mesh Chromosorb P stationary phase at 40 °C, 40 mL of N H_2/min., HWD. All manipulations involving air-sensitive organometallic compounds were carried out by using the usual anaerobic technique.[28] Reactions under 80 bar of CO were performed with 6-mL samples in a 20-mL stainless-steel rocking autoclave.

Materials. The solvents were dried in the usual way and stored under CO. Commercial dienes were freshly distilled under CO. Stock solutions of $HCo(CO)_4$ were prepared in *n*-octane from $Co_2(CO)_8$, DMF, and concentrated HCl.[23] $DCo(CO)_4$ was prepared from $HCo(CO)_4$ solutions by H–D exchange with a 50-fold molar excess of D_2O.[29] Isotopic purity was >95% as calculated from mass spectrometric measurements of its decomposition products. Dicobalt octacarbonyl was doubly recrystallized first from CH_2Cl_2 and then from *n*-heptane under CO.

Kinetic runs were performed in a gasometric apparatus fitted with a mercury-filled gas burette. A 5-L buffer flask was connected to the levelling vessel of the gas burette and kept at the pressure of the reaction vessel. All parts of the apparatus were thermostated (±0.05 °C). The actual total pressure was determined in millimeters of Hg by using an open mercury manometer measuring the pressure difference between the atmosphere and the reaction vessel. The reaction was started by injecting the diene into the vigorously stirred solutions of $HCo(CO)_4$. The initial rate of CO uptake and the initial rate of CO release were calculated from the change of gas volume with time.

Preparation of Aldehyde 2,4-Dinitrophenylhydrazones. To a solution of 0.33 mL of 2,3-dimethyl-1,3-butadiene (2.65 mmol) in 9 mL of *n*-heptane under CO at 10 °C was added 4.6 mL of a 0.65 M solution of $HCo(CO)_4$ in *n*-octane (3.0 mmol) dropwise in 50 min. During this time 0.8 mmol of CO was absorbed. The reaction mixture was stored on dry ice overnight and was filtered in the cold to separate crystalline $Co_2(CO)_8$. A solution of 198 mg (1 mmol) of 2,4-dinitrophenylhydrazine and 0.15 mL of concentrated HCl in 5 mL of methanol was added to the filtrate and the mixture evaporated to dryness in vacuo. The hydrazone was extracted with CH_2Cl_2, and after evaporation of the solvent it was recrystallized twice from benzene. A 50-mg (0.17-mmol) sample of yellow crystalline product resulted. TLC chromatography on Silicagel G (benzene–petroleum ether = 5:1) showed the presence of three isomers, all of which had the expected M^+ 292 in their mass spectra.

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Registry No. 1, 16842-03-8; 2, 513-81-5; *trans*-1,3-pentadiene, 2004-70-8; *cis*-1,3-pentadiene, 1574-41-0; *trans,trans*-2,4-hexadiene, 5194-51-4; *cis,trans*-2,4-hexadiene, 5194-50-3; isoprene, 78-79-5; 1,3-cyclohexadiene, 592-57-4; 1,3-cyclopentadiene, 542-92-7; α-terpinene, 99-86-5; (*R*)-α-phellandrene, 4221-98-1; D_2, 7782-39-0.

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Zirconocene-η^4-1,3-Pentadiene Complex and Its Higher Homologues. A New Synthetic Method Involving σ–π Rearrangement of the Hydrido-2,4-pentadienylzirconium Species

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The (1,3-pentadiene)zirconocene complex and its higher homologues of the type $(\eta^5\text{-}C_5H_5)_2Zr(CR^1(CH_3){=}CR^2CR^3{=}CR^4H)$ were prepared by reaction of $(\eta^5\text{-}C_5H_5)_2ZrHCl$ with alkyl-substituted or nonsubstituted pentadienyl anions through novel σ–π rearrangement of hydrido-2,4-pentadienylzirconium species. The ^1H NMR studies on these complexes revealed that the 1,3-pentadiene and 2,4-hexadiene complexes are composed of ca. 1:1 mixture of s-cis and s-trans isomers while each of the complexes containing 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 1-(trimethylsilyl)-1,3-pentadiene, and 1,5-bis(trimethylsilyl)-1,3-pentadiene ligands consists of a single isomer of s-cis structure. The process of hydrogen transfer was elucidated on the basis of the analysis of the stoichiometric reaction between $(\eta^5\text{-}C_5H_5)_2ZrDCl$ and (2-methylpentadienyl)potassium. The reaction of $(\eta^5\text{-}C_5H_5)_2Zr$(2,4-hexadiene) with 1-alkenes or 2-butyne showed that the coordinated diene is easily expelled to give zirconacyclopentanes or a zirconacyclopentadiene derivative, respectively. The addition of butanal or 3-pentanone resulted in double insertion into the 2,4-hexadiene moiety to selectively afford 3-hexene-1,6-diols through hydrolysis.

Introduction

Chemistry of diene complexes of group 4A early transition metals has received considerable attention in recent years because of their unique structural pattern coupled with their unusually high selectivity observed in the reaction with various electrophiles. For example, *s-trans*-η^4-diene coordination to mononuclear metal species was first discovered in the case of zirconocene complexes,[1,2] and the extremely high regioselective dienylation of saturated or unsaturated carbonyl compounds has been achieved with these complexes.[3,4] The following four procedures have been known for the preparation of a series of zirconium–diene complexes: (1) reaction of Cp_2ZrCl_2 (Cp =

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Table I. Characterization of Cp_2Zr(1,3-pentadiene) Complexes

		anal.				mass (M^+)	
		obsd		calcd			
complexes	mp, °C	C	H	C	H	obsd (distribution/%)	calcd for ^{90}Zr
1a + **1b**	96-97	62.01	6.31	62.33	6.27	288, ^{90}Zr (43.3); 289, ^{91}Zr (17.0); 290, ^{92}Zr (17.1); 292, ^{94}Zr (14.7)	288
2a + **2b**	107-109	62.71	6.46	63.31	6.64	302, ^{90}Zr (43.8); 303, ^{91}Zr (1717); 304, ^{92}Zr (1616); 306, ^{94}Zr (14.7)	302
3	95	62.89	6.72	63.31	6.64	302, ^{90}Zr (40.6); 303, ^{91}Zr (19.5); 304, ^{92}Zr (16.5); 306, ^{94}Zr (13.9)	302
4	110	62.10	6.68	63.31	6.64	302, ^{90}Zr (42.6); 303, ^{91}Zr (17.4); 304, ^{92}Zr (16.50; 306, ^{94}Zr (15.3)	302
5	99	63.38	6.98	64.29	6.98	316, ^{90}Zr (45.0); 317, ^{91}Zr (17.6); 318, ^{92}Zr (15.6); 320, ^{94}Zr (13.8)	316
6	101	59.73	7.24	59.77	7.24	360, ^{90}Zr (40.0); 361, ^{91}Zr (17.0); 362, ^{92}Zr (16.2); 364, ^{94}Zr (14.3)	360
7	95	56.23	7.69	58.13	7.90	432, ^{90}Zr (34.6); 433, ^{91}Zr (20.1); 434, ^{92}Zr (18.4); 436, ^{94}Zr (13.2)	432

Table II. Molar Ratio of *s-cis* to *s-trans*-1,3-Pentadiene Complexes and 1,3-Butadiene Derivatives

							molar ratio/%	
complexes	R^1	$R^{1'}$	R^2	R^3	R^4	$R^{4'}$	*s*-cis	*s*-trans
1a + **1b**	H	H	H	H	CH_3	H	42	58
2a + **2b**	CH_3	H	H	H	CH_3	H	35	64
2c + **2d**	H	H	H	H	C_2H_5	H	39	61
3	H	H	CH_3	H	CH_3	H	100	0
4	H	H	H	CH_3	CH_3	H	100	0
5	H	H	CH_3	H	CH_3	CH_3	100	0
6	$(CH_3)_3Si$	H	H	H	CH_3	H	100	0
7	$(CH_3)_3Si$	H	H	H	$CH_2Si(CH_3)_3$	H	100	0
Zr butadiene[a]	H	H	H	H	H	H	30-70	70-30
Zr isoprene[b]	H	H	CH_3	H	H	H	100	0
Zr 2,3-dimethylbutadiene[c]	H	H	CH_3	CH_3	H	H	100	0

[a] Cp_2Zr(butadiene). The s-cis/s-trans ratio varies depending on the temperature. [b] Cp_2Zr(isoprene). [c] Cp_2Zr(2,3-dimethylbutadiene). The numbering system is shown in eq 1.

