April, 1980] © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 1089—1100 (1980)

Chemistry of Dienyl Anions. II. Crystalline Bis(dienyl)magnesium. Selective Dienylation and Structure in Solution and in the Solid State

Hajime Yasuda, Michihide Yamauchi, Akira Nakamura,* Tsuyoshi Sei,† Yasushi Kai,† Noritake Yasuoka,† and Nobutami Kasai†

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560
†Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

(Received October 4, 1979)

Seven different crystalline bis(dienyl)magnesium·TMEDA complexes of open chain or cyclic structure were prepared by metal exchange reaction of corresponding potassium dienides. They are fluxional in solution due to the rapid 1,3-rearrangement. Terminally σ-bonded *trans* or (E) structure exists primarily in the open chain complexes while centrally σ-bonded *cis* structure in cyclic dienylmagnesium·TMEDA complexes. The former gave 1,3-dienes exclusively but the latter gave 1,4-dienes upon hydrolysis. Molecular structure of bis(2,4-dimethyl-2,4-pentadienyl)magnesium determined by X-ray crystallography showed that it has terminally σ-bonded structure. Addition of dienylmagnesium compounds to acetone followed by hydrolysis gave 1,4-diene derivatives regioselectively but that to diisopropyl ketone gave 1,3-diene derivatives selectively. Unsaturated alcohols with an elongated carbon chain were synthesized by thermal cracking of cyclic ether complexes. 1,3,7-Trienes can be obtained selectively by reaction of appropriate allyl halides in the presence of CuCl catalyst and regioselective dienylation occurred by using $TiCl_2(\eta^5\text{-}C_5H_5)_2$ as catalyst.

Allylic magnesium compounds have been utilized as an agent for introduction of olefin groups into various organic groups[1] or as a component of polymerization catalysts.[2] Stereoselective or regioselective introduction of the dienyl moiety into organic groups is also attractive especially for the synthesis of terpenoids or biologically active substances. Organic synthesis using dienylmetal compounds have been little developed due to the lack of suitable preparation methods though some diene syntheses catalyzed by transition metal compounds[3] and by Grignard type reaction[4] are recently reported. We present here a widely applicable novel route for the preparation of pure bis(dienyl)magnesium compounds, their structures, and some applications for organic synthesis. Bis(dienyl)magnesium compounds of five different linear dienes and of two cyclic dienes were prepared by transmetalation of dienyl anions with magnesium halides. All of these were isolated for the first time as crystals of N,N,N',N'-tetramethylethylenediamine (TMEDA) complexes. These dienylmagnesium compounds are fluxional in solution and their simple averaged ^{1}H-NMR spectra resemble well those of corresponding dienyl anions. Hence the fluxional structure is discussed in relation to the conformation[5] of the dienyl anions whose conformational stability was recently treated by extended Hückel MO calculations.[6]

Results and Discussion

Isolation of Crystalline Dienylmagnesium Compounds. Series of bis(dienyl)magnesium compounds and Grignard type dienylmagnesium halides were prepared by the metal exchange reaction. Bis(2,4-pentadienyl)magnesium was synthesized by the 2:1 reaction of potassium pentadienide[7] with anhydrous magnesium halide in THF in 85—95% yield and was isolated as pure crystals of TMEDA complex **1**. Deuteriolysis of **1** gave two moles of pentadiene-1-d or -3-d and one mole of TMEDA as evidenced by GC of the resulting solution. Grignard type pentadienylmagnesium bromide can also be prepared by the 1:1 reaction of potassium pentadienide with magnesium bromide. In the similar manner, TMEDA complexes of bis(2,4-hexadienyl)magnesium **2** and hexadienylmagnesium bromide were prepared in 90% yield. The direct reaction of magnesium with 1-bromo-2,4-hexadiene in THF gave hexadienylmagnesium bromide in only 30% yield. The formation of homo coupling products, $C_{12}H_{18}$, (70% yield) was predominant in the latter case even when 1-bromo-2,4-hexadiene was added to an excess (10 equivalent) magnesium turnings very slowly. Thus, the present method is widely applicable and superior to the known method with regard to the yield and purity. This paper mainly deals with bis(dienyl)magnesium compounds to avoid the complex problem arising from a Schlenk equilibrium observed for Grignard reagents. Other crystalline TMEDA complexes of bis(4-methyl-2,4-pentadien-1-yl)magnesium **3**, bis(3-methyl-2,4-pentadien-1-yl)magnesium **4**, bis(2,4-dimethyl-2,4-pentadien-1-yl)magnesium **5**, bis(2,6-cycloheptadien-1-yl)magnesium **6**, and bis(2,7-cyclooctadien-1-yl)magnesium **7** were prepared in essentially the same way as described for **1**. Their chemical characterization is given in Table 1. The molecular weights determined cryoscopically in benzene showed that they are all monomeric. Based on these facts, following formulae are given for **1**—**5** and **6**—**7**.

$$2\,C_5H_7K + MgX \xrightarrow{THF} (C_5H_7)_2Mg\cdot 2\,THF \xrightarrow{TMEDA} (C_5H_7)_2Mg\cdot TMEDA$$

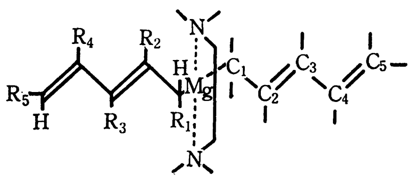
1

Population at Equilibria Existed in Bis(dienyl)magnesium. Monoalkyl substituted allylic Grignard reagents are known to be present in solution predominantly as γ-alkyl substituted species,[8] although it is equilibrating with the α-alkyl substituted one by rapid 1,3-rearrangement as evidenced by NMR spectroscopy and as deduced from structures of the products obtained by hydrolysis. The *cis*/*trans* ratio of the product decreased with an increase in bulkiness of the alkyl substituent,

