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Chemistry of Dienyl Anions. III. Crystalline Bis(2,4-pentadienyl)metal Compounds of Be and Zn. Terminally σ-Bonded Structure and Fluxional 1,5-Rearrangement

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A series of bis(dienyl)beryllium and bis(dienyl)zinc compounds were prepared by metal exchange reaction from seven different dienyl anions and were isolated as crystals of TMEDA complexes. Bis(dienyl)beryllium compounds of open chain structure obtained from pentadienyl, 2-methylpentadienyl, and 3-methylpentadienyl anions assume the terminally σ-bonded (*E*)-2,4-pentadienyl structure in solution as evidenced by ^{1}H-NMR and ^{13}C-NMR spectroscopies. Hydrolysis of these compounds gave 1,4-dienes regioselectively. The corresponding bis(dienyl)zinc compounds exist as a (*Z*), (*E*) mixture of teminally σ-bonded structures. An X-ray analysis of pentadienylzinc chloride·TMEDA complex showed that it had terminally σ-bonded (*E*)-2,4-pentadienyl structure with *s-trans* conformation. Steric effect of two methyl substituents in bis(2,4-dimethylpentadienyl)zinc induces the (*Z*) configuration which leads to the fluxional behavior by rapid 1,5-rearrangement above -80 °C.

In the previous paper, synthesis and chemical reaction of seven different bis(dienyl)magnesium compounds having fluxional structures in solution were reported.1) A rapid 1,3-rearrangement (1,3-shift) between the magnesium-terminal C-1 (or C-5) and magnesium-central C-3 carbon bonds explains the fluxional behavior assisted by the ionic character of the Mg–C bonds. Substitution of the magnesium atom with more electro-negative metals, beryllium or zinc, may freeze the rapid equilibrium since the covalency of the M–C bonds does not favor suprafacial 1,3-sigmatropic shift which is thermally forbidden when covalency of the bond is complete. The position of the metal-carbon bond may be fixed to either C-1, C-3, or C-5 carbon atoms of the dienyl group reflecting the radius and the electronegativity of the metals. The position of the metal-carbon bond should also be influenced by a change in bulkiness of the substituents on the pentadienyl group because no remarkable difference in electron density was observed by CNDO-II calculations2) among C-1, C-3, and C-5 of lithium pentadienide. Since the ionic radius of Zn (0.74 Å) is significantly larger than that of Be (0.41 Å), comparative studies on the structure of bis(dienyl)beryllium and bis(dienyl)zinc compounds will provide informations on the steric effect of the metal on the configuration or conformation of the dienyl group. Unique chemical behaviors of beryllium compounds resulting from its small ionic radius3) are of interest but no compounds related to this work are reported.

Understanding the difference in the position of the metal-carbon bond, configuration of dienyl group, process for the rearrangement and chemical reactivity between dienylmetal compounds of Be, Mg, and Zn will be essential for selective dienylation of organic groups using these reagents. Like some organozinc compounds used for addition to olefins,4) dienylzinc compounds reported here will be useful as the selective reagents for introducing a dienyl group to carbonyl compounds and olefins.

Results and Discussion

Preparation and Properties of Bis(dienyl)beryllium and -zinc Compounds. Bis(pentadienyl)beryllium and bis(pentadienyl)zinc compounds were prepared by the 2:1 reaction of potassium pentadienide5) with anhydrous beryllium chloride and zinc chloride, respectively, in THF. Zinc chloride readily reacts with dienyl anions at 0 °C while beryllium chloride requires higher temperatures (>40 °C). The resulting dienylmetal compounds are coordinated by two moles of THF as evidenced by NMR and by GC of the hydrolyzate. The 1:1 reaction of pentadienyl potassium with zinc chloride gave $C_5H_7ZnCl\cdot 2THF$ similar to $C_5H_7MgBr\cdot 2THF$ but that with beryllium chloride gave

$$\mathrm{KC_5H_7 + MX_2 \xrightarrow{THF} C_5H_7MX\cdot 2THF}$$
$$\mathrm{\xrightarrow{KC_5H_7} (C_5H_7)_2M\cdot 2THF}$$
$$\mathrm{M{=}Be,\ Zn}$$

mainly $(C_5H_7)_2Be\cdot 2THF$ presumably due to the instability of RMX type structure.6) Dienylzinc compounds are thermally the least stable among the Be, Zn, and Mg compounds. For example, bis(pentadienyl)zinc·2THF or bis(pentadienyl)zinc·$2N(C_2H_5)_3$ began to decompose at 10 °C giving metallic zinc and coupling dimers, $C_{10}H_{14}$.7) The corresponding magnesium compound, $(C_5H_7)_2Mg\cdot 2THF$, decomposed at 80—90 °C and the ring cleavage of the coordinated THF occurred to afford unsaturated alcohols with an elongated carbon chain1) while $(C_5H_7)_2Be\cdot 2THF$ was stable up to 100 °C in toluene. Remarkable difference in thermal stability was observed also for bis(cyclooctadienyl)metal compounds. The zinc compound was decomposed even at -20 °C but the magnesium and the beryllium compounds were stable at 50—60 °C. ^{1}H-NMR spectra of all the pentadienylmetal–THF complexes showed simple averaged AB_2X pattern signals (Table 1) due to the rapid 1,3-rearrangement as was observed for dienylmagnesium, allylmagnesium,8) and allylaluminium9) compounds. The chemical shifts (δ-values) of the protons at C-1 and C-3 increased with increasing covalent character of the M–C bond in the order Zn–C>Be–C>Mg–C.

The fluxionality can be frozen at room temperature by addition of bifunctional chelating ligands, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) or *N,N,N′*,

TABLE 1. CHEMICAL SHIFTS(δ-VALUES) AND COUPLING CONSTANTS OF FLUXIONAL PENTADIENYLMETAL COMPOUNDS[a)]

	C_1-H(C_5-H)	C_2-H(C_4-H)	C_3-H
$(C_5H_7)_2Be\cdot 2THF$	3.05 (11.1 Hz)	6.64	5.89 (12.2 Hz)
$(C_5H_7)_2Zn\cdot 2THF$	3.26 (11.1 Hz)	6.37	5.93 (11.5 Hz)
$C_5H_7ZnCl\cdot 2THF$	3.25 (11.1 Hz)	6.39	5.87 (11.5 Hz)
$(C_5H_7)_2Mg\cdot 2THF$	2.98 (11.3 Hz)	6.55	5.58 (12.0 Hz)

a) Data were collected at 38 °C in C_6D_6 and chemical shifts were calibrated using internal C_6H_6 signal assumed to be 7.20 ppm.

TABLE 2. CHARACTERIZATION OF BIS(DIENYL)BERYLLIUM·TMEDA COMPLEXES AND DISTRIBUTION OF THE HYDROLYSIS PRODUCTS

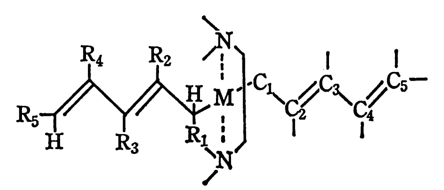
Complex	Mp/°C	Mol wt[a)] Found(Calcd)	Hydrolysis products 1,3-Diene/% (*E*)	Hydrolysis products 1,3-Diene/% (*Z*)	Hydrolysis products 1,4-Diene/%
1	80	250(259)	13.7	1.2	85.1
2	78	280(287)	41.0	4.5	54.5
3	64	—(287)	22.0	1.1 2.6[b)]	74.3
4	78	270(287)	5.8[c)]	0.3[d)]	93.8
5	61	335(316)	8.1		91.9
6	88	320(311)	0.0	4.5	95.5[e)]
7	83	335(340)	0.0	3.5	96.5[f)]

a) Determined cryoscopically in benzene. b) 4-Methyl-1,3-pentadiene. c) (*E,E*)-2,4-Hexadiene. d) (*E,Z*)-2,4-Hexadiene. e) 1,4-Cycloheptadiene. f) 1,4-Cyclooctadiene.