η^5-C_5H_5) with 2-butene-1,4-diylmagnesium;[5] (2) photochemical reaction of $Cp_2Zr(phenyl)_2$ in the presence of conjugated dienes;[2,6] (3) ligand exchange reaction between Cp_2Zr(diene) and dienes of higher π acidity;[5] (4) coordination of 1,3-butadiene to low-valent zirconium species generated by reduction with Li or Na amalgam.[7]

Extention from the butadiene complex $Cp_2Zr(C_4H_6)$ to higher homologues of the 1,3-pentadiene series is fundamentally important in the understanding of the scope of the chemistry of zirconium–diene complexes. However, the above four methods cannot be applied to the preparation of 1,3-pentadiene complexes of group 4 elements because the desired 2-pentene-1,4-diyldilithium or 2-pentene-1,4-diylmagnesium is not available and $Cp_2Zr(aryl)_2$ is completely inert to 1,3-pentadiene or its alkylated derivatives except for 2,4-hexadiene under photoirradiation.[2] Development of alternative methods is required for synthesizing a variety of zirconium–1,3-pentadiene complexes.

We describe herein a new method for the preparation of an extensive series of zirconium–1,3-pentadiene complexes together with NMR studies and characteristic reactions toward alkenes, alkynes, carbon monoxide, and carbonyl compounds. The key preparative strategy employed here is based on the σ–π rearrangement occurring in the reactive pentadienylhydridozirconium species, $ZrH(CH_2CR^1{=}CR^2CR^3{=}CHR^4)$, generated by the reaction of Cp_2ZrHCl with various pentadienyl anions, $(CH_2\underset{\cdots}{-}CR^1\underset{\cdots}{-}CR^2\underset{\cdots}{-}CR^3\underset{\cdots}{-}CHR^4)^-$.

Preparation of 1,3-Pentadiene Complexes of Zirconium. We have found that the reaction of Cp_2ZrHCl with 1 equiv of substituted or nonsubstituted pentadienyl anions affords a series of zirconium–1,3-pentadiene complexes in good yield (eq 1). To our knowledge, this is the first example of a η^4-1,3-pentadiene complex of early transition metals.[8] The result of chemical characterization of these complexes is given in Table I. The relative intensities of the parent peaks in MS are in good accord with the natural abundances of zirconium isotopes calculated for monomeric species. A typical experimental procedure is as follows. A pentadienyl anion was treated with 1 equiv of Cp_2ZrHCl in THF at 0–20 °C, and the solution was evaporated to dryness. The residue was then extracted with hexane and cooled to –20 °C to give Cp_2Zr(1,3-pentadiene) as air- and moisture-sensitive, deep red crystals. The ^1H NMR spectrum revealed that the 1,3-pentadiene complex **1** consists of a mixture of s-cis and s-trans isomers with an 18-electron configuration. The ratio did not depend on the identity of the metal (Li or K) or the geometry of the starting carbanions; i.e., pentadienyllithium,[9] which assumes the W form (*E,E* configuration) in THF, produced a 42/58 mixture of the *s-cis*-η^4-(*E*)-1,3-pentadiene complex

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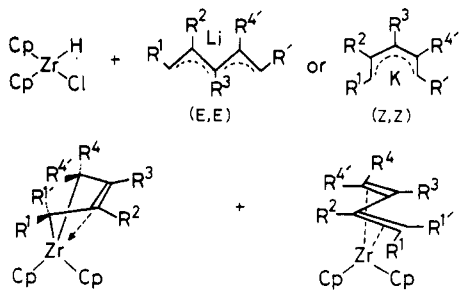


(1)

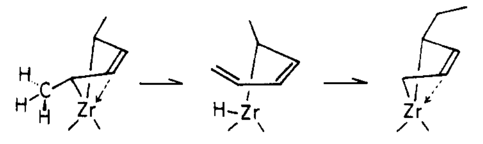
1a, $R^{1-3} = R^{1'} = R^{4'} = H$, $R^4 = CH_3$
2a, $R^{2,3} = R^{1'} = R^{4'} = H$, $R^1 = R^4 = CH_3$
2c, $R^{1-3} = R^{1'} = R^{4'} = H$, $R^4 = C_2H_5$
3, $R^1 = R^3 = R^{1'} = R^{4'} = H$, $R^2 = R^4 = CH_3$
4, $R^{1,2} = R^{4'} = R^{1'} = H$, $R^3 = R^4 = CH_3$
5, $R^1 = R^3 = R^{1'} = H$, $R^2 = R^4 = R^{4'} = CH_3$
6, $R^{2,3} = R^{1'} = R^{4'} = H$, $R^1 = Si(CH_3)_3$, $R^4 = CH_3$
7, $R^{2,3} = R^{1'} = H$, $R^1 = Si(CH_3)_3$, $R^4 = CH_2Si(CH_3)_3$
1b, $R^{1-3} = R^{1'} = R^{4'} = H$, $R^4 = CH_3$
2b, $R^{2,3} = R^{1'} = R^{4'} = H$, $R^1 = R^4 = CH_3$
2d, $R^{1-3} = R^{1'} = R^{4'} = H$, $R^4 = C_2H_5$

(**1a**) and *s-trans*-η^4-(*E*)-1,3-pentadiene complex (**1b**) as confirmed by NMR (see later). Treatment of Cp_2ZrHCl with pentadienylpotassium[10] of *Z,Z* configuration also provides a s-cis/s-trans mixture in nearly the same ratio (43/57). Though *s-trans*-Cp_2Zr(butadiene) is known to convert readily to the s-cis isomer on heating to 60–70 °C in solution,[2] heating of the 1,3-pentadiene complex **1** to 100 °C in toluene for 2 h did not change the ratio. Hexadienylpotassium[10c] also gave a mixture of the *s-cis*-2,4-hexadiene complex (**2a**) and *s-trans*-2,4-hexadiene complex (**2b**) of *E,E*-configuration under ordinary conditions (Table II).

EH-MO calculations predict that the total energy of the *s-trans*-(2,4-hexadiene)zirconium complex is slightly lower[11] than that of the s-cis isomer, in accord with the experimental observation. This indicates the relative ratio is determined thermodynamicly. The X-ray structure of Cp_2Zr(2,3-dimethylbutadiene)[6b] and Cp_2Zr(2,3-diphenylbutadiene)[6b] showed that the s-cis coordinated species assume the bent zirconacyclo-2-pentene structure rather than the conventional η^4-1,3-diene structure. Similarly the present pentadiene complexes may be expressed in the form of the bent zirconacyclopentene structure where the π electrons of the $CR^2{=}CR^3$ group are donated to the metal and at the same time the terminal carbon binds to the metal with σ bonding (eq 2).

(2)

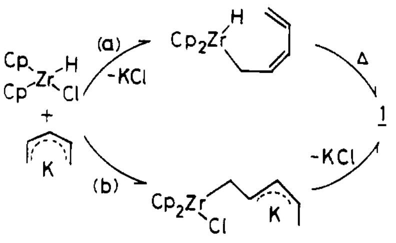
One of the characteristic properties of the 2,4-hexadiene complex lies in its irreversible conversion into 1,3-hexadiene derivatives on heating. Thus when a toluene solution of the 2,4-hexadiene complex (composed of a 36/64 mixture of s-cis and s-trans isomers) was kept at 90 °C for 2 h, isomerization occurred to give a 39/61 mixture of *s-cis*- and *s-trans*-1,3-hexadiene complexes (**2c** and **2d**) of *E* configuration (see Tables II–IV). A possible intermediate for this reaction is given in eq 3. β-Hydride elimination



(3)

at the terminal methyl forces migration to (1-methyl-2,4-pentadienyl)hydridozirconium that is readily converted to the sterically more stable 1,3-hexadiene complex. Recently clear evidence for a direct bonding interaction between Ti and β-C–H in $Ti{-}CH_2CH_3$ has been confirmed.[12] It is not clear at present which isomer of the 2,4-hexadiene complexes is selectively converted to the *s-trans*- or *s-cis*-1,3-hexadiene complex since the rate of isomerization of the *s-cis*-2,4-hexadiene complex is nearly identical with that of the s-trans isomer. Separation into individual isomers seems indispensable to get further insight into the isomerization mechanism.

