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The X-Ray and NMR Studies on the Regio- and Stereoselective Courses for Insertion of Ketones into the *s-cis*- and *s-trans*-Diene Complexes of Zirconium Leading to (*Z*)-1,2-Oxazirconacyclohept-4-enes

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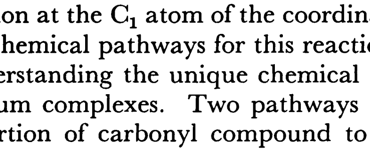
The *s-trans*-diene coordination in $(\eta^5\text{-}C_5Me_5)_2Zr$(butadiene) and the *s-cis*-diene coordination in $(\eta^5\text{-}C_5Me_5)_2Zr$(isoprene) were confirmed by the ^1H- and ^{13}C-NMR spectral studies. The reaction of 2,4-dimethyl-3-pentanone with these complexes occurred regio- and stereoselectively to give $(\eta^5\text{-}C_5Me_5)_2\overline{ZrOC(i\text{-}Pr)_2CH_2CR{=}CHCH_2}$ (**5**: R=H, **6**: R=Me). The X-ray crystal structure analysis of **5** and **6** revealed the (*Z*)-configuration with respect to the olefin part. Crystal data for **5**: monoclinic, space group $P2_1/n$ with $Z=4$, $a=11.650(2)$, $b=17.791(3)$, $c=13.612(2)$ Å, $\beta=92.20(2)°$, $R=0.111$ for 4308 non-zero reflections. Crystal data for **6**: monoclinic, space group $P2_1/n$ with $Z=4$, $a=10.279(3)$, $b=30.177(4)$, $c=9.955(2)$ Å, $\beta=108.67(2)°$, $R=0.104$ for 3526 non-zero reflections.

The unusual versatility of organozirconium complexes has led to many important developments in organic synthesis. In the preceding papers, we have reported that $(\eta^5\text{-}C_5H_5)_2Zr$(*s-cis*-isoprene) readily reacts with saturated or unsaturated ketones, aldehydes or esters; these reactions result in the regioselective C–C bond formation at the C_1 atom of the coordinated isoprene.[1,2] Stereochemical pathways for this reaction are of interest in understanding the unique chemical properties of the zirconium complexes. Two pathways are conceivable: a) insertion of carbonyl compound to the M–C bond with retention of the *s-cis*-diene conformation and b) insertion after conversion to the *s-trans*-diene coordination. Selective preparation of the *s-cis* and the *s-trans* zirconium-diene complexes is necessary to settle this problem. Though preparations of the *s-cis* and *s-trans* isomers of $(\eta^5\text{-}C_5H_5)_2Zr$(butadiene) complexes were recently reported by Erker[3,4] and by us,[5] purification of the respective isomers is difficult due to the existence of rapid equilibration between them. A thermally stable *s-trans* isomer of the butadiene complex was found to be obtained exclusively when the C_5H_5 ligand was replaced with C_5Me_5 ligand. The corresponding isoprene complexes, $(\eta^5\text{-}C_5R_5)_2Zr$(isoprene) (R=H, Me), assume the *s-cis*-diene coordination irrespective of the ligand. These findings prompted us to examine the reaction of carbonyl compounds with the *s-cis*- and the *s-trans*-diene complexes to define the stereochemical course by means of the X-ray structure analysis and chemical characterization.



(1)

1 R=H, L=C_5Me_5
2 R=Me, L=C_5Me_5
3 R=H, L=C_5H_5
4 R=Me, L=C_5H_5

5 R=H, L=C_5Me_5
6 R=Me, L=C_5Me_5

Experimental

All manipulations were conducted with Schlenk technique under argon atmosphere. The reagents and solvents were dried over appropriate drying agents and distilled before use. $(C_5Me_5)_2ZrCl_2$[6] and enediylmagnesiums[7] were prepared according to usual methods. Regioselectivity was determined by gas chromatographic analysis of hydrolysis products with a Yanagimoto Model G-80 gas chromatograph using a column packed with Silicone DC-550 on Uniport B. 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 Model JMS OISG-2 spectrometer. IR and electronic spectra were obtained on a Hitachi EPI-2 spectrometer and a JASCO Model UVIDEC-5A spectrometer, respectively.

*Preparation of $(C_5Me_5)_2Zr$(*s-trans-*butadiene) (1).* To a stirred solution of $(C_5Me_5)_2ZrCl_2$ (508 mg, 1.17 mmol) in 10 ml THF was added a THF slurry of 2-butene-1,4-diylmagnesium (f=0.32, 4.5 ml, 1.44 mmol) at −78 °C. The mixture was gradually warmed up to room temperature (25 °C). After stirring for 1 h, the solvent was evaporated under reduced pressure. The residue was extracted with hexane (25 ml) and salts were separated with a centrifuge to give an orange solution. After the solution was concentrated to *ca.* 1 ml, crystallization was carried out at 0 °C to give **1** as orange crystals. Yield 76% (370 mg, 0.89 mmol). Mp 196 °C, UV (hexane) λ_{max} (ε): 354 nm (1.61×10^3), 450 nm (4.33×10^2); IR (hexane) 1431, 1258, 1157, 1023, 944 and 803 cm^{-1}; MS (EI, 70eV), *m/e* 414 (M^+, ^{90}Zr); Found: C, 69.08; H, 8.50%. Calcd for $C_{24}H_{36}Zr$: C, 69.33; H, 8.73%.

*Preparation of $(C_5Me_5)_2Zr$(*s-cis-*isoprene) (2).* $(C_5Me_5)_2ZrCl_2$ (1.73 g, 4.0 mmol) was treated with 4.4 mmol (f=0.17, 26 ml) of 2-methyl-2-butene-1,4-diylmagnesium in essentially the same manner as described for **1**. Recrystallization from hexane gave **2** in 82% yield (1.41 g). Mp 208 °C. UV (hexane) λ_{max} (ε): 332 nm (2.54×10^3), 395 nm (1.12×10^3); IR (hexane) 1432, 1257, 1172, 1025 and 805 cm^{-1}; MS (EI, 70 eV), *m/e* 428 (M^+, ^{90}Zr); Found: C, 69.80; H, 8.87%. Calcd for $C_{25}H_{38}Zr$: C, 69.87; H, 8.91%.

*Reaction of **1** with 2,4-Dimethyl-3-pentanone.* To a benzene solution (5 ml) of **1** (1.25 g, 3.0 mmol) was added 2,4-dimethyl-3-pentanone (480 mg, 4.0 mmol). The color of the solution gradually turned into pale yellow. The insertion reaction became complete by stirring the mixture for 10 h at 30 °C or for 2 h at 80 °C, as revealed by gas chromatographic analysis. Concentration of solution to 1 ml resulted in the precipitation of complex **5** as yellow powder in >95% yield. Single crystals for X-ray structure analysis were obtained by recrystallization from hexane. Mp 206—211 °C; ^{1}H-NMR (C_6D_6) δ=1.18 (d, 6, J=7.0 Hz, $CH(C\underline{H}_3)_2$), 1.22 (d, 6, J=7.0 Hz, $CH(C\underline{H}_3)_2$), 1.40 (d, 2, J=8.0 Hz, $ZrCH_2$), 1.96 (m, 2, $C\underline{H}(CH_3)_2$), 2.09 (d, 2, J=8.5 Hz, $ZrCH_2CH{=}CH{-}C\underline{H}_2$), 5.15 (dt, 1, J=8.5 and 11.0 Hz, $ZrCH_2CH{=}C\underline{H}$), 6.65 (dt, 1, J=8.0 and 11.0 Hz, $ZrCH_2C\underline{H}{=}CH$), 1.91 (s, C_5Me_5); ^{13}C-NMR (C_6D_6) δ=12.3 ($C_5\underline{Me}_5$), 20.6, 22.3 ($CH(\underline{C}H_3)_2$), 37.7 ($ZrCH_2$), 39.9 ($\underline{C}H(CH_3)_2$), 46.2 ($ZrCH_2CH{=}CH\underline{C}H_2$), 94.5 ($ZrO\underline{C}(i\text{-}Pr)_2$), 115.3 ($ZrCH_2CH{=}\underline{C}H$), 119.0 ($\underline{C}_5Me_5$), 138.6 ($ZrCH_2\text{-}\underline{C}H{=}CH$); MS (FD, 70 eV), m/e 528 (M^+, ^{90}Zr); Found: C, 70.10; H, 9.65%. Calcd for $C_{31}H_{50}OZr$: C, 70.26; H, 9.51%.