TABLE 3. CHARACTERIZATION OF BIS(DIENYL)ZINC·TMEDA COMPLEXES AND DISTRIBUTION OF THE HYDROLYSIS PRODUCTS

Complex	Mp/°C	Mol wt Found(Calcd)	Hydrolysis products 1,3-Diene/% (*E*)	Hydrolysis products 1,3-Diene/% (*Z*)	Hydrolysis products 1,4-Diene/%
8	59	310(316)	59.9	8.3	31.8
9	32	350(344)	67.1	1.4	31.5
10	17	—(344)	13.2	3.9 30.0[a)]	52.9
11	73	—(344)	12.2[b)]	12.3[c)] 1.5[d)]	74.0
12	44	395(372)	31.1		68.9

a) 4-Methyl-1,3-pentadiene. b) (*E,E*)-2,4-Hexadiene. c) (*E,Z*)-2,4-Hexadiene. d) 1,3-Hexadiene.

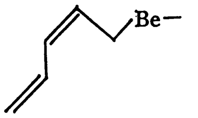


M; Be	Zn	
1	**8**	$R_1=R_2=R_3=R_4=R_5=H$
2	**9**	$R_3=CH_3$, $R_1=R_2=R_4=R_5=H$
3	**10**	$R_4=CH_3$, $R_1=R_2=R_3=R_5=H$
4	**11**	$R_5=CH_3$, $R_1=R_2=R_3=R_4=H$
5	**12**	$R_2=R_4=CH_3$, $R_1=R_3=R_5=H$

N'-tetramethyl-1,3-propanediamine (TMPDA) and a series of bis(dienyl)beryllium and bis(dienyl)zinc complexes which show the limiting structure in solution were isolated as crystals. They exist in monomeric form in benzene and the following formula are given for these complexes. Hydrolysis data are given in Tables 2 and 3. Formation of 1,4-dienes is remarkable as compared with that of 1,3-dienes especially for the beryllium compound. With respect to the 1,3-dienes, (*E*) structure predominated over (*Z*) structure for **1**—**4** and **8**—**10**. No information on the configuration of **5** and **12** was obtained by hydrolysis. If hydrolysis undergoes mainly through cyclic transition state[10)] and partially by direct cleavage just as found for hydrolysis mechanism of allylic magnesium compounds,[1)] terminally σ-bonded (*E*) structure is most plausible for **1**—**4** and **8**—**10**.

Nuclear Magnetic Resonance Studies on Bis(dienyl)beryllium Compounds. ^{1}H-NMR spectral data of seven different bis(dienyl)beryllium were measured and collected in Table 4. The assignment was done based on the values of chemical shift, relative intensities of the proton signals and the decoupling from the neighboring protons. It is clear that bis(pentadienyl)-beryllium·TMEDA complex **1** obtained from potassium pentadienide assumes terminally σ-bonded structure **1a** with (*E*) configuration ($J_{2,3}=14.6$ Hz). However, the TMEDA complex obtained from the reaction of $(C_5H_7)_2Mg\cdot 2THF$ with $BeCl_2$ comprises two species, (*E*) (**1a**) and (*Z*) (**1b**) isomers in an 8:1 ratio. The signals of major species are concordant in chemical shift with those of **1a** obtained from pentadienyl anion. Proton-proton coupling constant of $J_{2,3}$, 9.5 Hz, of minor signals corresponds to that of (*Z*) configuration.[11)] Any signals derived from the Be–C_3 carbon bond was not detected in the spectrum, although simple Hückel MO calculation suggests that the electron density of the pentadienyl anion is the highest on the C-3.[12)] Therefore, the regioselective 1,4-diene formation is rationalized by concerted mechanism as described for allylic magnesium compounds[1)] and the formation of 1,3-diene by direct cleavage of solvent-separated ionic species.[13)] Proton signals attached to C-2 and C-4 unfortunately overlap with each other. Therefore, the correct assignment was made from the decoupled spectra with reference to the spectrum of bis(2,4-pentadienyl-1,1,5,5-d_4)-beryllium·TMEDA complex (Fig. 1) which was prepared by the reaction of beryllium chloride with potassium penta-

1a (*E*)



1b (*Z*)

Table 4. ^{1}H-NMR chemical shifts(δ-values) and coupling constants of bis(dienyl)beryllium·TMEDA complexes$^{a)}$

Complex	C_1-H ($J_{1,2}$/Hz)	C_2-H	C_3-H ($J_{2,3}$/Hz)	C_4-H ($J_{3,4}$/Hz)	C_5-H ($J_{4,5}$/Hz)
1(*E*)	1.03 (d, 9.5)	6.69 (d of t)	5.89 (d of d, 15.3)	6.66 (d of q, 10.7)	4.92(d of d, 16.5) 4.72(d of d, 9.6)
1(*Z*)	1.16 (d, 9.5)	6.65 (d of d)	5.84 (d of d, 9.3)	6.66 (d of d)	5.04(d of d, 16.5) 4.85(d of d, 9.8)
2	1.01 (d, 9.3)	6.50 (t)	—	6.67 (d of d)	4.89(d of d, 16.5) 4.73(d of d, 10.0)
3	1.03 (d, 9.2)	6.70 (d of t)	6.05 (d, 15.0)	—	4.89 (d, 3.0)
4(*E*,*E*)	1.00 (d, 9.3)	6.53 (d of t)	5.89 (d of d, 14.9)	6.31 (d of d, 9.9)	5.37 (d of q, 13.5)
5	1.09(s) 1.38(s)	—	5.61(s) 5.40(s)	—	4.98(d, 3.6) 4.88(d, 3.6)
6$^{b)}$	2.77 (m, 9.6)	6.61 (d of d)	5.56 (d of d, 6.8)	6.16 (d of d, 10.8)	5.91 (d of t, 6.8)
7$^{c)}$	4.40 (m, 11.0)	5.92 (d of d)	5.32 (d of d, 9.7)	5.92	4.40

a) Measured in benzene-d_6 at 38 °C and calibrated using C_6H_6 peak, assumed to be 7.20 ppm. Assignments were made from the decoupled spectra. b) Bis(cycloheptadienyl)Be·TMEDA. c) Bis(cyclooctadienyl)Be·TMEDA.

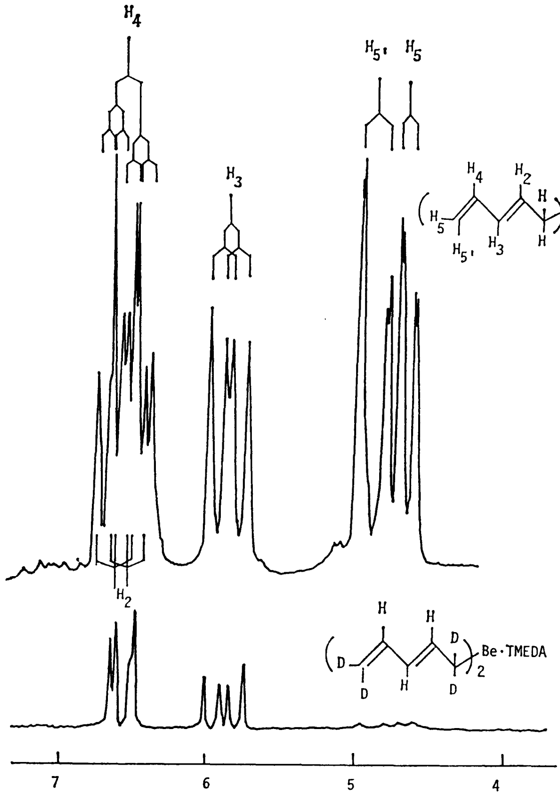


Fig. 1. ^{1}H-NMR spectra of $(C_5H_7)_2$Be·TMEDA and $(C_5H_3D_4)_2$Be·TMEDA in benzene-d_6 at 38 °C.