For formation of the 1,3-pentadiene complex, the following two reaction pathways are conceivable (eq 4). If



(4)

the elimination of KCl occurs rapidly prior to the hydrogen transfer, 2,4-pentadienylhydridozirconium should be formed as an intermediate product (path a). The reaction path b, via an allylic potassium derivative, may be also possible if insertion into the Zr–H bond precedes the elimination of KCl. This problem was solved by careful characterization of the product formed at –40 °C. The reaction of pentadienylpotassium with Cp_2ZrHCl at this temperature causes fading of the orange solution to pale yellow and the precipitation of 1 equiv of KCl. This marked change suggests the formation of the intermediate. On the basis of the characterization of the product thus formed, we can propose the reaction path a on the following grounds. (1) Alcoholysis of the product gave 1,3-pentadiene exclusively (>95%). If the reaction goes through process b, protonolysis should give rise to 1- or 2-pentene. (2) Addition of acetone to the product at this temperature resulted in the selective insertion at the C-3 atom of the pentadienyl group. The similar insertion has been reported for the reaction of $Cp_2Zr(\eta^1\text{-}1,3\text{-pentadienyl})_2$[13] and allylic zirconium complexes.[13,14] If $Cp_2Zr(\eta^4\text{-}1,3\text{-pentadiene})$ is already formed at this stage, the addition should occur at the C-1 or C-4 atom. (3) When the temperature was raised to ca. 0 °C, the color of the solution changed to deep red, indicating the formation of the η^4-pentadiene complex. No additional precipitation of the salt was observed during this procedure. In contrast to the presence of two isomers for 1,3-pentadiene and 2,4-hexadiene complexes, Cp_2Zr(diene) complexes **3–5** with

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Table III. Chemical Shifts Values (δ, ppm) for s-cis Coordinated Zirconium-η^4-1,3-Pentadiene Complexes and Related Complexes[a]

complexes	ν_1	$\nu_{1'}$	ν_2	ν_3	ν_4	$\nu_{4'}$	ν_{Cp}
1a	3.46	−0.81	4.52	4.52	2.08	−0.48	4.83, 5.31
2a	2.08	−0.52	4.46	4.47	2.09	−0.52	4.86, 5.40
2c	3.42	−0.81	4.57	4.56	2.10	−0.31	4.86, 5.34
3	3.27	−0.92	1.82	4.42	2.07	−0.52	4.92, 5.39
4	3.27	−0.81	4.44	1.81	2.00	−0.89	4.95, 5.46
5[b]	3.01	−0.40	1.84	4.28	1.78	0.92	5.01, 5.46
6	0.23	−1.44	4.63	4.63	2.04	−0.34	4.93, 5.46
7	0.24	−1.29	4.57	4.57	1.27	−0.20	4.97, 5.53
		–			1.97		
s-*cis*-Zr(C_4H_6)[c]	3.45	−0.61	4.78	4.78	3.45	−0.69	4.84, 5.37
s-*cis*-Zr(C_5H_8)[d]	3.32	−0.57	4.52		3.29	−0.73	4.96, 5.45
(*E*)-Fe(CO)$_3$(C_5H_8)[e]	?	1.08	5.17	5.17	1.64	0.22	
(*Z*)-Fe(CO)$_3$(C_5H_8)[f]	2.67	?	5.30	5.30	1.75	1.47	

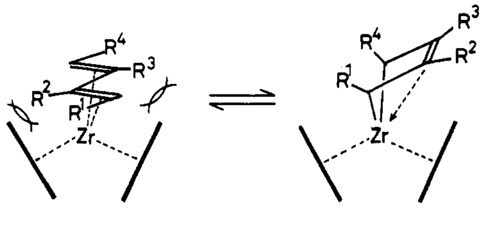
[a] Data were collected at 100 MHz in toluene-d_8 at 30 °C. The numbering system is given in eq 1. Chemical shift values were calibrated by using benzene as an internal standard assumed to be 7.20 ppm. [b] Measured at −40 °C. [c] Cp$_2$Zr(*s-cis*-butadiene) at −50 °C.[5] [d] Cp$_2$Zr(*s-cis*-isoprene). [e] The *E* isomer of Fe(CO)$_3$(*s-cis*-1,3-pentadiene).[18] [f] The *Z* isomer of Fe(CO)$_3$(*s-cis*-1,3-pentadiene).[18]

Table IV. Coupling Constants (Hz) for s-cis Coordinated η^4-1,3-Pentadiene Complexes[a]

complexes	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{1,3}$	$J_{1',3}$	$J_{1,4'}$	$J_{1',4'}$	$J_{2,3}$	$J_{2,4'}$	$J_{3,4'}$	$J_{4,4'}$
1a	−8.5	9.5	12.5	−1.2	−1.5	0.1	0.1	10.0	−1.5	12.0	5.8
2a	−5.7		12.0		−1.5		0.1	10.5	−1.5	12.0	
2c	−8.6	9.4	12.6	−1.5	−1.5	0.1	0.1	10.0	−1.5	11.8	5.9
3	−9.2			−1.9	−1.5	0.7	0.1			10.4	6.0
4	−9.5	10.5	10.9			0.5	1.5		−0.5		6.2
5[b]	−9.4			−2.1	−1.3						
6			15.0		−1.4		0.2	9.8	−1.4	11.0	5.9
7			15.0		−2.0		0.2	9.5	−2.0	12.0	10.0 2.4
s-*cis*-Zr(C_4H_6)	−10.0	9.5	10.5	−1.5	−0.8	0.2	0.5	8.0	−1.5	9.5	−10.0
s-*cis*-Zr(C_5H_8)	−9.6	10.2	11.0		−0.2	0.3	0.8		−1.5		−9.6

[a] Data were obtained at 30 °C and analyzed by the computer simulation. See eq 1 for the numbering system. [b] Data were obtained at −40 °C.

2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, and 2,4-dimethyl-1,3-pentadiene ligands are comprised of a single s-cis isomer as confirmed by the ^{1}H NMR spectra. This result is in line with the general trend observed in the 1,3-diene complexes where alkyl substitution at inner carbons always results in the *s*-cis coordination.[5] The extreme preference of the s-cis coordination may be ascribed to the steric repulsion between the Cp ring and alkyl group (R^2, R^3) on the dienes as confirmed by molecular model examination (eq 5). Introduction of an alkyl group on C-2 and/or C-3 of the *s-trans*-butadiene or *s-trans*-pentadiene complex causes severe steric congestion at the coordination sphere. However, this is not true for the s-cis-coordination.



(5)

Predominance of the s-cis coordination was also found for the complexes substituted with a bulky $(CH_3)_3Si$ group(s) at the C-1 and/or C-5 atoms; i.e., 1-(trimethylsilyl)-1,3-pentadiene complex **6** and 1,5-bis(trimethylsilyl)-1,3-pentadiene complex **7**. This can be accounted for by the steric repulsion between the $(CH_3)_3Si$ group and the Cp ring. The equilibrium shown in eq 5 shifts far to the right. The starting carbanion (1-(trimethylsilyl)pentadienyl)lithium assumes the *E,E,E* configuration and (1,5-bis(trimethylsilyl)pentadienyl)lithium has the *E,E,E,E* configuration as described before.[15] Thus, the s-cis coordination to zirconium involves rotation around the C_2–C_3 bond. The 1-(trimethylsilyl)-1,3-pentadiene complex unlike the hexadiene complex **2** showed no tendency for isomerization, and the interconversion into the 1-(trimethylsilyl)-2,4-pentadiene complex was not detectable even at high temperature (100 °C for 2 h in toluene). Bulkiness of the Me$_3$Si group together with stabilization of the Si–C bond by p_π–d_π interaction[16] may prevent isomerization.