*Reaction of **2** with 2,4-Dimethyl-3-pentanone.* To a benzene solution (5 ml) of **2** (1.29 g, 3.0 mmol) was added 2,4-dimethyl-3-pentanone (480 mg, 4.0 mmol) at 25 °C. After the mixture was stirred at 25 °C for 10 h and the solution was concentrated, complex **6** was obtained as pale yellow crystals in 95% yield. A single crystal for the X-ray diffraction was prepared by recrystallization from benzene. Mp 239—243 °C; ^{1}H-NMR (C_6D_6) δ=1.20 (d, 12, J=7.0 Hz, $CH(C\underline{H}_3)_2$), 1.31 (d, 2, J=8.5 Hz, $ZrC\underline{H}_2$), 1.91 (s, 30, C_5Me_5), 2.0 (m, 2, $C\underline{H}(CH_3)_2$), 2.09 (bs, 3, $CH{=}C(C\underline{H}_3)$), 2.13 (bs, 2, $CH{=}C(CH_3)C\underline{H}_2$), 6.61 (t, 1, J=8.5 Hz, $ZrCH_2C\underline{H}{=}C$); ^{13}C-NMR (C_6D_6) δ=12.3 ($C_5\underline{Me}_5$), 20.7, 22.4 ($CH(\underline{C}H_3)_2$), 27.5 ($CH{=}C(\underline{C}H_3)$), 39.6 ($\underline{C}H(CH_3)_2$), 41.3 ($Zr\underline{C}H_2$), 47.0 ($CH{=}C(CH_3)\text{-}\underline{C}H_2$), 93.2 ($ZrO\underline{C}(i\text{-}Pr)_2$), 118.8 ($\underline{C}_5Me_5$), 121.0 ($CH{=}\underline{C}(CH_3)$), 135.1 ($\underline{C}H{=}C(CH_3)$); MS (FD, 70eV), m/e 542 (M^+, ^{90}Zr); Found: C, 70.60; H, 9.66%. Calcd for $C_{32}H_{52}OZr$: C, 70.65; H, 9.64%.

*Hydrolysis of **5**.* To the complex **5** (1.06 g, 2.0 mmol) in diethyl ether solution (20 ml) was added acetic acid (1 ml), 4 mol dm^{-3} aq HCl or aq H_2SO_4 at 20 °C. After neutralization with aq $NaHCO_3$, the resulting 2-methyl-3-isopropyl-6-hepten-3-ol was isolated by distillation (120 °C/2 mmHg, 1 mmHg≈133.322 Pa). Isolated yield, 85%. When the complex **5** was hydrolyzed with 0.1 mol dm^{-3} aq NaOH, a mixture of 2-methyl-3-isopropyl-6-hepten-3-ol (35%) and 2-methyl-3-isopropyl-5-hepten-3-ol (65%) was obtained. The geometry of the latter could not be determined due to the failure in separation of the respective isomers using a preparative gas chromatograph. Therefore, the ^{1}H-NMR assignment of the latter was made with reference to the spectrum of 2-methyl-3-isopropyl-6-hepten-3-ol obtained by acid hydrolysis.

2-Methyl-3-isopropyl-6-hepten-3-ol: IR (neat) 3490, 3078, 2960, 1640, 1467, 1383, 1095, 992, 968, 950, and 908 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.95, 0.97 (d, 12, J=7.0 Hz, $CH(C\underline{H}_3)_2$), 1.48—2.25 (m, 7, others), 4.84—5.20 (m, 2, $CH{=}C\underline{H}_2$), 5.60—6.05 (m, 1, $C\underline{H}{=}CH_2$); ^{13}C-NMR ($CDCl_3$) δ=17.4, 17.6 ($CH(\underline{C}H_3)_2$), 28.8 ($\underline{C}H_2COH$), 33.0 ($CH_2{=}CH\underline{C}H_2$), 34.2 ($\underline{C}H(CH_3)_2$), 77.0 (COH), 114.1 ($\underline{C}H_2{=}CH$), 139.3 ($CH_2{=}\underline{C}H$); MS (EI, 70 eV) 170 ($M^+$); Found: C, 77.50; H, 13.02%. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02%.

2-Methyl-3-isopropyl-5-hepten-3-ol: ^{1}H-NMR ($CDCl_3$) δ=0.93, 0.95 (d, 12, J=7.0 Hz, $CH(C\underline{H}_3)_2$), 1.40—2.50 (m, 8, others), 5.40—5.70 (m, 2, $C\underline{H}{=}C\underline{H}$).

*Hydrolysis of **6**.* When the complex **6** was hydrolyzed with 0.1 mol dm^{-3} aq NaOH in diethyl ether at 20 °C, a mixture of (Z)-2,5-dimethyl-3-isopropyl-5-hepten-3-ol (97%) and 2,5-dimethyl-3-isopropyl-6-hepten-3-ol (3%) was obtained in 99% GC yield, while the protolysis with acetic acid gave 2,5-dimethyl-3-isopropyl-6-hepten-3-ol (94% isomeric purity) in 95% yield. The (Z)-structure was determined from the NOE measurement (8%) in $CDCl_3$ at 30 °C.

(Z)-2,5-Dimethyl-3-isopropyl-5-hepten-3-ol: IR (neat) 3560, 2960, 1467, 1383, 994, and 813 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=0.97, 0.99 (d, 12, J=6.5 Hz, $CH(C\underline{H}_3)_2$), 1.32 (s, 1, OH), 1.65 (d, 3, J=7.0 Hz, $C\underline{H}_3CH{=}$), 1.84 (bs, 3, $CH{=}C(C\underline{H}_3)$), 1.95 (sept, 2, J=6.5 Hz, $C\underline{H}(CH_3)_2$), 2.30 (bs, 2, $CH{=}C(CH_3)C\underline{H}_2$), 5.40 (q, 1, J=7.0 Hz, $CH_3C\underline{H}{=}$); ^{13}C-NMR ($CDCl_3$) δ=14.3 ($\underline{C}H_3CH{=}$), 17.8, 18.5 ($CH(\underline{C}H_3)_2$), 26.5 ($CH{=}C(\underline{C}H_3)$), 34.8 ($CH{=}C(CH_3)\underline{C}H_2$), 35.1 ($\underline{C}H(CH_3)_2$), 78.4 (COH), 123.5 ($CH_3\underline{C}H{=}$), 133.7 ($CH{=}\underline{C}(CH_3)$); MS (EI, 70 eV) 184 ($M^+$); Found: C, 78.07; H, 13.00%. Calcd for $C_{14}H_{24}O$: C, 78.20; H, 13.11%.

2,5-Dimethyl-3-isopropyl-6-hepten-3-ol: ^{1}H-NMR ($CDCl_3$) δ=0.90—1.05 (m, 15, $CH(C\underline{H}_3)_2$ and $CH_2{=}CHCH_2CHC\underline{H}_3$), 1.50—2.50 (m, 6, others), 4.80—5.20 (m, 2, $CH{=}C\underline{H}_2$), 5.55—6.10 (m, 1, $C\underline{H}{=}CH_2$).

*Crystal Structure Determination of **5** and **6**.* *Crystal Data for* $[(C_5Me_5)_2\overline{ZrOC(i\text{-}Pr)_2CH_2CH{=}CHC}H_2]$ ***(5)***: $C_{31}H_{50}OZr$, M=530.0, monoclinic, space group $P2_1/n$, a=11.650(2), b=17.791(3), c=13.612(2) Å, β=92.20(2)°, U=2819.3(9) Å^3, Z=4, D_c=1.248 g cm^{-3}, μ(Mo $K\alpha$)=4.06 cm^{-1}, F(000)=1136.

Crystal Data for $[(C_5Me_5)_2\overline{ZrOC(i\text{-}Pr)_2CH_2CMe{=}CHC}H_2]$ ***(6)***: $C_{32}H_{52}OZr$, M=544.0, monoclinic, space group $P2_1/n$, a=10.279(3), b=30.177(4), c=9.955(2) Å, β=108.67(2)°, U=2925.3(11) Å^3, Z=4, D_c=1.235 g cm^{-3}, μ(Mo $K\alpha$)=3.93 cm^{-1} F(000)=1168.