Table 5. ^{13}C-NMR chemical shifts(δ-values) and coupling constants(Hz) for complexes **1**, **2**, **3**, **5**, **6**, and **8**$^{a)}$

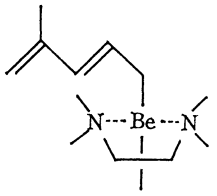
Complex	C-1	C-2	C-3	C-4	C-5
1(*E*)	25.7 (t, 115)	150.0 (t, 149)	119.2 (d, 153)	140.7 (d, 137)	103.3 (t, 158)
1(*Z*)	22.2 (t, 115)	146.6 (t, 147)	115.2 (d, 151)	135.3 (d, 137)	107.2 (t, 154)
2	24.6	149.9	122.3	147.0	103.2
3	25.4 (t, 115)	145.0 144.7 (d, 142)	121.1	137.0	105.1
5(*E*)	25.7	152.2	127.8	144.5	108.9
5(*Z*)	22.9	150.1	127.7	140.3	116.1
6	49.6 (d, 139)	151.0 (d, 139)	113.3 (d, 150)	150.0 (d, 138)	112.2 (d, 150)
8	20.5	147.1	118.2	141.0	105.0

a) Calibrated using internal benzene peak, assumed to be 128.0 ppm downfield from external TMS. Data were collected at 38 °C in C_6D_6 and assignment was made by the partial decoupling method.

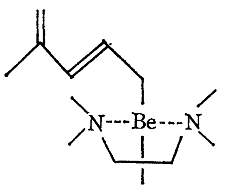
dienide-1,1,5,5-d_4. In a ^{13}C-NMR spectrum of **1** prepared from bis(pentadienyl)magnesium, two sets of five signals assignable to respective C_1—C_5 atoms of (*Z*) and (*E*) species were observed in an 8:1 ratio (Table 5) while **1** obtained from potassium pentadienide showed only five signals of (*E*) species consistent with the ^{1}H-NMR spectral data. Carbon-proton coupling constants obtained from non-decoupled spectra show no significant difference between (*Z*) and (*E*) structure.

The TMEDA complex of bis(3-methylpentadienyl)beryllium **2** had simple ^{1}H-NMR pattern which was readily attributed to the terminally σ-bonded structure and the ^{13}C-NMR spectrum showed expected six signals derived from either (*E*) or (*Z*) isomer. With reference to the exclusive production of (*E*)-3-methyl-1,3-pentadiene$^{5)}$ and 3-methyl-1,4-pentadiene upon hydrolysis of **2**, one can conclude that **2** assumes solely terminally σ-bonded structure with (E)-configuration.

Two different structures, bis(2-methyl-2,4-pentadienyl)beryllium and bis(4-methyl-2,4-pentadienyl)beryllium, are possible for the compound obtained from potassium 2-methylpentadienide. In the case of the corresponding magnesium compound hydrolysis gave nearly equal amounts of 2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene. However, the relative intensities of the signals of ^{1}H-NMR spectrum and the chemical shift values clearly show that bis[(E)-2-methyl-1,3-pentadienyl]beryllium **3** exists predominantly (95%) in the solution. It gave a 1,4-diene regioselectively by hydrolysis. Although a small amount of 4-methyl-1,3-pentadiene (2.6%) was formed by hydrolysis, their ^{1}H-NMR signals were too weak for making the correct assignment. All the expected six signals were observed also in the ^{13}C-NMR spectrum and their assignment was done by the partial decoupling method. Among the six signals, only that of C-2 splits into two peaks with a 1:1 intensity. Difference in chemical shift between the two signals (0.3 ppm) is too small to attribute them to (E) and (Z) isomers. Chemical shift difference between (Z) and (E) species observed for **1** is 3.4 ppm. Such predominance of (Z) isomer is ruled out in the present case by the hydrolysis data and the ^{1}H-NMR spectrum. Most plausible explanation is that those signals have arisen from the following two conformations (*s-cis* and *s-trans*). Free rotation around the C_3–C_4 bond would be hindered by the steric effect of the methyl group toward the TMEDA ligand. Thus, beryllium compounds **1**, **2**, and **3** assume *trans* or (E)-structure. For the compounds obtained by reaction of potassium 2,4-hexadienide with beryllium chloride, many isomers are to be considered but the abundant species (80%) was found to be bis[(E,E)-2,4-hexadienyl]beryllium·TMEDA complex **4** and minor species (20%) to be bis[(E,Z)-2,4-hexadienyl]beryllium. The results of hydrolysis of **4** [exclusive production of (E)-1,4-hexadiene and (E,E)-2,4-hexadiene] are concordant to the ^{1}H-NMR spectral data. Decoupled spectrum of **4** showed that the proton-proton coupling constants of $J_{2,3}$ and $J_{4,5}$ for (E,E)-isomer are 13.9 and 14.0 Hz and those for (E,Z)-isomer are 13.9 and 9.8 Hz, respectively. These coupling constants are in accord with the known values.[11,14] No methylene signals (CH_2=C) ascribable to C-3 or C-5 metalated species was detected.



3 (*s-trans*)



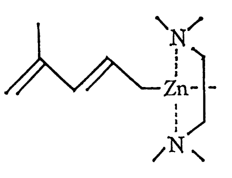
3 (*s-cis*)

NMR Studies on Crystalline Bis(dienyl)zinc Compounds of Open Chain Structure. For comparison with magnesium and beryllium compounds, the corresponding bis(dienyl)zinc·TMEDA complexes were prepared by the same method. The striking feature of the zinc compounds is that those are thermally unstable. For example, half-lives of bis(pentadienyl)zinc·2THF and bis(pentadienyl)zinc·2N$(C_2H_5)_3$ complexes at 30 °C were 10 and 15 min respectively in benzene as evidenced by ^{1}H-NMR and by gas chromatographic analysis of the hydrolyzate. These gave a 1:1 mixture of 1,3,7,9-dodecatetraene and 5-vinyl-1,3,7-octatriene quantitatively precipitating metallic zinc by raising the temperature to 80 °C. Radical coupling mechanism is most probable for this reaction. Indeed, CIDNP (chemically induced dynamic nuclear polarization) was detected on the ^{1}H-NMR spectrum at 38 °C. The two sets of resonances at 6.58, 5.12, 3.67 ppm and 6.02, 5.12, 2.78 ppm show A/E multiple polarizations[15] and are assigned to the pair of 1,4-pentadiene radicals and the pair of 1,4- and 1,3-pentadiene radicals respectively. Similar CIDNP has been reported for some organometallic compounds[16] and was recently detected for an allylzinc system[17] at higher temperatures (153 °C). By coordination with two moles of a strong donor, trimethylamine oxide, the thermal stability of bis(pentadienyl)zinc increased up to 100 °C but the rapid 1,3-rearrangement cannot be frozen even at −70 °C. The use of a chelating ligand such as TMEDA or TMPDA was essential to get the limiting structure. Another characteristic of bis(dienyl)zinc·TMEDA complex is that they comprise two or more isomeric species. The low mp of zinc compounds compared to beryllium compounds might be due to the contamination of the isomers.