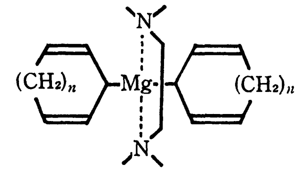
Table 1. Characterization of bis(dienyl)magnesium-TMEDA complexes

Dienyl Compound	Mp (°C)$^{a)}$	Mg/%		Diene/TMEDA$^{c)}$ (mol/mol)	Mol wt$^{d)}$	
		Found$^{b)}$	Calcd		Found	Calcd
1	74.8	8.8	8.8	2.01	282	274
2	66.2	8.2	8.0	2.05	310	302
3	35.2	8.2	8.0	2.03	320	302
4	60.7	8.1	8.0	2.00	302	302
5	86.6	7.3	7.3	2.02	335	330
6	91.1	—	7.4	2.02	340	326
7	93.5	6.7	6.8	2.02	370	354

a) Measured with sealed capillary. b) Determined by 8-quinolinol method. c) Determined by ^{1}H-NMR from relative signal intensities. d) Determined cryoscopically in benzene.

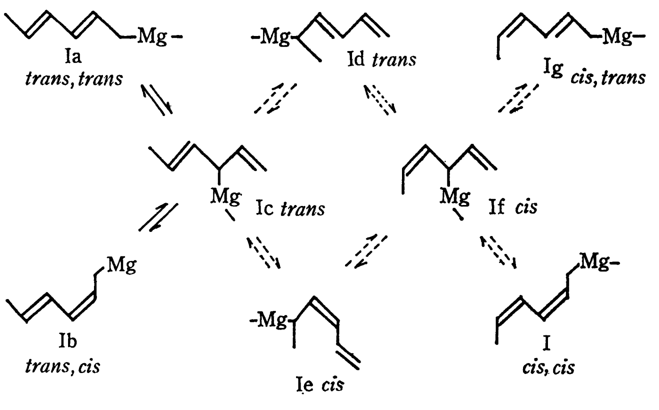


1: $R_1=R_2=R_3=R_4=R_5=H$
2: $R_5=CH_3$, $R_1=R_2=R_3=R_4=H$
3: $R_4=CH_3$, $R_1=R_2=R_3=R_5=H$
4: $R_3=CH_3$, $R_1=R_2=R_4=R_5=H$
5: $R_2=R_4=CH_3$, $R_1=R_3=R_5=H$



6: $n=2$
7: $n=3$

Equilibria for the dienylmagnesium compounds are rather complex because dienyl group has three reactive carbon atoms, C_1, C_3, and C_5. For example, following eight species are possible for the hexadienylmagnesium compounds (Scheme 1). To get the information on the configuration of the diene group and on the position at which the magnesium atom is bonded, hydrolysis of the bis(dienyl)magnesium compounds was carried out (Table 2). Compounds **1** and **4** gave 1,3-dienes primarily but the cyclic dienylmagnesium compounds **6** and **7** gave 1,4-dienes exclusively in line with hydrolysis data of the starting dienyl anions.7) Other magnesium compounds **2**, **3**, and **5** gave nearly equal amounts of 1,3- and 1,4-dienes, although the corresponding dienyl anions gave only 1,3-dienes.7) Thus dienylmagnesium compounds exist as an equilibrium mixture and the alkyl substitution on the pentadienyl group influences the ratio of resulting 1,3- to 1,4-dienes. Characteristic feature of the hydrolysis of **1**, **3**, and **4** is that *trans*(or *E*)-1,3-diene was produced in preference to *cis*(or *Z*)-1,3-diene. This result sharply contrasts to the hydrolysis of the corresponding potassium dienides which gave *cis*-1,3-diene selectively. In the case of **2**, nearly equal amounts of *trans,trans*- and *trans,cis*-2,4-hexadiene were produced upon hydrolysis. Two routes are possible for the production of *trans,cis*-2,4-hexadiene (from Ib and Ig in Scheme 1) but the route *via* Ib is more plausible. If Ig is equilibrating with Ia and the *trans,cis*-isomer is formed from Ig, other isomers (*i.e.*, 1,3-hexadiene derived from Id or Ie, *cis*-1,4-hexadiene from If and *cis,cis*-2,4-hexadiene from Ih) should be produced simultaneously but those yields were negligible. *Trans* configuration of 1,4-hexadiene obtained from **2** together with the configuration of above mentioned 2,4-hexadiene supports the postulate of equilibration between Ia and Ib. In contrast to the open chain dienylmagnesium compounds, cyclic dienylmagnesium compounds **6** and **7** gave *cis,cis*-1,4-dienes exclusively, indicating the negative charge being high on the C_3 atom.



Scheme 1.

Table 2. Hydrolysis of bis(dienyl)magnesium-TMEDA complexes in benzene at 10 °C

Complexes	1,3-Dienes/%		1,4-Dienes/%
	trans,(*E*)	*cis*,(*Z*)	
1	64.5	14.5	21.0
2	24.5$^{a)}$	21.6$^{b)}$	53.9$^{c)}$
3	29.5	2.0$^{d)}$	44.8
	23.7$^{e)}$		
4	62.5	3.4	34.1
5	41.2		58.8
6	0	7.9	92.1
7	0	6.5	93.5

a) *trans,trans*-2,4-Hexadiene. b) *trans, cis*-2,4-Hexadiene. c) *trans*-1,4-Hexadiene. d) 2-Methyl-1,3-pentadiene. e) 4-Methyl-1,3-pentadiene

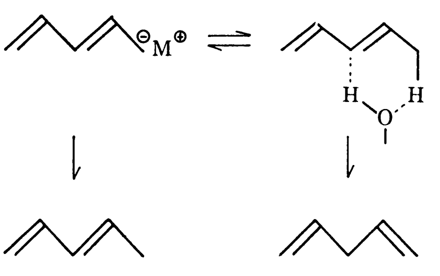
The position of equilibrium was altered by change