Data Collection and Structure Analysis: The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation. As the compounds are very air-sensitive, the crystals were sealed in thin-walled glass capillary tubes under argon atmosphere. The crystals with dimensions of 0.50×0.50×0.30 mm for **5** and 0.45×0.40×0.35 mm for **6** were used for the data measurements. The integrated intensities were measured by the θ-2θ scan technique with background countings at each end of the scan range for 5 s. The total numbers of reflections measured were 6478 for **5** (2θ up to 55°) and 5134 for **6** (2θ up to 50°), among which non-zero reflections are 4308 and 3526, respectively. Three monitor reflections were measured for each block of 61 reflections to check for radiation damage and for any change in orientations of the crystals. No radiation damage of the crystals was found. The measured intensities were corrected for Lorentz and polarization effects but not for absorption, because of the relatively small absorption effects of these compounds for Mo $K\alpha$ radiation.

The crystal structures were solved by the conventional heavy atom method and refined by the block-diagonal least-squares (*HBLS*-V).[8] The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[9] Hydrogen atoms were searched for on the difference Fourier maps calculated after the anisotropic refinements of non-hydrogen atoms. Methyl hydrogen atoms, however, could not be located on the maps and were excluded in the final stage of refinements. The weighting scheme applied was $w=[\sigma(F_o)^2+a|F_o|+b|F_o|^2]^{-1}$ for non-zero reflections and $w=c$ for zero reflections, respectively. The final R indices defined by $R=\sum(|F_o|-|F_c|)/\sum|F_o|$ were 0.111 (non-zero reflections) and 0.219 (all reflections) for **5**, and 0.104 and 0.202 for **6**, respectively. The weighted R indices defined by $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 0.160 for **5** with the weighting parameters of a=0.368, b=0.00002, and c=0.014, and 0.094 for **6** with a=0.503, b=−0.002, and c=0.011, respectively. The

Table 1. Fractional atomic coordinates of **5** and **6** with estimated standard deviations in parentheses

a) $[(C_5Me_5)_2\overline{\mathrm{ZrOC}(i\text{-}\mathrm{Pr})_2\mathrm{CH_2CH{=}CHC}}\mathrm{H_2}]$ (**5**).

Atom	x	y	z	$B_{eq}/Å^2$ [10]
Zr	0.29990(8)	0.37823(5)	0.28324(7)	2.70
O	0.4643(6)	0.3586(4)	0.2706(5)	2.7
C(1)	0.2565(9)	0.3052(6)	0.1480(8)	2.9
C(2)	0.3397(12)	0.3180(7)	0.0701(8)	4.2
C(3)	0.4495(10)	0.3012(7)	0.0703(8)	3.4
C(4)	0.5157(10)	0.2640(6)	0.1533(9)	3.4
C(5)	0.5627(9)	0.3203(6)	0.2337(7)	2.7
C(7)	0.6405(10)	0.3760(7)	0.1848(8)	3.6
C(8)	0.7485(13)	0.3443(9)	0.1346(12)	5.9
C(9)	0.6788(12)	0.4458(8)	0.2484(11)	5.1
C(10)	0.6173(10)	0.2738(7)	0.3220(8)	3.6
C(11)	0.6932(16)	0.2037(10)	0.2918(13)	7.4
C(12)	0.6806(11)	0.3203(9)	0.4003(10)	4.9
C(21)	0.3321(9)	0.4989(6)	0.1804(7)	2.6
C(22)	0.3269(9)	0.5192(6)	0.2810(8)	2.7
C(23)	0.2107(9)	0.5129(5)	0.3094(8)	2.8
C(24)	0.1473(10)	0.4849(7)	0.2284(9)	3.6
C(25)	0.2215(9)	0.4765(6)	0.1485(7)	2.8
C(26)	0.4290(11)	0.5135(7)	0.1137(9)	4.1
C(27)	0.4246(11)	0.5520(7)	0.3451(10)	4.2
C(28)	0.1652(12)	0.5525(8)	0.3987(9)	4.6
C(29)	0.0155(11)	0.4804(10)	0.2156(14)	6.3
C(30)	0.1782(12)	0.4634(8)	0.0444(9)	4.7
C(31)	0.2696(9)	0.2508(6)	0.3802(8)	2.9
C(32)	0.3198(9)	0.3033(6)	0.4481(7)	2.6
C(33)	0.2374(10)	0.3610(6)	0.4623(8)	3.0
C(34)	0.1383(9)	0.3432(6)	0.4055(8)	2.8
C(35)	0.1623(9)	0.2779(7)	0.3520(8)	3.1
C(36)	0.3175(11)	0.1742(6)	0.3526(10)	4.3
C(37)	0.4298(11)	0.2936(8)	0.5111(8)	4.3
C(38)	0.2501(13)	0.4163(7)	0.5477(8)	4.3
C(39)	0.0195(11)	0.3755(8)	0.4195(11)	4.9
C(40)	0.0689(11)	0.2348(9)	0.2911(11)	5.0

Atom	x	y	z	$B/Å^2$
H(11)	0.261(9)	0.261(6)	0.178(8)	3(3)
H(12)	0.180(9)	0.320(6)	0.120(8)	3(3)
H(2)	0.319(10)	0.322(7)	0.000(9)	4(3)
H(3)	0.500(9)	0.320(6)	-0.000(8)	3(3)
H(41)	0.582(9)	0.219(7)	0.121(8)	4(3)
H(42)	0.470(9)	0.230(6)	0.180(8)	3(3)
H(7)	0.590(10)	0.400(6)	0.142(8)	4(3)
H(10)	0.558(9)	0.242(6)	0.359(8)	3(3)

b) $[(C_5Me_5)_2\overline{\mathrm{ZrOC}(i\text{-}\mathrm{Pr})_2\mathrm{CH_2CMe{=}CHC}}\mathrm{H_2}]$ (**6**).

Atom	x	y	z	$B_{eq}/Å^2$ [10]
Zr	0.02683(11)	0.13713(4)	0.37664(12)	2.66
O	-0.1373(8)	0.1066(3)	0.2551(8)	2.3
C(1)	-0.0573(14)	0.2031(4)	0.2646(13)	3.1
C(2)	-0.1129(14)	0.1974(4)	0.1074(14)	3.0
C(3)	-0.2218(14)	0.1745(5)	0.0330(12)	3.0
C(4)	-0.3165(13)	0.1500(5)	0.0994(13)	3.3
C(5)	-0.2719(12)	0.1027(5)	0.1513(13)	2.8
C(6)	-0.2675(18)	0.1743(6)	-0.1306(14)	5.2
C(7)	-0.2618(13)	0.0745(5)	0.0276(13)	3.1
C(8)	-0.3996(17)	0.0671(6)	-0.0929(17)	6.0
C(9)	-0.1885(16)	0.0270(5)	0.0728(16)	4.4
C(10)	-0.3715(12)	0.0869(5)	0.2335(15)	3.5
C(11)	-0.5284(16)	0.0977(7)	0.1595(21)	6.1
C(12)	-0.3535(19)	0.0364(6)	0.2781(17)	5.2
C(21)	0.1464(12)	0.1140(5)	0.1925(13)	2.6
C(22)	0.1937(12)	0.0862(5)	0.3090(12)	2.6
C(23)	0.2824(13)	0.1108(5)	0.4272(14)	3.1
C(24)	0.2819(12)	0.1544(5)	0.3806(14)	3.0
C(25)	0.2003(12)	0.1568(5)	0.2379(15)	3.3
C(26)	0.0780(15)	0.1018(6)	0.0423(14)	4.3
C(27)	0.1765(14)	0.0354(5)	0.3086(15)	3.8
C(28)	0.3827(17)	0.0890(6)	0.5552(15)	5.7
C(29)	0.3754(17)	0.1929(6)	0.4608(21)	6.1
C(30)	0.2047(17)	0.1975(6)	0.1461(17)	5.3
C(31)	-0.1037(13)	0.1646(5)	0.5519(12)	2.9
C(32)	-0.0714(14)	0.1205(5)	0.5833(12)	2.9
C(33)	0.0720(14)	0.1151(5)	0.6397(13)	3.1
C(34)	0.1308(13)	0.1569(5)	0.6482(12)	3.2
C(35)	0.0237(14)	0.1893(5)	0.5868(12)	3.0
C(36)	-0.2440(13)	0.1872(6)	0.5028(14)	4.4
C(37)	-0.1723(18)	0.0838(5)	0.5886(16)	4.7
C(38)	0.1419(18)	0.0728(6)	0.7079(16)	5.0
C(39)	0.2734(15)	0.1711(7)	0.7392(17)	5.4
C(40)	0.0375(17)	0.2383(5)	0.5914(16)	4.4