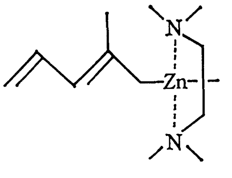
Assignments of proton signals of the isomers were done by reference to the spectra of beryllium compounds (Table 6). Bis(pentadienyl)zinc·TMEDA **8** exists as a mixture of (E) and (Z) isomers in a 4:1 ratio, but C_5H_7ZnCl·TMEDA **8′** has solely (E) structure in solution below 80 °C. The importance of this finding prompted the determination of the crystal structure of C_5H_7ZnCl·TMEDA as the typical example of the pentadienyl metal compounds for the present work. While complex **8** decomposed at 70 °C, C_5H_7ZnCl·TMEDA was thermally more stable and it displayed fluxional behavior at 90—120 °C (*i.e.*, simple averaged spectrum was obtained) and finally decomposed at 125 °C.

Bis(3-methylpentadienyl)zinc·TMEDA **9** obtained from potassium 3-methylpentadienide also comprises (E) and (Z) isomers in a 4:1 ratio.

In sharp contrast with **3**, zinc complex **10** prepared from potassium 2-methylpentadienide are composed of three isomeric species, (E)-4-methyl-2,4-pentadienyl-(45%), (Z)-4-methyl-2,4-pentadienyl-(5%), and 2-methyl-2,4-pentadienylzinc (50%) species. Their assignments shown in Table 6 could be made with a decoupled spectrum by reference to the spectrum of beryllium compound **3**. It could not be determined



10a



10b

Table 6. ^{1}H-NMR spectral data of bis(dienyl)zinc·TMEDA complexes(δ-values)[a)]

Complex	C_1-H ($J_{1,2}$/Hz)	C_2-H	C_3-H ($J_{2,3}$/Hz)	C_4-H ($J_{3,4}$/Hz)	C_5-H ($J_{4,5}$/Hz)
8(*E*)	1.47 (d, 9.3)	6.57 (d of t)	6.02 (d of d, 14.6)	6.61 (d of q, 10.8)	4.99(d of d, 16.5) 4.74(d of d, 10.1)
8(*Z*)	1.50 (d, 9.3)	6.60 (d of t)	5.78 (d of d, 9.5)	6.58 (d of q, 10.6)	4.94(d of d, 16.0) 4.70(d of d, 10.3)
8'(*E*)	1.59 (d, 9.3)	6.53 (d of t)	6.02 (d of d, 14.1)	6.60 (d of q, 10.0)	4.96(d of d, 16.1) 4.74(d of d, 9.6)
9(*E*)[b)]	1.56 (d, 9.5)	6.31 (t)	—	6.72 (d of d)	4.94(d of d, 16.3) 4.78(d of d, 10.3)
9(*Z*)	1.36 (d, 9.6)	6.27 (t)	—	6.58 (d of d)	4.94(d of d, 16.3) 4.79(d of d, 10.2)
10a	1.47 (d, 8.9)	6.34 (d of t)	5.94 (d, 15.6)	—	4.63(d, 7.0)
10b	1.49 (s)	—	5.46 (d)	6.83 (d of q, 10.8)	4.82(d of d, 14.2) 4.70(d of d, 11.0)
11(2*E*, 4*E*)	1.48 (d, 8.7)	6.09 (d of t)	5.64 (d of d, 9.8)	6.18 (d of d, 11.1)	5.29 (d of q, 14.0)
11(2*Z*, 4*E*)	1.57 (d, 8.7)	6.18 (d of t)	5.15 (d of d, 14.0)	6.17 (d of d, 11.1)	5.29 (d of q, 13.8)
12a	5.01(bs)	—	5.76(s)	—	1.48(bs)
12c	3.45(bs)	—	5.37(s)	—	3.45(s)

a) Data were collected at 38 °C in C_6D_6 and assignments were made from decoupled spectra by reference to the spectrum of the corresponding beryllium compound. b) Major signals were tentatively assigned to 9(*E*) based on the hydrolysis data.

from NMR data at hand whether **10** was composed of an asymmetric species of the type RZnR',[18)] 2-methylpentadienyl-4-methylpentadienylzinc, or a mixture of equal amounts of symmetric bis(4-methylpentadienyl)zinc (**10a**) and bis(2-methylpentadienyl)-zinc complex (**10b**)

Decoupled spectrum of bis(hexadienyl)zinc·TMEDA complex **11** showed that bis[(*E*,*E*)-2,4-hexadienyl]zinc (50%), bis[(*Z*,*E*)-2,4-hexadienyl]zinc (40%) and the other dienyl compound of unknown structure [10%, presumably (*E*,*Z*)-isomer] existed in the system. Thus, selective formation of the dienylmetal compound was not observed in cases of **10** and **11**. The poor selectivity should be ascribed to the large ionic radius of zinc atom compared to beryllium. Similar size effect of metal is known for the alkali-metal-catalyzed stereospecific polymerization of isoprene, Li favoring over Na or K for stereoregulation.[19)] Thus, the use of beryllium is suitable for selective formation of one particular isomer of the dienylmetal compound.

The predominant formation of the (*E*) species observed for dienylberyllium compounds **1**—**4** and dienylzinc compounds **8**—**9** may be ascribed to the covalency in the M–C bonding. Similar behavior is also known for allylic metal compounds; *i.e.*, 2-butenylaluminium compounds assumes (*E*) structure[9)] while more ionic allylic magnesium compounds[20)] prefer the (*Z*) structure.

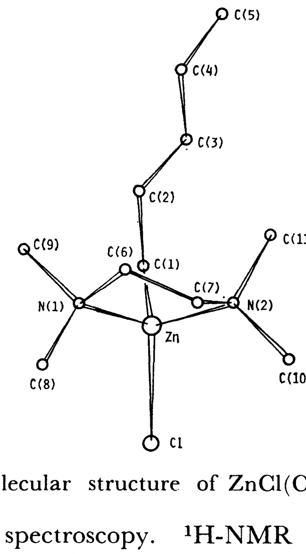


Fig. 2. Molecular structure of $ZnCl(C_5H_7)$·TMEDA.

X-Ray Structural Study of Pentadienylzinc Chloride·TMEDA. TMEDA complexes of bis(pentadienyl)beryllium, bis(pentadienyl)zinc, and pentadienylzinc chloride have (*E*)-structure in solution as evidenced by ^{1}H-NMR spectroscopy. ^{1}H-NMR spectrum of the fluxional bis(pentadienyl)magnesium indicated that the rapid 1,3-shift occurs keeping *s-trans-*(*E*) conformation.[1)] To determine whether they assume *s-trans-*(*E*) or *s-cis-*(*E*)-conformation (which corresponds to W-shaped or sickle-shaped structure for the pentadienyl anion[5)]), X-ray analysis of C_5H_7ZnCl·TMEDA was done since it showed much more reflections compared to $(C_5H_7)_2$-Zn·TMEDA and $(C_5H_7)_2$Be·TMEDA. The molecular structure is given in Fig. 2. Bond lengths and bond angles are listed in Table 7. The coordination geometry around the zinc atom is essentially tetrahedral and the C(1)–Zn–Cl angle is slightly deviated [118.8(4)°] from the standard tetrahedral angle.

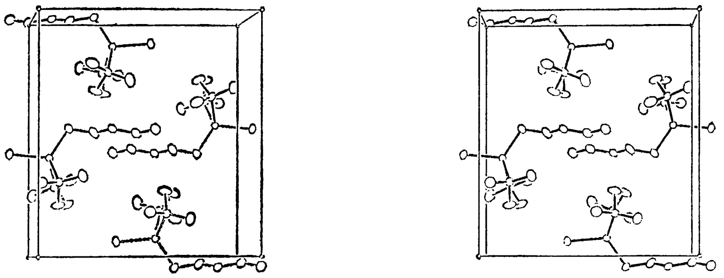


Fig. 3. A stereoscopic drawing[36] of the crystal strcuture of $ZnCl(C_5H_7)\cdot TMEDA$.

