1,3-Diene Complexes of Zirconium and Hafnium Prepared by the Reaction of Enediylmagnesium with MCl_2Cp_2. A Remarkable Difference between the Zirconium and Hafnium Analogues As Revealed by ^1H NMR and Electronic Spectra

H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, K. Lee, and A. Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

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1,3-Butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene complexes of Zr and Hf were prepared by the 1:1 reaction of $ZrCl_2Cp_2$ or $HfCl_2Cp_2$ with the corresponding enediylmagnesium $[MgCH_2CR{=}CRCH_2]_n$, where R is H or CH_3. The variable ^1H NMR spectra of the zirconium–diene complexes showed a limiting *s-cis*-η^4-1,3-diene structure below −40 °C, although they are fluxional at higher temperatures. The ^1H NMR parameters for these Zr complexes at −70 °C were determined by computer simulation. The corresponding Hf complexes showed a strong preference for the metallacyclopentene structure in the temperature range of −90 to +80 °C. A clear difference between the Zr and Hf complexes was also observed in the electronic spectra. In contrast, the Cp_2Zr(1,4-diphenyl-1,3-butadiene) complex favored the *s-trans*-η^4-diene structure at −80 to +50 °C, although the Hf analogue preferred the *s-cis*-η^4-diene structure. All these complexes released the coordinated 1,3-dienes quantitatively on reaction with oxygen. 3,4-Dideuterated butene (or 1,4) or its methyl or phenyl derivatives were formed on treatment of these complexes with D_2O.

Introduction

The 1,3-diene complexes of group 4A metals reported so far show enhanced chemical reactivity. Zirconium(0)– and zirconium(II)-diene complexes with bidentate phosphine ligands are among the well-characterized examples of the 4A metal–diene complexes.[1,2] We have previously communicated (1) a novel method for preparation of a series of Cp_2M(diene) complexes (where M = Zr of Hf) utilizing enediylmagnesium,[3] (2) solution structure,[3] and (3) some regioselective reactions of these complexes with nitriles, carbonyl compounds,[4] alkenes, dienes, and alkynes.[5] Independent of our work, Erker and Krüger recently have reported the synthesis and structure of a series of Cp_2Zr(diene) complexes which were obtained by photochemical reactions between $Cp_2Zr(C_6H_5)_2$ and conjugated dienes.[6]

In this paper, we wish to report the details of our method, the unique reactivity of the resulting diene complexes, and the remarkable difference in fluxional behavior between the Zr and Hf complexes as observed in the variable-temperature ^1H NMR spectra. Since some of the complexes involve a new type of mononuclear *s-trans*-diene structure, the NMR data are compared with those of zirconium, hafnium, and related metal complexes having the *s-cis*-diene structure.

Preparation and Characterization of Cp_2M(1,3-diene) Complexes

A zirconium complex of isoprene was prepared by the 1:1 reaction of $ZrCl_2Cp_2$ with $[Mg(C_5H_8)]_n$ in THF at 20 °C for 2–3 h. After evaporation of the reaction mixture to dryness, the Cp_2Zr(isoprene) complex was extracted into hot benzene–hexane (1:2) and was isolated in the form of extremely air-sensitive dark red crystals by recrystallization from hexane in ca. 70% yield. When the original reaction mixture was cooled to −40 °C, orange crystals of an adduct formulated as $[Cp_2Zr(\text{isoprene})][MgCl_2{\cdot}2THF]$ precipitated in high yield (65–75%). The adduct of Cp_2Zr(isoprene) with magnesium salts is thermally unstable, and hence heating the crystals in refluxing hexane resulted in the precipitation of the magnesium salt. From the hexane-soluble fraction, red crystals of Cp_2Zr(isoprene) were obtained in good yield when the solution was concentrated and cooled to −20 °C. The Zr complexes obtained by this method did not contain any magnesium salt as checked by chemical analysis. The process for the formation of the diene complexes is summarized in eq. 1.

In the case of the hafnium products, the complexes are readily separated from salts by extraction with hexane at 20–30 °C. The interaction of 4–6 with magnesium salts seems to be weaker than that of the Zr derivatives 1–3.

$$MCl_2Cp_2 + [MgCHR^1CR^2{=}CR^3CHR^1]_n \xrightarrow{THF} [Cp_2M(CHR^1{=}CR^2CR^3{=}CHR^1)][MgCl_2{\cdot}2THF] \xrightarrow{\Delta} Cp_2M(CHR^1CR^2{=}CR^3CHR^1) + MgCl_2{\cdot}2THF \quad (1)$$

M = Zr	M = Hf
1, $R^1 = R^2 = R^3 = H$	4, $R^1 = R^2 = R^3 = H$
2, $R^1 = R^2 = H$, $R^3 = CH_3$	5, $R^1 = R^2 = H$, $R^3 = CH_3$
3, $R^1 = H$, $R^2 = R^3 = CH_3$	6, $R^1 = H$, $R^2 = R^3 = CH_3$
7, $R^2 = R^3 = H$, $R^1 = C_6H_5$	8, $R^2 = R^3 = H$, $R^1 = C_6H_5$

A series of butadiene, isoprene, 2,3-dimethylbutadiene, and 1,4-diphenyl-1,3-butadiene complexes of Zr and Hf thus was prepared by the reaction with the corresponding enediylmagnesium $[MgCHR^1CR^2{=}CR^3CHR^1]_n$ where R^1, R^2, and R^3 are H, CH_3, and/or C_6H_5.[7,8] The compositions of the complexes were established by chemical analysis, molecular weight determination, and the ^1H NMR spectra (Table I). All the Zr and Hf complexes exist in monomeric form as proved by the cryoscopic method or by mass spectroscopy.

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Table I. Characterization of Cp_2M(diene)

complex	mp, °C	metal content,[a] % calcd	metal content,[a] % found	Cp/diene ratio,[b] mol/mol calcd	Cp/diene ratio,[b] mol/mol found	mol wt[c] calcd	mol wt[c] found
1	73	33.1	33	2.00	1.98	275	291
2	64	31.5	32	2.00	2.00	290	301
3	101 dec	30.0	30	2.00	2.01	304	325
4	78	49.2	48	2.00	2.00	363	374
5	68	47.4	48	2.00	2.02	377	388
6	115 dec	45.7	45	2.00	1.99	391	401
7	231 dec	21.3	21	2.00	2.00	426.4 (^{90}Zr), 39.3[d]	426
						427.4 (^{91}Zr), 20.0	427
						428.4 (^{92}Zr), 17.8	428
						430.4 (^{94}Zr), 13.1	430
8	233 dec	34.7	33	2.00	2.00	513.4 (^{177}Hf), 16.8	513
						514.4 (^{178}Hf), 26.4	514
						515.4 (^{179}Hf), 17.5	515
						516.4 (^{180}Hf), 31.3	516

[a] Determined by the metal oxide method and calculated by using atomic weight defined by IUPAC rule. [b] Determined from ^{1}H NMR signal intensity ratio. [c] Molecular weight for **1–6** were determined cryoscopically in benzene and that for **7** and **8** by MS. [d] Intensity ratio (%) of the parent peaks for individual isotopes.