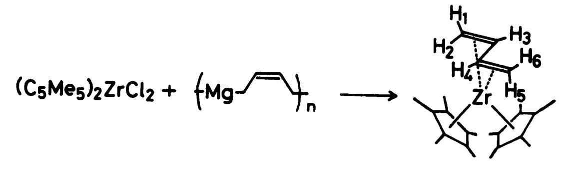
Atom	x	y	z	$B/Å^2$
H(11)	-0.135(12)	0.218(4)	0.288(12)	3(3)
H(12)	0.025(12)	0.230(4)	0.306(11)	3(3)
H(2)	-0.083(10)	0.211(4)	0.039(9)	1(3)
H(41)	-0.415(12)	0.148(4)	0.026(12)	3(3)
H(42)	-0.325(11)	0.168(4)	0.182(11)	2(3)
H(7)	-0.183(11)	0.089(4)	-0.016(11)	3(3)
H(10)	-0.340(12)	0.109(4)	0.337(11)	3(3)

final atomic coordinates for **5** and **6** are listed in Table 1.[††]

All the computations were carried out on an ACOS-S900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

NMR Studies on the $(C_5Me_5)_2Zr(diene)$ Complexes. Most mononuclear transition metal complexes of acyclic or cyclic dienes assume the *s-cis-η^4*-diene coordination. However, we and Erker *et al.* recently found by X-ray analysis that the *s-trans* coordination is possible for 1,4-diphenyl-1,3-butadiene[11] and butadiene[3,4] when these are coordinated to $(C_5H_5)_2Zr$ fragments. More recently, preparation of the corresponding hafnium-*s-trans*-butadiene complex has been reported.[12] A photochemically generated $(C_5H_5)_2Zr$(*s-trans*-butadiene) complex is thermally unstable and is readily converted to the *s-cis*-diene complex at ambient temperature.[3] Seeking for preparation of thermally stable *s-trans*-butadiene complexes, we have found that the 1 : 1 reaction of $(C_5Me_5)_2ZrCl_2$ with 2-butene-1,4-diylmagnesium predominantly gave a pure *s-trans* isomer (>99%), $(C_5Me_5)_2Zr$(*s-trans*-butadiene) (**1**), in good yield (Eq. 2).



1

(2)

The *s-trans* structure was confirmed by iterative computer simulation of the ^{1}H-NMR spectrum (Table 2). The magnitude of the proton-proton coupling constant, 16.0 Hz for $J_{3,4}$, clearly shows that the complex **1** has the *s-trans* structure. This value is consistent with the values of 15—16 Hz observed for the *s-trans* isomer of $(C_5H_5)_2Zr$(butadiene) and $(C_5H_5)_2Zr$(1,4-diphenyl-1,3-butadiene).[5] The coupling constant of $J_{3,4}$ for the *s-cis* isomer is known to be 8.0 Hz for $(C_5H_5)_2$-Zr(*s-cis*-butadiene) (**3-*s-cis***). Chemical shift values for **1** are also comparable with those for $(C_5H_5)_2Zr$(butadiene) (**3-*s-trans***).[5]

The corresponding isoprene complex, $(C_5Me_5)_2Zr$-(isoprene) **2**, was prepared in the same way (Eq. 3) and the geometry was determined to be *s-cis* based upon the ^{1}H-NMR chemical shift values (Table 2). It is noteworthy that the spectrum of **2** was not changed by

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[††] Tables of observed and calculated structure factors and anisotropic thermal parameters are deposited as Document No. 8348 at the Chemical Society of Japan.

Table 2. ^{1}H-NMR parameters for complexes **1** and **2** obtained by computer simulation[a)]

Complex	Chemical shift, ν/ppm							
	$\underline{H}_1$	$\underline{H}_2$	$\underline{H}_3$	$\underline{H}_4$	$\underline{H}_5$	$\underline{H}_6$	ν_{CH_3}[b)]	ν_{CH_3}[c)]
1	2.75	1.21	2.14	2.14	2.75	1.21	—	1.69
2	0.87	0.87	5.74	—	0.75	0.75	1.92	1.85

Complex	Coupling constant, J/Hz										
	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	$J_{1,5}$	$J_{2,6}$	$J_{3,5}$	$J_{3,6}$
1	−4.2	7.3	16.2	16.0	7.3	16.2	−4.2	1.0	0.2	−0.5	−1.2
2	−5.0	4.8	4.8	—	—	—	−5.0	0.6	0.6	−0.8	−0.8

a) Spectra were observed at 100 MHz in toluene-d_8 at 30 °C. Chemical shifts were calibrated by using the internal benzene peak, assumed to be 7.20 ppm. The numbering system follows that shown in Eqs. 2 and 3. b) Methyl proton signals of isoprene. c) Methyl proton signals of C_5Me_5 group.

Table 3. ^{13}C-NMR chemical shift values (ν/ppm) and ^{13}C–^{1}H coupling constants (in parentheses, J/Hz) for **1** and **3**[a)]

Complex	Temp/°C	$C_1(C_4)$	$C_2(C_3)$	Ligand	$\Delta(C_2-C_1)$
1	30	64.95 (146.0)	100.71 (143.9)	10.45(125.7) [Me] 108.64 [ring]	35.76
1	−50	64.54 (150.5)	100.57 (148.9)	10.37(125.7) [Me] 108.05 [ring]	36.03
3-*s-trans*	30	57.72 (145.3)[b)] (156.3)[c)]	94.56 (148.9)	100.79 (172.1)	36.84
3-*s-cis*	30	48.35 (144.7)	110.86 (153.8)	98.08 (170.9)	62.52
3-*s-trans*	−50	57.66	94.09	97.92	36.73
3-*s-cis*	−50	48.29	110.38	102.41	62.09

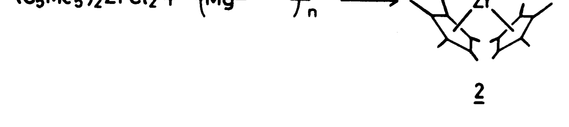
a) Spectra were recorded at 25.2 MHz in toluene-d_8 and chemical shifts were calibrated by using internal toluene peak (CH_3-proton signal), assumed to be 19.20 ppm. b) Coupling constant between ^{13}C at $C_1(C_4)$ and terminal proton at the *syn*-position with respect to the proton at $C_2(C_3)$. c) Coupling constant for ^{13}C–^{1}H at *anti*-position (see Ref. 22 for the assignment).

Table 4. ^{13}C-NMR chemical shift values and ^{13}C–^{1}H coupling constants (in parentheses) for **2** and **4**[a)]

Complex	Temp/°C	C_1	C_2	C_3	C_4	C_5[d)]	Ligand	$\Delta(C_3-C_4)$
2	30	45.96 (123.9)	136.65	124.68 (148.9)	47.37 (123.0)	30.68 (127.0)	10.04(126.1) [Me] 115.85 [ring]	77.31
2	−50	44.82 (123.3)	136.76	124.62 (141.6)	46.29 (122.1)	31.06 (123.3)	9.94(126.1) [Me] 115.36 [ring]	78.33
4	30	46.67 (143.4)	122.19	109.83 (156.3)	52.19 (140.4)	27.81 (125.7)	101.22(170.9)	57.64
4	−50	46.45 (157.5)[b)] (128.2)[c)]	121.48	109.51 (153.8)	51.87 (157.5)[b)] (128.2)[c)]	27.81 (125.7)	99.11(172.1) 102.68(170.9)	57.64

a) Recorded at 25.2 MHz in toluene-d_8. Chemical shift values are expressed by ppm and coupling constants by Hz. Assignments of each atom were made with reference to the ^{1}H NMR chemical shift values (see. Ref. 5a). b) Coupling constant for ^{13}C–^{1}H at the *syn*-position with respect to the proton at C_2 or C_3 atoms (see Ref. 22). c) Coupling constant for ^{13}C–^{1}H at the *anti*-position with respect to the proton at C_2 or C_3 atoms. d) Methyl carbon of isoprene.

lowering the temperature from 50 °C to −70 °C while $(C_5H_5)_2Zr$(isoprene) **4** showed the limiting η^4-diene structure when it was cooled to −30 °C, as reported previously.[5)] This behavior indicates enhanced fluxionality of **2** compared to that of **4**.



