$

Table II. Composition of the Deuterated Methylcyclohexanes from the Reaction of **2a** with D_2

time, min	volatiles d_0	$d_1{}^0$	$d_1{}'$	d_2	$\Sigma(d_1{}^0 + d_2)$[a]	$\Sigma(d_1{}' + d_2)$[b]	hydrolysate[c] d_0	$d_1{}'$
120	26	63	3	8	71	11	86	14
210	25	62	3	10	72	13	80	20
300	19	61	3	17	78	20	72	28
540[d]	17	50	11	22	72	33		

[a] % of the methylcyclohexane product has incorporated an atmosphere label in its methyl group. [b] % of the methylcyclohexane product that has incorporated an atmosphere label at the 1-position. [c] The % of d_0 and $d_1{}'$ methylcyclohexanes in the hydrolysate is a measure of the label incorporation at the β position of the cyclohexylmethyl group on the unreacted zirconium(IV) alkyl hydride. [d] From a separate experiment.

Compound **2a** can be stored as a solid for long periods under nitrogen at −30 °C. However, in solution it decomposes at room temperature over several days to methylcyclohexane (80%, 14 h, 45 °C) and a purple solid that shows strong Zr–H vibrations in the IR (1250 cm^{-1}) and has been shown to contain η^5-Cp and bridging $\eta^1{:}\eta^5C_5H_4$ ligands.[19] The relatively insoluble complexes **2d** and **2e** are reasonably stable at room temperature, and **2c** slowly metathesizes to $Cp_2Zr(CH(CH_2)_4CH_2)_2$ and highly insoluble Cp_2ZrH_2.[20]

Study of the labeled compounds **2a**′ and **2b**′ has revealed the occurrence of two equilibration processes: (1) The hydride ligand and the β-hydrogen of the cyclohexylmethyl group exchange intramolecularly.[21] In solutions of **2a**′ the deuterium label is approximately equally distributed between these two positions after 3 h at room temperature (during which time only 6% decomposition has occurred). (2) Hydride ligands exchange *inter*molecularly. This is implied by the observation that the hydride ligands exchange between **2a** and Cp_2ZrD_2, even though this latter compound is of very low solubility.[11] Because of these scrambling processes, which are fast *relative to autodecomposition* (which occurs to 6% in 3.25 h at room temperature), solutions of **2a**′ or of an equimolar mixture of **2a** and **2b**′ decompose at approximately equal rates and give similar distributions of deuterated methylcyclohexanes. This mixture of methylcyclohexanes consists largely of d_0 and d_1 isomers.[22]

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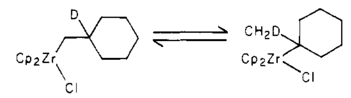
(14) In the preparation of **1b** by the reaction of methylenecyclohexane with $Cp_2Zr(D)Cl$, no deuteration of the α-methylene group is observed. The initial addition is therefore regiospecific, and the equilibrium



1b

does not operate.

(15) Molecular weights of **2c** and **2d** have not been determined. However, **2e** is polymeric, perhaps accounting for its low solubility; see ref 11.

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(17) The synthesis of the hydride-bridged dimer $[(Cp_2Zr[CH(SiMe_3)_2]$-μ-$H)_2]$ has recently been reported. For this complex, ν_{ZrH} is 1590 cm^{-1}. It is not clear why this frequency differs so markedly from that for **2a**. Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1081.

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(21) In contrast, no *observable* β-H elimination occurs in $Cp_2Zr(R)Cl$ complexes (R = primary alkyl). If it does occur, the olefin which forms does not leave the coordination sphere of the Zr(IV), as the hydride is redelivered to the same face of the olefin; Hart, D. W. Ph.D. Dissertation, Princeton University, Princeton, NJ, 1975.

Table III. Analysis of the Products of Hydrogenation of **2b**′

		$Cp_2Zr(OPr\text{-}i)_2$			$Cp_2Zr(CH_2R')(OPr\text{-}i)$[a]					
			composition[c]			composition[c]				
time, min	MCH yield, %[b]	yield, %	% H	% D	yield, %	% H	% D[d]	ΣH	ΣD	$\Sigma H/Cp_2ZrH_2$, mmol
35[e]	15[f]	10	26	74	90	25	75	0.15	0.40	2.5 ± 0.5
70	30	23	38	62	77	41	59	0.25	0.36	2.1 ± 0.2
130	57	46	56	44	54	59	41	0.42	0.32	1.8 ± 0.1
360[g]	80	90–100	72	28						

[a] $R' = \overline{CH_2(CH_2)_4C}X$; X = H, D. [b] % methylcyclohexane (MCH) based on 0.47 mmol of methylcyclohexane in the hydrolysate. [c] % H/D at the α-carbon of the isopropoxy groups. [d] Yields for each isopropoxy compound are calculated, assuming (as independently shown) that equivalent amounts of the zirconium(IV) dihydride and of methylcyclohexane are produced. [e] Reaction mixture cloudy; in other aliquots a white precipitate of Cp_2ZrH_2 was present; accurate sampling was difficult. [f] When this aliquot was taken, 0.06 mmol of hydrogen had been absorbed. [g] Second experiment.

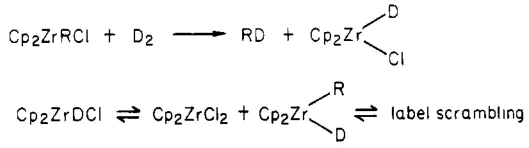
Table IV. Hydrogenation of $Cp_2Zr(R)Cl$

			isotope ratios					isotope ratios			
gas pressure, (psig)[a]	R-Cl, mmol	yield[c] of RX, mmol	d_0	$d_1{}^0$	$d_1{}'$	d_2	yield of RX, mmol	d_0	$d_1{}^0$	$d_1{}'$	d_2
D_2 1200	1.21	0.16	≈0	79	18	3	0.83	97	0	3	0
D_2 600	1.19	0.05	16	40	42	2	0.90	≈100	0	0	0
D_2 300	1.21	0.02	≈0	57	43	0	1.05	≈100	0	0	0
H_2 1200	1.27	0.24[d]					0.78				
D_2 550[b]	2.57	0.58[d]	27	69	1	3	1.17	84	0	16	0

[a] Standard conditions, 0 °C, 10 h. [b] 24 °C, 10 h. [c] Yields are recorded after evaporative distillation from samples recovered upon hydrogenation, before hydrolysis (corrected for background hydrolysis); X = H or D. [d] Not corrected for background hydrolysis. [e] After hydrolysis.

Hydrogenation of $Cp_2Zr(CH_2\overline{CH(CH_2)_4C}H_2)H$ (2a). Solutions of **2a** react in aromatic solvents with H_2 (1 atm) at room temperature over several hours, producing methylcyclohexane (ca. 1 equiv on the basis of H_2; 0.8 equiv on the basis of **2a**) and Cp_2ZrH_2 (Scheme II). The hydrogenation can be followed by monitoring H_2 uptake, methylcyclohexane production, or the formation of Cp_2ZrH_2 [analyzed as $Cp_2Zr(OPr\text{-}i)_2$]. The reaction rate shows an apparent first-order dependence on H_2 pressure over the small pressure range studied (1–4.6 atm); the rate of alkane formation is *more than an order of magnitude greater than that for autodecomposition of **2a***. Hydrogenation is approximately twice as fast as the corresponding reaction with D_2. The mechanism of hydrogenation has been investigated by performing a series of mixed-label experiments: (1) **2b**′ + H_2, (2) **2a**′ + H_2, and (3) **2a** + D_2. In each of these reactions a large fraction of the methylcyclohexane product incorporates a single atmosphere label into its methyl group (Table I.)[23] Atmosphere label is also incorporated at the 1-position of the methylcyclohexane (see Table I) in increasing amounts during hydrogenation (Table II) of **2a**. The hydride ligand and the β-H position of the (cyclohexyl)methyl group of the *unreacted* alkylzirconium(IV) hydride show a parallel incorporation of atmosphere label during this reaction (Table II). Several aspects of these data are significant: (1) Under slightly elevated pressure (55 psig), at short reaction times (20 min), when no Cp_2ZrH_2 is detectable (as $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ on acetone treatment), the unreacted zirconium(IV) alkyl hydride shows substantial incorporation of atmosphere label at the hydride position. (2) In reactions at 1 atm, the *total* atmosphere label incorporation at the hydride positions of the zirconium(IV) dihydride and unreacted zirconium(IV) alkyl hydride *substantially exceeds* the yield of methylcyclohexane throughout the reaction (Table III). (3) In these reactions label incorporation at the hydride positions increases during hydrogenations but at any given time is approximately the same in each of these compounds.