Table 3. Effect of protonolysis agents on the distribution of the protonolysis products of $(C_5H_7)_2Mg\cdot 2THF$[a)]

Agent	1,3-Pentadiene/%		1,4-Pentadiene/%
	trans	*cis*	
CH_3COOH	48	8	44
CH_3OH	52	6	42
H_2O	75	5	20
Pyrrolidine	95	5	0
Piperidine	96	4	0

a) Protonolysis was carried out in benzene at 10 °C.

of basicity of the protonolysis agents and of the ligands as shown in Table 3. The variation in distribution of the protonolysis products may be explained by considering both ionic species and covalent species which are equilibrating with each other as was described for magnesium–diene adducts;[9)] *i.e.*, protonation with bases occurs at $C_1(C_5)$ position exclusively while that with acid occurs also at C_3 position. The former may be explained by the predominant cleavage of ionic Mg–C bond and the latter by the cleavage of covalent Mg–C bond presumably by a concerted mechanism. Based on this assumption, the effect of the ligand to the structure of the hydrolysis product was examined.



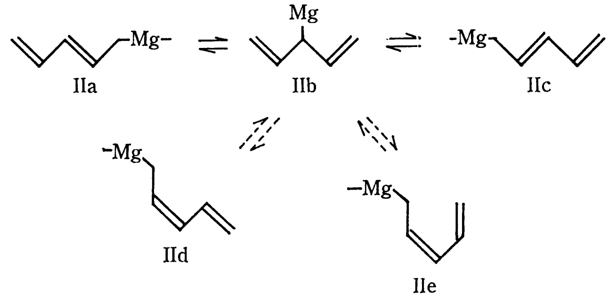
Coordination of strong donor such as 1,4,8,11-tetramethyl-1,4,8,11-tetraazatetradecane(tetramethylcyclam) and 1,4,7,10,13-pentaoxacyclopentadecane(15-crown-5) increases the ionic nature of the Mg–C bond and hence the dienyl group behaved similarly to the dienyl anion[7)] giving 1,3-diene exclusively upon hydrolysis (Table 4). Linear polyethers bearing aromatic end groups are also being increasingly used for complexing the metal cations[10)] but the polyethers shown in Table 4 have relatively little interaction with metal.

A typical example of the regioselective 1,4-diene formation is observed in hydrolysis of $K[(C_5H_7)_4Al]$ which was prepared by the 4: 1 reaction of potassium pentadienide with aluminium chloride (see experimental). It has terminaly-σ-bonded structure as evidenced by ^{1}H-NMR and it gave 1,4-pentadiene quantitatively (99%) upon hydrolysis. Thus, the complete conversion of a 1,3-diene to the thermally more unstable 1,4-diene was realized by the metalation of 1,3-diene with alkali metals, followed by the aluminium assisted reaction. Similar regioselectivity is found also for allylaluminium compounds and enediylaluminium compounds[11)] obtained from endiylmagnesium compounds. The high regioselectivity should be ascribed to the larger covalent character of the Al–C bond compared to the Mg–C bond.

Table 4. Distribution of the hydrolysis products of $(C_5H_7)_2Mg$ coordinated with macromolecular ligands

Ligand		1,3-Pentadiene/%		1,4-Pentadiene/%
		trans	*cis*	
$CH_3O(CH_2CH_2O)_nCH_3$	$n=1$	37	8	55
	$n=2$	37	9	54
	$n=3$	35	11	54
	$n=4$	42	13	45
15-Crown-5		94	6	0
18-Crown-6		81	13	7
Tetramethylcyclam		95	5	0

Nuclear Magnetic Resonance Studies. ^{1}H-NMR spectra of TMEDA complexes **1**—**7** are collected to know the correlation between the population at equilibrium obtained by hydrolysis and the structure of the complexes in solution (Table 5). The values of chemical shifts of **1** clearly shows that the terminally σ-bonded structure (IIa and IIc) exists predominantly,



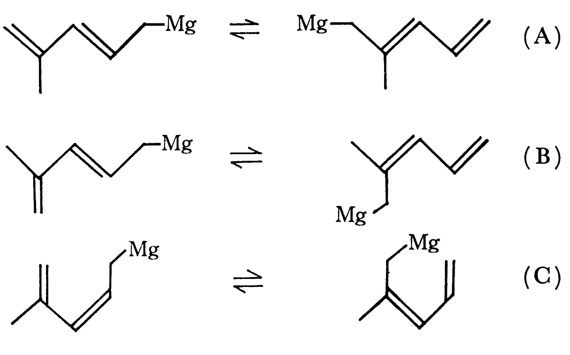
although it is equilibrating rapidly with IId or IIe *via* IIb the presence of which was not detected on the NMR time scale, a simple averaged A_2BX type spectrum being observed. Proton-proton coupling constant J_{23} (or J_{34}), of 11.7 Hz corresponds to the J_{23} of internal olefin protons of pentadienyl anions (11.5—13.5 Hz)[12)] whose conformation is W-form (*trans* configuration). The coupling constant J_{23} for dienyl anions having *cis*-configuration is known to be 7—9 Hz.[13)] The *cis/trans* ratio of **1** calculated from the magnitude of the coupling constant (assuming *trans* $J_{H,H}$ to be 12.5 Hz and *cis* $J_{H,H}$ to be 7.0 Hz) with a linear equation is 0.21 in line with the hydrolysis data (0.22). Thus **1** was concluded to be in equilibrium between IIa and IIc keeping *trans* configuration. The rapid equilibrating structure may be correlated to the W-form of the pentadienyl anion which also shows A_2BX spectrum. Based on the coupling constant, we may conclude that sickle(IId) and U(IIe) formed compounds which result by the rotation around the C_2–C_3 or C_3–C_4 bond have minor populations at equilibrium. Assignment of the signals of **2** was made in part from a decoupled spectrum and **2** was concluded to be terminally-σ-bonded structure. The value of proton-proton coupling of J_{45}, 13.1 Hz, indicates that C_4H=C_5H group assumes *trans* structure while that of J_{23} shows C_2H=C_3H group being in equilibrium between *trans* and *cis* structure (*cis*/*trans*=0.41). The higher field shift of C_1-proton