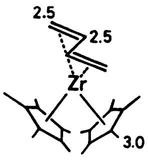
2

(3)

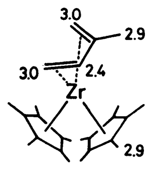
The geometry of **1**, **2**, **3-*s-cis***, **3-*s-trans*** and **4** was also confirmed by the ^{13}C-NMR spectra. Chemical shift values and the ^{13}C–^{1}H coupling constants for **1**, **3-*s-cis*** and **3-*s-trans*** are given in Table 3 and those for **2** and **4** are given in Table 4. It is apparent from these data that the chemical shift difference, $\Delta(C_2-C_1)$, between terminal carbons $C_1(C_4)$ and central carbon atoms $C_2(C_3)$ is rather small (*ca.* 36 ppm) for the *s-trans*-diene complexes, **1** and **3-*s-trans***, while the corresponding difference, $\Delta(C_3-C_4)$, for the *s-cis*-diene complexes **2**, **4** and $\Delta(C_2-C_1)$ for **3-*s-cis*** is significantly larger (57.6—

77.3 ppm) regardless of temperature. Thus, geometries are readily determined from chemical shift differences. It is important to note here that the ^{13}C chemical shift values of **4** at 30 °C for the fluxional diene molecule are essentially the same as the values for the η^4-coordinated diene observed at -50 °C. This result suggests that most of the coordinated isoprene remains η^4-bonded even when some of it is flipping. Such information could not be obtained from the ^1H-NMR spectrum since the proton signals of **4** coalesce at 0—-30 °C.

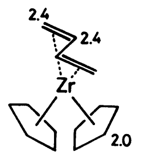
The ^{13}C–^1H coupling constant offers important information on the extent of hybridization in the diene carbons. Based upon Newton's semiempirical rule,[13] it is possible to calculate the s-% of carbon atoms of the dienes and hence the hybridization. The hybridization approximated by $n=(1-s)/s$ for sp^n is shown below. The sp^3 character of CH_2 carbon at isoprene termini of **2** is higher than that of **4**. Thus, greater contribution of the zirconacyclopent-3-ene structure was inferred for **2** when compared with that of **4**. This will account for the higher fluxionality of **2**. The sp^3 character of carbon atoms at *s-trans*-diene termini of **1** is smaller than that of the terminal atom of the *s-cis*-diene complex **2**, indicating that the Zr–C_1 and Zr–C_4 σ-bonding of **1** is less than that of **2**. The sp^n parameter for $C_1(C_4)$ atoms of ***3-s-trans*** and **4** (at -50 °C) was obtained from the avaraged coupling constant values of ^{13}C–^1H(*syn*) and ^{13}C–^1H(*anti*). See footnote in Tables 3 and 4 and Ref. 22 for the assignment.



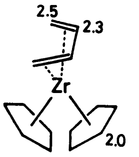
1



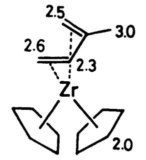
2



3-s-trans



3-s-cis



4

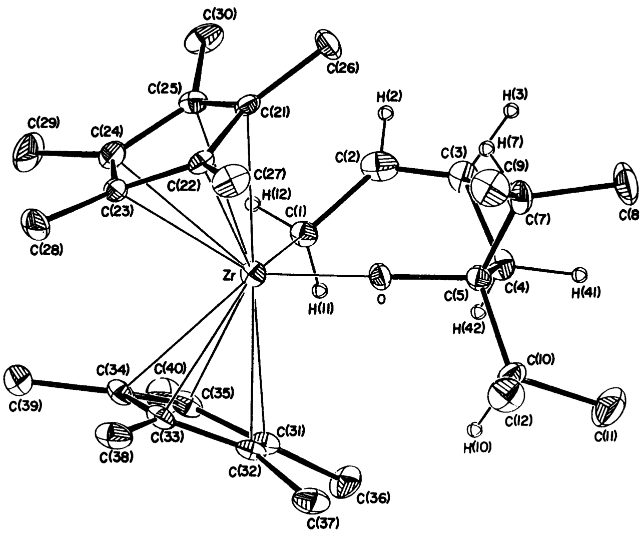


Fig. 1. Molecular structure of $[(C_5Me_5)_2ZrOC(i\text{-}Pr)_2CH_2CH{=}CHCH_2]$ (**5**) with the numbering scheme of the atoms. Thermal ellipsoids for non-hydrogen atoms are drawn at the 20% probability level. Hydrogen atoms are shown as the spheres with arbitrary temperature factor of 1.0 Å².

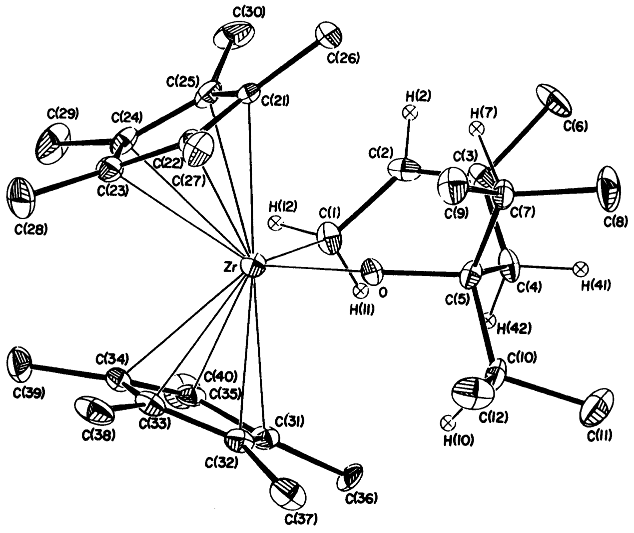


Fig. 2. Molecular structure of $[(C_5Me_5)_2ZrOC(i\text{-}Pr)_2CH_2CMe{=}CHCH_2]$ (**6**) with the numbering scheme of the atoms. Drawing parameters are same as those for Fig. 1.

*Molecular Structures of **5** and **6**.* Single crystals of 1,2-oxazirconacyclohept-4-enes (**5** and **6**) were prepared by the 1 : 1 reaction of $(C_5Me_5)_2Zr$(*s-trans*-butadiene) **1** or $(C_5Me_5)_2Zr$(*s-cis*-isoprene) **2** with 2,4-dimethyl-3-pentanone at 30 °C in benzene to define the stereochemistry of the insertion reaction in terms of X-ray crystal structure analysis.

The molecular structures of **5** and **6** determined in this work are shown in Figs. 1 and 2 which give the *ORTEP* drawings[14] together with the atomic numberings. The bond distances and angles are listed in Table 5. The molecular structure of **5** shows that the 2,4-dimethyl-3-pentanone inserts regioselectively into the bond between zirconium and one of terminal carbon atoms of butadiene [Zr–C(4) bond]. The molecular structure of **6** shows that the insertion of ketone with $(C_5Me_5)_2Zr$(isoprene) occurred into the bond between zirconium and C_1 atom of isoprene [C(4) atom in Fig. 2]. Thus, the insertion occurred regioselectively into the sterically hindered Zr–C(4) bond rather than into the less hindered Zr–C(1) bond. These molecular structures coincided with the oxametallacycloheptene structures determined by the mass and ^1H-NMR spectra (see Experimental) and the structures of the base hydrolysis products.