Scheme III



Hydrogenation of $Cp_2Zr(CH_2\overline{CH(CH_2)_4C}H_2)Cl$ (1a). To determine if a metal hydride ligand were necessary for hydrogenolysis to succeed, we investigated the reaction between **1a** and H_2. Under conditions for which hydrogenolysis of **2a** occurred readily (room temperature, 50 psig of H_2), **1a** reacted only very slowly with hydrogen (<5% over 2 days). Convenient rates for hydrogenolysis of **1a** were achieved at a higher temperature and slightly higher pressure (80 °C, 70 psig); however, GC/MS analysis of the methylcyclohexane produced under D_2 under these conditions revealed a large amount of deuterium incorporation into the β position. This label scrambling increased with increasing reaction time. Hydrolysis of the residues of evaporative distillation yielded some methylcyclohexane-$d_1{}'$. Such behavior is reminiscent of that of **2a**. Scheme III can account for this scrambling; this exchange process, which requires the production of Cp_2ZrCl_2 (the presence of which was noted by ^1H NMR analysis) and which results in a less than stoichiometric production of Cp_2ZrHCl on the basis of **1a** consumed, can confuse interpretation of hydrogenation results. It was therefore important to investigate hydrogenolysis of **1a** under conditions of minimized scrambling. Higher pressures of H_2 (or D_2) and lower temperatures were therefore employed; higher pressures should accelerate the hydrogenolysis reaction *relative to label scrambling*, while lower temperatures should slow ligand exchange by decreasing the solubility of the Cp_2ZrHCl required for this process. These predictions were corroborated experimentally (see Table IV). The rate of hydrogenation of **1a** showed a nearly linear dependence on pressure of D_2 applied (300–1200 psig); unfortunately, the solubility of D_2 in toluene, under these conditions of greatly varying presure, could not be

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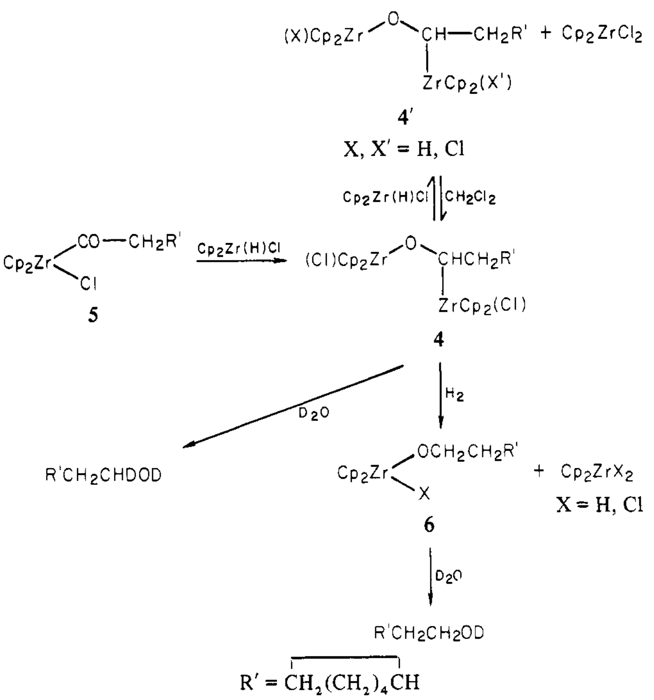
(22) The labeling patterns of the methylcyclohexane produced from **2a** + **2b**′ (or from **2a**′) are consistent with that observed for **2b**′ alone. For example, after 18 h in the decomposition of **2b**′, 37% of the product shows a proton at the α-position (RCH_2–H, $d_0 + d_1{}^0$) while 63% shows a deuterium (original hydride label) at this position (RCH_2–D, $d_1{}^0 + d_2$). Assume that the original mixture of **2a** + **2b**′ (or **2a**′) has equilibrated and is composed of approximately equal amounts of **2a**, **2a**′, **2b**, and **2b**′. Assume that each of these compounds decomposes to give methylcyclohexane with 37% proton at the α position, the remaining 63% containing the hydride label originally on Zr; then **2a** → d_0; **2a**′ → 0.37 d_0 + 0.63 $d_1{}^0$; **2b** → $d_1{}'$; and **2b**′ → 0.37 $d_1{}'$ + 0.63 d_2; which gives a distribution: d_0 (34%); $d_1{}^0$ (16%); $d_1{}'$ (34%); d_2 (16%).

(23) In the reaction of **2a** with D_2, approximately 20% of the methylcyclohexane is unlabeled (d_0), apparently retaining the label originally at the hydride position of **2a**. Although this result may be significant to a detailed understanding of the hydrogenation mechanism, it should be noted that any adventitious hydrolysis will increase the yield of methylcyclohexane-d_0 in this reaction.

Scheme IV



ascertained. A slight isotope effect was measured ($k_H/k_D \simeq 1.3$). The amount of label-scrambled methylcyclohexane was very small ($\ll$4% -d_2 of methylcyclohexane obtained; some unlabeled methylcyclohexane, arising from adventitious hydrolysis of **1a**, was noted).[23]

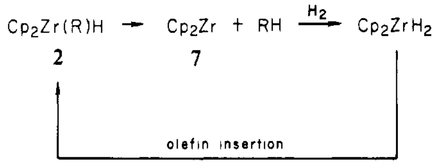
Preparation, Characterization, and Hydrogenation of (Alkoxyalkyl)zirconium(IV) Complex: (Cl)Cp$_2$Zr-μ-(OCHCH$_2$-CH(CH$_2$)$_4$CH$_2$)ZrCp$_2$(Cl) (4). This compound was prepared by the reaction of the isolable acyl complex Cp$_2$Zr(COCH$_2$CH-(CH$_2$)$_4$CH$_2$)Cl (**5**) with Cp$_2$Zr(H)Cl in which the acyl group of **5** is reduced and dimeric compound **4** (contaminated by a small amount of a hydridic species which may have structure **4′**) is produced.[24] This mixture of compounds is converted to pure **4** on treatment with methylene chloride.[25]

Hydrolysis of **4** with D$_2$O gives 2-cyclohexyl-1-deuterioethanol, demonstrating that the alkoxy ligand is both C- and O-bound to Zr. ^{1}H and ^{13}C NMR spectra confirm this finding and, in addition, show that this ligand is bridging, being C- and O-bonded to two different Zr centers;[26] the alkoxyalkyl complex is fluxional, as has been noted.[24] Dimeric species **4** reacts with H$_2$ (95 atm) very slowly at room temperature (24 h) to cleave the Zr–C bond, giving a zirconium alkoxide, **6** (^{1}H NMR identification), as the major product (Scheme IV).[27] Hydridic species, spectrally resembling **3**, are generated, together with some Cp$_2$ZrCl$_2$. Hydrolysis with D$_2$O of the hydrogenation products gives 2-cyclohexylethanol containing no deuterium at the α-carbon, and some H$_2$ is evolved. Under these conditions acyl complex **5** was not hydrogenated.

Discussion

Reductive elimination of alkane from **2**, followed by hydrogenation of "zirconocene" product **7** (Scheme V), has been proposed as a mechanism for the catalytic hydrogenation of olefins by Cp$_2$ZrH$_2$.[11] Our results for autodecomposition and hydrogenation of **2a** differ from the predictions of this scheme in several important ways: (1) Simple reductive elimination,[13,28] the first step of this mechanism, is not a major pathway for the autodecomposition of this isolable alkyl hydride complex.[29] (2) The acceleration of the rate of alkane formation from **2a** in the presence of H$_2$, the nearly first-order dependence of this rate on H$_2$ pressure (even over small pressure ranges), and the high incorporation of atmosphere label into *either* the *starting material* or the alkane product are additional observations which are at variance with Scheme V and suggest that **2a** interacts with H$_2$ *prior* to the formation of alkane.

Scheme V



Our results involving alkylzirconium chloride complexes demonstrate that a hydride ligand (on Zr) is not necessary for hydrogenolysis of the C–Zr bond and show that hydrogenolysis of Cp$_2$Zr(R)Cl can occur by direct interaction between the organometallic species and H$_2$. Relative rates for hydrogenolysis of Cp$_2$Zr(R)H and Cp$_2$Zr(R)Cl show, though, that the nature of X in Cp$_2$Zr(R)X does play a role in modulating this H$_2$ activation pathway.

Three elementary mechanisms have been demonstrated for the activation of H$_2$ by simple metallic complexes: heterolytic or homolytic cleavage of H$_2$ by a metal complex or oxidative addition of H$_2$ to a reduced metal center. A formal oxidative addition of H$_2$ to **2a**, a d^0 species with no accessible higher oxidation states, seems improbable. Dihydrogen in theory can, however, interact *directly* with a metal center *without* net oxidation of that metal center via a *vacant* orbital on the metal. The orbitals of bent-sandwich complexes, Cp$_2$MX$_2$, have been defined from a series of spectroscopic and structural studies.[30] For d^1 and d^2 systems, the highest occupied molecular orbital (HOMO) is populated by the nonbonding electrons and is chiefly d$_{y^2}$ in character, lying in the plane of the ligands X, and with significant extent along the *y* axis (using the terminology of ref 30). Provided that the lowest unoccupied molecular orbital (LUMO) in d^0 Cp$_2$MX$_2$ complexes qualitatively resembles HOMO in the d^1 and d^2 systems, attack by a nucleophile or, we suggest, by H$_2$ could occur at this orbital. (This might occur along the *y* axis, the "external" lobe of LUMO. This direction of attack on LUMO gives better overlap with the H$_2$ σ bond than does attack at the relatively small central lobe.)[31-33]

In a preliminary account of this work,[34] we proposed that H$_2$ is polarized by this interaction with the Lewis acid Zr(IV) center. The consequences of this interaction, which can occur at two stereochemically distinct sites with regard to the hydride on Zr, are illustrated in Scheme VI. Attack cis to the alkyl group (**8**) and transfer of proton to the front side of the Zr–C bond forms

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[24] Gell, K. I.; Williams, G. M.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1980**, 550.