Stereochemistry of Coordination in (1,3-Pentadiene)zirconium Complexes. The configurational analysis of a series of 1,3-pentadiene complexes has been made in terms of ^{1}H NMR spectroscopy. All of the NMR parameters were determined by iterative computer simulation. Tables III and IV show chemical shift values and the coupling constants, respectively, of the *s-cis*-1,3-pentadiene derivatives. The corresponding parameters for the *s-trans*-1,3-pentadiene derivatives are given in Tables V and VI. As typical examples, the spectrum of **1a** and **1b** are shown in Figures 1 and 2, respectively. The coupling constant $J_{2,3}$ for the s-cis isomers is 9.5–10.5 Hz while that for the s-trans isomer is 14.5–15.2 Hz in line with the data reported for *s-cis*- or *s-trans*-Cp$_2$Zr(1,3-butadiene).[5] The chemical shift values of H^1 (the syn proton with respect to the H^2 atom) and $H^{1'}$ (the anti proton) also serve as a useful tool in making a correct assignment of the structure. The H^1 signals of the s-cis isomers (**1a**, **2a**, and **3**–**7**) appear at 3.24 ± 0.23 ppm, and the $H^{1'}$ signal appears at −0.66 ±

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(15) H. Yasuda, T. Nishi, K. Lee, and A. Nakamura, *Organometallics*, 2, 21 (1983).

(16) (a) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill, New York, 1969, p 410. (b) E. W. Calvin, "Silicon in Organic Synthesis", Butterworths, London, 1981.

Table V. Chemical Shift Values (δ, ppm) for s-trans Coordinated η^4-1,3-Pentadiene Complexes[a]

complexes	ν_1	$\nu_{1'}$	ν_2	ν_3	ν_4	$\nu_{4'}$	ν_{Cp}
1b	3.12	1.72	2.54	2.86	2 08	1.72	4.77, 4.78
2b	2.05	1.66	2.61	2.62	2.05	1.67	4.94
2d	3.13	1.72	2.56	2.86	2.07	1.72	4.75
Cp_2Zr(butadiene)[b]	3.22	1.22	2.90	2.90	3.22	1.22	4.92
Cp^*_2Zr(butadiene)[b]	2.75	1.21	2.14	2.14	2.75	1.21	

[a] Data were collected at 100 MHz in toluene-d_6. Chemical shift values were calibrated by using the internal benzene peak (7.20 ppm). Numbering system follows that given in eq 1. [b] For the values of the s-trans isomer, see ref 5.

Table VI. Coupling Constants (Hz) for s-trans Coordinated η^4-1,3-Pentadiene Complexes of Zirconium[a]

complexes	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{1,3}$	$J_{1',3}$	$J_{1,4'}$	$J_{1',4'}$	$J_{2,3}$	$J_{2,4'}$	$J_{3,4'}$	$J_{4,4'}$
1b	−4.0	7.0	16.1	−0.3	−1.0	0.1	0.1	15.0	−1.0	15.5	5.8
2b	5.9		15.2		−1.1		0.1	14.5	−1.1	15.2	5.9
2d	−4.0	7.1	16.0	−0.3	−1.1	0.05	0.2	15.2	−1.0	15.6	5.9
Cp_2Zr(butadiene)[b]	−4.0	7.1	16.4	−0.5	−1.1	0.02	0.5	15.5	−1.1	16.4	−4.0
Cp^*_2Zr(butadiene)[b]	−4.2	7.3	16.2	−0.5	−1.2	0.05	0.2	16.0	−1.2	16.2	−4.2

[a] Data were obtained at 30 °C and analyzed by the computer simulation. [b] Values for the s-trans isomers.[5]

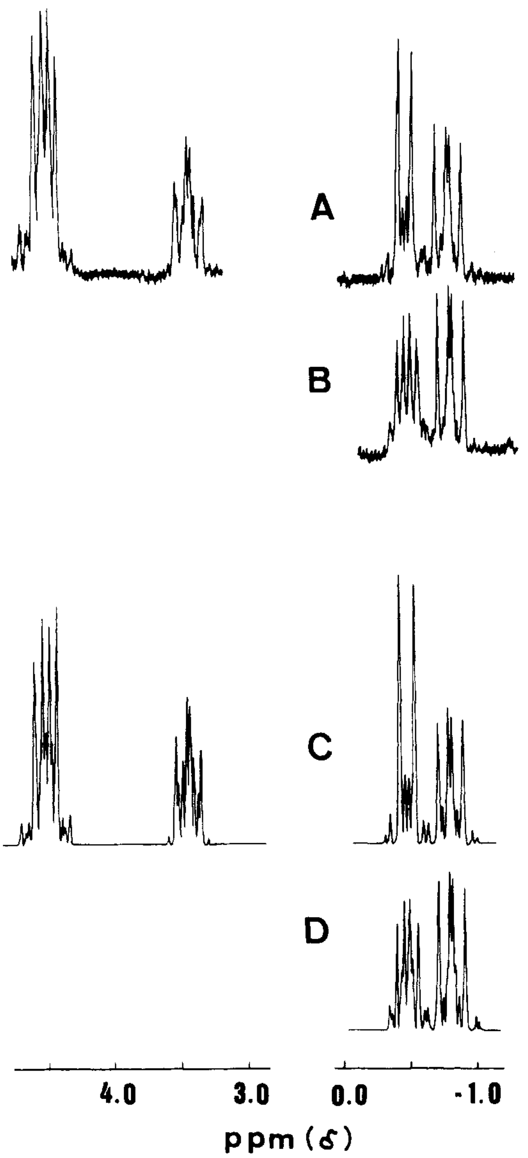


Figure 1. ^1H NMR spectrum of Cp_2Zr(*s-cis*-η^4-1,3-pentadiene) (**1a**) at 30 °C in toluene-d_8. Spectrum A shows observed signals assigned to H_2, H_3 (left), H_1 (center), and $H_{4'}$, $H_{1'}$ (right), measured after decoupling from the methyl protons at the C_4 atom, and spectrum C indicates its simulated spectrum. Spectrum B expresses the spectral region for $H_{1'}$ and $H_{4'}$ measured without the decoupling procedure, and spectrum D illustrates the simulated spectrum.

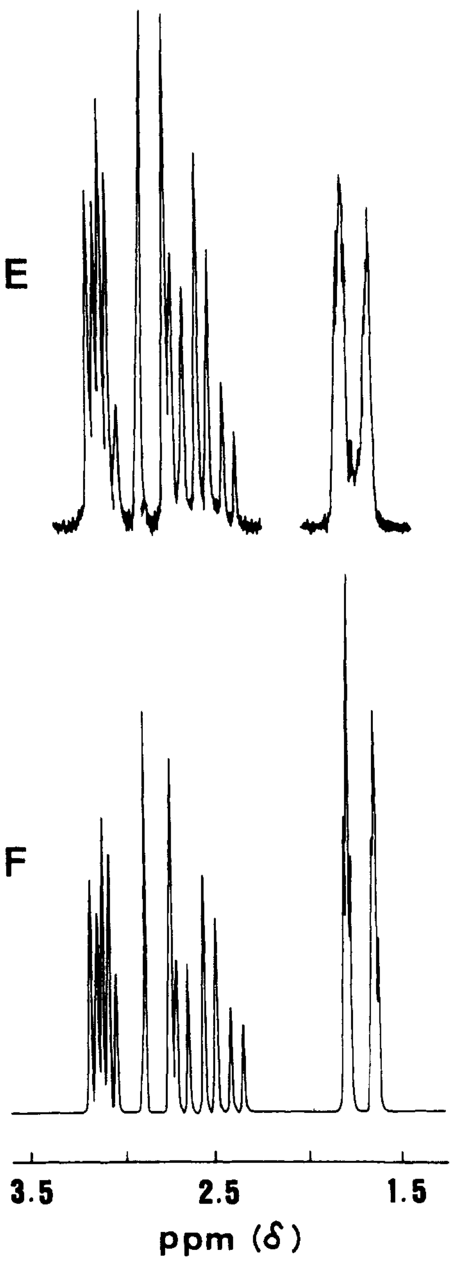
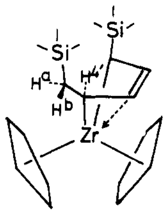


Figure 2. ^1H NMR spectrum of Cp_2(*s-trans*-η^4-1,3-pentadiene) (**1b**) at 30 °C in toluene-d_8 decoupled from the methyl group: observed (E) and simulated (F) spectra. Signals of H_1(left), H_3, H_2(center), and $H_{4'}$, $H_{1'}$ (right) are shown.