Table II. Hydrolysis and Air Oxidation Product of Cp_2M(diene) Complexes (M = Zr, Hf)

complex	hydrolysis products (distribution, %)	combined yield,[a] mol %	oxidation product	yield,[a] mol %
1	1-butene (98) 2-butene (2)	99	1,3-butadiene	94
2	3-methyl-1-butene (94) 2-methyl-2-butene (4)	99	isoprene	99
3	2,3-dimethyl-1-butene (96) 2,3-dimethyl-2-butene (4)	100	2,3-dimethyl-1,3-butadiene	97
4	1-butene (91) 2-butene (9)	98	1,3-butadiene	95
5	3-methyl-1-butene (94) 2-methyl-1-butene (1) 2-methyl-2-butene (5)	98	isoprene	96
6	2,3-dimethyl-1-butene (92) 2,3-dimethyl-2-butene (8)	100	2,3-dimethyl-1,3-butadiene	95
7	1,4-diphenyl-1-butene (24) 1,4-diphenyl-2-butene (76)	100	(*E*,*E*)-1,4-diphenylbutadiene	93
8	1,4-diphenyl-1-butene (18) 1,4-diphenyl-2-butene (82)	98	(*E*,*E*)-1,4-diphenylbutadiene	99

[a] Yields were determined by gas chromatographic analysis and are given in mol % to the diene complexes.

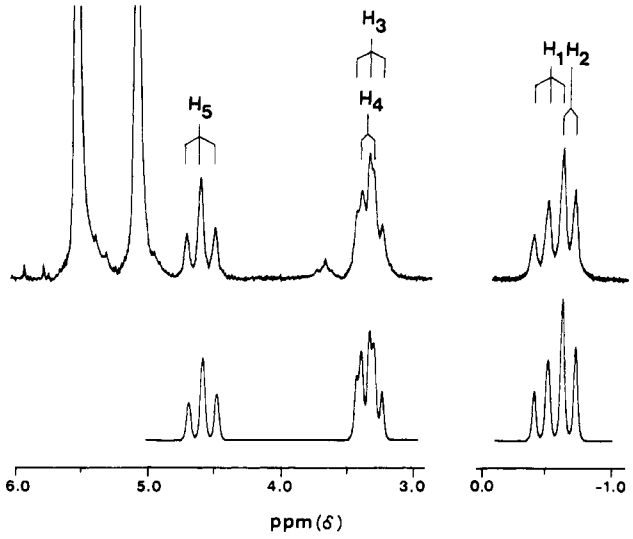
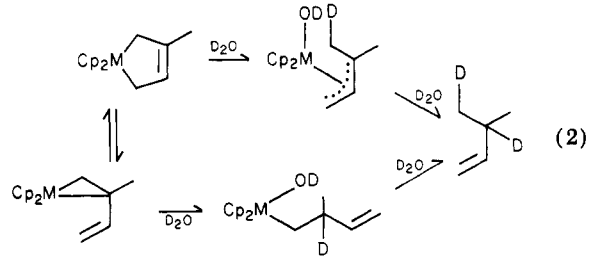


Figure 1. ^{1}H NMR (100-MHz) spectrum of Cp_2Zr(*s-cis*-η^4-isoprene) (**2**) at −70 °C in toluene-d_8 (above) and the simulated spectrum (below).

The diene complexes **1–8** immediately released the coordinated diene quantitatively when the benzene solution was exposed to dry air or oxygen (Table II). The complexes are sensitive also to water and readily hydrolyzed with aqueous HCl. The distribution of hydrolysis products is given in Table II. Addition of deuterium oxide decomposes the Zr and Hf complexes **1–6** to give dideuterated olefins where two deuterons occupy the 3,4-positions regioselectively; e.g., 3,4-dideuterio-1-butene, 3,4-dideuterio-3-methyl-1-butene, or 3,4-dideuterio-2,3-dimethyl-1-butene was produced, respectively. No difference was observed in the hydrolysis between Zr and Hf complexes. Production of 1,4-dideuterated isomer was only 1–9% and of 1,2-dideuterated compounds, which are possible for **2** and **5**, was negligible. Exceptional are the 1,4-diphenyl-1,3-butadiene complexes **7** and **8**, which produced a 1,4-dideuterated olefin exclusively (80%), with minor amounts of a 1,2-dideuterated one. Intermediacy of metallacyclopropane, which may be in equilibrium with a metallacyclo-3-pentene (eq 2) or deuterioxy (η^3-allyl)-



(2)

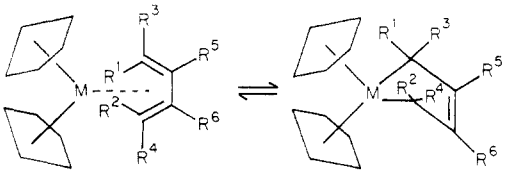
metal species, is invoked to account for the selective deuteration of **1–6**. Equation 2 illustrates possible routes for the selective deuteration of **2** to afford 3,4-di-

deuterio-3-methyl-1-butene.

Thermolysis of metallacyclopentanes of Ti,[9] Zr,[10] Pt,[11] Ta,[12] and Ni[13] is known to proceed by (a) β-hydrogen elimination, (b) reductive elimination, or (c) C–C bond cleavage, depending critically on the transition metals and ligands present in the complex. Such types of elimination or C–C bond cleavage were not observed in the thermolysis of **1–6** at 130 °C for 8 h in toluene or decane. The sole products obtained in thermolysis were coupling products between the Cp ligand and the diene. For example, complex **2** gradually decomposed at this temperature to give a mixture of $C_{10}H_{14}$ isomers (which corresponds to the 1:1 cyclopentadiene–isoprene adduct) as confirmed by MS (M^+ = 134) and by gas chromatography (three components in 15–25% yield).

Nuclear Magnetic Resonance of Cp_2M(1,3-diene) Complexes with *s-cis*-η^4-Diene Structure. The ^1H NMR (100-MHz) spectra of **1–3** were temperature dependent and revealed the fluxional character of the zirconium–diene bonding at room temperature. When the temperature was lowered, the signals broadened at 0–10 °C and split into two groups assignable to syn and anti protons at the diene termini below −40 °C to reach the limiting η^4-1,3-diene structure. For example, Cp_2Zr(2,3-dimethyl-1,3-butadiene) (**3**) in toluene-d_8 at 30 °C showed three broad singlets at 1.19, 1.80, and 5.31 ppm in a 2:3:5 ratio assignable to CH_2, CH_3, and Cp groups, respectively. At −40 °C, the terminal CH_2 signal split into two doublets of equal intensity at 3.16 (syn) and −0.72 ppm (anti).

Chemical shift values of the complexes **1–3** (at −70 °C in toluene-d_8) and a set of ^1H NMR parameters determined by iterative computer simulation are given in Table III. Parameters for related (*s-cis*-diene)metal complexes also are given for comparison. On the basis of the proton coupling constants, $J_{15(26)}$, $J_{35(46)}$, and J_{56}, the butadiene complex **1** most likely has a *s-cis*-η^4-1,3-diene structure rather than a metallacyclopentene structure.



(3)

If **1** favored the metallacyclo-3-pentene structure, the value of $J_{15(26)}$ and $J_{35(46)}$ must be smaller and J_{12} should be larger. We note that magnitude of $J_{15(35)}$ and J_{12} for 1,1-dimethylsilacyclo-3-pentene, 1,1-dimethylgermacyclo-3-pentene,[14] oxo- or thiacyclo-3-pentene[15] and cyclopentene[16] are known to be 1.6–4.6 and 1.7–7.0 Hz, respectively.