Table 5. Chemical shifts and coupling constants in ^{1}H-NMR spectra of complexes **1**—**7**[a)]

	C_1-H(J_{12}/Hz)	C_2-H	C_3-H(J_{23}/Hz)	Others
1	2.98 (d, 11.3)	6.55 (d of d)	5.58 (d of d, 11.7)	C_4-H=C_2-H, C_5-H=C_1-H
2	1.95 (d, 9.9)	6.51 (d of t)	5.76 (d of d, 10.9)	6.51 (d of d, 13.0, C_4-H) 5.24 (d of q C_5-H) 1.50 (d 9.9, CH_3)
3	2.88 (d, 11.5)	6.77 (d of t, 12.3)	5.72 (d)	3.21 (s, C_5-H) 1.91 (s, CH_3)
4	3.02 (d, 11.5)	6.54 (d of d)	—	1.91 (s, CH_3)
5	3.33 (s)	—	5.22 (s)	2.12 (s, CH_3)
6	4.68 (bd 9.7)	6.31 (d of d)	3.85 (d of d, 7.4)	2.77 (m, CH_2)
7	4.22 (d of d, 9.3)	6.40 (d of d)	3.34 (d of d, 6.5)	3.10 (d of t, 6.4, CH_2C=C) 1.62 (t of t, 6.3, CH_2CH_2)
1[b)]	1.49 (d, 8.9)	6.28 (m)	5.60 (d of d, 14.0)	6.18 (C_4-H, m) 4.91 (C_5-H, d of d, 15.8) 4.77 (C_5-H, d of d, 10.0)

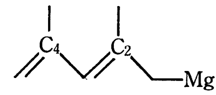
a) Calibrated using benzene as internal standard (benzene peak, 7.20 ppm downfield from external TMS). Data were collected at 38 °C in C_6D_6. b) Bis(pentadienyl)magnesium-15-crown-5 complex at −60 °C in THF-d_8.

and lower field shift of C_5-proton compared to the values of **1**, suggest that the equilibrium in Scheme 1 are shifted to Ia and Ib in line with the hydrolysis data. The spectrum of **3** was composed of both A_2BX pattern signals and broad singlet assignable to the terminal CH_2 group. Magnitude of J_{23} corresponds to that of *trans* structure. Protons attached to C_1 and C_5 carbon atoms shifted to higher field by 1.9—2.1 ppm from C_1 and C_5-protons of the starting diene showing the presence of the equilibrium. Therefore, the following equilibria (A) and/or (B) which include *trans* configuration are considered for **3**. Equilibrium (C) including *cis* configuration may exist in only minor population, if any.

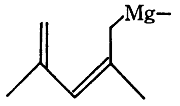


Although ^{1}H-NMR data of **4** gave no information about the configuration, it is possible to conclude based on chemical shift value that **4** has also terminally σ-bonded structure primarily. Hydrolysis data of **4** (exclusive production of (*E*)-3-methyl-1,3-pentadiene) strongly suggest that rapid 1,3-rearrangement occurs in solution keeping (*E*)-structure. If the conformation changes from (*E*) to (*Z*) during the rearrangement, (*Z*)-3-methyl-1,3-pentadiene should be produced in lager amounts.

In contrast to **1**—**4**, (*Z*)-configuration is most plausible for 2,4-dimethylpentadienylmagnesium **5** due to the steric repulsion between the two methyl groups. The double bonds in (*E*)-2,4-dimethylpentadienyl group can not be coplanar since the van der Waals radius of methyl group (*ca.* 2.0 Å) is much larger than the C_2–C_4 carbon distance (1.3 Å). The X-ray analysis of bis(2,4-dimethylpentadienyl)magnesium·TMEDA **5**, actually, showed that it has (*Z*)-configuration (details are given later in this paper). Chemical shift of **5** shows that it has terminally σ-bonded structure also in solution.



5 (*E*)



5 (*Z*)

Thus, (*E*)- and (*Z*)-pentadienylmagnesium compounds of open chain structure were realized. This finding prompted further interest in comparison of electron density distribution of **5** with that of (*Z*)-pentadienylmagnesium compounds of cyclic structure. Proton-proton coupling constants, J_{23} (7.4 Hz for **6** and 6.5 Hz for **7**) show that cyclic dienylmagnesium **6** and **7** have (*Z*)-structure as expected. The increased coupling constants of J_{12} (9.7 Hz for **6** and 9.3 Hz for **7**) may be explained by the torsion around the C_1–C_2 carbon bond derived from the nonplanar structure[14)] rather than the equilibrium between *cis* and *trans* structure because *cis,trans* (or *trans,trans*) conformation is much higher in energy than the *cis,cis* conformation in a ring system,[15)] especially for 1,3-cycloheptadiene.

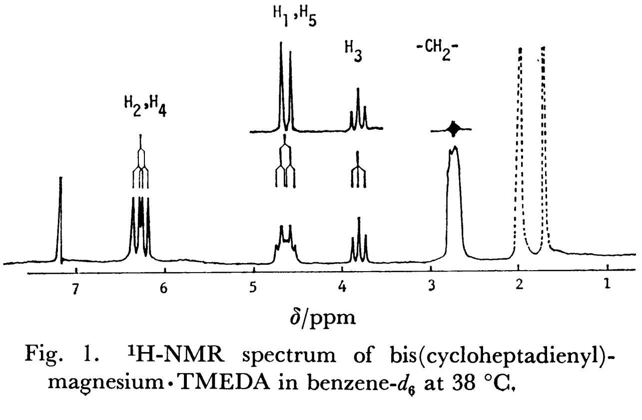


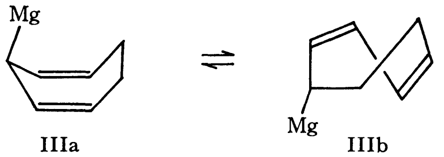
Fig. 1. ^{1}H-NMR spectrum of bis(cycloheptadienyl)-magnesium·TMEDA in benzene-d_6 at 38 °C.