TABLE 7. BOND LENGTHS [l/Å] AND BOND ANGLES [ϕ/°] IN $ZnCl(C_5H_7)\cdot TMEDA$
Estimated standard deviations in parentheses

Bond lengths			
Zn-Cl	2.263(3)	N(1)-C(6)	1.480(12)
Zn-N(1)	2.161(6)	N(1)-C(8)	1.482(13)
Zn-N(2)	2.151(6)	N(1)-C(9)	1.506(13)
Zn-C(1)	2.03(12)	N(2)-C(7)	1.460(12)
C(1)-C(2)	1.460(17)	N(2)-C(10)	1.509(11)
C(2)-C(3)	1.293(15)	N(2)-C(11)	1.482(12)
C(3)-C(4)	1.399(13)	C(6)-C(7)	1.498(15)
C(4)-C(5)	1.273(15)		
Bond angles			
Cl-Zn-C(1)	118.8(4)	Zn-N(1)-C(6)	104.7(6)
Cl-Zn-N(1)	105.04(17)	Zn-N(1)-C(8)	112.9(6)
Cl-Zn-N(2)	104.59(17)	Zn-N(1)-C(9)	111.6(6)
N(1)-Zn-N(2)	84.5(3)	C(6)-N(1)-C(8)	111.4(8)
N(1)-Zn-C(1)	118.2(4)	C(6)-N(1)-C(9)	107.6(8)
N(2)-Zn-C(1)	120.0(4)	C(8)-N(1)-C(9)	108.4(8)
Zn-C(1)-C(2)	114.9(9)	Zn-N(2)-C(7)	105.6(6)
C(1)-C(2)-C(3)	132.8(9)	Zn-N(2)-C(10)	113.3(5)
C(2)-C(3)-C(4)	132.3(10)	Zn-N(2)-C(11)	111.1(5)
C(3)-C(4)-C(5)	137.2(11)	C(7)-N(2)-C(10)	107.0(7)
N(1)-C(6)-C(7)	112.8(9)	C(7)-N(2)-C(11)	113.9(7)
N(2)-C(7)-C(6)	112.8(9)	C(10)-N(2)-C(11)	106.0(7)

The N(1)–Zn–N(2) angle [84.5(3)°] which is equal to the corresponding angle in $(C_7H_{11})_2Mg\cdot TMEDA$ [84.2(5)°][1] is largely deviated from the tetrahedral angle. The N–Zn–N angle in $ZnCl_2\cdot TMEDA$ is 87.9°.[21]

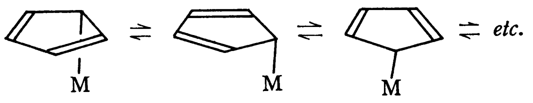
The remarkable feature of the molecular structure is that the pentadienyl group is σ-bonded to the zinc atom by the terminal C(1) [Zn–C(1)=2.031(12) Å] similar to the dimethylpentadienyl group in $(C_7H_{11})_2$-$Mg\cdot TMEDA$, but the pentadienyl group in the present complex has the *s-trans-*(*E*) conformation (W-shaped structure). The Zn–C bond length is nearly equal to those of EtZnI(1.95 Å),[22] $(MeZnOMe)_4$ (1.94 Å),[23] $LiZn(CH_3)_4$(2.07 Å),[24] but shorter than the bond length of Zn–C(Cp) in $(C_5H_5)ZnCH_3$(2.28 Å).[25] The bond lengths in the pentadienyl group show the bond alternation, C(1)–C(2)=1.460(17), C(2)–C(3)=1.293 (15), C(3)–C(4)=1.399(13) and C(4)–C(5)=1.273(15) Å. Thus, C(2)–C(3) and C(4)–C(5) double bond and C(3)–C(4) single bond lengths are slightly shorter than the ordinary C–C bond (1.33 Å for C–C double bond and 1.5 Å for single bond). All the bond angles are more than 10° larger than that of the C(sp^2) bond angle. The pentadienyl group is planar within ±0.02 Å and the dihedral angle between this plane and the plane defined by the Zn, Cl, and C(1) is 71.2°. The bond length of Zn–Cl [2.263(3) Å] is reasonable value. The Zn–Cl bond length for $ZnCl_2(CH_3CN)_2$[26] and $ZnCl_2\cdot TMEDA$[21] are 2.17 and 2.208(4)Å, respectively.

The TMEDA coordinates to the zinc atom by two nitrogen atoms. The two Zn–N lengths are almost equal [Zn–N (1)=2.161 (6) and Zn–N (2)=2.151 (6) Å]. The TMEDA moiety has the similar structure as that in $(C_7H_{11})_2Mg\cdot TMEDA$ except the two-fold symmetry.

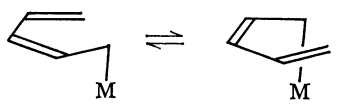
The crystal structure is shown in Fig. 3. No close intermolecular atomic contacts less than the van der Waals distance is observed.

1,5-*Metallotropic Rearrangement Induced by σ-π Conjugation.* The pathway of the metallotropic rearrangement of η^1-cyclopentadienylmetal compounds has been described as 1,2-shift,[27] although the equivalent pathway, 1,5-shift is prefered on the ground of orbital symmetry rules (*i.e.*, suprafacial 1,5-sigmatropic rearrangement).[28] If the stereochemistry required for the 1,5-shift is realized using dienylmetal compound of open chain structure (see Scheme 1), the 1,5-shift should be observable at a reasonable rate. Taking advantage of steric effect of two methyl substituents on C-2 and C-4 positions, we could realize the required geometry in bis(2,4-dimethyl-2,4-pentadienyl)zinc·TMEDA **12** as described below.

1,2- or 1,5-Metallotropic rearrangement in η^1-cyclopentadienyl compd.



1,5-Metallotropic rearrangement in (*Z*)-2,4-dimethylpentadienylmetal compd.



Scheme 1.

In the spectrum of **12**, two sets of signals (10:9 ratio) were observed. The similar ratio (10:7) was also observed for monodienyl substituted zinc compound, $C_7H_{11}ZnCl\cdot TMEDA$. One is very close in shape and in chemical shift values to bis(2,4-dimethylpentadienyl)magnesium compound of fluxional

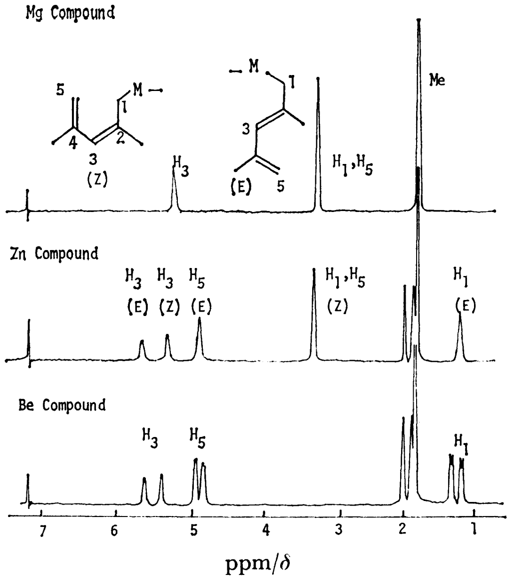
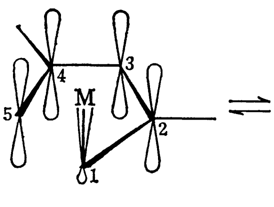
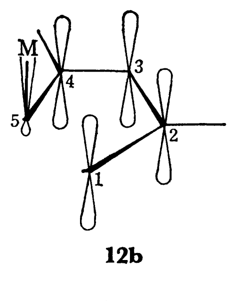