Computer analysis of the spectrum of the isoprene complex **2** offered parameters comparable to **1**, although the NMR pattern is rather complicated due to the overlap of the proton signals at C_1 and C_4 (Figure 1). Chemical shift and coupling constant values for **3** also resemble those for **1**. The ^1H NMR data on **1–3** compare closely with those of tricarbonyliron and -ruthenium complexes of *s-*

Table III. ^1H NMR Parameters for *s-cis*-η^4-Diene Complexes at −70 °C and for Related Complexes[a]

complexes	chemical shift, ppm				coupling constant, Hz							
	ν_1 (ν_2)	ν_3 (ν_4)	ν_5 (ν_6)	ν_{Cp}	J_{12}	$J_{13(24)}$	$J_{14(23)}$	$J_{15(26)}$	$J_{16(25)}$	J_{34}	$J_{35(46)}$	$J_{36(45)}$	J_{56}
1 (cis isomer)	−0.69	3.45	4.78	4.84 5.37	0.5	−10.0	0.2	10.5	−0.8	0.2	9.5	−1.5	8.0
2	−0.57 (R_1) −0.73 (R_2)	3.32 (R_3) 3.29 (R_4)	4.52 (R_5) 1.88 (R_6 = CH_3)	4.96 5.45	0.8	−9.6	0.3	11.0 (J_{15})	−0.2	0.4	10.2 (J_{35})	−1.5 (J_{45})	
3	−0.72	3.16		5.03 5.44	1.0	−10.0	0.2			0.5			
8 (cis isomer)	0.90		5.57	4.84 5.38	0.5			11.1	−1.8				10.7
$Fe(CO)_3(C_4H_6)$[b]	−0.03	1.46	4.89		−0.31	−2.42	−0.09	9.33	−1.11	0.05	6.93	1.14	4.70
$Ru(CO)_3(C_4H_6)$[b]	0.12	1.44	4.88		−0.30	−2.77	−0.13	8.65	−1.10	0.02	6.94	1.10	4.60
$Os_3(CO)_{10}(C_4H_6)$[c]	0.49	2.32	5.27		?	2.89	?	8.53	−0.79	?	7.17	1.02	4.66

[a] Spectra were observed at 100 MHz in toluene-d_8 and were analyzed by the computer simulation. Chemical shifts were calibrated by using the internal benzene peak, assumed to be 7.20 ppm. The numbering system follows that shown in eq 3. [b] Data by Philipsborn.[17,18] [c] Data by Shapley.[26]

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Table IV. ^{1}H NMR (100 MHz) Spectral Data for *s-cis*-Diene Complexes at 38 °C[a]

complexes	chemical shift, ppm				coupling constant, Hz		
	ν_1 (ν_3)	ν_2 (ν_4)	ν_5 (ν_6)	ν_{Cp}	$J_{15(26)}$	$J_{35(46)}$	J_{56}
1[b]	1.43 (b s)	1.43 (b s)	4.74 (dt)	5.25	9.9	9.9	10.7
2	1.27 (d)	1.23 (s)	4.58 (t)	5.28	10.1 (J_{15})	10.1 (J_{35})	
3	1.19 (s)	1.19 (s)		5.31			
4[c]	1.14 (m)	1.14 (m)	5.04 (m)	5.23	10.1	10.1	11.1
5	1.00 (d)	1.05 (s)	4.90 (t)	5.27	9.9 (J_{15})	9.9 (J_{35})	
6	0.93 (s)	0.93 (s)		5.36			

[a] Toluene-d_8 was used as a solvent. [b] Measured at 60 °C. [c] Simulated spectrum was given in ref 3. Numbering system follows that for metallacyclopentene given in eq 3.

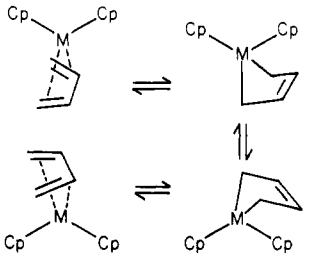
Table V. ^{1}H NMR Parameters for *s-trans*-η^4-Diene Complexes at 38 °C[a]

complexes	chemical shift, ppm				coupling constant, Hz							
	ν_1 (ν_2)	ν_3 (ν_4)	ν_5 (ν_6)	ν_{Cp}	J_{12}	$J_{13(24)}$	$J_{14(23)}$	$J_{15(26)}$	$J_{16(25)}$	J_{34}	$J_{35(46)}$	$J_{36(45)}$
1 (trans isomer)	3.22	1.22	2.90	4.92	0.5	−4.0	0.02	7.1	−0.5	0.5	16.4	−1.1
7		3.23	3.91	4.89						0.2	15.8	−0.8
8 (trans isomer)		3.11	3.87	4.88						0.2	15.5	−0.8
$Os_3(CO)_{10}(C_4H_6)$[b]	1.43	2.26	3.40		?	2.47	?	7.38	−0.65	?	11.13	−0.48
C_4H_6[c]	4.97	5.08	6.25		1.3	1.7	0.6	10.1	−0.8	0.7	16.9	−0.8

[a] Spectral data were collected at 100 MHz in toluene-d_8 and analyzed by simulation. [b] Data by Shapley.[26] [c] Data by Segre.[25] The numbering system follows that given in eq 7.

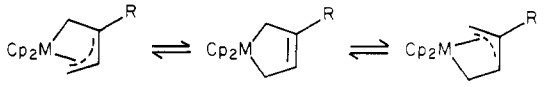
cis-butadiene.[17-19] On the basis of these facts, the solution structure of 1–3 was concluded to be the conventional *s-cis*-η^4-diene structure below −40 °C, in line with the crystal structure of Cp_2Zr(2,3-dimethyl-1,3-butadiene).[6]

The chemical shift difference between the syn and anti protons for 1, 2, and 3 at −70 °C was found to be exceedingly large (3.88–4.14 ppm) compared with those (1.3–2.3 ppm) for $[Zr(C_4H_6)_2(dmep)](dmep)$,[1] $Fe(CO)_3(C_4H_6)$,[17] $RhCp(C_4H_6)$, $RhCp(C_5H_8)$,[20] or similar complexes. The resonance of the anti protons appears at remarkably high magnetic field, indicating their presence in a magnetically highly shielded environment. The diamagnetic shielding zone due to the Cp–Zr bond seems responsible for this observation. The chemical shift of the syn protons was significantly lowered compared with that of $M(CO)_3(C_4H_6)$ (M = Fe, Ru, Os) but is similar to that of tricarbonyl(cyclic diene)iron complexes.[21] The chemical shift values of the terminal protons at diene termini observed at 38 °C fit well to the averaged value of chemical shifts of syn and anti protons observed at −70 °C. A single Cp proton resonance at 38 °C also showed the averaged chemical shift value of the two Cp resonances detected at −70 °C (Table V).



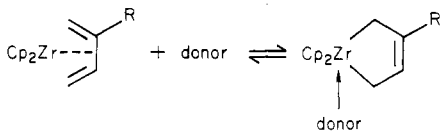
(4)

Therefore, the fluxional mode of the 1,3-diene coordinated to Zr may be explained in terms of the equilibrium between (*s-cis*-η^4-diene)metal and metallacyclo-3-pentene species (a flip mechanism) rather than the rotation of the diene group around the coordination axis. Equation 4 illustrates the fluxional mode of the butadiene complex as an example. The rate of fluxionalization seems to be in an order 1 < 2 ≃ 3 because the coalescence temperature observed for the butadiene complex (ca. 0 °C) is higher than those (ca. −40 °C) observed for the isoprene and 2,3-dimethyl-1,3-butadiene complexes. The ^{1}H NMR data gave no evidence in support of a fluxionalization process via (η^3-allyl)metal species shown in eq 5.



(5)

Since the metallacyclopentene is a 16-electron species with an electron-rich alkenyl group, complexation with electron donors or electron acceptors seems plausible. If an electron donor occupies the vacant d orbital of the metal, the equilibrium (eq 6) may shift to the right to give



(6)

a stable metallacyclo-3-pentene which has two Zr–C σ bonds, as in $Cp_2Zr(CH_3)_2$ or dicyclopentadienylzirconacyclopentane. To examine this possibility, an excess of an electron donor such as $P(Bu)_3$, $P(C_6H_5)_3$, pyridine, or triethylamine was added to 2. However, no remarkable change was observed on the variable-temperature NMR spectra. An electron acceptor such as trimethylaluminium or triethylaluminium also showed no interaction with 2 although 2 forms an adduct with $MgCl_2$·2THF as noted above. Thus, the addition of usual electron donors or acceptors had no effect on the presumed equilibration (eq 6, cf. eq 4).