0.27 ppm, the values being entirely consistent with those for Cp_2Zr(*s-cis*-butadiene) and Cp_2Zr(*s-cis*-isoprene).[5] The $H^{1'}$ signal for the s-trans isomers (**1b**, **2b**, and **2d**) generally appears at a lower field (1.6–1.7 ppm), which is roughly comparable to the magnitude of the H^1 chemical shift observed for Cp_2Zr(*s-trans*-butadiene) and Cp^*_2Zr(*s-trans*-butadiene) ($Cp^* = C_5Me_5$) (Table V). On this basis, the s-cis/s-trans ratio was estimated. The ^1H NMR spectrum of the 1,5-bis(trimethylsilyl)-1,3-pentadiene complex 7 indicates that the bulky $(CH_3)_3Si$ group restricts



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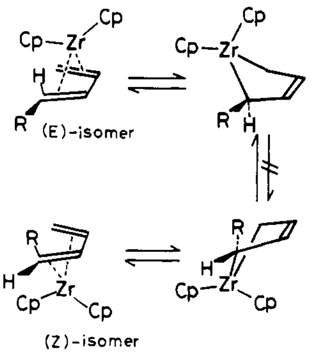
the rotation around the C_4–C_5 bond as illustrated. Steric congestion between the $(CH_3)_3Si$ group and the Cp ring is reflected in the significantly small coupling constant of $J_{H^a,H^{4'}}$ (2.4 Hz) and the large coupling constant of $J_{H^b,H^{4'}}$ (10.0 Hz).

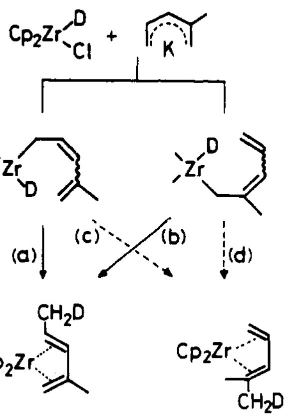
Among complexes 1–7, only the 2,4-dimethyl-1,3-pentadiene complex **5** was found to be fluxional as confirmed by variable-temperature NMR studies. Similar dynamic behavior has been already reported for Cp_2Zr(butadiene), Cp_2Zr(isoprene), and Cp_2Zr(2,3-dimethylbutadiene).[5,6,17] A broad resonance assignable to terminal methylene protons (H^1 and $H^{1'}$) appeared at 1.81 ppm at 30 °C while at −40 °C it splits into two well-resolved doublets (−0.40 and 3.01 ppm, respectively) to show the extreme bent zirconacyclo-2-pentene structure. The mode of fluxionalization may be rationalized by the flipping the pentadiene molecule around an axis passing through the C_1 and C_4 atoms. A similar flip mechanism has been proposed for zirconium complexes of the 1,3-butadiene series.[17] By contrast, discrete molecules 3, 4, 6, and 7 are not fluxional in the temperature range from −80 to +60 °C. This difference may be ascribed to the great configurational stability of the s-cis coordinated *E* isomer. The fluxionalization process requires the rapid interconversion between (*Z*)- and (*E*)-1,3-pentadiene complexes (eq 6); nevertheless the *E*



(6)

configuration is thermodynamicly more stable than the *Z* configuration as was found for iron–1,3-pentadiene complexes.[18] The *Z* isomer of $Fe(CO)_3$(*s-cis*-1,3-pentadiene) converts irreversibly into the *E* isomer on heating. Therefore, the high barrier present between the *E* and *Z* isomers of the s-cis structure seems responsible for inhibition of the flipping and hence the fluxionality. Since the 2,4-dimethyl-1,3-pentadiene complex has no configurational isomers, the molecule can flip rapidly on the NMR time scale through the low-energy barrier. Such fluxional behavior has not been found for simple diene complexes of the later transition metals. This is due to the strong preference of the σ M–C bonding character of the zirconium–diene complexes as evidenced by the relatively large absolute values of geminal coupling ($J_{1,1'}$) in comparison with 2.0–4.5 Hz observed for $M(CO)_3$(diene) (M = Fe, Ru).

Scheme I



Reaction Pathway for the Formation of (1,3-Pentadiene)zirconium Complexes. The success in isolation of the isomerically pure 2-methyl-1,3-pentadiene complex **3** raises the possibility of getting a closer look at the hydrogen transfer mechanism. Since the starting carbanion has a nonsymmetrical structure, the labeling experiment with Cp_2ZrDCl gives definitive evidence for the reaction pathway. The sole product obtained from Cp_2ZrDCl and (2-methylpentadienyl)lithium was found to be the s-cis coordinated (*E*)-2-methyl-1,3-pentadiene-*5-d* complex. Thus it is unequivocal that the attack of the deuteride occurred preferentially on the C-5 atom of the 2-methylpentadienyl anion. No scrambling of the deuteride to C-1 and C-3 atoms was observed as confirmed by ^1H NMR. On the basis of these facts, the following two reaction pathways in Scheme I are postulated for the formation of the η^4-pentadiene complexes.

One is the σ–π rearrangement (path a) through (4-methyl-2,4-pentadienyl)hydridozirconium, and the other is the intramolecular hydrozirconation (path b) through (2-methyl-2,4-pentadienyl)hydridozirconium. Reaction paths c and d can be ruled out because the 4-methyl-1,3-pentadiene-*5-d* complex was not formed. Process a involves the initial reductive elimination (coupling of deuteride with the 4-methyl-2,4-pentadienyl group) followed by coordination to the metal. Such reductive elimination has been proposed for the photolysis of $Cp_2Zr(aryl)_2$ to give low-valent "Cp_2Zr" species[19] and for the thermal rearrangement of $CpZr(2\text{-butenyl})_3$ leading to $CpZr(\eta^4$-butadiene)(η^3-2-butenyl) where elimination of 2-butene occurs.[20] The intramolecular hydrozirconation process b should prefer the *Z* configuration of the pentadienyl group, but process a will be not greatly affected by the geometry. The mode of deuteride transfer proposed in process b is against the usual pattern of hydrozirconation where hydrogen transfers to sterically more crowded carbon atoms of alkenes, dienes, or alkynes.[21] However, the hydrozirconation

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(17) H. Yasuda, Y. Kajihara, K. Mashima, K. Lee, and A. Nakamura, *Chem. Lett.*, 519 (1981).

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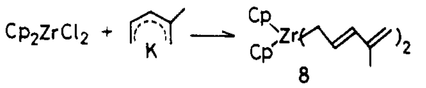
that follows process b has recently been found in the reaction of Cp_2ZrHCl with allyloxy anions.[22]

To specify the site of Zr–C bonding and the geometry of the intermediate, a thermally more stable compound $Cp_2Zr(methylpentadienyl)_2$ was prepared by reaction of Cp_2ZrCl_2 with (2-methylpentadienyl)potassium. The exclusive formation of (4-methyl-2,4-pentadienyl)zirconium compound (eq 7) rather than the (2-methyl-2,4-pentadienyl)zirconium derivative favors hydrogen transfer via process a since the site of Zr–C bonding is the same as that proposed in reaction path a. The *E* configuration of the product also supports the above process. Though dipentadienylmetal complexes of Fe, Ru, and Mn assume the *Z* configuration (open metallocene structure),[23] the present molecule $Cp_2Zr(C_6H_9)_2$ has a linear structure with respect to the pentadienyl group.