The overall geometry of complexes **5** and **6** is essentially the same. The zirconium atom is coordinated with two C_5Me_5 ligands and bonded with the C(1) atom of the diene part and the oxygen atom of the ketone part

Table 5. Bond lengths and angles in **5** and **6** with their estimated standard deviations in parentheses

Bond length	l/Å		Bond length	l/Å	
	5	**6**		**5**	**6**
Zr -O	1.961(7)	1.964(8)	C(24)-C(25)	1.423(16)	1.401(20)
Zr -C(1)	2.294(10)	2.311(14)	C(21)-C(26)	1.498(16)	1.481(21)
C(1) -C(2)	1.482(17)	1.494(20)	C(22)-C(27)	1.523(16)	1.542(19)
C(1) -H(11)	0.89(10)	1.01(12)	C(23)-C(28)	1.519(17)	1.509(22)
C(1) -H(12)	1.00(10)	1.16(12)	C(24)-C(29)	1.541(21)	1.556(25)
C(2) -C(3)	1.313(17)	1.324(20)	C(25)-C(30)	1.504(17)	1.541(23)
C(2) -H(2)	0.97(11)	0.93(10)	C(31)-C(32)	1.425(14)	1.384(19)
C(3) -C(4)	1.499(16)	1.530(19)	C(31)-C(35)	1.380(15)	1.449(19)
C(3) -C(6)		1.545(22)	C(32)-C(33)	1.423(14)	1.408(19)
C(3) -H(3)	1.19(10)		C(33)-C(34)	1.400(15)	1.389(20)
C(4) -C(5)	1.567(15)	1.536(18)	C(34)-C(35)	1.405(15)	1.452(19)
C(4) -H(41)	1.20(11)	1.04(12)	C(31)-C(36)	1.524(17)	1.527(21)
C(4) -H(42)	0.90(10)	1.02(11)	C(32)-C(37)	1.524(17)	1.530(22)
C(5) -O	1.440(12)	1.442(14)	C(33)-C(38)	1.525(18)	1.515(23)
C(5) -C(7)	1.514(15)	1.529(18)	C(34)-C(39)	1.518(17)	1.517(23)
C(5) -C(10)	1.573(15)	1.576(19)	C(35)-C(40)	1.546(18)	1.487(22)
C(7) -C(8)	1.560(20)	1.552(22)	Zr -C(21)	2.598(10)	2.608(13)
C(7) -C(9)	1.569(18)	1.614(20)	Zr -C(22)	2.527(10)	2.549(12)
C(7) -H(7)	0.92(11)	1.13(11)	Zr -C(23)	2.641(10)	2.635(13)
C(10)-C(11)	1.592(22)	1.577(25)	Zr -C(24)	2.687(12)	2.660(14)
C(10)-C(12)	1.518(19)	1.583(24)	Zr -C(25)	2.669(10)	2.649(15)
C(10)-H(10)	1.04(10)	1.19(12)	Zr -C(31)	2.654(10)	2.652(13)
C(21)-C(22)	1.420(14)	1.388(18)	Zr -C(32)	2.613(10)	2.614(13)
C(21)-C(25)	1.401(14)	1.420(20)	Zr -C(33)	2.589(11)	2.596(14)
C(22)-C(23)	1.427(14)	1.442(18)	Zr -C(34)	2.635(10)	2.638(14)
C(23)-C(24)	1.395(16)	1.394(19)	Zr -C(35)	2.597(11)	2.626(14)

Bond angle	ϕ/°		Bond angle	ϕ/°	
	5	**6**		**5**	**6**
O -Zr -C(1)	90.8(4)	89.6(5)	C(5) -C(10)-C(12)	114.9(10)	113.6(12)
Zr -O -C(5)	155.2(7)	156.5(8)	C(5) -C(10)-H(10)	114(6)	104(6)
Zr -C(1) -C(2)	110.9(8)	111.4(9)	C(11)-C(10)-C(12)	110.4(11)	109.9(13)
Zr -C(1) -H(11)	97(6)	119(7)	C(11)-C(10)-H(10)	95(6)	104(6)
Zr -C(1) -H(12)	109(6)	109(6)	C(12)-C(10)-H(10)	106(6)	109(6)
C(2) -C(1) -H(11)	116(6)	103(7)	C(22)-C(21)-C(25)	107.4(10)	106.7(12)
C(2) -C(1) -H(12)	107(6)	117(6)	C(22)-C(21)-C(26)	126.9(10)	128.2(13)
H(11)-C(1) -H(12)	117(9)	98(9)	C(25)-C(21)-C(26)	124.5(10)	124.0(13)
C(1) -C(2) -C(3)	128.9(12)	128.1(13)	C(21)-C(22)-C(23)	108.5(10)	109.4(12)
C(1) -C(2) -H(2)	124(7)	128(6)	C(21)-C(22)-C(27)	126.2(10)	126.1(12)
C(3) -C(2) -H(2)	103(7)	104(6)	C(23)-C(22)-C(27)	124.8(10)	123.8(12)
C(2) -C(3) -C(4)	125.1(11)	123.5(13)	C(22)-C(23)-C(24)	107.1(10)	106.3(12)
C(2) -C(3) -C(6)		120.6(13)	C(22)-C(23)-C(28)	122.9(10)	123.2(13)
C(4) -C(3) -C(6)		115.7(12)	C(24)-C(23)-C(28)	127.5(11)	128.4(13)
C(2) -C(3) -H(3)	116(5)		C(23)-C(24)-C(25)	108.8(10)	108.9(13)
C(4) -C(3) -H(3)	118(5)		C(23)-C(24)-C(29)	127.1(12)	126.7(14)
C(3) -C(4) -C(5)	113.6(9)	115.5(11)	C(25)-C(24)-C(29)	122.7(12)	123.5(14)
C(3) -C(4) -H(41)	110(5)	109(6)	C(21)-C(25)-C(24)	108.2(10)	108.7(13)
C(3) -C(4) -H(42)	108(7)	109(6)	C(21)-C(25)-C(30)	127.4(10)	128.2(14)
C(5) -C(4) -H(41)	118(5)	107(6)	C(24)-C(25)-C(30)	123.0(10)	121.4(14)
C(5) -C(4) -H(42)	110(7)	109(6)	C(32)-C(31)-C(35)	107.2(10)	107.9(12)
H(41)-C(4) -H(42)	96(8)	106(9)	C(32)-C(31)-C(36)	127.0(10)	129.5(13)
O -C(5) -C(4)	106.6(8)	106.3(10)	C(35)-C(31)-C(36)	125.5(10)	122.4(13)
O -C(5) -C(7)	110.0(8)	109.0(10)	C(31)-C(32)-C(33)	107.4(10)	110.2(12)
O -C(5) -C(10)	106.7(8)	106.6(10)	C(31)-C(32)-C(37)	127.3(10)	126.0(13)
C(4) -C(5) -C(7)	108.1(10)	109.7(11)	C(33)-C(32)-C(37)	124.3(10)	122.6(13)
C(4) -C(5) -C(10)	108.5(10)	106.4(11)	C(32)-C(33)-C(34)	108.0(10)	107.5(13)
C(7) -C(5) -C(10)	116.6(9)	118.2(10)	C(32)-C(33)-C(38)	121.4(10)	124.1(14)
C(5) -C(7) -C(8)	117.6(10)	115.0(11)	C(34)-C(33)-C(38)	128.3(11)	127.1(13)
C(5) -C(7) -C(9)	115.9(10)	114.6(11)	C(33)-C(34)-C(35)	107.3(10)	109.2(12)
C(5) -C(7) -H(7)	102(7)	109(6)	C(33)-C(34)-C(39)	125.5(10)	127.7(13)

Table 5. (Continued)

Bond angle	φ/°		Bond angle	φ/°	
	5	6		5	6
C(8) -C(7) -C(9)	108.1(10)	108.5(12)	C(35)-C(34)-C(39)	125.4(10)	121.3(13)
C(8) -C(7) -H(7)	113(7)	111(6)	C(31)-C(35)-C(34)	110.0(10)	105.1(12)
C(9) -C(7) -H(7)	99(7)	97(6)	C(31)-C(35)-C(40)	125.9(10)	126.1(13)
C(5) -C(10)-C(11)	115.4(10)	115.6(12)	C(34)-C(35)-C(40)	122.6(10)	127.3(13)

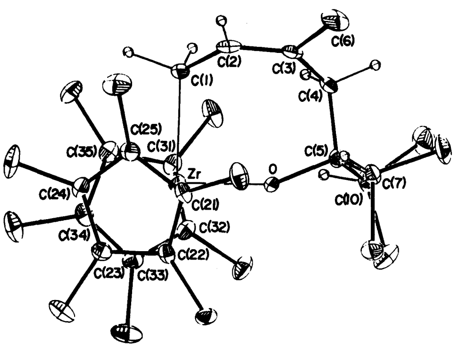


Fig. 3. Molecular structure of **6** projected onto the plane defined by Zr, O, and C(1) atoms. Drawing parameters are same as those for Fig. 1.