Table 6. ^{13}C-NMR spectral data of the complexes **1**,**3**,**4**,**5**, and **7**$^{a,b)}$

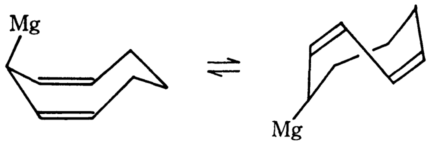
	C_1 (C_5)	C_2 (C_4)	C_3	Others
1	63.1	143.9	112.0	
3	57.8 (C-1) (140)	140.8 (C_2) (145) 139.7 (C_2) (150)	112.1 (148) 111.3 (148)	147.9 (C_4) 69.1 (C_5) (141) 22.1 (CH_3) (128)
4	60.9	144.7	114.4	20.8 (CH_3)
5	67.8 (150)	143.9	109.3 (138)	28.4 (CH_3) (129)
7	98.5 (151)	139.7 (140)	66.5 (135)	26.3 (CH_2) (128) 19.1 (CH_2) (128)

a) In ppm downfield from external TMS (calibrated using benzene peak, assumed to be 128.0 ppm). b) Measured at 38 °C in C_6D_6.

The most striking feature in the spectra of **6** (Fig. 1) and **7** is that the signals of the proton attached to the central C_3-carbon atom appeared at higher field than that of C_1 and C_5 carbon stoms. This means that centrally bonded 1,4-diene type structure exists primarilly in **6** and **7** and the electron density on the C_3 carbon atom is higher than those on the C_1 and C_5 carbon atoms. Based on these facts, structure IIIa is considered for **6** as the abundant species although it is in equilibrium with the minor species IIIb of 1,3-dienyl type structure. For the structure IIIb, twisted structure is most plausible from view of the conformational stability.[16] Stereochemistry around the Mg–C bond in IIIa and IIIb could not be determined by spectral data. Since the boat-chair conformation[17] is known for 1,4-cyclooctadiene to be much more stable than the boat-boat conformation, structure IVa is reasonably considered as the predominant species for **7**. The minor species IVb which is equilibrating with IVa should have also nonplanar 1,3-diene structure because double bonds in 1,3-cyclooctadiene can not be coplanar.[18] Thus, a sharp contrast in electron density (or the position at which the metal bonds to a carbon atom) was observed between acyclic dienylmagnesium compound and cyclic dienylmagnesium compounds with (*Z*) structures. That is, the former has high electron density on the terminal carbon atoms while the latter on the central carbon atom.



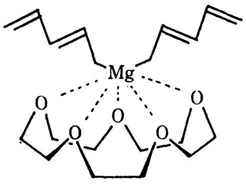
IIIa IIIb



IVa IVb

^{13}C-NMR chemical shifts for dienyl anions have been reported[19] and provide the best measure of electron density distribution and the configuration of dienyl anions. ^{13}C-NMR spectral data of bis(dienyl)magnesium were collected in this view as shown in Table 6. Assignment of the spectrum was done with nondecoupled spectrum and by partial decoupling. The striking feature of these data is that signals of C_1 and C_5 atoms of linear dienylmagnesium compounds **1**—**5** appeared in higher field than that of C_3 atom, while those of cyclic compound **6** and **7** appeared in lower field than the signal of C_3 carbon atoms consistent to the ^{1}H-NMR data. The values of the carbon-proton coupling constant were useless for the determination of the configuration. Based on ^{13}C-NMR, ^{1}H-NMR, and hydrolysis data, it is reasonable to conclude that bis(dienyl)magnesium of open chain structure except **5** assume primarily the terminally σ-bonded (*E*) structure but those of cyclic dienyl structure assume the centrally σ-bended (*Z*) structure.

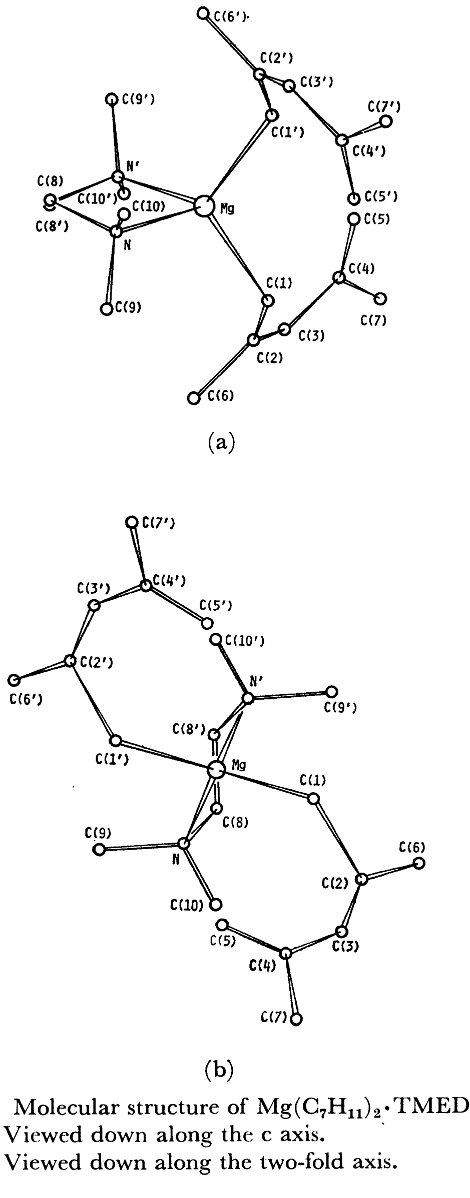
Although no appreciable change in chemical shift was observed for **1**—**7** over a 100 °C temperature (−80—50 °C) within 10 Hz and no limiting structure was realized even at −100 °C, freezing of the dynamic equilibrium was realized by coordination of a bulky ligand such as 15-crown-5 or 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6). ^{1}H-NMR spectrum of 1 : 1 complex of 15-crown-5 or 18-crown-6 showed A_2BX pattern at 0—30 °C but it showed the limiting structure (see Table 5) below −40 °C. Chemical shift and relative intensity of the signals observed at −60 °C are characteristic of the terminally σ-bonded structure and resemble well to that of bis(pentadienyl)zinc·TMEDA complex.[20] This is the first example of freezing out of the equilibrium of allylic type magnesium compound. The complete equilibrium shift may be attained by the steric repulsion between the crown ether and the pentadienyl group. Examination of models which permits the 1,3-rearrangement showed the following structure to be the most plausible for this complex.