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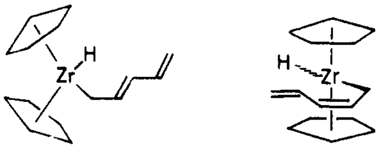
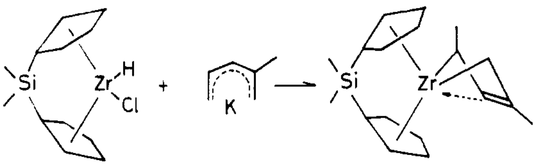
(7)

Two different stereochemical pathways are probable at the metallocene moiety.[24a] One is the wedged metallocene species A, and the other is the parallel metallocene species B that has been proposed for hydrogenation of alkenes with Cp_2MoH_2.[24b]



(A) (B)

To address this problem, the corresponding reaction with silylene-bridged chlorohydridozirconocene was examined because the transition state with the parallel metallocene is not allowed for this molecule. The reaction between the silylene-bridged zirconocene and (2-methylpentadienyl)potassium occurred smoothly to give a 2-methylpentadiene complex (**9**) under the same reaction conditions as described for Cp_2ZrHCl. The ^1H NMR parameters of the product were found to be essentially the same as that of **3**. Thus, it is unambiguous that the reaction proceeds by way of wedged metallocene species.



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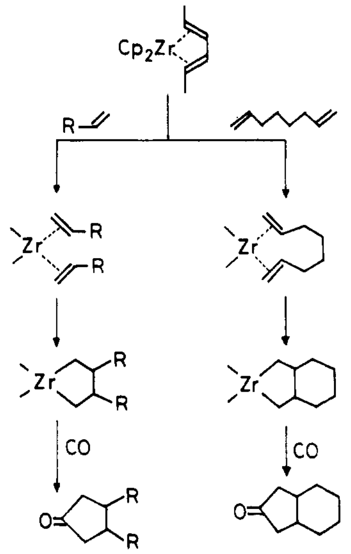
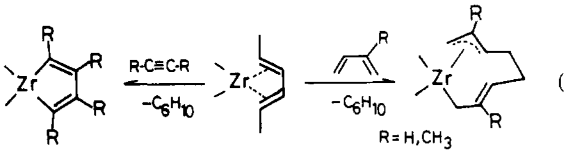
Unique Chemical Properties of 1,3-Pentadiene Complexes. To clarify the unique chemical properties of 1,3-pentadiene complexes, the reactions with alkenes, alkynes, and carbonyl compounds were examined by using Cp_2Zr(2,4-hexadiene) (**2**) as a representative example. When the complex was treated with excess 1-pentene at 30 °C, the coordinated 2,4-hexadiene was expelled and a zirconacyclopentane derivative was generated in 87% yield. This result is in sharp contrast to the reactions of Cp_2Zr(isoprene) or Cp_2Zr(butadiene) with alkenes[25,26] or alkynes[25,27] that performs the 1:1 addition reaction preferentially. By taking advantage of the weak coordination of the 2,4-hexadiene ligand, 3,4-dialkylcyclopentanones were prepared by the addition of 3 equiv of 1-pentene, 1-heptene, or 1,7-octadiene followed by treatment with CO. The addition of 1 equiv of 1,7-octadiene provides an access to the bicyclic complex and hence hydrindanone. An alternative titanium-assisted hydrindanone synthesis has been reported recently.[28] The sequence shown in Scheme II provides a very convenient synthetic route to alkylated cyclopentanones and appears to be of wide applicability. Since the cyclopentanone derivatives are not formed without protonolysis of the product, the reaction should proceed through a zirconium enolate as has been proposed for the carbonylation of a zirconacyclopentane.[29]

Scheme II



Addition of excess 2-butyne to **2** also resulted in the release of 2,4-hexadiene quantitatively and the formation of zirconacyclopentadiene by the successive insertion of 2 mol of 2-butyne (eq 9). Correspondingly, zirconacyclopentadiene derivatives are also available by the direct reaction of Cp_2ZrHCl with alkynes.[30] The addition of 3 equiv of butadiene or isoprene also results in the release of coordinated 2,4-hexadiene. In this case, complexes of the butadiene dimer or the isoprene dimer were formed by metallacyclic expansion from monodiene complexes (see



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(21) (a) D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, **96**, 8115 (1974); (b) J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.*, **15**, 333 (1976); (c) B. Katzner, P. C. Wailes, and H. Weigold, *J. Chem. Soc., Chem. Commun.*, 1105 (1969).

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(26) G. Erker, K. Engel, U. Dorf, J. L. Atwood, and W. E. Hunter, *Angew. Chem., Int. Ed. Engl.*, **21**, 914 (1982).

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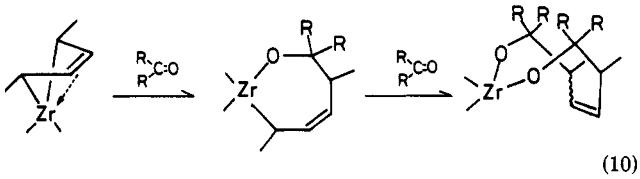
ref 25). Generation of "$(C_5R_5)_2Zr$" (76–82%) from 1,3-pentadiene complexes **1**–**7** and **9** was also observed by mass spectroscopy studies.

The mode of reaction of the 2,4-hexadiene complex **2** toward aliphatic ketones or aldehydes is quite different from above. In these reactions double insertion of electrophiles predominates even under the mild reaction conditions and 2,4-hexadiene was not released in this case. For example, 2 mol of 3-pentanone or 2-methyl-1-propanal readily reacts with the coordinated 2,4-hexadiene at both the C_2 and C_4 positions selectively at 25 °C according to eq 10. This sequence is useful for the facile synthesis of unsaturated 1,6-diols, the preparation of which usually requires multiple steps by conventional methods.[31] It should be noted here that the corresponding isoprene complex can react with only 1 equiv of carbonyl compounds at the C_1 atom even under the vigorous reaction conditions (80 °C, 10 h) in the presence of excess carbonyl compound. Further investigation currently in progress will lead to a more detailed mechanistic insight into the insertion reaction. The unique chemical reactivity of 2,4-hexadiene complexes is caused by the polar metal–carbon bond, and such reactivity has not been seen for group 8 metal–diene complexes.



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Experimental Section

All operations were performed under argon atmosphere by using Schlenk techniques. Tetrahydrofuran, benzene, toluene, and hexane, dried over Na/K alloy, were distilled and degassed by vacuum transfer before use. NMR spectra were recorded on a Varian XL-100 instrument with a VFT-100-620L Fourier transform accessory and analyzed with a Varian spin simulation program. Mass spectra (EI) were recorded on a JEOL Model 01SG-2 spectrometer, samples being transferred into the inlet under nitrogen atmosphere. Elemental analysis of the pentadiene complexes were carried out with a Yanagimoto Model MT-2 CHN analyzer by weighing the samples quickly under nitrogen. Gas chromatographic analysis and the melting points were conducted in the same manner as described before.[5]

Preparation of Cp_2Zr(1,3-pentadiene) (1). To a stirred suspension of Cp_2ZrHCl (1.0 g, 3.9 mmol) in THF (10 mL) was added a THF solution (15 mL) of pentadienylpotassium (3.9 mmol) or pentadienyllithium (3.9 mmol) at −78 °C. The mixture was allowed to warm to room temperature with magnetic stirring. The solution turned to deep red at ca. 0 °C. After continued stirring for 3 h, the solution was evaporated to dryness and the residue was extracted with hexane (200 mL). The solution was then concentrated to 8 mL and cooled to −20 °C to induce the precipitation of deep red crystals of **1**. Typical yield is 70%.