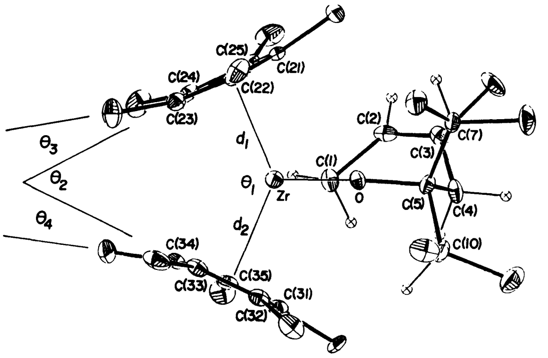


Fig. 4. Molecular structure of **6** viewed along the plane defined by Zr, O, and C(1) atoms. Drawing parameters are same as those for Fig. 1.

in a pseudo-tetrahedral manner. The Zr–C(1) lengths, 2.294(10) Å in **5** and 2.311(14) Å in **6**, are similar to the Zr–C(alkyl) distances in $(\eta^5\text{-}C_9H_7)_2Zr(CH_3)_2$ [2.255(5) Å],[15] $(\eta^5\text{-}C_5H_5)_2Zr(CH_2SiMe_3)_2$ [2.279(4) Å],[16] and $(\eta^5\text{-}C_5H_5)_2Zr(CH_2CMe_3)_2$ [2.288(10) Å],[16] and also to the Zr–C (terminal) distance in $(\eta^5\text{-}C_5H_5)_2$-Zr(2,3-dimethylbutadiene) [2.300 Å].[3] The Zr–O distances are 1.961(7) and 1.964(8) Å for **5** and **6**, respectively. These distances are slightly shorter than the expected Zr–O single bond distance estimated from the sum of the covalent radii for zirconium (1.45—1.48 Å) and oxygen (0.66 Å). The Zr–O–C(5) angles have relatively large values of 155.2(7)° for **5** and 156.5(8)° for **6**, respectively. The C(2)–C(3) bond distances, 1.313(17) Å in **5** and 1.324(20) Å in **6**, show that these bonds are the localized carbon-carbon double bonds, whose standard value is 1.337±6 Å.[17] The interatomic distances between zirconium and C(2) and/or C(3) atoms [Zr–C(2): 3.144(13) Å in **5**, 3.177(14) Å in **6**; Zr–C(3): 3.702(11) Å in **5**, 3.729(14) Å in **6**] indicate that there is no direct interaction between zirconium and the C(2)–C(3) double bond. Thus, the oxametallacycloheptene part in these complexes is described as having the 1,2-oxazirconacyclohept-4-ene structure.

The characteristic views of the molecular structure of **6** are shown in Figs. 3 and 4. The corresponding views of **5** are essentially the same as those of **6** in these Figures. The most interesting features in the oxametallacycloheptene part in these complexes are the conformations of C(1)–C(2)–C(3)–C(4) moieties, which correspond to the 1,3-dienes in the original complexes into which the ketone inserts. The torsional angles about C(2)–C(3) double bonds, C(1)–C(2)–C(3)–C(4), are 0.0° in **5** and 2.3° in **6**, respectively. Thus, the C(1) to C(4) moiety takes the *s-cis* structure in both complexes. The oxametallacycloheptene parts in **5** and **6** are divided into two planar moieties, the plane of diene moiety [C(1) to C(4), including also C(6) in **6**] and the approximate plane defined by C(1), Zr, O, C(5), and C(4) with the maximum atomic deviations from the plane of 0.088 Å in **5** and 0.051 Å in **6**, the dihedral angles being 62.7° in **5** and 61.1° in **6**, respectively. All the methyl groups in 2,4-dimethyl-3-pentanone moieties locate away from the oxametallacycloheptene part to release the possible nonbonded interatomic repulsions in both complexes.

The mean distances between zirconium and carbon atoms of C_5Me_5 ligands are 2.623 Å in **5** and 2.621 Å in **6**, and those between zirconium and the centroids of C_5Me_5 ligands [d_1 and d_2 in Fig. 4] are 2.331 Å in both complexes. These distances are slightly longer than the corresponding distances in $(\eta^5\text{-}C_5H_5)_2ZrCl_2$[18] of 2.522(2) and 2.20 Å or those in $(\eta^5\text{-}C_5H_5)_2Zr(CHPh_2)_2$[16] of 2.513(15) and 2.22 Å. The CCP(1)–Zr–CCP(2) [CCP(1) and CCP(2), which are the centroids of C(21) to C(25) and C(31) to C(35)] angles [θ_1 in Fig. 4], 129.0° in **5** and 129.4° in **6**, are similar to those in $(\eta^5\text{-}C_5H_5)_2Zr(CHPh_2)_2$[19] [128.4°], $(\eta^5\text{-}C_5H_5)_2ZrF_2$[20] [127.8°], and $(\eta^5\text{-}C_5H_5)_2$Zr(2,3-dimethylbutadiene)[3] [124°]. Figure 3 shows that the two C_5Me_5 ligands are in a staggered conformation so as to release the nonbonded repulsion between the methyl groups of facing C_5Me_5 ligands. However, all the methyl groups in C_5Me_5 ligands in **5** and **6** bend back from the zirconium atom with the angular deviations from the C_5 plane [θ_3 or θ_4 in Fig. 4] of 3.7 to 16.1° [av. 10.2°] in CP(1) [ring defined by C(21) to C(25)] and of 7.2 to 15.2° [av. 10.2°] in CP(2) [ring defined by C(31) to C(35)] for **5**, and of 6.1 to 14.6° [av. 9.9°] in CP(1) and of 5.9 to 15.7° [av. 9.6°] in CP(2) for **6**, respectively. Some short contacts are found between these methyl groups, resulting in the large angular deviations from the C_5

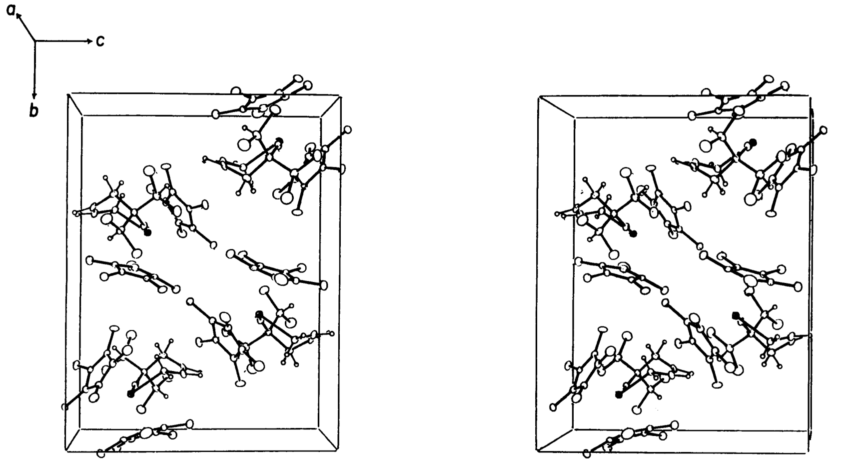


Fig. 5. Stereoscopic view of the crystal structure of **5**.

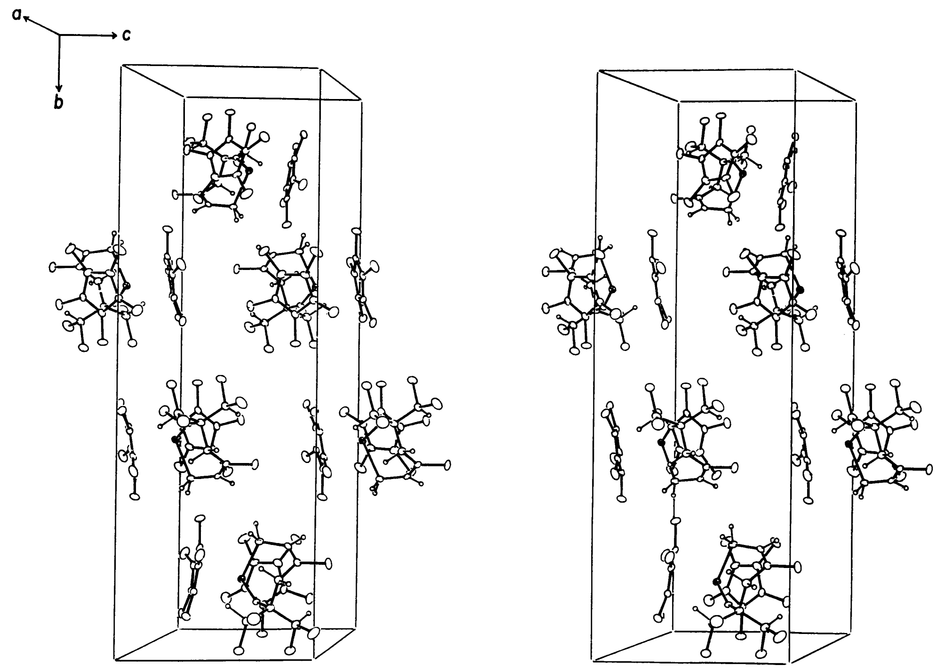
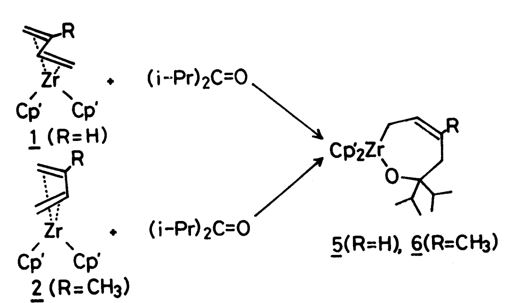
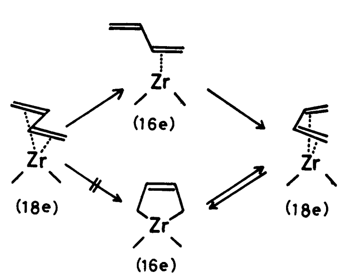


Fig. 6. Stereoscopic view of the crystal structure of **6**.