Solubility of the 1 : 1 crown ether complex in benzene becomes less than 1/5 of that of THF complex due to the increase in ionic character, being different from the behavior of the usual crown ether complexes.[21] Linear polyethers had no ability to freeze out the equilibrium even at −80 °C. Coordination of strong coordinating

Table 7. Bond lengths [l/Å] and bond angles [ϕ/°] in $Mg(C_7H_{11})_2\cdot$TMEDA
Estimated standard deviations are in parentheses.

Bond lengths			
Mg–N	2.202(12)	C(2)–C(3)	1.402(19)
Mg–C(1)	2.179(15)	C(2)–C(6)	1.55(3)
N–C(8)	1.49(3)	C(3)–C(4)	1.466(20)
N–C(9)	1.475(20)	C(4)–C(5)	1.356(22)
N–C(10)	1.49(3)	C(4)–C(7)	1.54(3)
C(1)–C(2)	1.467(20)	C(8)–C(8′)	1.48(5)
Bond angles			
N–Mg–N′	84.2(5)	C(3)–C(4)–C(7)	114.1(13)
N–Mg–C(1′)	118.0(6)	C(5)–C(4)–C(7)	119.7(14)
N–Mg–C(1)	110.4(6)	Mg–N–C(8)	104.4(11)
C(1)–Mg–C(1′)	113.1(6)	Mg–N–C(9)	112.5(9)
C(1)–C(2)–C(3)	129.4(13)	Mg–N–C(10)	111.8(10)
C(1)–C(2)–C(6)	116.1(13)	C(8)–N–C(9)	110.8(13)
C(3)–C(2)–C(6)	114.5(13)	C(8)–N–C(10)	106.4(13)
C(2)–C(3)–C(4)	127.1(13)	C(9)–N–C(10)	110.5(12)
C(3)–C(4)–C(5)	126.3(14)	C(8′)–C(8)–N	114.5(18)



(a)

(b)

Fig. 2. Molecular structure of $Mg(C_7H_{11})_2\cdot$TMEDA.
(a) Viewed down along the c axis.
(b) Viewed down along the two-fold axis.

ligand, trimethylamine oxide, was unable to shift the equilibrium and no significant changes in chemical shift were observed over a temperature range from 50 °C to −80 °C. Thus, steric factor rather than the donor property was considered to be dominant to bring about the complete shift of the equilibrium.

X-Ray Structural Studies of Bis(2,4-dimethyl-2,4-pentadienyl)magnesium·TMEDA. The molecular structure of **5** is given in Fig. 2. Bond lengths and bond angles are listed in Table 7. The molecules has a two-fold symmetry. The magnesium atom lies on a crystallographic two-fold axis parallel to the b axis, and is tetrahedrally coordinated by the two carbon atoms from two pentadienyl groups and two nitrogen atoms from the TMEDA. The dihedral angle between planes defined by Mg, C(1), and C(1′) and Mg, N, and N′ is 83.6°.

The remarkable feature of the structure is that the 2,4-dimethylpentadienyl group is terminally σ-bonded (1-η-C_7H_{11} structure) to the magnesium atom by the C(1) atom and has the (Z)-configuration (U-shape) but not the (E)-configuration (W-shape) like that observed for **1**—**4** in solutions by ^{1}H-NMR. The Mg–C(1) distance [2.179(15) Å] is the reasonable value. The Mg–C distances in $C_2H_5MgBr\cdot 2C_4H_{10}O$,[22] $[C_2H_5MgBr\cdot N(C_2H_5)_3]_2$,[23] $[C_2H_5Mg_2Cl_3\cdot (C_4H_8O)_3]_2$,[24] and $[(C_2H_5)_2Mg]_\infty$[25] are 2.15(2) Å, 2.18(2) Å, 2.19(3) Å, and 2.2$_6$ Å, respectively. Expected Mg–C covalent bond length for $C_6H_5MgBr\cdot 2C_4H_{10}O$[26] is 2.17 Å. Two double bonds in the dimethylpentadienyl group is not coplanar, the plane defined by the C(1), C(2), C(3), and C(6) atoms makes an angle of 22.6° with the plane made by C(3), C(4), C(5), and C(7). This is probably due to the steric repulsion between two methyl groups as mentioned before. In the pentadienyl moiety the bond alternation in bond length is observed, C(1)–C(2) = 1.467(20), C(2)–C(3) = 1.402(19), C(3)–C(4) = 1.466(20), and C(4)–C(5) = 1.356(22) Å. The C(2)–C(3) and C(4)–C(5) bond lengths are significantly smaller than the C–C bond (1.43 Å) of η^5-cyclopentadienyl group in $C_5H_5MgBr\cdot(C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$.[27]

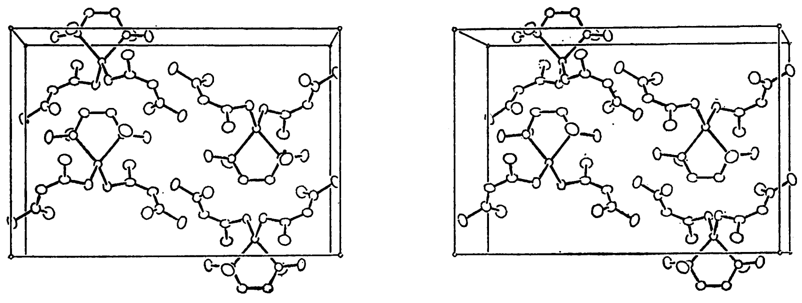


Fig. 3. A stereoscopic drawing of the crystal structure of $Mg(C_7H_{11})_2 \cdot TMEDA$.