The ^{1}H NMR patterns of the Hf complexes 4–6 were very simple and did not (Table IV) change on lowering the temperature from +60 °C to −85 °C. However, when the temperature was lowered to −110 °C, the spectra of 4 and 6 were converted to the pattern of *s-cis*-η^4-diene coordination as has been found for 1 and 3 at −40 °C, respectively. Broad signals of the anti and syn protons of 4 appeared at −0.65 and 3.36 ppm and Cp proton signals at 4.78 and 5.21 ppm. Corresponding signals of 6 appeared

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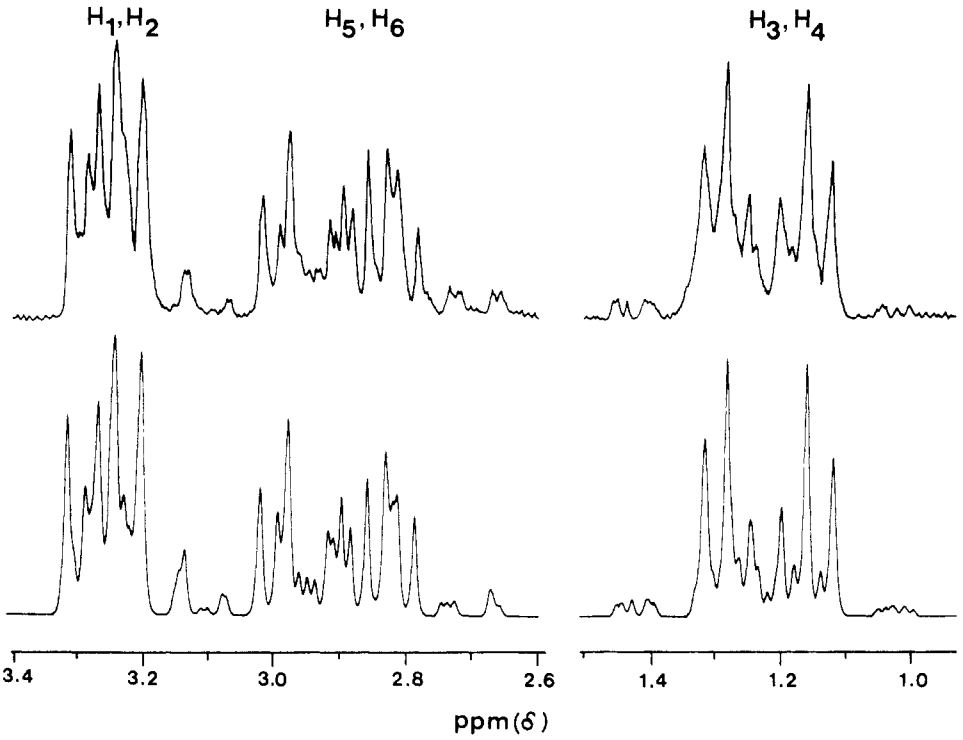

Figure 2. ^{1}H NMR (100-MHz) spectrum of Cp_2Zr(*s-trans*-η^4-butadiene) at 38 °C in toluene-d_8 (above) and the simulated spectrum (below).

at −0.65 (anti), 3.05 (syn), 4.98, and 5.30 (Cp) ppm, respectively, at this temperature. Thus, the rate of fluxionalization of the hafnium–diene complexes is very rapid at temperatures above −85 °C.

When the chemical shift values of the Hf complexes 4–6 were compared with those of the Zr complexes 1–3 at 38 °C, the resonance of the terminal protons appears at a higher field by 0.26–0.29 ppm. This difference may be attributed to the stronger M–C σ-bonding character of Hf than Zr, in accord with the general trend that the metal–hydrogen or metal–carbon σ bond is stronger for the third-row transition-metal complexes than the corresponding bond in the second-row isostructural ones. For example, calculation of the Cotton–Kraihanzel force constants for the CO vibration of $M(CO)_2Cp_2$ (M = Ti, Zr, Hf)[22] showed that the force constants (mdyn/Å) decrease from Ti, 15.18, and Zr, 15.06, to Hf, 14.96. The interaction force constants increase in the order Ti, 0.61, Zr, 0.70, Hf, 0.71, to indicate enhanced bonding with CO for the Hf derivative. In the related pentamethylcyclopentadienyl compounds, $M(CO)_2(Me_5C_5)_2$,[22] the same trend was observed. Thus, the remarkably different NMR temperature dependency observed between Zr and Hf complexes is reasonably explained as follows: The hafnium complexes prefer the σ-M–C bonding (when compared with the isostructural Zr complexes), while the Zr complexes prefer the π-M–C bonding.

The detection of subtle differences in the electronic properties between Zr and Hf is worth noting because these two elements are known to have similar electronegativities, ionic potentials, and ionic radii due to the lanthanide contraction. The difference is amplified in the dynamic structure of organometallic complexes with multicenter ligands. Similar spectral differences have been observed between tetrakis(η-allyl)zirconium and tetrakis(η-allyl)-hafnium.[23] The former showed the limiting AM_2X_2 pattern at temperatures below −40 °C, while the latter has an AX_4 pattern even at −60 °C, suggesting ease in rotation at the CH_2 group. The X-ray structures of $(C_5H_5)_4M$ also showed a critical difference; i.e., $(C_5H_5)_4Hf$ was formulated with two η^1- and two η^5-cyclopentadienyl units, while $(C_5H_5)_4Zr$ has one η^1- and three η^5-bonded Cp ligands.[24] Lack of X-ray analyses of organozirconium and -hafnium complexes does not allow meaningful comparisons of the metal–carbon bond distances at present.

Despite the presence of a clear spectral difference between Zr and Hf complexes, these complexes showed no difference in the hydrolysis and air oxidation as noted above. This is presumably due to the ease in conversion of the η^4-diene species to the metallacyclic form by the attack (coordination) of H_2O or O_2 that results in the production of the same compounds from the Zr and Hf analogues.

Nuclear Magnetic Resonance of Cp_2M(1,3-diene) with *s-trans*-η^4-Diene Structure. Cp_2Zr(butadiene), which was recrystallized from hot hexane, showed the *s-cis*-η^4-diene structure as mentioned above. However, when the Cp_2Zr(butadiene) was prepared and extracted into hexane below 30 °C, it comprises two species: *s-cis*-η^4-butadiene (75%) and *s*-trans-η^4-butadiene (25%). The ^{1}H NMR parameters for the latter were obtained by computer simulation (Figure 2) and are given in Table V. The large values of $J_{35(46)}$ and J_{56} clearly show that this species has the *s-trans*-η^4-diene structure. The magnitude of both J_{35} and J_{56} is larger than those for butadiene[25] and a trinuclear osmium–*s-trans*-butadiene complex.[26]

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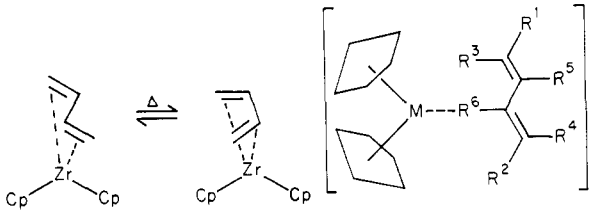