[25] Gell, K. I.; Schwartz J. *Inorg. Chem.* **1980**, *19*, 3207.

[26] At low temperature four sharp singlets for the Cp ligands are seen in both the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **4**. The pairs of ligands Cp$_{A_1}$, Cp$_{A_2}$ and Cp$_{B_1}$, Cp$_{B_2}$ are diastereotopic because of the chiral center of C$_1$ of the alkoxy group. The downfield pair of singlets in the ^{1}H NMR (δ 6.12, 6.04; Cp$_{A_1}$, Cp$_{A_2}$) are assigned to the Cp ligands on the Zr bound to oxygen, and the upfield pair (δ 5.76, 5.73; Cp$_{B_1}$, Cp$_{B_2}$) are assigned to the Cp ligands on the Zr bound to carbon.

[27] Gray, D. R.; Brubaker, C. H., Jr. *Inorg. Chem.* **1971**, *10*, 2143.

[28] Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

[29] For a list of other isolable metal alkyl hydride complexes, see: (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (b) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966, and ref 10b and 23.

[30] Lauher, J. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729, and references therein.

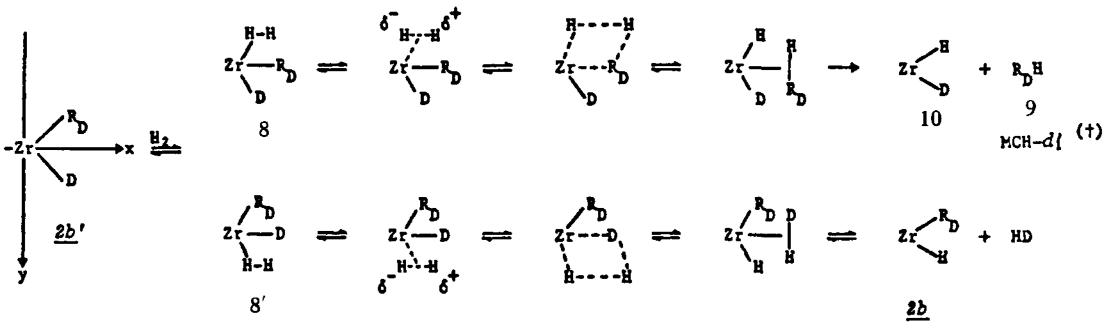
[31] (a) Analogous coordination of conventional two-electron ligands to monomeric (C$_5$Me$_5$)$_2$ZrH$_2$ has been reported.[7e] In these adducts the donor ligand is coordinated between the two hydride ligands. At low temperature CO coordination is reversible;[7c] these adducts are probably thermodynamic rather than kinetic products (see ref 32 and 33). (b) See also: Marsella, J. A.; Curtis, C. J.; Bercaw, J. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 7244.

[32] A theoretical description of this process has appeared: Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337.

[33] Carbonylation of analogues has been described: (a) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Am. Chem. Soc., Dalton Trans.* **1977**, 1946. (b) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605.

[34] Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246.

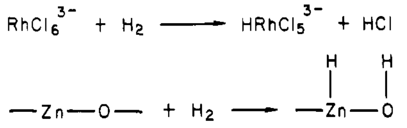
Scheme VI



R_D = $\overline{CH_2(CH_2)_4CD}CH_2$-

† = methylcyclohexane-α-d

Scheme VII



$RhCl_6^{3-} + H_2 \longrightarrow HRhCl_5^{3-} + HCl$

$—Zn—O— + H_2 \longrightarrow —\overset{H}{\overset{|}{Zn}}—\overset{H}{\overset{|}{O}}$

a C–H bond (**9**) followed by alkane loss via the central lobe of LUMO. The alkane is specifically labeled from the atmosphere, and the zirconium(IV) dihydride product (**10**) carries an atmosphere label and the label originally on **2b'**. The alternative site of attack, cis to the hydride (**8'**), provides a mechanism for exchange of the hydride on the starting material with the atmosphere by loss of HD in the series of equilibria **8'** → **2b**. (Exchange of the β hydride of the alkyl group with the hydride on starting material which has *itself* exchanged with the atmosphere results in incorporation of increasing amounts of atmosphere label at the 1-position of the methylcyclohexane product.)

The mechanism proposed above is an example of a general class of heterolytic cleavage reactions of H_2. This process has been demonstrated for certain aqueous Cu(I), Ag(I), Ru(III), and Rh(III) complexes[35] and for many metal oxides (see Scheme VII).[36] It results in formation of a metal hydride and a proton stabilized by interaction with a basic species. For hydrogenolysis of **2a**, the Zr–C bonding electron pair may be the proton receptor (this leads to C–Zr cleavage). For **1a** a lone pair on the chloride ligand may be the kinetically favored site of protonation; transfer of this proton to the Zr–C bond would lead to its cleavage.

From the literature[16,37g,i] and from our studies, it is clear that $Cp_2Zr(R)X$ complexes (R = alkyl, X = Cl or alkyl) are more difficult to hydrogenate than are soluble Zr(IV) alkyl hydrides, e.g., **2a**. The ease of hydrogenation by the direct interaction mechanism should depend on steric and electronic factors influencing the availability of LUMO. This orbital must be accessible in **2a** because it is used in dimerization of the compound. However, $Cp_2Zr(R)Cl$ complexes are monomeric; the chloride ligand can donate electron density to Zr(IV) by $p\pi$ overlap with LUMO.[30,31b,38] Partial electronic saturation of the metal center by this π donation may prevent effective interaction with H_2. Slow hydrogenation of a dialkyl species could be attributed to steric factors. The dimer **4**, in which the vacant coordination site on each Zr is partially occupied as a result of the fluxional motion of the alkoxyalkyl ligand, can be hydrogenated (slowly), but the zirconium(IV) acyl complex, **5** in which the vacant coordination site is occupied by the oxygen of the η^2-carbonyl group, fails to hydrogenate.

Zirconium(IV) alkyls are probably not unique examples of organometallic species which activate H_2 "heterolytically". In fact, numerous d^0 alkyl metal complexes can be hydrogenated.[37] Schrock and Parshall[39] have noted that *direct* reaction of a d^0 alkyl with H_2 by a mechanism analogous to our proposal for the hydrogenation of **2a** could operate exclusively (or could initiate subsequent autocatalysis of hydrogenation). Hydrogenation of actinide analogues may proceed in similar fashion.[40] In some cases, e.g., the hydrogenation of Zr(IV) alkyls bound to silica[37k,41] or the hydrogenation of LiPh,[37a,f] there is no obvious alternative to a direct interaction of the d^0 complex with H_2.[39]

Conclusion

Qualitative relative rates of carbonylation or hydrogenation of Zr(IV) complexes follow a similar trend, $Cp_2Zr(R)H$[42] > $Cp_2Zr(R)Cl$[43] ≃ Cp_2ZrR_2[9,44] > $[(Cp_2ZrCl)_2$-μ-OCHR][42] > $Cp_2Zr(COR)Cl$,[44] and likely reflect the availability of a vacant site on the metal of monomeric Zr(IV) complex **2**; CO or H_2 compete for this site with the hydride ligand on another molecule of **2** (which forms the observed dimer). The interaction, then, between the cleavage reagent and the metal complex, involving the availability of this vacant orbital, provides the conceptual link between these two pathways.

Hydrogenolysis of many metal alkyls has generally been discussed in terms of an oxidative addition process, one which is not feasible for the Zr(IV) complexes under consideration herein. Rather, on the basis of rate and labeling trends, a *direct* interaction between H_2 and Zr(IV) via its *vacant* valence orbital is postulated (a similar interaction with CO would initiate carbonylation). This hydrogen activation process, which requires *no* oxidation state change for the metal but depends on the availability of a vacant orbital on the metal, is reminiscent of "heterolytic" activation of H_2 which is known for a variety of Lewis-acid complexes studied in solution and for a number of insoluble metal oxides. The heterolytic activation of H_2 in these cases is facilitated by the

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(35) (a) Halpern, J. *J. Phys. Chem.* **1959**, *63*, 398; (b) *Annu. Rev. Phys. Chem.* **1965**, *16*, 103.

(36) For example, see: Kokes, R. J.; Dent, A. L.; Chang, C. C.; Dixon, L. T. *J. Am. Chem. Soc.* **1972**, *94*, 4429.