The TMEDA coordinates to the magnesium atom by two nitrogen atom [Mg–N=2.202(12) Å]. The N–Mg–N′ angle[84.2(5) Å] largely deviates from tetrahedral angle and is comparable to that of $C_5H_5MgBr \cdot (C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$ (82.5±0.5°) and that of $Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]_2C_{10}H_8$(85.2°).[28] The Mg–N–C(8) angle[104.4(11)°] is also slightly smaller than the tetrahedral angle.

The crystal structure is shown in Fig. 3. No close intermolecular atomic contact less than the van der Waals distance(3.6 Å) was observed.

Regioselective Dienylation of Carbonyl Compounds.
Addition of bis(dienyl)magnesium to carbonyl compounds was examined to check whether the abundancy of the solution species of **1**—**7** reflects the structure of the addition products. The result of the reaction with a simple ketone, acetone, is given in Table 8.

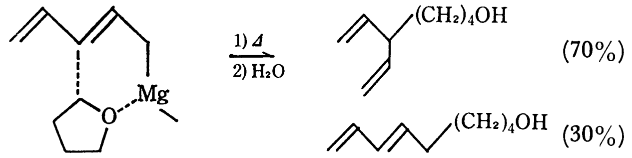
TABLE 8. ADDITION OF KETONES ON THE C_1 AND C_3 CARBON ATOMS OF BIS(DIENYL)MAGNESIUM·TMEDA COMPLEXES[a)]

Complex	Acetone		DIPK	
	C_1/%	C_3/%	C_1/%	C_3/%
1	2	98	100	0
2	2	98	100	0
3	5	95	65 35[b)]	0
4	1	99	95	5
5	5	95	100	0
6	1	99	8	92
7	20	80	25	75

a) Reaction was carried out at 10 °C for 2 h in benzene.
b) 2,5-Dimethyl-3-isopropyl-5,7-octadien-3-ol.

Regioselective addition occurred for **1**—**7**. The regioselectivity also depends on the ligand property. For example, compound **1** coordinated with THF, 1,2-dimethoxyethane, $CH_3O(CH_2CH_2O)_2CH_3$, $CH_3O(CH_2CH_2O)_3CH_3$, and $CH_3O(CH_2CH_2O)_4CH_3$ reacted with acetone on the C_3 carbon atom in 67, 81, 83, 78, and 77% conversion respectively in line with the hydrolysis data. The regioselectivity increased up to 99—100% by using 15-crown-5,18-crown-6, and tetramethylcyclam. The behavior to acetaldehyde was the same with that to acetone. In contrast to above, the reaction of **1**—**5** with a bulky ketone, diisopropyl ketone, gave 1,3-diene derivatives selectively presumably due to the steric repulsion between the isopropyl group and the diene moiety. The configuration of the dienyl group of the products obtained from **1**—**3** was trans. Similar behavior of the bulky ketone was found for the reaction with allylmagnesium compounds and is explained by S_E2' mechanism based on the kinetic studies.[29] Cyclic dienylmagnesium compounds also allow the selective reaction in this case.

Formation of Unsaturated Alcohols by Thermal Cracking of Bis(dienyl)magnesium·Cyclic Ether Complexes.
Thermal cracking of bis(dienyl)magnesium·THF adduct followed by hydrolysis provided a novel route for the synthesis of unsaturated alcohols. Heating of THF complex of **1** in toluene at 120 °C for 3 h and hydrolysis of the reaction mixture gave 6,8-nonadien-1-ol (30%) and 5-vinyl-6-hepten-1-ol (70%) in 40—60% yield.



THF molecule was cleaved. By taking advantage of this reaction, synthesis of a precursor of an insect pheromone for *carpocapsa pomonella*[30] was attempted. Thermal cracking of oxepane complex of **2** gave 7-vinyl-8-decen-1-ol(63%) and its isomer, 8,10-dodecadien-1-ol in 6% yield. Thus, this reaction has an extensive utility in the synthesis of unsaturated alcohols with an elongated carbon chain. The order in reactivity of cyclic ethers followed that described for acid-catalyzed cleavage of cyclic ethers.[31]

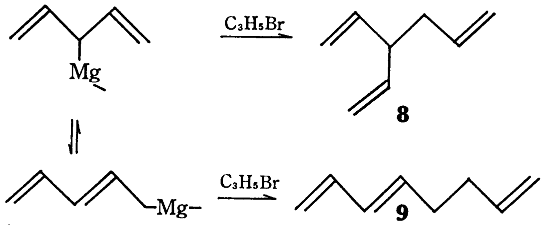
Selective Synthesis of Trienes. Though transition

TABLE 9. COUPLING REACTION OF ALLYL BROMIDE WITH $(C_5H_7)_2$ Mg·2THF CATALYZED BY TRANSITION METAL COMPOUNDS[a)]

Catalyst	Products/%	
	8	**9**
None	10	90
CuCl	1	99
$TiCl_2(\eta^5\text{-}C_5H_5)_2$	92	8
$ZrCl_2(\eta^5\text{-}C_5H_5)_2$	88	12
$NbCl_2(\eta^5\text{-}C_5H_5)_2$	60	40

a) Reaction conditions; 0 °C, 20 h in benzene, catalyst; 2 mol% for the magnesium compound. b) Reaction was carried out at 30 °C for 2 h.