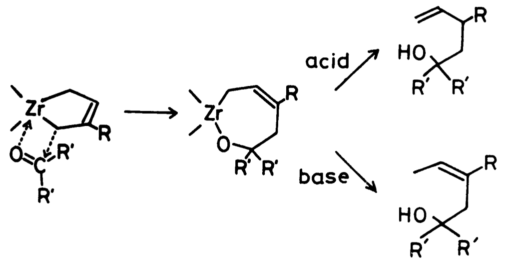
(4)



(5)

rings: C(28)···C(38) 3.288(20) Å, θ_3 16.1° [C(28)], θ_4 12.2° [C(38)] in **5**, and 3.329(25) Å, θ_3 14.6° [C(28)], θ_4 8.1° [C(38)] in **6**; C(29)···C(39) 3.344(23) Å, θ_3 9.5° [C(29)], θ_4 15.2° [C(39)] in **5**, and 3.327(28) Å, θ_3 7.3° [C(29)], θ_4 15.7° [C(39)] in **6**. Some short contacts are also found between the methyl groups in the C_5Me_5 ligands and the oxametallacycloheptene part; C(1)···C(30) 3.262(17) Å in **5** and 3.273(22) Å in **6**; C(9)···C(26) 3.588(18) Å in **5** and 3.635(23) Å in **6**; and C(12)···C(37) 3.372(20) Å in **5** and 3.374(26) Å in **6**. The shortest nonbonded contact of the methyl group on C(3) in **6** is the C(6)···C(7) of 3.392(22) Å.

The comparison between the molecular structures of **5** and **6** showed that these complexes take essentially the same structure in spite of the different coordination modes of the 1,3-diene in (η^5-$C_5Me_5)_2$Zr(butadiene) and (η^5-$C_5Me_5)_2$Zr(isoprene).



(6)

*Crystal Structures of **5** and **6**.* The crystal structures of **5** and **6** are shown in Figs. 5 and 6, respectively. No intermolecular nonbonded contact shorter than 3.5 Å is found between the non-hydrogen atoms in either crystal structure.

Pathways for Regio- and Stereoselective Reaction of Ketones with s-cis *and* s-trans *Zirconium–Diene Complexes.* It is evident from the X-ray work that both the *s-cis*-diene and the *s-trans*-diene complexes gave oxametallacycloheptenes with (*Z*)-structure. Thus, the insertion of ketone caused the conversion of butadiene from *s-trans* to *s-cis* and the retention of isoprene in *s-cis* structure The interconversion occurs presumably *via* 1,2-η^2-diene metal species with 16e configuration and the process *via* 1,4-η^2-diene metal species (16e) can be ruled out (Eq. 5).

Since the Zr-η^4-diene complex has 18e configuration and leaves no vacant coordination site, the insertion of 2,4-dimethyl-3-pentanone may take place after its conversion to zirconacyclopent-3-ene structure with 16e configuration. Direct conversion of η^2-diene species to metallacyclopentene can not be ruled out when a ketone is present in the system. An MO calculation predicts that wedged $(C_5H_5)_2M$ fragment has three in-plane orbitals of d-character.[21] The $2a_1$ and b_2 orbitals are used for forming the zircona ring and the remaining vacant orbital ($1a_1$) may be used for the coordination of the ketone. Therefore, a zircona ring coordinated through oxygen atom of carbonyl group may be postulated as the intermediate. Insertion of ketone will then take place *via* four-centered transition state (Eq. 6). Hydrolysis of **6** with protic acid (aq HCl) gave 2,5-dimethyl-3-isopropyl-6-hepten-3-ol but hydrolysis with bases such as aq NaOH and Et_2NH gave (*Z*)-2,5-dimethyl-3-isopropyl-5-hepten-3-ol quantatively, in line with the X-ray structure. The high regioselectivity observed in the formation of **6** is explained by the inductive effect of the methyl group of isoprene, which causes the higher negative charge on the C_1 atom.

Other ketones, such as 2-propanone or 3-pentanone, and aldehydes such as ethanal or propanal, also react with **1**—**4** in the same fashion (these will be published in a separate paper). Therefore, the present reaction mechanism seems applicable in general for these reactions.

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References

1) H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, and A. Nakamura, *Chem. Lett.*, **1981**, 671.

2) M. Akita, H. Yasuda, and A. Nakamura, *Chem. Lett.*, **1983**, 217.

3) G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich, and C. Krüger, *J. Am. Chem. Soc.*, **102**, 6346 (1980).

4) G. Erker, J. Wicher, K. Engel, and C. Krüger, *Chem. Ber.*, **115**, 3300 (1982).

5) a) H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, K. Lee, and A. Nakamura, *Organometallics*, **1**, 388 (1982); b) *ibid.*, **2**, 478 (1983); c) H. Yasuda, Y. Kajihara, K. Mashima, K. Lee, and A. Nakamura, *Chem. Lett.*, **1981**, 519.

6) J. M. Manriquez, D. R. McAlister, E. Rosenberg, A. M. Shiller, K. L. Silliamson, S. I. Chan, and J. E. Bercaw, *J. Am. Chem. Soc.*, **100**, 3087 (1978).

7) a) H. Fujita, Y. Ohnuma, H. Yasuda, and H. Tani, *J. Organomet. Chem.*, **113**, 201 (1976); b) H. Yasuda, Y. Nakano, K. Natsukawa, and H. Tani, *Macromolecules*, **11**, 589 (1978).

8) T. Ashida, *HBLS*-V, "The Universal Crystallographic Computing System-Osaka," 2nd ed, The Computation Center, Osaka Univ. (1979), pp. 53—59.

9) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, p. 71.

10) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

11) Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, K. Nagasuna, H. Yasuda, and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, **1982**, 191.

12) R. Benn and G. Schroth, *J. Organomet. Chem.*, **228**, 71 (1982).

13) M. D. Newton, T. M. Shulmann, and M. M. Manus, *J. Am. Chem. Soc.*, **96**, 17 (1974).

14) C. K. Johnson, *ORTEP*-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee (1974).

15) J. L. Atwood, W. E. Hunter, D. C. Hrncir, E. Samuel, H. Alt, and M. D. Rausch, *Inorg. Chem.*, **14**, 1757 (1975).

16) J. Jeffery, M. F. Lappert, and N. T. Luong-Thi, *J. Chem. Soc., Chem. Commun.*, **1978**, 1081.

17) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1968), Vol. III, p. 276.

18) I. A. Ronova, N. V. Alekseev, N. I. Gapotcheko, and Yu. T. Struchkov, *J. Organomet. Chem.*, **25**, 149 (1970); A. Clearfield and I. Bernal, personal communication cited in Ref. 15.

19) J. L. Atwood, G. K. Barker, J. Holton, W. E. Hunter, M. F. Lappert, and R. Pearce, *J. Am. Chem. Soc.*, **99**, 6645 (1977).

20) M. A. Bush and G. A. Sim, *J. Chem. Soc., Sect. A*, **1971**, 2225.

21) J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729 (1976).

22) a) K. Bachmann and W. von Philipsborn, *Org. Magn. Res.*, **8**, 648 (1976); b) B. E. Mann and B. F. Taylor, "^{13}C NMR Data for Organometallic Compounds," Academic Press, New York (1981).