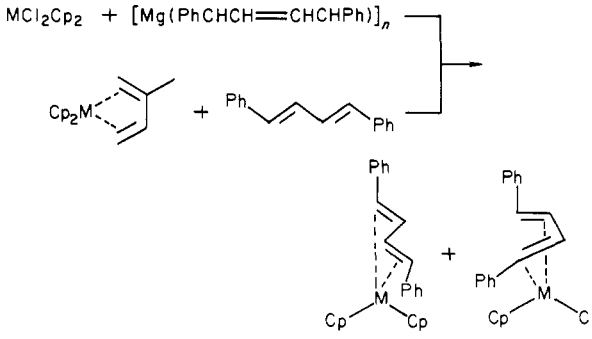
(7)

M = Zr, Hf

Athough the coordination of a *s-trans*-diene to metals was already reported for dinuclear manganese[27] and trinuclear osmium complexes,[26] the coordination of a *s-trans*-diene to mononuclear complexes now has confirmed by ^{1}H NMR studies for the first time. An X-ray analysis of Cp_2Zr(*s-trans*-butadiene) has recently been reported. However, there is some uncertainty with respect to the *s-trans* conformation because of the large positional ambiguity of the central two carbon atoms of the diene.[6]

The *s-trans*-butadiene complex is thermally unstable and readily can be converted to the *s-cis*-butadiene complex by heating in toluene at 80 °C for 30 min. The complexes **2–6** which were prepared at low temperature (25 °C) showed no contamination with the isomer of the *s-trans*-η^4-diene structure as revealed by ^{1}H NMR. The ratio of the *s-cis*- to *s-trans*-diene complex prepared by the present method at 25 °C is summarized in Table VI.

When 1,4-diphenyl-1,3-butadiene was used as a ligand, the *s-trans*-diene coordination to Zr becomes predominant. The NMR parameters of Cp_2Zr(1,4-diphenyl-1,3-butadiene) (**7**) which was prepared from (1,4-diphenyl-2-butene-1,4-diyl)magnesium fit well to those for $Os_3(CO)_{10}$(*s-trans*-C_4H_6) in their chemical shifts while J_{56} is larger.



(8)

We have found a novel method for preparation of **7** by a ligand-exchange reaction. The reaction of the isoprene complex with an equimolar amount of (*E,E*)-1,4-diphenylbutadiene gave **7** quantitatively (>90%) when the mixture was heated to 60 °C in benzene (eq 8). Release of isoprene was confirmed by GC. This is the first example for the synthesis of zirconium(IV)–diene complexes by a ligand exchange reaction. The ratio of *s-trans*- to *s-cis*-diene species (97/3) observed for **7** was the same irrespective of the two different synthetic routes described above. Although Cp_2Zr(*s-trans*-butadiene) can readily be converted into Cp_2Zr(*s-cis*-butadiene) by heating at 80 °C in toluene, no such transformation was observed for **7** even when it was heated at 120 °C for 16 h. Complex **1** represents the thermally stable mononuclear *s-trans*-diene complexes.

Surprising was the observation that Cp_2Hf(1,4-diphenyl-1,3-butadiene) (**8**) favors the *s-cis*-η^4-diene structure (76%) over the *s-trans*-η^4-diene structure (24%) even when the complex was prepared by the ligand-exchange reaction under mild reaction conditions (60 °C in benzene). Complex **8** prepared by reaction of [Mg(PhCHCH=CHCHPh)]$_n$ with Cp_2HfCl_2 also favored the *s-cis*-diene configuration. The ratio of *s-cis* to *s-trans* was 75/25, in good agreement with the ratio obtained by the ligand-exchange reaction.

Table VI. Molar Ratio of *s-cis*- to *s-trans*-Diene Species for Cp_2M(diene) Prepared from Enediylmagnesium at 25 °C[a]

complex	M	diene	*s-cis*- to *s-trans*-diene, mol/mol	
1	Zr	butadiene	75	25
2		isoprene	100	0
3		2,3-dimethylbutadiene	100	0
4		1,4-diphenylbutadiene	3	97
5	Hf	butadiene[b]	100	0
6		isoprene[b]	100	0
7		2,3-dimethylbutadiene[b]	100	0
8		1,4-diphenylbutadiene	75	25

[a] Determined by ^{1}H NMR at −70 °C in toluene-d_8. [b] Species of hafnacyclo-3-pentene structure is counted as *s-cis*-diene species.

Table VII. IR and Electronic Spectral Data for Cp_2M(*s-cis*-diene) Complexes in THF[a]

complex	λ_{max}, nm	ϵ mol^{-1}/L cm^{-1}	$\nu_{C=C}$ of diene, cm^{-1}	$\nu_{C=C}$ of Cp, cm^{-1}
1	432	1080	1479 (m) 1515 (w)	1442
2	438	1110	1477 (m) 1516 (w)	1443
3	448	1140	1477 (m) 1516 (w)	1444
4	350	970	1487 (m) 1515 (w)	1442
5	370	990	1480 (m) 1516 (w)	1442
6	394	1040	1476 (m) 1516 (w)	1443
7	385 495	3180 1500		1443
8[b]	438	1130		1443

[a] Spectral data were collected at 25 °C, and the absorption of THF were compensated with a variable cell. [b] A mixture (25/75) of *s-cis*- and *s-trans*-diene species.

Computer simulation of the ^{1}H NMR spectrum of the *s-cis*-diene species of **8** (cf. Figure 3) revealed J values similar to those for **1** and **2** of the *s-cis*-diene structure, indicating similar bonding. However, the fluxionalization rate for **8** of *s-cis*-diene structure was extremely slow when compared to **1–6** and no significant spectral change was observed in the temperature range −40 to +60 °C. Interconversion of the *s-cis*- to the *s-trans*-diene structure has not been achieved by irradiation of UV in benzene. It is not clear at present why **7** prefers the *s-trans*-diene and **8** prefers the *s-cis*-diene coordination.

The IR and the Electronic Spectrum of Cp_2M(diene) in THF. The IR data on the complexes **1–6** were collected (Table VII) in order to obtain more information on the fluxional structure since IR data on metal complexes of mono- and polyolefins have revealed that the vibrational frequencies associated with C=C bond are correlated to the σ- or π-type of M–C bonding.[28] The C=C frequencies of η^4-butadiene coordinated to metals such as Co, Mn, V, and Fe generally appears at 1380–1480 cm^{-1}[29] and of metallacyclo-3-pentenes at 1550–1600 cm^{-1},

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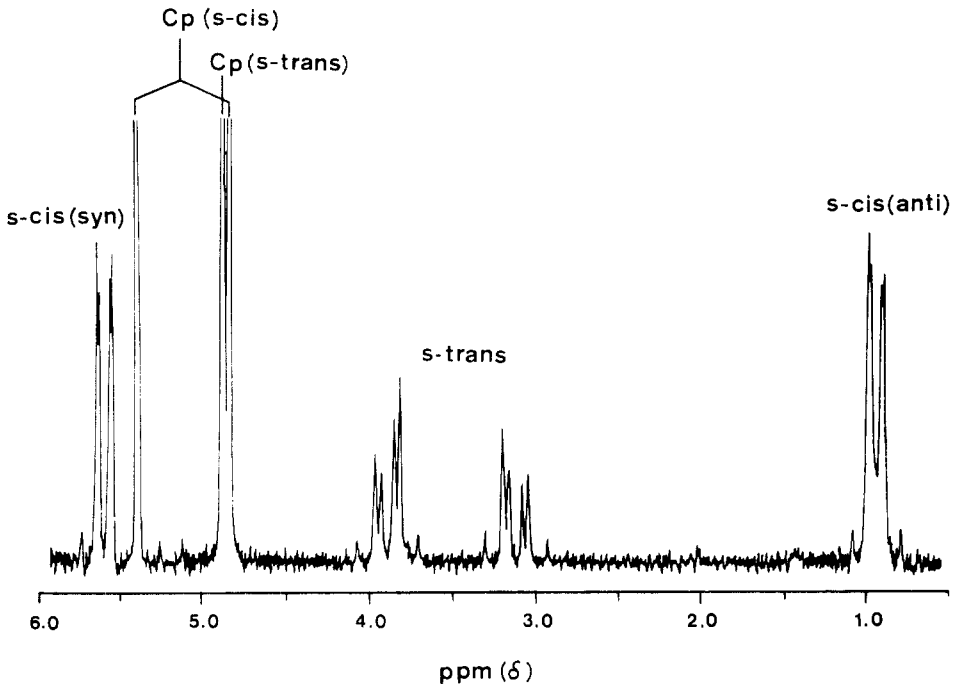