(37) See, for example: (a) Gilman, H.; Jacoby, A. J.; Ludeman, H. *J. Am. Chem. Soc.* **1938**, *60*, 2336 (alkali metal organometallics). (b) Hein, F.; Weiss, R. *Z. Anorg. Allg. Chem.* **1958**, *295*, 145 (Li_3CrPh_6). (c) Podall, H. E.; Petree, H. E.; Zeitz, J. R. *J. Org. Chem.* **1959**, *24*, 1222 (main group organometallics). (d) Köster, R.; Bruno, G.; Binger, P. *Liebigs Ann. Chem.* **1961**, *644*, 1 (BR_3·NR'_3). (e) Klein, R.; Bliss, A.; Schoen, L.; Nadeau, H. G. *J. Am. Chem. Soc.* **1961**, *83*, 4131 (Et_3B). (f) Clauss, K.; Bestian, H. *Liebigs Ann. Chem.* **1962**, *654*, 8 (Cp_2TiMe_2, LiPh, LiMe, Li_3CrPh_6). (g) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 155 (Cp_2ZrMe_2). (h) Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 5823 ($LiTaPh_6$). (i) Shortland, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 872 (WMe_6). (j) Couturier, S.; Gautheron, B. *J. Organomet. Chem.* **1978**, *157*, C61 ($(\eta^5$-$C_5H_4R)_2ZrMe_2$). (k) Zakharov, V. A.; Dudchenko, V. K.; Paukshtis, E. A.; Karakchiev, L. G.; Yermakov, Yu, I. *J. Mol. Catal.* **1977**, *2*, 421.

(38) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389.

(39) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243.

(40) (a) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *100*, 3939. (b) Maatta, E. A.; Marks, T. J. *Ibid.* **1981**, *103*, 3576.

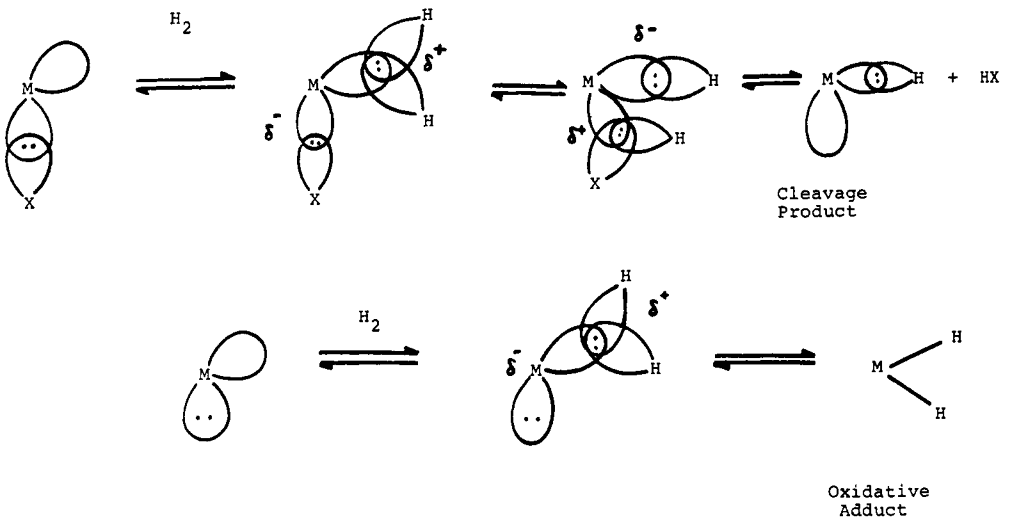
(41) Ward, M. D.; Schwartz, J. *J. Mol. Catal.* **1981**, *11*, 397.

(42) Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *162*, C11.

(43) Bertelo, C. A.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 228.

(44) Gell, K. I. Ph.D. Dissertation, Princeton University, Princeton, NJ, 1980.

Scheme VIII



presence of a base to stabilize the proton thus liberated. As in heterolytic H_2 activation, conventional "oxidative addition" of H_2 requires a vacant site on the metal (as well as a lone electron pair). It may be then that "oxidative addition" of H_2 and its "heterolytic" activation, as described herein, are but two aspects of the *same* reaction; in the latter case, interaction of H_2 with the metal may occur via its vacant orbital, to be followed by proton transfer either to a basic electron pair of the medium or to a bonding electron pair of the complex; in the former, the proton is simply transferred to a *lone* electron pair of the metal (Scheme VIII).).

Experimental Section

General Procedures and Techniques. Reactions were performed under purified argon by using standard Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres drybox. Solvents were distilled from sodium benzophenone ketyl under nitrogen and were routinely tested with sodium and benzophenone in the drybox. If necessary, further purification was effected in the drybox by passing the solvent down a column of alumina (Woelm Activity 1, 20 × 1 in.), which had been dried at 180 °C under high vacuum for 12 h. Methylene chloride, bromobenzene, and olefins were distilled from calcium hydride; acetone was dried over molecular sieves (3 Å) for several days prior to vacuum distillation. NMR solvents (benzene-d_6, toluene-d_8) were vacuum distilled from lithium aluminum hydride. Dichlorobis(η^5-cyclopentadienyl)zirconium(IV) (Cp_2ZrCl_2, Boulder Scientific) was used as received to prepare $Cp_2Zr(H)Cl$, $Cp_2Zr(D)Cl$, $(Cp_2ZrCl)_2O$, Cp_2ZrH_2, and Cp_2ZrD_2 by standard methods. The purity of these hydrides was determined by reaction with acetone and ^1H NMR analysis of the resulting zirconium(IV) isopropoxide. Trimethylaluminum was purchased from Ethyl Corporation. Carbon monoxide and hydrogen were dried by passage through a column of molecular sieves (Matheson, 4 Å). Deuterium and carbon-^{13}C monoxide were obtained from Merck Sharp and Dohme, Canada Ltd., Isotopes, and were used without purification. Hydrogen chloride and deuterium chloride (Matheson) were dried by passage through calcium chloride. A mercury-filled gas buret was used for hydrogenations and carbonylations at 1 atm. Reactions at pressures from 1 to 4 atm were performed in a standard Fischer–Porter apparatus. A rocking autoclave (Autoclave Engineers) or a Parr "Mini" reactor was used at higher pressures. The bomb for this autoclave was fitted with a glass liner; solutions were loaded in the drybox where the bomb was sealed.

Mass spectra were obtained on an AEI MS-9 instrument, and gas chromatographic/mass spectral (GC/MS) analyses were performed on a Du Pont 21-490 system or a Hewlett-Packard 5992B. Several GC/MS analyses were carried out by Hoffmann-La Roche, Inc., Nutley, NJ. The composition of mixtures of deuterated methylcyclohexanes was determined by GC/MS using authentic deuterated samples as reference compounds.

Molecular weights were measured cryoscopically in benzene under argon with a jacketed cell fitted with a calibrated thermocouple. Elemental analyses were performed by Alfred Bernhardt, West Germany, using drybox sampling techniques, and by Hoffmann-La Roche, Inc., Nutley, NJ.

Preparation of Alkylchlorobis(η^5-cyclopentadienyl)zirconium(IV) Complexes (1a–e). The general method of synthesis of these compounds has been described[45] and is illustrated for the preparation of $Cp_2Zr(CH_2\overline{CH(CH_2)_4C}H_2)Cl$ (**1a**). The ^1H NMR spectra of these compounds are reported in Table V.

(A) Methylenecyclohexane (4.8 mL, 40 mmol) was added to a suspension of $Cp_2Zr(H)Cl$ (10.2 g, 39.6 mmol) in toluene (50 mL). After 3 h the solution was yellow-brown, and only a small amount of insoluble material remained. The mixture was filtered, and acetone (1 mL) was added to react with any soluble hydridic species which, in trace amounts, decompose, cauing discoloration of the product. The resulting bright yellow solution was concentrated to 20 mL, and after the addition of hexane (10 mL), the mixture was cooled (−30 °C). Two crops of small yellow crystals of **1a** (8.2 g, 23.2 mmol, 60%) were obtained. The actual yield is higher (ca. 85%), as the purity of the $Cp_2Zr(H)Cl$ reagent is approximately 70%.[45] An analysis sample of **1a** was prepared by recrystallization from toluene–hexane. IR (KBr) 3100, 2920 (s), 2840 (m), 1440 (m), 1020 (s), 810 (s), 340 (m) cm^{-1}.

Anal. Calcd for $C_{17}H_{23}ClZr$: C, 57.67; H, 6.55; Cl, 10.01; Zr, 25.77. Found: C, 57.61; H, 6.53; Cl, 10.25; Zr, 25.82.

(B) $Cp_2Zr(\overline{CH(CH_2)_4C}H_2)Cl$ (**1c**) was made by an analogous procedure. $Cp_2Zr(C_2H_5)Cl$ (**1d**) was made by stirring a suspension of $Cp_2Zr(H)Cl$ in THF at 0 °C under ethylene (1 atm). This procedure minimized the ethylene homologation that occurs if the reaction is carried out in toluene at room temperature.