Preparation of Cp_2Zr(2,4-hexadiene) (2a,b). To a slurry of Cp_2ZrHCl (1.0 g, 3.9 mmol) in THF (10 mL) was added a THF solution (15 mL) of hexadienylpotassium (3.9 mmol) at −20 °C over a 10-min period with vigorous stirring. The mixture was stirred for 3 h at 20 °C and then evaporated to dryness. The crude product was extracted with three portions of degassed hexane (30 mL × 3), and the combined hexane solution was concentrated to 8 mL. On cooling the solution to −20 °C, and 2,4-hexadiene complex precipitated as a deep red microcrystalline product in 73% yield.

Preparation of Cp_2Zr(1,3-hexadiene) (2c,d). A toluene solution (15 mL) of Cp_2Zr(2,4-hexadiene) (1.0 g, 3.9 mmol) was kept at 90 °C for 2 h to perform the isomerization. Further heating should be avoided because the yield is decreased significantly due to the thermal decomposition of the complex. For isolation of the complex, the solvent was removed by trap-to-trap distillation and the residue was extracted with hexane (60 mL). The extract was then concentrated and cooled to −20 °C to give Cp_2Zr(1,3-hexadiene) as deep red crystals in 86% yield. The *s*-cis/*s*-trans ratio of the complex thus isolated is comparable to that determined by NMR methods for complexes **2a,b** after being heated at 90 °C for 2 h in toluene-d_8. The product contained 12% of unreacted complexes **2a,b**: mass (EI); M^+ 302 (^{90}Zr). Anal. Calcd for $C_{16}H_{20}Zr$: C, 63.31; H, 6.64. Found: C, 63.21; H, 6.60.

Preparation of 3–7. Zirconium complexes **3**–**7** were synthesized in essentially the same way as described for **1**, and all the complexes were isolated as deep red crystals in 65–85% yield by recrystallization from hexane at −20 °C. Elemental analyses are shown in Table I. See ref 10b,c and 15 for preparation of alkylated or silylated pentadienyl anions.

Preparation of Cp_2Zr(2-methyl-1,3-pentadiene-d_1) (3-d_1). A THF solution (10 mL) of (2-methylpentadienyl)potassium (3.9 mmol, 0.5 g) was syringed into a stirred suspension of Cp_2ZrDCl (1.0 g, 3.9 mmol) in THF (10 mL) at −78 °C. The solution was stirred at 20 °C for 3 h and then evaporated to dryness. The residue was extracted with hexane (200 mL) at 30–40 °C. The hexane solution was concentrated to 8 mL and cooled to −20 °C to give deep red crystals of complex **3**-d_1 in 65% yield: mp 96 °C; ^1H NMR (δ, toluene-d_8) −0.92 (d of d, 1, $H^{1'}$), −0.50 (d of t, 1, $H^{4'}$), 1.85 (s, 3, CH_3), 2.05 (d of t, 2, CH_2D), 3.25 (d of d, 1, H^1), 4.47 (d, 1, H^3), 4.98 (s, 5, Cp), 5.45 (s, 5, Cp); mass (EI) M^+ 303 (40.6%) for ^{90}Zr, 304 (19.5%) for ^{91}Zr, 305 (16.5%) for ^{92}Zr, 307 (13.9%) for ^{94}Zr, calcd for ^{90}Zr species, 303. Anal. Calcd for $C_{16}H_{19}DZr$: C, 63.10; H, 6.29; D, 0.66. Found: C, 62.72; H, 6.35; D, 0.65. For preparation of Cp_2ZrDCl, see ref 32.

Preparation of Cp_2Zr(4-methyl-2,4-pentadienyl)$_2$ (8). To a stirred solution of Cp_2ZrCl_2 (0.5 g, 1.7 mmol) in THF (10 mL) was added a THF solution of (2-methylpentadienyl)potassium (3.5 mmol, 0.4 g) at −78 °C. The solution was gradually warmed to 20 °C with stirring. After being stirred for 3 h, the solution was evaporated to dryness and the residue was extracted with hexane (90 mL) and the salt was separated with a centrifuge. Cooling the concentrated solution to −20 °C gave complex **8** as pale yellow crystals: mp 102 °C; ^1H NMR δ, toluene-d_8, 30 °C) 1.59 (d, 4, CH_2, $J_{1,2}$ = 9.6 Hz), 1.83 (s, 6, CH_3), 4.74 (s, 4, $CH_2{=}C$), 5.24 (d, 2, $CH{=}CH$, $J_{2,3}$ = 15.0 Hz), 5.71 (d of t, 2, $CH{=}CH$), 5.32 (s, 10, Cp); mass (EI), M^+ 382 (39.1%) for ^{90}Zr, 383 (21.3%) for ^{91}Zr, 384 (16.7%) for ^{92}Zr, 386 (14.1%) for ^{94}Zr, calcd for ^{90}Zr, 382. Anal. Calcd for $C_{22}H_{28}Zr$: C, 68.87; H, 7.36. Found: C, 67.84; H, 7.36.

Preparation of $(CH_3)_2Si(C_5H_4)_2ZrCl_2$. The starting material dicyclopentadienyldimethylsilane was prepared by the dropwise addition of dimethyldichlorosilane (32.5 g, 250 mmol) to a stirred suspension of cyclopentadienylsodium (500 mmol) in hexane (300 mL) at 0 °C followed by stirring for 30 min at 25 °C, quenching with 4 mol/L aqueous HCl, and distillation (56 °C/2 torr); yield 67%. Lithiation of Cp_2SiMe_2 was conducted by the addition of butyllithium (100 mmol, 61 mL of 1.64 mol/L hexane solution) to a stirred THF solution (60 mL) of Cp_2SiMe_2 (9.4 g, 50 mmol) at 0 °C. The solution was stirred at 25 °C for 2 h and then dropwise added to a suspension of $ZrCl_4$ (9.3 g, 40 mmol) in a mixture of THF/benzene (1/1 volume ratio, total 30 mL) at 0 °C. After being stirred for 2 h at 25 °C, the solution was evaporated and the residue was extracted with chloroform (300 mL). Cooling the solution to −20 °C afforded $(CH_3)_2Si(C_5H_4)_2ZrCl_2$ as pale yellow crystals in 48% yield: ^1H NMR ($CDCl_3$) 0.75 (s, 6, $SiMe_2$), 5.96 (t, 4, J = 2.5 Hz, C_5H_4), 6.95 (t, 4, J = 2.5 Hz, C_5H_4); IR (KBr) 3105, 3065, 1398, 1372, 1323, 1256, 1167, 1068, 1050, 902, 815, 682, 453, 418 cm^{-1}. Anal. Calcd for $C_{12}H_{14}Cl_2SiZr$: C, 41.36; H, 4.05. Found: C, 41.16; H, 4.03.

Preparation of $(CH_3)_2Si(C_5H_4)_2ZrHCl$. To a THF solution (5 mL) of $(CH_3)_2Si(C_5H_4)_2ZrCl_2$ (1.0 g, 1.4 mmol) was added $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (0.42 g, 1.4 mmol, 70% toluene solution) at 20 °C in the dark. After being stirred for 4 h, the solution was concentrated to ca. 1 mL and anhydrous diethyl ether (5 mL) was added to induce the precipitation of $(CH_3)_2Si(C_5H_4)_2ZrHCl$

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[31] For example, R. J. Tedeshi and A. E. Brown, *J. Org. Chem.*, **29**, 2051 (1964).

[32] P. C. Wailes and H. Weigold, *J. Organomet. Chem.*, **24**, 405 (1970).

as a white solid, which was then filtered, washed with diethyl ether, and dried in vacuo; yield 58–60%. The complex is very sensitive to light and moisture, and treatment with acetone gave 2-propanol (0.9 equiv) through subsequent hydrolysis: ^{1}H NMR (THF-d_8) δ 0.20, 0.22 (s, 6, $SiCH_3$), 6.0, 6.4, 6.6, 6.8 (m, 8, C_5H_4).

Preparation of $(CH_3)_2Si(C_5H_4)_2Zr$(2-methyl-1,3-pentadiene) (9). To a solution of $(CH_3)_2Si(C_5H_4)_2ZrHCl$ (250 mg, 0.8 mmol) in THF (5 mL) was added (2-methylpentadienyl)potassium (0.8 mmol) in THF (3 mL) at −78 °C. the mixture was allowed to warm to room temperature, and stirring was continued for 3 h.