Figure 3. ^{1}H NMR (100-MHz) spectrum of Cp_2Hf(1,4-diphenyl-1,3-butadiene) (8) in toluene-d_8 at 38 °C.

as observed for silacyclo-3-pentene (1600 cm^{-1})[30] or (2-butene-1,4-diyl)magnesium (1550 cm^{-1}).[7]

Although *s-cis*-η^4-diene coordination is unambiguous for 1–6 at low temperatures (−80 ± 30 °C) from the ^{1}H NMR data, it is not clear how much η^4 diene species exists at ambient temperature when they are fluxional in solution. The observed C=C frequencies of 1–6 in THF at 30 °C (1515 and 1481 ± 5 cm^{-1}) are close to the values reported for η^4-diene structures rather than the metallacyclopentene structures. Therefore, on this basis, one can conclude that both the zirconium complexes 1–3 and hafnium complexes 4–6 prefer the η^4-diene structure even when they become fluxional at higher temperatures (0–60 °C). No clear difference in bonding character between zirconium and hafnium complexes has been revealed from the IR data.

The electronic spectra of 1–6, however, showed a remarkable difference between them. The absorption maxima of the zirconium complexes appeared at longer wavelength than those of the corresponding hafnium complexes (Table VII). This result suggests that electronic delocalization over the diene group in the Zr complexes is higher than that in the corresponding Hf derivatives. This means that the zirconium complexes have less σ-bonding character compared to the Hf analogues, in line with the conclusion obtained from the NMR studies. Substitution of phenyl groups at the η^4-diene (complexes 7 and 8) results in longer wavelength shift of the maximum. Meaningful comparison between 7 and 8 cannot be made because the former has the *s-trans*-diene species while the latter involves the *s-cis*-diene species.

Experimental Section

All operations were conducted with Schlenk techniques under argon atmosphere. All the reagents and solvents were distilled after being dried over appropriate drying agents: calcium hydride for olefins and dienes; Na/K alloy for THF and toluene. $ZrCl_2Cp_2$ and $HfCl_2Cp_2$ were prepared by the known method and purified by recrystallization or sublimation. The purity of these complexes was confirmed to be >97% by elemental analysis, mass and ^{1}H NMR spectroscopies, and measurement of melting point: 249 °C for $ZrCl_2Cp_2$ (lit.,[31] 247–249 °C); 305 °C dec for $HfCl_2Cp_2$ (lit.[32] 300 °C). The gas chromatographic analysis of the reaction products was made with a Hitachi Model 163 gas chromatograph equipped with a capillary column, HB-2000 or CW (45 m), and the separation of the products with a Varian-Aerograph Model 700 gas chromatograph using a column packed with Celite-silicone DC-550. 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 were recorded on a JEOL OISG-2 spectrometer. IR spectra were obtained on a Hitachi EPI-2 spectrometer and the electronic spectra on a JASCO Model UVIDEC-5A spectrometer. Elemental analyses of the diene complexes were carried out only for 1,4-diphenylbutadiene complexes with a Yanagimoto Model MT-2 CHN analyzer since other complexes were decomposed immediately in the air. Melting points were measured with a sealed glass capillary and were uncorrected.

Activation of Magnesium. The activation of magnesium was carried out in essentially the same way as described previously.[4] To 6.1 g (0.25 mol) of magnesium turnings (suitable for Grignard reaction) in 80 mL of dried THF was added at ambient temperature 0.3 g (2.5 mmol) of iodine and 2.5 mL (0.025 mol) of dry isoprene or 2,3-dimethyl-1,3-butadiene. The mixture was shaken for 30 h at 70 °C in a temperature-controlled water bath, the resulting yellow-green solution was removed by using a syringe, and the residual magnesium was washed with 20 mL of THF. The resulting lusterless magnesium turnings (5.4 g) were used as the activated magnesium for reaction with 1,3-dienes. When the magnesium is inactive, the above-mentioned procedure should be repeated again or the above-mentioned yellow green solution (0.3 mL) should be added to the magnesium. The use of commercial turnings without activation or the use of insufficiently dried THF resulted in no reaction between magnesium and the dienes even at 60 °C. Increase of the reaction temperature exceeding 15 °C or further addition of iodine for activation of magnesium turnings should be avoided because it causes contamination by the magnesium–1,3-diene (1/2) addition compound.

Preparation of (2,3-Dimethyl-2-butene-1,4-diyl)magnesium. Magnesium–butadiene (1/1) adduct ((2-butene-1,4-diyl)magnesium–bis(tetrahydrofuran)) and magnesium–isoprene (1/1) adduct ((2-methyl-2-butene-1,4-diyl)magnesium–bis(tetrahydrofuran)) were prepared as previously reported.[3,4] Magnesium–2,3-dimethyl-1,3-butadiene (1/1) adduct, [$MgCH_2C$-

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$(CH_3)=C(CH_3)CH_2 \cdot 2THF]_n$, was prepared in exactly the same way. Freshly distilled 2,3-dimethyl-1,3-butadiene (5.6 mL, 50 mmol) was added to an excess of activated magnesium (12 g, 0.5 mol) in THF (100 mL) and a mixture was shaken for 5 days at 10 °C at a water bath incubator. The resulting yellow solution was evaporated to dryness, and the residue was washed with anhydrous benzene to give the 1/1 adduct as pale yellow powder in 77% yield; mp 71 °C dec. The adduct is flammable in the air and immediately decomposes upon hydrolysis in toluene to give 2,3-dimethyl-1-butene (38%) and 2,3-dimethyl-2-butene (62%) besides 2 mol of THF originally coordinated to the magnesium atom: M content, 9.5% by 8-quinolinol method; 9.7% calcd for $C_{14}H_{28}O_2Mg$. ^1H NMR (THF-d_8): 1.03 (s, 4 H, CH_2) 1.81 ppm (s, 6 H, CH_3). The CH_3 proton signal was measured by WEFT (water eliminated Fourier transform) method because it overlapped partially the signal of coordinated THF.

Preparation of (1,4-Diphenyl-2-butene-1,4-diyl)magnesium. A mixture of (*E,E*)-1,4-diphenyl-1,3-butadiene (5 g, 25 mmol) and activated magnesium turnings (6.1 g, 250 mmol) in THF (120 mL) was shaken for 5 days at 15 °C in a shaking apparatus. The resulting deep red solution was separated from magnesium turnings with a syringe, concentrated to 50 mL and cooled to −20 °C to induce the precipitation of (1,4-diphenyl-2-butene-1,4-diyl)magnesium–tris(tetrahydrofuran) as an orange powder in 80% yield. One recrystallization from THF was sufficient for purification (0.6 g of sample per 10 mL of THF). The structure determination was based on the GC analysis of the hydrolysis products, 1,4-diphenyl-2-butene (55%) and 1,4-diphenyl-1-butene (45%), and on the analysis of the metal content (5.4% by 8-quinolinol method; 5.44%, calcd for $C_{28}H_{38}O_3Mg$). The X-ray structure will be reported elsewhere.