Fig. 4. ^{1}H-NMR spectra of bis(2,4-dimethylpentadienyl)metal·TMEDA complexes of Mg, Zn, and Be in benzene-d_6 at 10 °C (proton signals of TMEDA were neglected).

structure and the other corresponds to the terminally σ-bonded structure observed for bis(2,4-dimethylpentadienyl)beryllium·TMEDA (Fig. 4). Chemical shift values and the relative proton signal intensity ratio were independent of the concentration and temperature (−70—50 °C). Possibility of the equilibrium mixture is thus excluded. The effect of aggregation is negligible because **12** is monomeric in benzene independent of the concentration of the solution. Therefore, above two sets of signals can reasonably be assinged to independent (Z) and (E) species. Based on these facts, fluxional proton signals can be assigned to the (Z) species of **12** and are explained by rapid 1,5-rearrangement between **12a** and **12b**.

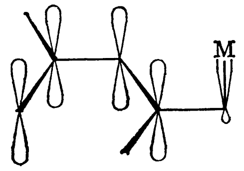


12a



12b

The U-shaped geometry is also found for bis(2,4-dimethylpentadienyl)magnesium in solid state.[1] The polarized σ-bond M–C_1 or M–C_5 is in σ-π conjugation[29] with the p-orbital of C-2 or C-4 atom and hence the metal attached to the C-1 in **12a** can easily move to C-5 by least motion. In contrast, the stereochemistry of the (E) species **12c** does not allow such a facile rearrangement since the metal is far apart from C-5. The (E) structure is limited to the following sickle-shaped structure due to the steric repulsion between two methyl groups.

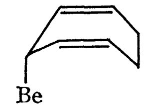


12c

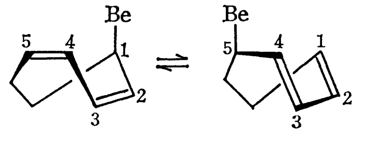
If rapid 1,3-rearrangement occurs, the species **12c** should be in equilibrium also with **12a** to give a simple averaged spectrum as was found for dienylmagnesium compounds.

Bis(2,4-dimethylpentadienyl)beryllium·TMEDA **5** is not fluxional and two sets of resonances (7:5 ratio) attributable to (Z) and (E) terminally σ-bonded species were observed. Chemical shift values of ^{13}C-NMR spectrum support this explanation. Resonances appearing at lower field may be assigned to those of (E) species of **5** by reference to the chemical shift of **12**. The relatively small ionic radius of beryllium atom may be inadequate for 1,5-rearrangement at room temperature. At 80 °C, **5** displays the fluxional behavior similar to **12**.

This guide line appears to be generally applicable and unexpected simple ^{1}H-NMR spectral pattern of bis(cycloheptadienyl)beryllium·TMEDA **6** and bis(cyclooctadienyl)beryllium·TMEDA **7** complexes may be explained by the predominant occurrence of the 1,5-pathway. As previously noted, electron density of cycloheptadienyl and cyclooctadienyl metal compound of Mg[1] and alkali metals[5] is highest on the central C-3. Considering the distribution of the electron density, the centrally σ-bonded structure **6a** may be preferred for **6**. However, chemical shifts of **6** (Fig. 5)



6a



6b

indicate that it assumes (Z)-2,4-dienylmetal type structure **6b** at room temperature contrary to the prediction. Since 1,3-cycloheptadiene[30] and 1,3-cyclooctadiene are known to have twisted structure[31], C-1 atom is close to C-5 to allow the direct 1,5-shift by transannular interaction rather than sequential 1,2- or 1,3-shift observed for η^1-cyclopentadienylmetal compounds or dienylmagnesium compounds.

If this consideration is correct, the negative charge density on C-1 and C-5 should increase by the effect of metal in sharp contrast with the negative charge distribution of the magnesium compound. Thus, simple averaged spectra of **6** (at 90 °C) and that of bis(cycloheptadienyl)beryllium·2THF are measured. Indeed, a remarkable difference in chemical shifts between proton signals of the beryllim compound and magnesium compound (Table 8) was observed. Proton at C_1 and C_5 of beryllium compound appeared at 3.9 ppm and C_3-H at 5.1 ppm while the C_1-H

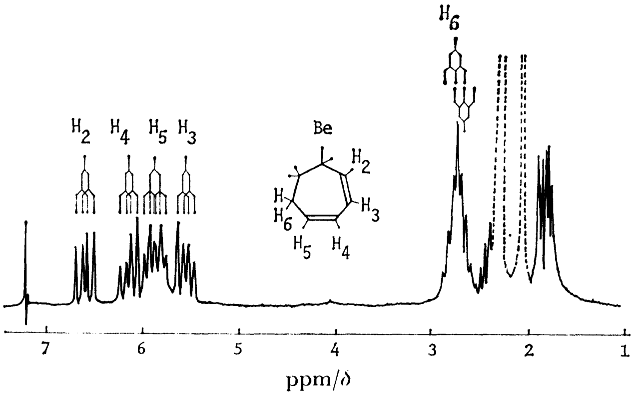


Fig. 5. ^{1}H-NMR spectrum of bis(cycloheptadienyl)beryllium·TMEDA complex in benzene-d_6 at 38 °C.

and C_5–H signals of the magnesium compound appeared at 4.6 ppm and C_3–H signal at 3.5—3.9 ppm. Negative charge density is thus highest on the C-1 and C-5 for the beryllium compound **6** but highest on the C-3 for the magnesium compound. Bis(cyclooctadienyl)beryllium·TMEDA **7** also has the highest negative charge density on C-1 and C-5 atoms and is fluxional at room temperatures (see Table 4). Conformation of **7** will be more suited for the rapid rearrangement than that of **6**. Thus, the remarkably high chemical shift values of C_1- and C_5-protons of cyclic dienylberyllium compounds and their fluxionality can be explained by the rapid transannular 1,5-rearrangement induced by σ-π conjugation. Rearrangement observed for the magnesium compound should occur by the 1,3-pathway induced by dπ-pπ conjugation[32] due to the higher ionicity of the Mg–C bond. Bis(cycloheptadienyl)zinc·2THF also showed similar chemical shift values at −20 °C to that of the beryllium compound. The information on the conformation of the crystalline TMEDA complexes of bis(cycloheptadienyl)zinc **13** and bis(cyclooctadienyl)zinc **14** cannot be obtained at present due to their thermal instability. However, the location of the metal on the cyclooctadienyl group can be inferred by the reaction with carbonyl compounds. That is, reaction of **14** with acetone or acetaldehyde gave regioselectively 2-(2,7-cyclooctadienyl)-2-propanol or 1-(2,7-cyclooctadienyl)ethanol respectively at −30 °C (regioselectivity, 98% in both cases). Since six-membered cyclic transition state is generally assumed for this type of reaction, the above result indicates that the metal–C_1 bond is involved in the compound **14**. Corresponding beryllium compound **7** also reacted with acetone regioselectively. Regioselectivity of bis(dienyl)metal compounds of open chain structure **1**—**5**, **8**—**12** toward acetone is as high as that of cyclic dienylmetal compounds (Table 9). It is noteworthy that regioselectivity of **10** is high since **10a** and **10b** gave the same products. Chemical characterization of these addition compounds were reported in Ref. 1.