After evaporation of the mixture, the residue was extracted with hexane and purified by recrystallization at −20 °C to give deep red crystals of the *s-cis*-2-methyl-1,3-pentadiene complex in 62% yield: mp 120 °C; mass (EI), M$^+$ 358 for ^{90}Zr (37.3%), 359 for ^{91}Zr (17.7%), and 360 for ^{92}Zr (16.6%); ^{1}H NMR (toluene-d_8) δ −1.13 (d, 1, $J_{1,1'}$ = 9.2 Hz, $H_{1'}$), −0.51 (d of q, 1, $J_{3,4}$ = 10.5 Hz, $J_{4,4'}$ = 6.0 Hz, $H_{4'}$), 0.43 (s, 3, $SiCH_3$), 0.52 (s, 3, $SiCH_3$), 1.83 (s, 3, CH_3), 2.08 (d, 3, CH_3), 3.39 (d of d, $H_{1'}$), 4.49 (d, 1, H_3), 4.74, 5.07, 5.41, 5.74 (m, 8, C_5H_4).

Reaction of 1-Pentene with 2 and Carbonylation. Into a benzene solution (10 mL) of Cp_2Zr(2,4-hexadiene) (0.9 g, 3 mmol) was syringed 1-pentene (0.9 mL, 10 mmol) at 20 °C under argon. When the solution was stirred for 2 h, 80% of coordinated (*E*,*E*)-2,4-hexadiene was expelled as confirmed by GLC analysis of an aliquot of the solution taken for monitoring. The vessel was then cooled to −78 °C, evacuated, and filled with CO through a rubber balloon. After the mixture was stirred for 6 h, the solvent was removed by trap-to-trap distillation and replaced with diethyl ether (20 mL). The cleavage of the product with acetic acid (1 mL) followed by distillation gave 3,4-dipropylcyclopentanone (310 mg, 1.85 mmol) in 78% yield. No cyclic ketone was formed without hydrolysis: ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 6, J = 6.0 Hz, CH_3), 1.04–1.54 (m, 8, CH_2 of Pr), 1.54–2.00 (m, 4, CH_2CO), 2.44 (d of d, J_{gem} = 11.0 Hz, $J_{vicinal}$ = 17.5 Hz, CH_2CO) (see ref 33 for the assignment); ^{13}C NMR ($CDCl_3$) δ 14.26 (CH_3), 21.45 (CH_2 of Pr),36.42 (CH_2 of Pr), 42.59 (CH), 45.14 (CH_2COCH_2), 218.71 (CO); IR (neat) 2955, 2930, 2870, 1745, 1468, 1407, 1380, 1241, 1197, 1160 cm^{-1}; mass (EI), m/z 168 (M$^+$). Anal. Calcd for $C_{11}h_{20}O$: C, 78.51; H, 11.98. Found: C, 78.55; H, 11.53.

Reaction of 1,7-Octadiene with 2 and Carbonylation. Into a solution of Cp_2Zr(2,4-hexadiene) (0.9 g, 3 mmol) in benzene (10 mL) was syringed 1,7-octadiene (0.7 mL, 5 mmol) at 25 °C. After the mixture was stirred for 5 h, CO was admitted over the solution through a rubber balloon and stirring was continued for additional 5 h. Vacuum distillation gave no product containing a cyclic ketone, but acid cleavage of the residue with acetic acid (1 mL) in ether gave *cis*-hydrindanone in 63% yield (GC yield, 75%). The cis/trans ratio (90/9) was determined based on the ^{13}C NMR spectrum with reference to the literature:[34] ^{1}H NMR ($CDCl_3$) δ 1.05–1.80, 2.00–2.50; ^{13}C NMR ($CDCl_3$) δ 22.39, 27.37, 35.44, 43.13, 219.84; IR (neat) 2920, 2845, 1743, 1450, 1405, 1160 cm^{-1}; mass (EI), m/z 138 (M$^+$). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.62; H, 10.67.

Reaction of 2-Butyne with 2. Into a stirred benzene solution (10 mL) of Cp_2Zr(2,4-hexadiene) (0.9 g, 3 mmol) was syringed 2-butyne (0.5 mL, 8 mmol). The mixture was stirred for 12 h at room temperature and then distilled in vacuo. The distillate contained the expelled (*E*,*E*)-2,4-hexadiene (93%) as confirmed by GC analysis. The residue was dissolved in diethyl ether and cleaved with 4 mol/L aqueous HCl to give (*E*,*E*)-3,4-dimethyl-2,4-hexadiene (304 mg, 2.7 mmol) in 98% yield: ^{1}H NMR ($CDCl_3$) δ 1.68 (d, 6, J = 7.0 Hz, $=CHCH_3$), 1.72 (s, 6, $=CCH_3$), 5.52 (q, 2, J = 7.0 Hz, $CHCH_3$); IR (neat) 3055, 2990, 2930, 2870, 1445, 1370, 1255, 794 cm^{-1}; mass (EI), m/z 110 (M$^+$). Anal. Calcd for C_8H_{14}: C, 87.34; H, 12.94. Found: C, 87.34; H, 12.94.

Reaction of Complex 2 with 2-Methyl-1-propanol. To a THF solution (10 mL) of Cp_2Zr(2,4-hexadiene) (0.9 g, 3 mmol) was added dropwise a solution of 2-methyl-1-propanal (0.5 mL, 7 mmol) in THF (3 mL) at 0 °C. The mixture was allowed to warm to room temperature and kept for 3 h with stirring. Solvent was removed by flash distillation and replaced with diethyl ether (20 mL). The resulting product was cleaved with 4 mol/L aqueous HCl and distilled in vacuo to give 2,4,7,9-tetramethyl-3,8-dihydroxy-5-decene in 72% yield: mass (EI), M$^+$ 228, M$^+$ − 2 226; ^{1}H NMR ($CDCl_3$) δ 0.88 (d, 12, CH_3), 0.96 (d, 6, CH_3), 1.72 (m, 2, CH), 1.74 (s, 2, OH), 2.26 (m, 2, CH), 3.10 (d of d, 2, CHO), 5.43 (m, 2, CH=CH).

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Registry No. **1a/1b**, 91128-46-0; **2a/2b**, 75361-75-0; **2c/2d**, 91128-47-1; **3**, 91128-48-2; **3**-d_1, 91128-49-3; **4**, 91128-50-6; **5**, 91128-51-7; **6**, 91128-52-8; **7**, 91128-53-9; **8**, 91128-54-0; **9**, 91128-55-1; Cp_2Zr(B) (B = butadiene), 75374-50-4; Cp_2Zr(B) (B = isoprene), 75361-73-8; Cp_2Zr(B) (B = 2,3-dimethylbutadiene), 75361-74-9; $(CH_3)_2Si(C_5H_4)_2ZrCl_2$, 86050-32-0; $(CH_3)_2Si(C_5H_4)_2ZrHCl$, 91157-80-1; Cp_2ZrHCl, 37342-97-5; Cp_2ZrDCl, 80789-51-1; Cp_2ZrCl_2, 1291-32-3; $ZrCl_4$, 10026-11-6; Cp_2SiMe_2, 18053-74-2; 2-butyne, 503-17-3; 3,4-dipropylcyclopentanone, 91128-56-2; *cis*-hydrindanone, 2826-65-5; *trans*-hydrindanone, 16783-22-5; (*E*,*E*)-3,4-dimethyl-2,4-hexadiene, 18265-39-9; 2,4,7,9-tetramethyl-3,8-dihydroxy-5-decene, 91128-57-3; pentadienylpotassium, 51391-25-4; pentadienyllithium, 54962-98-0; hexadienylpotassium, 74206-01-2; (2-methylpentadienyl)potassium, 91128-58-4; cyclopentadienylsodium, 4984-82-1; 1-pentene, 109-67-1; 1,7-octadiene, 3710-30-3; 2-methyl-1-propanal, 78-84-2; dimethyldichlorosilane, 75-78-5.

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