(C) $Cp_2Zr(Me)Cl$ (**1e**) was prepared in 85% yield by a literature procedure from $(Cp_2ZrCl)_2O$ and Me_3Al.[46]

(D) $Cp_2Zr(CH_2\overline{CD(CH_2)_4C}H_2)Cl$ (**1b**) was prepared from $Cp_2Zr(D)Cl$ and methylenecyclohexane. GC/MS analysis of the hydrolysate (aqueous sulfuric acid, 1 M) of this compound showed methylcyclohexane-*1-d* (97%) and methylcyclohexane (3%).

Preparation of Alkylbis(η^5-cyclopentadienyl)hydridozirconium(IV) Complexes (2a–e). These compounds were prepared by reduction of the corresponding Zr(IV) alkyl chloride complexes (**1a–e**) with $LiAlH(OBu\text{-}t)_3$ or $LiAlD(OBu\text{-}t)_3$. The synthesis is described for $Cp_2Zr(CH_2\overline{CH(CH_2)_4C}H_2)H$ (**2a**). The procedure is analogous for the other compounds. However, **2d** and **2e** are thermally stable and can be prepared at room temperature.

(A) A solution of **1a** (14.8 g, 41.3 mmol) in DME (100 mL) was cooled (−30 °C) and stirred as a solution of $LiAlH(OBu\text{-}t)_3$ (47 mL of a 0.88 M solution, 1 equiv of hydride per Zr) in DME was added dropwise over 30 min. Toward the end of this addition, white crystals of **2a** began to form in the yellow solution. After 12 h at −30 °C, the solution was pink-yellow and contained a heavy white precipitate. This was isolated by rapid low-temperature (−50 °C) filtration and washed (−50 °C) with DME (50 mL, 20 mL) and then with hexane (2 × 20 mL). It was dried under vacuum (−20 °C), taken rapidly into the drybox, and stored at −30 °C. The crude material (12 g, 37.6 mmol, 90%) was used in all reactions; at −30 °C in an inert atmosphere it slowly turns pink. ^1H NMR (see Table V). $^{13}C\{^1H\}$ NMR (benzene-d_6, 15 °C) δ 106.6 (Cp), 48.9 (1), 43.3 (1), 38.2 (2), 27.8 (2), 17.5 (1); $\overline{CH_2(CH_2)_4C}HCH_2$ group. IR (KBr) 2900 (s), 2820 (m), 1380 (br s, ν_{ZrH}), 1000 (m), 800 (s) cm^{-1}. M_r (cryoscopic, benzene) 568 ± 40; calculated for dimer, 638.

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(45) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

(46) Surtees, J. R. *Chem. Commun.* **1965**, 567.

Table V. ^1H NMR Data for the Compounds Cp_2ZrRR''

compd[a]	R	R''	solvent	δ	multiplicity, J (Hz)	integral	assignment
1a	$R'CH_2$	Cl	benzene-d_6	5.80	s	10	Cp
				2.0–0.7	br m	11	R'
				1.02	d, $^3J = 6$	2	$ZrCH_2$
1c	R'	Cl	toluene-d_8	5.80	s	10	Cp
				2.0–1.0	br m	11	R'
1d	C_2H_5	Cl	benzene-d_6	5.80	s	10	Cp
				1.7–1.0	A_3B_2	5	C_2H_5
1e	Me	Cl	benzene-d_6	5.70	s	10	Cp
				0.37	s	3	Me
2a	$R'CH_2$	H	THF-d_8, −30 °C	5.82	s	10	Cp
				1.7–0.9	br m	11	R'
				0.35	br	2	$ZrCH_2$
				−2.35	br, $\nu_{1/2} = 4.5$	1	ZrH
2a'	$R'CH_2$	D	THF-d_8, −10 °C	5.82	s	10	Cp
				1.8–0.9	br m	11	R'
				0.20	br d, $^3J = 4$	2	$ZrCH_2$
2d	C_2H_5	H	THF-d_8, 0 °C	5.86	s	10	Cp
				1.23	t, $^3J = 7$	3	CH_2Me
				0.51	q, $^3J = 7$	2	$ZrCH_2$
				−2.15	br	1	ZrH
3a	$R'CH_2$	$OCHMe_2$	benzene-d_6	5.71	s	10	Cp
				4.02	sept, $^3J = 6$	1	OCH
				2.2–1.0	br m	11	R'
				0.89	d, $^3J = 6$	6	$CHMe_2$
				0.84	d, $^3J = 6$	2	$ZrCH_2$
3a'	$R'CH_2$	$OCDMe_2$	THF-d_8	5.97	s	10	Cp
				1.8–1.1	br m	11	R'
				1.00	t, $^3J_{HD} \simeq 1$	6	$CDMe_2$
				0.72	d, $^3J = 6$	2	$ZrCH_2$
3b'	R'_DCH_2	$OCDMe_2$	benzene-d_6	5.74	s	10	Cp
				2.2–1.0	br m	10	R'
				0.90	t, $^3J_{HD} \simeq 1$	6	$CDMe_2$
				0.85	br s	2	$ZrCH_2$
3c	R'	$OCHMe_2$	benzene-d_6	5.73	s	10	Cp
				3.95	sept, $^3J = 6$	1	OCH
				2.2–1.1	br m	11	R'
				0.90	d, $^3J = 6$	6	$CHMe_2$
3d	C_2H_5	$OCHMe_2$	benzene-d_6	5.73	s	10	Cp
				4.00	sept, $^3J = 6$	1	OCH
				1.57	t, $^3J = 6.5$	3	CH_2Me
				1.03	q, $^3J = 6.5$	2	$ZrCH_2$
				0.95	d, $^3J = 6$	6	$CHMe_2$
3e	Me	$OCHMe_2$	benzene-d_6	5.74	s	10	Cp
				4.00	sept, $^3J = 6$	1	OCH
				0.98	d, $^3J = 6$	6	$CHMe_2$
				0.26	s	3	$ZrMe$
	$OCHMe_2$	$OCHMe_2$	benzene-d_6	6.01	s	10	Cp
				4.10	sept, $^3J = 6.5$	2	OCH
				1.04	d, $^3J = 6.5$	12	$OCHMe_2$
	$OCDMe_2$	$OCDMe_2$	benzene-d_6	6.01	s	10	Cp
				1.03	t, $^3J_{HD} \simeq 1$	12	$CDMe_2$
	$OCHMe_2$	Cl	benzene-d_6	5.99	s	10	Cp
				4.04	sept, $^3J = 6.5$	1	OCH
				0.95	d, $^3J = 6.5$	6	$CHMe_2$

[a] $R' = \overline{CH_2(CH_2)_4CH}$; $R'_D = \overline{CH_2(CH_2)_4CD}$.

Elemental analysis of **2a** was not attempted; the solid rapidly discolors at room temperature in inert atmosphere. It was characterized by a series of reactions, which show that the crude material is approximately 90% pure. All weight calculations are per equiv of monomer.

(i) In a 5-mm NMR tube, **2a** (24 mg, 0.08 mmol) was dissolved in benzene-d_6 (1 mL), and methylene chloride (50 μL, 10 equiv) was added. The colorless solution turned yellow over 30 min. Methyl chloride (δ 2.30, s) and **1a** were the only products detected by ^1H NMR. The molar ratio of **1a**:methyl chloride was 1.02:1.

(ii) A solution of **2a** (30 mg, 0.09 mmol) in toluene-d_8 (0.3 mL) was treated with bromobenzene (4 equiv). After 22 h, no starting material remained. The products of the reaction were $Cp_2Zr(CH_2\overline{CH(CH_2)_4CH_2})Br$ (90%) and benzene. ^1H NMR (toluene-d_8) δ 5.8 (s, 10, Cp), 1.09–0.7 (br m, 13, $\overline{CH_2(CH_2)_4C}HCH_2$ group; δ 1.0, d, $ZrCH_2$, $^3J_{HH} = 6$ Hz). The mixture was hydrolyzed (aqueous sulfuric acid, 1 M), and GC analysis showed benzene and methylcyclohexane in a 4:5 ratio.

(iii) Water (2 mL, 1.1 mmol) was vacuum distilled onto a degassed solution of **2a** (0.34 g, 1.07 mmol) in toluene (15 mL). After the solution was stirred several hours, H_2 (0.95 mmol, 90%) was collected via a Toepler pump.