Preparation of Cp_2Zr(butadiene) Complex 1. To a stirred slurry of $ZrCl_2Cp_2$ (2.9 g, 10 mmol) in THF (25 mL) in a 100-mL Schlenk tube was added a suspension of (2-butene-1,4-diyl)-magnesium, $[Mg(butadiene) \cdot 2THF]_n$ (2.2 g, 10 mmol), in THF (150 mL) at −40 °C. The mixture was stirred for 1 h at 30 °C and then heated to 60 °C for 10 min. The solution turned from pale yellow to deep red. After evaporation of the solution to dryness, a mixture of hexane (50 mL) and benzene (15 mL) was added and the mixture was heated at reflux for 10 min under an argon atmosphere. The precipitated $MgCl_2 \cdot 2THF$ was separated by centrifugation using a two-necked glass tube fitted with rubber stoppers. Removal of benzene–hexane by trap-to-trap distillation gave Cp_2Zr(butadiene) as deep red crystals in 70% yield. The sample was purified by recrystallization from hexane at −20 °C. Characterization of the complex was based on the ratio of metal to hydrolysis product (analyzed by GC) in addition to the ratio of Cp to the diene group determined by ^1H NMR as shown in Tables I and II.

Preparation of Cp_2Zr(isoprene) Complex 2. A solution of (2-methyl-2-butene-1,4-diyl)magnesium, $[Mg(C_5H_8) \cdot 2THF)]_n$ (2.4 g, 10 mmol), dissolved in THF (80 mL) was added at once at −40 °C to a stirred slurry of $ZrCl_2Cp_2$ (2.9 g, 10 mmol) in THF (25 mL). The mixture was allowed to warm to ambient temperature, stirred for 2h, heated to 60 °C for 5 min, and evaporated to dryness. Hexane (50 mL) was added to the residue, and the mixture was refluxed for 10 min and separated from the salts with a syringe. The products were further extracted from the salts with two portions of 1/2 benzene–hexane (40 mL). Evaporation of the combined solutions gave deep red crystals of Cp_2Zr-(isoprene) in 70% yield. The pure complex was obtained by recrystallization from hexane at −20 °C. When the above-mentioned THF solution was kept at −20 °C for 20 h, prismatic orange crystals were precipitated in 70% yield. The metal content of the crystals agreed with the value calculated for $[Cp_2Zr(C_5H_8)][MgCl_2 \cdot 2THF]$: Zr, 16.5% by oxidation method (calcd 17.2%) and Mg, 5.1% by 8-quinolinol method (calcd 4.5%). When hexane (40 mL) was added at 30 °C to the concentrated THF solution (30 mL) and the mixture was kept at −20 °C for 1 day, orange crystals whose metal content agreed with that of $[Cp_2Zr(C_5H_8)][MgCl_2 \cdot 2THF]_{2.2}$ were precipitated: Zr, 11.1% (calcd 11.17%) and Mg, 6.5% (calcd 6.55%); yield 55%. When the isolated adduct $[Cp_2Zr(C_5H_8)][MgCl_2 \cdot 2THF]$ (5.3 g, 10 mmol) was heated for 10 min in refluxing hexane (80 mL), it decomposed to release Cp_2Zr(isoprene) into the hexane. The hexane solution was concentrated to 6 mL and cooled to −20 °C to give crystals of pure $Cp_2Zr(C_5H_8)$ which contained no magnesium salts as checked by chemical analysis. The yield of **2** was 65%. No appreciable difference was observed between $[Cp_2Zr(C_5H_8)]$-$[MgCl_2 \cdot 2THF]$ and **2** in the ^1H NMR and electronic spectra in THF.

Preparation of Cp_2Zr(2,3-dimethylbutadiene) (3). A solution of (2,3-dimethyl-2-butene-1,4-diyl)magnesium, $[Mg(C_6H_{10}) \cdot 2THF]_n$ (2.5 g, 10 mmol), in THF (80 mL) was added to finely divided $ZrCl_2Cp_2$ (2.9 g, 10 mmol) stirred in THF (30 mL) at −20 °C. The mixture was stirred for 2 h at 30 °C and heated to 60 °C for 5 min. The resulting orange solution was evaporated to dryness, and the residue was extracted with two portions of hot hexane (50 mL). Evaporation of the solution gave **3** as orange crystals in 75% yield. Further purification was effected by recrystallization from hexane at 0 °C.

Preparation of Cp_2Hf(butadiene) (4). A suspension of (2-butene-1,4-diyl)magnesium (2.2 g, 10 mmol) in THF was syringed onto finely divided $HfCl_2Cp_2$ (3.8 g, 10 mmol) stirred in THF at 0 °C, and the mixture was stirred for 2 h at 25–30 °C. The resulting orange-colored homogeneous solution was evaporated to dryness, and the residue was extracted with a mixture of benzene (10 mL) and hexane (40 mL). Separation of the solution from salts by centrifugation followed by trap-to-trap distillation gave Cp_2Hf(butadiene) as orange crystals in 80% yield. Recrystallization was carried out in hexane at −20 °C.

Preparation of Cp_2Hf(isoprene) (5). A solution of (2-methyl-2-butene-1,4-diyl)magnesium (2.4 g, 10 mmol) in THF (80 mL) was syringed onto a stirred suspension of $HfCl_2Cp_2$ (3.8 g, 10 mmol) at 0 °C. The mixture was stirred for 1 h at 30 °C and then refluxed for 5 min. The solution was evaporated to dryness and the desired complex was extracted into hexane (60 mL) at 30 °C. The solution was concentrated to 3 mL and kept at −20 °C to induce the precipitation of orange crystals of Cp_2Hf-(isoprene). Typical isolated yield was 82%.

Preparation of Cp_2Hf(2,3-dimethylbutadiene) (6). A solution of (2,3-dimethyl-2-butene-1,4-diyl)magnesium (2.5 g, 10 mmol) in THF (80 mL) was syringed onto a stirred suspension of $HfCl_2Cp_2$ (3.8 g, 10 mmol) at 0 °C. The mixture was stirred for 2 h at 30 °C and then heated to 60 °C for 5 min. After evaporation of the solution to dryness, the desired complex was extracted with hexane (60 mL). Concentration of the solution to 10 mL and cooling to −20 °C gave orange crystals of Cp_2Hf-(2,3-dimethyl-1,3-butadiene) in 85% yield. Recrystallization was done in hexane at 20 °C.

Preparation of 7 and 8 by Reaction with Enediylmagnesium. To a suspension of powdered $ZrCl_2Cp_2$ (2.9 g, 10 mmol) in THF (30 mL) was added at 0 °C a solution of 1,4-diphenyl-2-butene-diyl)magnesium–tris(tetrahydrofuran) (4.5 g, 10 mmol) in THF (100 mL). The mixture was stirred at ambient temperature for 3 h, heated to 60 °C for 10 min, and then evaporated to dryness. Benzene (60 mL) was added to the residue, and the solution was separated from the salts by centrifugation. Concentration of the solution to 10 mL gave deep red crystals of Cp_2Zr(1,4-diphenyl-1,3-butadiene) (**7**) in 75% yield. A pure sample was obtained by recrystallization from benzene. Anal. Calcd for $C_{26}H_{24}Zr$: C, 73.03; H, 5.62. Found: C, 72.95; H, 5.81. Preparation of Cp_2Hf(1,4-diphenyl-1,3-butadiene) (**8**) was carried out in exactly the same manner as described for **7**; yield 80% based on $HfCl_2Cp_2$. Anal. Calcd for $C_{26}H_{24}Hf$: C, 60.64; H, 4.70. Found: C, 60.42; H, 4.72.