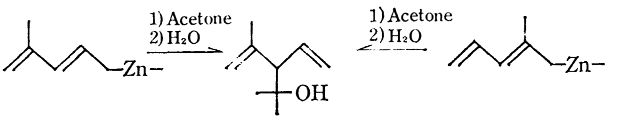


Table 8. Chemical shifts(δ-values) and coupling constants(Hz) of fluxional bis(cycloheptadienyl)metal compounds[a)]

Compound	C_1-H(C_5-H) ($J_{1,2}$)	C_2-H(C_4-H)	C_3-H ($J_{2,3}$)
$(C_7H_9)_2Be\cdot 2THF$	3.85 (8.9)	6.26	5.12 (8.5)
$(C_7H_9)_2Be\cdot TMEDA$[b)]	3.75 (8.8)	6.35	5.10 (8.4)
$(C_7H_9)_2Zn\cdot 2THF$	3.80 (bs)	6.15	5.12 (8.2)
$(C_7H_9)_2Mg\cdot 2THF$	4.55 (10.0)	6.15	3.45 (7.8)
$(C_7H_9)_2Mg\cdot TMEDA$	4.68 (9.7)	6.31	3.85 (7.4)

a) Measured in toluene-d_8 at −20 °C (in ppm downfield from external TMS). b) Measured at 90 °C. Assignment was done from decoupled spectra and relative signal intensity ratios.

Table 9. Regioselective addition of dienyl group in bis(dienyl)metal compounds to acetone giving 1,4-diene derivatives[a)]

Be compd	Regioselectivity %	Zn compd	Regioselectivity %
1	99	**8**	98
2	98	**9**	97
3	98	**10**	97
4	98	**11**	98
5	98	**12**	97
6	98	**13**	98
7	99	**14**	98

a) In benzene at 5 °C.

In summary, unambiguous evidence for symmetry-allowed 1,5-shift was obtained for covalently-bonded linear dienylmetal compounds. The absence of the corresponding 1,3-shift also indicated the unimportance of ionic character and d-orbital participation in the zinc-dienyl bonding. The covalency in the bonding in dienylberyllium or dienylzinc compounds thus dictates terminally bonded structure which in turn induces regioselective reaction of the dienyl group.

Experimental

Anhydrous zinc chloride and zinc bromide (Wako Pure Chem.) were used after drying at 140—150 °C for 20 h *in vacuo*. Anhydrous beryllium chloride was purified by dissolution of the commercial sample (needle crystals, Kishida Chem. Co.) in diethyl ether and then evaporation of the ether soluble fraction. Hydrates of beryllium chloride was thus removed. Benzene-d_6 (99.5%, Merck Co.) and toluene-d_8 (99%, Merck Co.) were dried over sodium/potassium alloy and distilled. All the procedures were done in an argon atmosphere with the high vacuum technique. ^{1}H-NMR spectra were recorded at 100 MHz and ^{13}C-NMR spectra at 25.2 MHz on a Varian XL-100 instrument with a VFT-100-620L Fourier transform accessory. All the other instrumental analyses were done as previously reported.[1] Melting points were measured in a sealed tube and were uncorrected.

Preparation of Bis(2,4-pentadienyl)beryllium·TMEDA ***1***. To a chilled solution of beryllium chloride·diethyl ether complex (2.3 g, 10 mmol) in THF (30 ml) was added a THF solution (40 ml) of potassium pentadienide (2.2 g, 20 mmol) using a syringe over a 20 min period at 5—10 °C with vigorous stirring. The mixture was allowed to react at 50 °C for 1 h and pentane (100 ml) was added at 10 °C to induce the precipitation of the salt. The supernatant liquid was separated from the salt by centrifugation using a two-necked glass tube protected with plastic cover and equipped with two small rubber stoppers and then it was evaporated *in vacuo*. Extraction of the residue with a mixture of diethyl ether (100 ml) and pentane (30 ml) followed by evaporation gave bis(pentadienyl)beryllium·2 THF as a pale yellow oil. Typical yield: 80% (2.3 g). TMEDA complex **1** was prepared by the addition of TMEDA (2.2 ml, 15 mmol) to the THF complex (2.8 g, 10 mmol) in diethyl ether (10 ml) at 20 °C. After the addition of pentane (30 ml), the mixture was cooled to −20 °C to induce the precipitation of colorless needle crystals. Yield: 92% (2.2 g) based on the THF complex. Recrystallization was carried out in 1:3 ether–pentane solution. Found: pentadiene, 53.0%; TMEDA, 43.2% (by GC); Be, 3.10% by beryllium oxide method. Calcd for $BeC_{16}H_{22}N_2$, pentadiene, 53.39%; TMEDA, 43.03%; Be, 3.58%.

Preparation of Bis(2,4-pentadienyl-1,1,5,5-d$_4$*)beryllium·TMEDA.* In essentially the same way as **1**, bis(pentadienyl-1,1,5,5-d_4)beryllium·TMEDA was prepared by reaction of potassium pentadienide-1,1,5,5-d_4($KC_5H_3D_4$) with beryllium chloride. Preparation of $KC_5H_3D_4$ is as follows. A solution of dimethyl glutarate (32 g, 0.2 mol) in diethyl ether (50 ml) was added dropwise to the suspension of $LiAlD_4$ (10 g, 0.24 mol, Merck Co.) in ether (300 ml) at 0 °C. After stirring for 5 h at 0 °C, the mixture was hydrolyzed with 2M HCl and distilled to give 1,5-pentanediol-1,1,5,5-d_4 (110 °C/1 mmHg, 20.5 g, 95% yield). Resulting pentanediol was esterified with acetic anhydride by the known method and then pyrolysis of the 1,5-pentanediyl diacetate was carried out by passing it through a Pyrex tube heated to 575± 5 °C to produce 1,4-pentadiene-1,1,5,5-d_4. Yield: 57% based on diol (8 g). After purification by distillation and drying over calcium hydride, resulting deuterated 1,4-diene (4 g, 6 mmol) was allowed to react with metallic potassium (1.2 g, 3 mmol) in THF (7 ml) in the presence of triethylamine (5 ml) at 10 °C to give $KC_5H_3D_4$.

Preparation of Bis(dienyl)beryllium·TMEDA Complex ***2—7***. In essentially the same way as described above, a series of bis(dienyl)beryllium·TMEDA complexes were prepared from the corresponding potassium dienide. Yield: 75—85%.

Preparation of Bis(2,4-pentadienyl)zinc·TMEDA ***8***. To a solution of potassium pentadienide (2.2 g, 20 mmol) in THF (40 ml) cooled by ice-water was added powdered zinc chloride (1.4 g, 10 mmol) over a 30 min period with stirring. The mixture was stirred at 5 °C for 1 h and then the volume of the solution was reduced to 1/5 by evaporation. Pentane (80 ml) was added to the residue for complete precipitation of the salt, which was then separated by quick filtration with a glass filter or by centrifugation at 5—15 °C for 10 min. All the procedures were done below 15 °C to prevent thermal decomposition. The supernatant liquid was evaporated and washed with a small portion of pentane (10 ml) at −70 °C to give bis(pentadienyl)zinc·2THF as oily substance. Yield: 84% (2.9 g). Bis(pentadienyl)zinc·TMEDA **8** was prepared by the addition of TMEDA (2.2 ml, 15 mmol) to bis(pentadienyl)zinc·2THF (2.7 g, 8 mmol) in ether (8 ml) at 0 °C. After stirring for 30 min at 30 °C, pentane (15 ml) was added and the solution was allowed to stand at −20 °C to induce the precipitation of the crystals. Yield: 98% based on the THF complex (2.3 g). Recrystallization was carried out at −20 °C from THF–pentane (1:10 vol ratio).