(iv) A solution of **2a** (53 mg, 0.17 mmol) in toluene (3 mL) containing octane (17.1 mg, 0.15 mmol) was connected to a gas buret (10 mL) via a trap at 0 °C. Aqueous sulfuric acid (0.2 mL, 1 M) was added to the clear stirred solution via syringe through a septum cap on the side arm

Table VI. Composition of Mixtures of Deuterated Methylcyclohexanes Formed in the Autodecomposition of the Deuterated Compounds **2b**′, **2b**′ + **2a**, and **2a**′

entry[a]	time, h	yield,[b] %	methylcyclohexane d_0	d_1	$d_1{}'$	d_2	R'_HMe $d_0 + d_1{}^0$	R'_DMe $d_1{}' + d_2$	$R''H$ $d_0 + d_1{}'$	$R''D$[d] $d_1{}^0 + d_2$	% H	% D[c]
i	18	10	2	0	35	63	2	98	37	63	19	81
	46	30	6	4	48	42	10	90	54	46	32	68
	117	72										
ii	6[e]		14	5	48	33	19	81	62	38	41	59
iii	6[e]		19	3	48	30	22	78	67	33	45	55
iv	18	18	36	7	49	8	43	57	85	15	64	36
	46	58	42	7	45	6	49	51	87	13	68	32
	117	81										
v	*f*	*f*	51	4	44	1	55	45	95	5	75	25
	22	35	39	10	42	9	49	51	81	19	65	35
	65	60	43	10	38	9	33	47	81	19	67	35

[a] (i) **2b**′ in toluene; (ii) **2b**′ in toluene-d_8; (iii) **2b**′ in benzene-d_6; (iv) an equimolar mixture of **2a** and **2b**′ in toluene; (v) **2a**′ in toluene. [b] % yield based on Zr. [c] $\% H = 0.5(2d_0 + d_1{}^0 + d_1{}')$; $\% D = 0.5(d_1{}^0 + d_1{}' + 2d_2)$. Only two positions of the methylcyclohexane product (a single substituent at the α position and that at the 1-position) can show H/D incorporation. $R'_X = \overline{CH_2(CH_2)_4C}X$; X = H, D; $R'' = R'_XCH_2$. [e] Time in days. [f] Hydrolysate.

of the Schlenk flask. Hydrogen (4.45 mL, 0.18 mmol, 105%) was evolved. After 4 h the solution was analyzed by GC. Methylcyclohexane (0.15 mmol, 88%) was detected.

(v) Acetone (0.1 mL, 1.4 mmol, 8 equiv) was added to a solution of **2a** (50 mg, 0.16 mmol) in toluene (2 mL). Reaction was rapid, and after 15 min the volatiles were removed and the white crystalline residue was redissolved in benzene-d_6. ^1H NMR showed only $Cp_2Zr(CH_2\overline{CH(CH_2)_4CH_2})(OPr\text{-}i)$ (**3a**) (Table V). This method was used to characterize each of the compounds **2a–e**.

(vi) A solution of **2a** (0.17 g, 0.54 mmol) in toluene (10 mL) containing octane (34.8 mg, 0.31 mmol) was treated with hydrogen chloride (1.5 mmol) at −80 °C. A rapid reaction occurred, hydrogen was evolved, and a white solid precipitated. After 45 min, the mixture was warmed slowly to room temperature. Volatiles were removed from the clear colorless solution and analyzed by GC. Methylcyclohexane (0.47 mmol, 87%) was detected. The white solid was identified by ^1H NMR comparison with an authentic sample as Cp_2ZrCl_2 (0.14 g, 0.5 mmol, 90%). ^1H NMR (toluene) δ 5.90 (s).

(B) The deuterated compound **2a**′ was prepared by reducing **1a** with $LiAlD(OBu\text{-}t)_3$. Deuterium (>95%) at the hydride position was detected with acetone to give **3a**′ (Table V). IR (KBr) 2900 (s), 2825 (m), 1435 (m), 990 (br, s, ν_{ZrD}), 800 (s) cm^{-1}.

Similarly, **2b**′ was made from **1b** by reduction with $LiAlD(OBu\text{-}t)_3$.

Preparation of $Cp_2Zr(COCH_2\overline{CH(CH_2)_4CH_2})Cl$ (5). A bright yellow solution of **1a** (0.95 g, 2.9 mmol) in methylene chloride (15 mL) was carbonylated (4 atm) and after 30 min it was colorless. After 3 h the solution was transferred via cannula to a Schlenk flask and reduced in volume to 5 mL. Hexane (5 mL) was added, the solution was cooled (−30 °C), and cream crystals of **5** (1.1 g, 2.7 mmol, 95%) were obtained. Recrystallization from methylene chloride–hexane gave an analysis sample. ^1H NMR (benzene-d_6) δ 5.60 (s, 10, Cp), 2.72 (d, 2, $COCH_2$, ^3J = 6.5 Hz), 1.9–0.7 (br m, 11, $CH_2(CH_2)_4CH$). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 238.7 (ZrCO), 109.4 (Cp), 54.8 ($COCH_2$), 33.9, 33.5, 33.4, 26.3. IR (methylene chloride) 2933 (s), 2856 (m), 1548 (m), 1098, 1018 (s), 814 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{23}ClOZr$: C, 57.06; H, 6.06; Cl, 9.28; Zr, 23.88. Found: C, 56.60; H, 6.13; Cl, 9.35; Zr, 24.08.

Preparation of $(Cl)Cp_2Zr(\mu\text{-}(O\text{-}CHCH_2\overline{CH(CH_2)_4CH_2}))ZrCp_2(Cl)$ (4). A suspension of $Cp_2Zr(H)Cl$ (1.10 g, 3 mmol for 70% purity)[45] in a colorless solution of **4** (1.0 g, 2.7 mmol) in toluene (20 mL) was stirred for 12 h. Most of the $Cp_2Zr(H)Cl$ had dissolved, and the dark yellow solution was filtered. An aliquot was pumped down and analyzed by ^1H NMR (benzene-d_6), which showed a complex pattern in the Cp region (δ 6.5–5.5), a distorted triplet (δ 3.6), the cyclohexyl group, and broad singlets ($\nu_{1/2}$ = 3 Hz) at δ −1.40 and −1.60. Cp_2ZrCl_2 (δ 5.9) was present. Hydrolysis with D_2SO_4/D_2O (1 M) evolved hydrogen and produced 2-cyclohexyl-1-deuterioethanol (GC/MS, comparison with authentic sample; no molecular ion was observed, and it is assumed that deuterium was originally present at the alkoxy position).

The toluene solution of the crude material was treated with methylene chloride (2 mL). It rapidly turned bright yellow. After 2 h, the solvent was removed and the major compound **4** was isolated as yellow crystals (1.4 g, 50%). Fractional crystallization from toluene–octane removed most of the Cp_2ZrCl_2 contaminant.

Anal. Calcd for $C_{28}H_{34}Zr_2Cl_2O$: C, 52.55; H, 5.36. Found: C, 52.29; H, 5.20.

Hydrolysis of **4** with D_2SO_4/D_2O (1 M) gave 2-cyclohexyl-1-deuterioethanol and $(Cp_2ZrCl)_2O$ [^1H NMR (benzene-d_6) δ 6.10; comparison with authentic sample]. ^1H NMR (100 MHz) (toluene-d_8, −22 °C) δ 6.12 (s, 5, Cp), 6.04 (s, 5, Cp), 5.76 (s, 5, Cp), 5.73 (s, 5, Cp), 3.36 (d of d, X part of an ABX, 1, OCH, $|^3J_{AX} + {}^3J_{BX}|$ = 14 Hz), 3.06 (br m, 1), 2.2–1.0 (br m, 12, cyclohexylmethyl group); the broad resonance at δ 3.06, which appears to belong to a proton of the cyclohexylmethyl group, has not been assigned. $^{13}C\{^1H\}$ NMR (toluene-d_8, −50 °C) 116.0 (s, Cp), 115.5 (s, Cp), 109.1 (s, Cp), 108.5 (s, Cp), 92.6 (s, OCH), 45.2 (s, $OCHCH_2$), 37.0 (C_3)*, 35.2 (C_4)*, 33.6 ($C_{4'}$)*, 26.9 (C_5, $C_{5'}$, C_6)*; (*) $CH_2(CH_2)_4CH$, broadened singlets.

Hydrogenation and Decomposition Reactions. In all hydrogenations of **2**, a weighted amount (ca. 0.5 equiv) of octane and hexane was used as an internal GC standard; an aliquot of the solution of **2** was taken prior to hydrogenation and hydrolyzed (aqueous sulfuric acid, 1 M) to determine accurately the amount of **2** present. Unless otherwise stated, yields of methylcyclohexane are based on the amount of methylcyclohexane in the hydrolysate. Mixtures of methylcyclohexane and octane were analyzed by GC and by GC/MS.

Authentic samples of $Cp_2Zr(OCHMe_2)_2$, $Cp_2Zr(OCDMe_2)_2$, and alkylzirconium alkoxide were prepared by the reaction of the corresponding Zr(IV) hydride or deuteride with acetone, and their ^1H NMR spectra are recorded in Table V.

Decomposition of 2a Derivatives. Solutions of (i) **2b**′ (95 mg, 0.3 mmol) in toluene (5 mL) and (ii) **2b**′ (36 mg, 0.1 mmol) and **2a** (38 mg, 0.1 mmol) in toluene (3.8 mL) were stirred at room temperature, and they turned pink through red to purple over several days. Aliquots were periodically removed and analyzed by GC and GC/MS for the amount (octane internal standard) and composition of the methylcyclohexane product [Table VI (i), (iv)]. A trace (ca. 3%) of methylenecyclohexane (undeuterated) was detected in the first two aliquots (GC/MS identification).