Preparation of 7 and 8 by Ligand Exchange Reaction. To a stirred benzene solution (5 mL) of (*E,E*)-1,4-diphenyl-1,3-butadiene (0.7 g, 3.6 mmol) was added a benzene solution (10 mL) of complex **2** (1.1 g, 3.5 mmol) at ambient temperature. The mixture was stirred for 10 h at 40 °C and concentrated to 4 mL by trap-to-trap distillation. Addition of excess hexane (20 mL) resulted in the precipitation of complex **7**. The hexane-soluble part was taken out by a syringe, and the residue was recrystallized from benzene to give deep red needles of **7** in 75% yield based on the complex **2**. Anal. Calcd for $C_{26}H_{24}Zr$: C, 73.03; H, 5.62. Found: C, 72.83; H, 5.90. Preparation of **8** by reaction of **5** (1.3 g, 3.5 mmol) with (*E,E*)-1,4-diphenyl-1,3-butadiene (0.7 g, 3.6 mmol) was carried out under the same reaction conditions as those for **7** except for the reaction temperature (60 °C); yield 82% based on **2**. Anal. Calcd for $C_{26}H_{24}Hf$: C, 60.64; H, 4.66. Found: C, 60.39; H, 4.84.

Hydrolysis and Oxidation of Cp_2M(diene) Complexes. All the complexes were hydrolyzed with 2 N HCl or 2 N DCl in benzene at 5–10 °C. The resulting 1-butene, 2-butene, 2-methyl-1-butene, 3-methyl-1-butene, 2,3-dimethyl-1-butene, or the dideuterated compounds were isolated with a preparative gas chromatograph and were identified by comparison of their MS and ^{1}H NMR spectra with those of authentic samples previously identified.[4,5] 1,4-Diphenyl-1-butene and 1,4-diphenyl-2-butene obtained by hydrolysis of 7 and 8 were identified with reference to the data reported by Bumgardner.[33] The yield of each olefin (Table II) was determined by gas chromatographic analysis within an error of 3%. The purity of the dideuterated olefins was determined to be 96–99% by mass spectroscopy with the use of the corresponding undeuterated olefins as standards. Oxidation was carried out in a closed system; i.e., an excess of dry oxygen (300 mL, dried over P_2O_5) was introduced into the reaction tube containing a toluene solution of a diene complex (3 mmol in 30 mL of toluene) (Schlenk technique). The solution turned colorless after being stirred, for 1–10 min at 25 °C. The formation of 0.93–0.97 molar equiv of the respective conjugated diene was confirmed by GC. Addition of dried air gave the identical result.

(33) C. L. Bumgardner and H. Iwerks, *J. Am. Chem. Soc.*, **88**, 5518 (1966).

Registry No. 1, 75374-50-4; 2, 75361-73-8; 3, 75361-74-9; 4, 80185-89-3; 5, 80161-02-0; 6, 80161-03-1; 7, 75361-76-1; 8, 80161-04-2.

Communications

An Intramolecular Silene Ene Reaction

Robert T. Conlin,* Mel P. Bessellieu, Paul Ronald Jones,* and Richard A. Pierce

Department of Chemistry, North Texas State University Denton, Texas 76203

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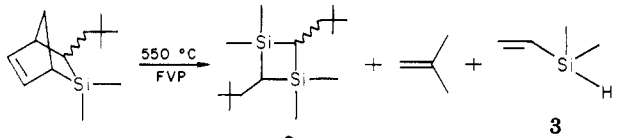
Summary: The flash vacuum pyrolysis of 2,2-dimethyl-3-neopentyl-2-silabicyclo[2.2.1]hept-5-ene (1) gives nearly quantitative yields of cyclopentadiene. In addition to the 1,3-disilacyclobutane dimers of 1,1-dimethyl-2-neopentylsilene (4), two novel silene-derived products, isobutene and dimethylvinylsilane, are produced. Evidence that the latter products are formed in an intramolecular ene-type reaction of the silene, 4, is presented.

To a large extent, the resurgence of interest in the intramolecular ene reactions derives from the facility with which heteroatom π bonds undergo pericyclic processes.[1] With the widespread recognition of the extraordinary reactivity of π bonds between silicon and carbon,[2] it is somewhat surprising that there are no demonstrated examples of ene reactions initiated by a silicon–carbon π bond. In this communication we report a new and mild thermal method for generating silenes in the gas phase as well as an example of an intramolecular ene reaction of a silene.

Flash vacuum pyrolysis[3] of a mixture of the endo and exo isomers of 2,2-dimethyl-3-neopentyl-2-silabicyclo[2.2.1]hept-5-ene (1)[4] at 550 °C leads cleanly to cyclopentadiene in nearly quantitative yield. Four other products are isolated: the cis and trans isomers of 1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutane (2),[5] isobutene, and dimethylvinylsilane (3).[6] These products were all characterized by comparison of their spectral and chromatographic properties with those of authentic samples.



1 2 3

The formation of cyclopentadiene and the 1,3-disilacyclobutanes (2) is consistent with a [2 + 4] cycloreversion of 1, giving cyclopentadiene and 1,1-dimethyl-2-neopentylsilene (4) which undergoes the usual head-to-tail dimerization[2] to form 2. Analogous, possibly concerted, retro Diels–Alder eliminations are known for both the parent hydrocarbon bicyclo[2.2.1]heptene[8] and the related 7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,5-diene.[9] It is noteworthy that the ratio of *cis*- and *trans*-disilacyclobutanes formed in the gas phase at 550 °C, 1.15, is the *same ratio* observed when the silene, 4, is generated at low temperature in hydrocarbon solvents by the reaction of *tert*-butyllithium with chlorodimethylvinylsilane.[5] The absence of a temperature effect on this cis/trans ratio is consistent with earlier reports that there is no appreciable energy barrier to silene dimerization[10] and that 4 is produced in the low-temperature reaction.[4,5]

Especially intriguing is the mechanism of formation of isobutene and 3, which are isolated in nearly equal amounts from the reaction mixture.[11] We have established that the disilacyclobutanes, 2, do not give rise to these

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(2) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(3) Pyrolyses were carried out at 10^{-4}–10^{-5} torr, employing a seasoned hot zone consisting of 10-mm i.d. × 30 cm quartz tube. Residence time in the hot zone was on the order of milliseconds.

(4) Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970.

(5) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 2013, **1977**, *99*, 8447.

(6) Recently, Auner and Grobe[7] have reported that 2,2-dimethyl-2-silabicyclo[2.2.1]hept-5-ene, formed as a transient by the addition of 1,1-dimethylsilene to cyclopentadiene, isomerizes through a series of unprecedented steps and eventually leads to benzene as the only isolated product. We have not been able to reproduce their results.

(7) Auner, N.; Grobe, J. *J. Organomet. Chem.* **1980**, *190*, 129.

(8) Herndon, W. C.; Cooper, W. B.; Chambers, M. J. *J. Phys. Chem.* **1964**, *68*, 2016.

(9) Barton, T. J.; Kline, E. *J. Organomet. Chem.* **1972**, *42*, C21.

(10) (a) Gusel'nikov, L. E.; Konobeevski, V. M.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 1086. (b) Basu, S.; Davidson, I. M. T.; Laupert, R.; Potzinger, P. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1282.

(11) In all of our experiments the yield of isobutene appears to be higher than that of 3. This might be due to the difficulty in determining an accurate response factor for the highly volatile isobutene. It is also possible that side reactions provide another source of isobutene or that some of 3 is consumed by subsequent reactions. We have no evidence which resolves this discrepancy at this time.

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