The other complexes of triethylamine, TMPDA, and trimethylamine oxide were prepared in the same procedure as that for the THF complex and were recrystallized from pentane at −40 °C, ether–pentane at −20 °C, and toluene at 0 °C, respectively.

Preparation of Bis(dienyl)zinc·TMEDA ***9—12***. A series of bis(dienyl)zinc·TMEDA complexes were prepared in the same procedure described for **8** from corresponding potassium dienides. The reaction of potassium 2,4-dimethylpentadienide with zinc chloride gave THF free bis(2,4-dimethylpentadienyl)zinc as evidenced by ^{1}H-NMR while the reaction of potassium 2-methylpentadienide, 3-methylpentadienide, and hexadienide gave the complexes coordinated with 2 moles of THF.

Preparation of Pentadienylzinc Chloride·TMEDA Complex. The sample for X-ray structural analysis was prepared as follows. A solution of potassium pentadienide (2.2 g, 20 mmol) in THF (40 ml) was added with a syringe over a 30 min period to a stirred solution of anhydrous zinc chloride (2.88 g, 20 mmol) in THF (30 ml) at 5 °C. The mixture was stirred for additional 1 h at 30 °C and then the salt was separated by centrifugation. THF fraction was evaporated to give $C_5H_7ZnCl\cdot 2THF$ as semi-solid, which was then extracted with two portions of toluene (20 ml). Addition of a mixture of TMEDA (3.3 ml, 22 mmol) and pentane (80 ml) to the toluene solution followed by cooling to −20 °C produced $C_5H_7ZnCl\cdot TMEDA$ quantitatively as needle crystals; mp, 77 °C. Yield: 85% based on zinc chloride (4.6 g).

Dienylation of Acetaldehyde and Acetone. To the solution of **1—12** (5 mmol) in benzene (8 ml) was added a solution of acetaldehyde (0.6 ml, 12 mmol) or acetone (0.8 ml, 12 mmol) in benzene (3 ml) at 5 °C. Resulting mixture was hydrolyzed at 0 °C and distilled *in vacuo*. In cases of **13** and **14**, corresponding reaction was carried out in THF at −30 °C without isolating the complex. After the mixture was allowed to stand at 0 °C for 1 h it was quenched with 2 M HCl. Resulting alcohols were analyzed by GC using authentic samples (chemical characterization was previously reported. see Ref. 1). Yield by GC: 98%. Both acetaldehyde and acetone attacked the C-3 atom of dienyl group regioselectively in all cases.

Crystal Data and Structure Determination of Pentadienylzinc Chloride·TMEDA. $C_{11}H_{19}N_2ClZn$, *F. W.* 280.1, monoclinic, space group $P2_1/c$, $a=8.935(2)$, $b=13.587(2)$, $c=12.096(2)$ Å, $\beta=95.50(2)°$, $V=1461.7(5)$ Å^3, $D_c=1.272$ g cm^{-3} for $Z=4$.

Unit-cell dimensions and reflection intensities were measured on a Rigaku automated, four-circle diffractometer using graphite monochromatized Mo $K\alpha$ radiation. The θ-2θ scan technique was applied at a 2θ scan rate of 4 °min^{-1}. The scan width was $\Delta 2\theta=(2.0+0.7\tan\theta)°$. Backgrounds were counted for 5 s before and after the scan of each peak. Intensities of three standard reflections were measured after every 60 reflections. A total of 2296 (1852 non-zero) reflections was collected up to $\Delta 2\theta=48°$. Usual Lorentz and polarization corrections were applied but no absorption correction was made [μ(Mo $K\alpha$)$=17.1$ cm^{-1}].

The structure was established by the heavy atom method and refined isotropically by the block-diagonal least-squares procedure (HBLS V).[33] After the R value decreased to 0.15, anisotropic refinements were carried out. Final R

Table 10. Atomic positional and thermal parameters of ZnCl(C_5H_7)·TMEDA
Estimated standard deviations in parentheses

Atom	X	Y	Z
Zn	0.23418(10)	0.07752(6)	0.41436(6)
Cl	0.2632(3)	0.06375(15)	0.60165(15)
N (1)	0.0773(7)	0.1974(5)	0.3810(5)
N (2)	0.4004(7)	0.1838(5)	0.3768(5)
C (1)	0.2038(14)	−0.0467(6)	0.3216(7)
C (2)	0.1782(15)	−0.0303(7)	0.2020(8)
C (3)	0.2607(11)	−0.0439(6)	0.1211(7)
C (4)	0.2353(12)	−0.0266(7)	0.0069(7)
C (5)	0.3044(14)	−0.0412(8)	−0.0789(8)
C (6)	0.1642(10)	0.2742(7)	0.3285(10)
C (7)	0.3249(10)	0.2791(6)	0.3765(9)
C (8)	0.0156(14)	0.2347(9)	0.4823(9)
C (9)	−0.0521(12)	0.1682(8)	0.2985(10)
C (10)	0.5329(11)	0.1889(7)	0.4638(8)
C (11)	0.4630(11)	0.1598(8)	0.2710(8)

Atom	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
Zn	0.01822(13)	0.00426(5)	0.00563(6)	0.00064(12)	0.00506(13)	0.00021(8)
Cl	0.0306(5)	0.00687(13)	0.00580(13)	0.0045(4)	0.0054(4)	0.00201(19)
N (1)	0.0143(9)	0.0066(4)	0.0078(5)	0.0013(10)	0.0038(10)	0.0037(7)
N (2)	0.0155(9)	0.0059(4)	0.0075(5)	0.0009(9)	0.0045(10)	−0.0001(7)
C (1)	0.041(3)	0.0058(5)	0.0071(7)	−0.0063(18)	0.0053(19)	−0.0029(9)
C (2)	0.044(3)	0.0079(7)	0.0110(9)	−0.019(3)	0.019(3)	−0.0084(12)
C (3)	0.0266(16)	0.0046(4)	0.0083(6)	−0.0018(13)	0.0005(16)	−0.0029(9)
C (4)	0.031(2)	0.0066(6)	0.0107(8)	−0.0069(16)	0.010(2)	−0.0042(10)
C (5)	0.034(3)	0.0083(7)	0.0104(9)	−0.009(2)	0.008(3)	−0.0031(12)
C (6)	0.0167(13)	0.0063(6)	0.0193(12)	−0.0026(14)	0.0000(19)	0.0088(13)
C (7)	0.0190(14)	0.0047(5)	0.0185(11)	0.0026(13)	0.004(2)	0.0037(12)
C (8)	0.040(3)	0.0139(10)	0.0120(10)	0.027(3)	0.024(3)	0.0063(16)
C (9)	0.0216(17)	0.0094(8)	0.0197(13)	−0.0075(18)	−0.015(3)	0.0062(16)
C (10)	0.0196(15)	0.0097(7)	0.0132(10)	−0.0025(16)	−0.0075(19)	0.0002(13)
C (11)	0.0274(19)	0.0115(8)	0.0098(8)	−0.007(2)	0.0186(19)	−0.0039(13)

value was 0.068 for non-zero reflections. Atomic scattering factors were taken from International Tables for X-Ray Crystallography, Vol. IV.[34] The weighting schemes used in the final refinement were $w=[\sigma^2(F_o)+a|F_o|+b|F_o|^2]^{-1}$ for $|F_o|>0$ and $w=c$ for $|F_o|=0$, where, $a=0.0067$, $b=0.002$, and $c=0.111$. The final atomic positional and thermal parameters are listed in Table 10. Calculations were done on an ACOS series 77 NEAC system 700 computer at Osaka University.[35]

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