In control experiments small samples of **2b**′ (ca. 15 mg, 0.05 mmol) were stirred in toluene-d_8 (5 mL) and in benzene-d_6 (5 mL) for 6 days. The evaporative distillates were analyzed by GC/MS [Table VI (ii), (iii)].

Hydrogenations. (A) Hydrogenation of $Cp_2Zr(CH_2\overline{CH(CH_2)_4CH_2})H$ (2a). A solution of **2a** (0.28 g, 0.88 mmol) in toluene (15 mL) was divided into three 5-mL aliquots, which were hydrogenated at 1, 2.1, and 4.6 atm. The solutions were sampled during the initial stages of the reaction. Aliquots were withdrawn rapidly from the Fischer-Porter apparatus by cannula transfer to an argon-filled evaporative distillation apparatus. During this transfer the system was depressurized for a short time (<45 s). Samples from the reaction at 1 atm were withdrawn via an argon-flushed syringe and then the buret was rapidly releveled. The samples were immediately degassed and stored under argon at −78 °C until evaporative distillation for GC analysis (Table VII). The residues were resuspended in toluene and reacted with acetone (ca. 5 equiv), and the crude products $Cp_2Zr(OPr\text{-}i)_2$ and **3a** were analyzed by ^1H NMR spectroscopy (Table VII).

(B) Hydrogenation of 2a′. A solution of **2a**′ (80 mg, 0.25 mmol) in toluene (4 mL) was hydrogenated (1 atm) at room temperature. After 40 min the solution was cloudy, and H_2 (15%, 0.04 mmol) had been absorbed. In 10 h, H_2 (ca. 0.15 mmol) had been absorbed and me-

Table VII. Methylcyclohexane Formed in the Hydrogenations of **2a** at Various Pressures

pressure, atm	temp, °C	time, min	methylcyclohexane		Cp_2ZrH_2,[b] %	$Cp_2Zr(R)H$,[b,c] %
			mmol	%[a]		
1.0	22	0	0.03	4		
		15	0.11	15		
		30	0.14	19		
		47.5	0.22	30	24	76
		81	0.33	45		
		150	0.40	55	60	40
		210	0.46	63		
		270	0.47	65		
2.1	23	15	0.15	20		
		30	0.24	34		
		45	0.33	45		
4.6	23	15	0.26	34		
		30	0.42	58		
		47	0.53	73		

[a] % relative to methylcyclohexane in the hydrolysate (0.73 mmol, 85% on the basis of **2a**). [b] Measured from ^1H NMR integration of the $Cp_2Zr(OPr\text{-}i)_2$ and **3a** formed from the reaction of the residues with acetone. [c] $R = \overline{CH_2(CH_2)_4CH}CH_2$.

Table VIII. Analysis of the Products of the Reaction of **2a** with D_2 at 1 atm

time, min	% reaction[a]	$Cp_2Zr(OPr\text{-}i)_2$			$Cp_2Zr(CH_2R')(OPr\text{-}i)$[c]		
		yield, %	composition[b]		yield, %	composition[b]	
			% H	% D		% H	% D
17	2	2	*f*	*f*	98	86	14
30	3	3	73	27	97	78	22[d]
60	5[d]	5	69	31	95	70	30
120	20	20	58	42	80	61	39
210	46[e]	33	46	54	67	56	44
300	65[e]	57	41	59	43	44	56

[a] Estimated from ^1H NMR integration of $Cp_2Zr(OPr\text{-}i)_2$ and $Cp_2Zr(CH_2R')(OPr\text{-}i)$. [b] % H/D at the α-carbon of the isopropoxy groups. [c] $R' = \overline{CH_2(CH_2)_4CX}$–; X = H or D. [d] Estimates at these early stages may be in error. [e] GC yields of methylcyclohexane are based on methylcyclohexane (1.8 mmol) in the hydrolysate. [f] Small.

thylcyclohexane (0.19 mmol) was detected. Methylcyclohexane was analyzed by GC/MS (Table I); the inorganic residue was reacted with excess acetone as above; the $Cp_2Zr(OPr\text{-}i)_2$ which formed was analyzed by ^1H NMR spectroscopy and showed 17% incorporation of deuterium at the α-carbon of the isopropoxy group.

(C) Hydrogenation of $Cp_2Zr(CH_2\overline{CD(CH_2)_4CH_2})D$ (2b′). A solution of **2b′** (ca. 0.2 g, 0.6 mmol) in toluene (8 mL) was stirred under H_2 (1 atm) on a 10-mL gas buret. Three aliquots were withdrawn from the mixture during the reaction, quenched with acetone (0.1 mL), stirred until all the precipitate had reacted (ca. 45 min), and then evaporatively distilled. The distillates were analyzed by GC (Tables I, VIII). The white residues were redissolved in benzene-d_6 and then analyzed by ^1H NMR spectroscopy (Table III).

In an analogous reaction, the hydrogenation of **2b′** (92 mg, 0.29 mmol) in toluene (5 mL) was monitored on a gas buret. After 6 h the H_2 uptake was 0.21 mmol (73%) and methylcyclohexane (0.23 mmol, 80%) had been formed. The volatiles were analyzed by GC/MS (Table I), and the residue was reacted with acetone. The resulting $Cp_2Zr(OPr\text{-}i)_2$ was analyzed by ^1H NMR spectroscopy.

(D) Reaction of 2a with D_2. (i) A similar reaction was performed with **2a** (0.57 g, 1.8 mmol) in toluene (23 mL), and GC/MS analysis of the methylcyclohexane produced is presented in Table I.

(ii) A solution of **2a** (0.1 g, 0.32 mmol) in toluene (10 mL) was stirred under D_2 (4.5 atm) for 20 min. The resulting clear, very pale yellow solution was reacted with acetone (0.1 mL) under nitrogen for 1 h. No $Cp_2Zr(OPr\text{-}i)_2$ was detected by ^1H NMR analysis of this product. The major (>95%) product was the zirconium(IV) alkyl isopropoxide, which was shown by ^1H NMR spectroscopy, and by GC/MS analysis of its hydrolysate (H_2O, room temperature, 8 h), to be a mixture of $Cp_2Zr(CH_2R')(OCHMe_2)$ (44%) and $Cp_2Zr(CH_2R')(OCDMe_2)$ (56%); $R' = \overline{CH_2(CH_2)_4CH}$.

(E) Reaction of Cp_2ZrH_2 with D_2. (i) Cp_2ZrH_2 (0.14 g, 0.62 mmol) was suspended in toluene (6 mL) and stirred vigorously under D_2 (1 atm) at room temperature for 18 h. The appearance of the mixture did not change. Excess acetone was added, and the products were analyzed by ^1H NMR spectroscopy. The product, $Cp_2Zr(OPr\text{-}i)_2$, contained no deuterium at the α-carbon of the isopropoxy group.

(ii) A solution of $(Cp_2ZrCl)_2O$ (0.4. g, 0.93 mmol) in THF (20 mL) was stirred under D_2 (1 atm) for 1 h. A solution of $LiAlH_4$ (0.39 mL of a 2.4 M solution, 2 equiv of hydride per Zr) in THF was added dropwise to the stirred solution over 10 min, and the mixture turned pink. No precipitation of Cp_2ZrH_2 occurred for over 30 min. After 15 h under D_2, the white precipitate was isolated by filtration from the red solution and washed with toluene. It was resuspended in toluene and reacted with excess acetone for 1 h. The resulting $Cp_2Zr(OPr\text{-}i)_2$ was analyzed by ^1H NMR, which showed 14% deuterium incorporation at the α-carbon of the isopropoxy groups.

(F) Reaction of 2a with Cp_2ZrD_2. A suspension of Cp_2ZrD_2 (50 mg, 0.22 mmol) in a solution of **2a** (50 mg, 0.16 mmol) in toluene (3 mL) was stirred for 2 h. Acetone (0.1 mL) was added to the pale purple-pink solution, and after 1 h the volatiles were removed and the residue analyzed by ^1H NMR spectroscopy (benzene-d_6) for deuterium incorporation at the α-carbon of the isopropoxy groups:

	$Cp_2Zr(OPr\text{-}i)_2$	$Cp_2Zr(CH_2R')(OPr\text{-}i)$
% H	30	52
% D	70	48

$R' = \overline{CH_2(CH_2)_4CX}$;
X = H, D

The mixture was hydrolyzed, and the methylcyclohexane which formed was analyzed by GC/MS as a mixture of d_0 (66%) and d_1' (34%) compounds. An equimolar mixture of $Cp_2Zr(OPr\text{-}i)_2$ and **3a′** showed no evidence of exchange of isopropoxy ligands over 2 days at room temperature.

Hydrogenation of $Cp_2Zr(CH_2\overline{CH(CH_2)_4CH_2})Cl$ (1a). (a) Reactions at Elevated Temperature. Complex **1a** (370 mg, 1.07 mmol) was dissolved in 10 mL of toluene, and *n*-hexane was added as an internal standard. The solution was transferred via syringe to a H_2-filled Fischer-Porter bottle. Stirring and heating were begun, and the reactor was pressurized to the desired level (the reactor bottle was wrapped with Al foil to minimize photochemical decomposition of the Cp_2ZrHCl product). The reaction was stopped by cooling the vessel to room temperature, depressurization, and injection of a solution of 2–3 equiv of acetone (in toluene). After 2 h, the reaction mixture was removed by syringe and was transferred to an Ar-filled flask for evaporative distillation. Volatiles were collected and were analyzed by GC and GC/MS. Distillation solid residues were analyzed by ^1H NMR spectroscopy and by analysis of volatiles produced by hydrolysis with 2 N H_2SO_4.

(b) High-Pressure Work (0 °C). A solution of **1a** was prepared as described above and was loaded into the Parr "Mini Reactor" autoclave, which was then placed in an ice bath for 1 h. The autoclave was then pressurized. After 10 h it was depressurized and the reaction mixture was poured into a 50-mL Schlenk flask. Acetone was then added, and samples were analyzed as described above. Results are summarized in Table IV.

(G) Hydrogenation of $(Cl)Cp_2Cr(\mu\text{-}(O\text{-}CHCH_2\overline{CH(CH_2)_4CH_2}))ZrCp_2(Cl)$ (3). A dark yellow solution of **4** (0.23 g, 0.36 mmol) in benzene (15 mL) was reacted with H_2 (95 atm) at room temperature for 24 h. The resulting pale yellow solution, which contained a pale prepcipitate, was concentrated and analyzed by ^1H NMR spectroscopy. One major Cp-containing compound (δ 5.98, s) and a triplet (δ 3.93, *J* = 7 Hz) were present in a ratio of approximately 4.5:1. Several minor Cp products, including Cp_2ZrCl_2 and three peaks at δ 5.65, 5.58, and 5.35 in a 1:1:2 ratio, which had been present in the crude product of the reaction of **5** with $Cp_2Zr(H)Cl$, were also formed.

Hexadecane (22 μl, 0.11 mmol) was added to the combined solution which was hydrolyzed with excess D_2O. Hydrogen was evolved and the major inorganic products was $(Cp_2ZrCl)_2O$ [^1H NMR (benzene) δ 6.10]. The layers were separated, and the aqueous phase was washed several times with small volumes of diethyl ether. The combined organic layers were analyzed by GC (120 °C). 2-Cyclohexylethanol (0.3 mmol, 90%) was detected. It contained no deuterium at C_1.

(H) Hydrogenation of $Cp_2Zr(CH_2CH_2Bu\text{-}t)_2$. (i) Preparation of $Cp_2Zr(CH_2CH_2Bu\text{-}t)_2$. 3,3-Dimethyl-1-butene (1 mL, 7.8 mmol) was added to a suspension of Cp_2ZrH_2 (0.88 g, 4 mmol) in benzene (10 mL), and the mixture was heated at 45 °C for 8 h. Black finely divided material was removed by filtration through Celite, and the filtrate was pumped down to a green yellow oil. The product could not be crystallized, but ^1H NMR spectra showed only one major component (>95%). ^1H NMR (benzene) δ 5.75 (s, 10, Cp), 1.5–1.1 (m, 4, CH_2Bu-*t*), 0.88 (s, 18, Me), 0.5–1.0 (m, 4, $ZrCH_2$).

(ii) A solution of $Cp_2Zr(CH_2CH_2Bu\text{-}t)_2$ (0.5 g, 1.3 mmol) was dissolved in toluene (20 mL) and stirred under H_2 (1 atm) attached to a gas buret (50 mL). After 2 days, most of the starting material was recovered.

(I) Hydrogenation of $Cp_2Zr(CO\overline{CH_2CH(CH_2)_4CH_2})Cl$ (5). $Cp_2Zr(CO\overline{CH(CH_2)_4CH_2})Cl$ (5) (0.55 g, 1.4 mmol) was dissolved in toluene (20 mL). It failed to react with H_2 (92 atm) over 2 days at room temperature.

Acknowledgment. We acknowledge generous support for this work by the National Science Foundation (Grant No. CHE-79-00996). K.I.G. also acknowledges support from a University Travelling Scholarship from the Australian National University.

Registry No. 1a, 54634-15-0; **1b**, 80789-41-9; **1c**, 37343-38-7; **1d**, 12109-84-1; **1e**, 1291-45-8; **2a**, 69058-71-5; **2a′**, 67063-44-9; **2b**, 67077-97-8; **2b′**, 67660-04-2; **2c**, 80789-42-0; **2d**, 80789-43-1; **2e**, 67659-92-1; **3a**, 80789-44-2; **3a′**, 80789-45-3; **3b′**, 80789-46-4; **3c**, 80789-47-5; **3d**, 80789-48-6; **3e**, 80789-49-7; **4**, 69106-29-2; **5**, 71068-71-8; **6** (X = Cl), 80789-50-0; $Cp_2Zr(H)Cl$, 37342-97-5; $Cp_2Zr(D)Cl$, 80789-51-1; Cp_2ZrH_2, 37342-98-6; Cp_2ZrD_2, 80789-52-2; $Cp_2Zr(OPr\text{-}i)_2$, 78091-18-6; $Cp_2Zr(OCDMe_2)_2$, 80789-53-3; $(Cp_2ZrCl)_2O$, 12097-04-0; $Cp_2Zr(OCDMe_2)Cl$, 80789-54-4; $Cp_2Zr(CH_2CH_2Bu\text{-}t)_2$, 80789-55-5; 3,3-dimethyl-1-butene, 558-37-2; **6** (X = H), 80789-56-6.

Stereochemically Nonrigid Silanes, Germanes, and Stannanes. 9.[1] Chiral Silylcyclopentadienes and Related Compounds: Mechanistic and Stereochemical Definition of Fluxional Behavior

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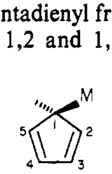
Abstract: Chirality at the Si atom in the silylcyclopentadienes $C_5H_5Si^*H(R)Cl$ (R = Me, *n*-Bu, or Me_3SiCH_2) and $C_5H_5Si^*H(i\text{-}Pr)(Me)$ results in anisochronicity among both pairs of olefinic ring nuclei ($C^{2,5}$ and $C^{3,4}$) in slow-limit ^{13}C NMR spectra. The larger diastereotopic shift is attributed in each system to that between those nuclei nearest to the chiral Si center, i.e., C^2 and C^5. With increasing temperature the pair of resonances so distinguished coalesces more rapidly with C^1 than do $C^{3,4}$, corresponding to fluxional characteristics qualitatively interpretable only in terms of a 1,2 pathway as the lowest energy rearrangement. This conclusion is supported by comparison with data simulated by using a five-site exchange program which (a) substantiate that 1,2 and 1,3 pathways are distinguishable and (b) yield $\Delta G^{\ddagger}$ = 61.3 (±1.3) and 59.8 (±2.7) kJ mol^{-1} for the Me_3SiCH_2 and *i*-Pr compounds, respectively. For the latter and in $C_5H_5M^*Me(i\text{-}Pr)(Ph)$ (M = Ge or Sn), ^1H and ^{13}C NMR spectra show magnetically nonequivalent methyl resonances for the *i*-Pr substituent; these diastereotopic shifts are temperature invariant, establishing that intramolecular metallotropic rearrangement occurs with retention of configuration at the migrating center M. Relationships with Woodward–Hoffmann [1,5] sigmatropic behavior are discussed.

Structural chemistry has been transformed by the advent of variable-temperature NMR spectroscopy, which has demonstrated that for certain kinds of molecules more than one configuration is thermally accessible at or near ambient temperature, resulting in facile intramolecular rearrangement between degenerate or nondegenerate states. The consequent dynamic stereochemistry has been termed *fluxional behavior*[3] where a structure alternates between two or more identical configurations (i.e., those having identical free energy), while we have called related systems[4] for which nonidentical configurations are accessed *"quasi-fluxional"*. The development of organometallic chemistry has presented a fascinating array of such molecules,[5] although important examples also exist which are strictly organic[3,6] or inorganic[7] in type.

Perhaps the class of compounds most closely identified with the initial recognition and subsequent characterization of fluxional behavior has been the *monohapto*cyclopentadienyl (η^1-C_5H_5) compounds of transition and nontransition metals. Cotton has provided a definitive perspective on initial developments in this area in several review articles[5,8,9] (of which one[8] is splendidly informal), in which the difficulties inherent in identifying the rearrangement pathway whereby a metal atom migrates around a cyclopentadienyl framework are explained. Thus differentiation between 1,2 and 1,3 movement of M in compounds (**1**) is a



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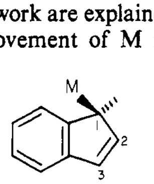

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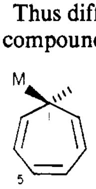

3

nontrivial problem, the solution of which depends on distinguishing between NMR signals due to the two pairs of *chemically* (but not magnetically) equivalent nuclei in the C_5 ring. Various experiments directed toward this end have been documented,[10] all of which are consistent with, but do not prove, a 1,2-type rearrangement. Further indirect evidence to support this conclusion has been adduced from the nonrigid characteristics[11] of η^1-indenyl

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