metal-catalyzed triene synthesis are known for several conjugated dienes,[32] novel triene synthesis by the coupling reaction of dienylmagnesium compound with allyl halides is attractive since it has wider applicability. As a typical example, the reaction of pentadienylmagnesium bromide with allyl bromide catalyzed by transition metal compounds was examined (Table 9). The reaction catalyzed by $MX_2(\eta^5\text{-}C_5H_5)_2$(M=Zr,[33] Ti[34]) gave 3-vinyl-1,5-hexadiene **8** regioselectively while with copper(I) chloride catalyst it gave 1,3,7-octatriene **9** selectively. The poor selectivity by $NbCl_2(\eta^5\text{-}C_5H_5)_2$[35] may be due to its poor solubility. This type of reaction will be useful for obtaining desired trienes by an appropriate combination of dienylmegnesium compounds with allyl halides. The selectivity by Ni(II) chloride, Co(II) chloride, or $NiBr_2(PPh_3)_2$ catalyzed reaction was low while these were active for selective synthesis of linear tetraenes from dienyl anions.[7]



Experimental

Anhydrous magnesium bromide and magnesium chloride were prepared by the reaction of magnesium (1.0 mol) with 1,2-dibromoethane (1.0 mol) or 1,2-dichloroethane (1.0 mol) in ether at 0 °C and were stored in argon.[36] Commercial anhydrous magnesium halides were unsuitable for this examination because they include hydrates. All ethers were dried over Na/K alloy and distilled. Crown ethers (Nisso Chem. Corp.) were used without further purification or drying. TMEDA was dried over calcium hydride and distilled. Trimethylamine oxide was prepared according to the method of Meisenheimer[37] and was sublimed (140 °C/10^{-4} mmHg). Tetramethylcyclam was synthesized by the known method.[38] 1-Bromo-2,4-hexadiene was prepared from sorbic acid[39] in the usual manner. Potassium dienides were prepared by the procedure previously reported.[7] Melting points were measured in a sealed tube and were uncorrected. GC analysis and the separation of the reaction products were made with a Hitachi Model 163 gas chromatograph using a capillary column OV-1 or HB 2000 and a Varian-Aerograph Model 700 gas chromatograph using a column packed with Silicone DC-550. NMR spectra were recorded on a Varian XL-100 instrument with a VFT-100-620L Fourier transform accessory. IR spectra were recorded on a Hitachi EPI-2 spectrometer. All the procedures were conducted in an argon atomosphere by using flow system. Elemental analysis was carried out for the key substances with Yanagimoto Model MT-2 CHN-analyzer.

Preparation of Bis(pentadienyl)magnesium·TMEDA Complex 1. A THF solution (40 ml) of anhydrous magnesium bromide (6.4 g, 35 mmol) was added over a 20 min period to potassium pentadienide (6.4 g, 60 mmol) dispersed in THF (100 ml) in a 300 ml Schlenk tube with stirring at 0—5 °C. The magnetic stirring continued for 3 h at 10 °C and the orange color of the solution changed to pale yellow. After the addition of pentane (100 ml), the resulting precipitate of magnesium bromide was separated by centrifugation with the use of a two-necked glass tube fitted with rubber stoppers. The supernatant liquid was evaporated to dryness and a mixture of diethyl ether (100 ml) and pentane (50 ml) was added to the residue for complete separation of the salt. Evaporation of the ether–pentane soluble fraction gave $(C_5H_7)_2Mg\cdot 2THF$ as pale yellow oil. Yield; 70—80% (6.3—7.2 g). Toluene solution of this complex gave pentadiene and THF in a 1: 1 molar ratio upon hydrolysis as evidenced by GC. TMEDA complex was prepared by the addition of TMEDA (7.5 ml, 50 mmol) dissolved in pentane (40 ml) to the THF complex (6.0 g, 20 mmol) in THF (10 ml), stirring the mixture for 2 h at room temperature and then cooling to −20 °C to induce the crystallization. Yield; 85% (5.2 g). Concentration by evaporation and cooling of the supernatant solution further gave TMEDA complex (0.6 g). Recrystallization was made in 5: 1 hexane–THF at −20 °C.

Preparation of Bis(pentadienyl)magnesium·diethyl ether Complex. Diethyl ether (150 ml) was added to the THF-free potassium pentadienide (5.3 g, 50 mmol) in 300 ml Schlenk tube cooled with ice–water (addition of potassium pentadienide to ether should be avoided since the THF-free potassium dienide is very explosive in the air). Anhydrous magnesium bromide (5.2 g, 28 mol) was added at once and magnetic stirring was continued for 10 h at 30 °C until the yellow solid changes to a white powder. The supernatant pale yellow solution was evaporated and the resulting oily ether complex was washed with two portions of pentane (30 ml) at −78 °C. Yield; 60% (4.7 g) based on potassium dienide. This ether complex can not be prepared from the THF complex **1** by ligand exchange reaction.

Preparation of Bis(pentadienyl)magnesium·15-crown-5 ether Complex. A solution of 15-crown-5 (2.2 g, 10 mmol) in benzene (10 ml) was added to bis(pentadienyl)magnesium·ethyl ether complex (3.2 g, 10 mmol) dissolved in benzene (20 ml) at room temperature with magnetic stirring, crystals of the complex being precipitated instantly. The precipitate was washed with two portions of pentane (20 ml) and recrystallized in toluene. Yield; 98%. The relative signal intensity ratio in ^{1}H-NMR spectrum showed the formation of 1: 1 complex.

Preparation of Pentadienylmagnesium Bromide. In the same reaction conditions and the same procedures to the preparation of **1**, Grignard type dienylmagnesium bromide can be prepared by 1: 1 reaction of a dienyl anion and magnesium bromide. For example, the reaction of potassium pentadienide (5.3 g, 50 mmol) with magnesium bromide (10.1 g, 55 mmol) in THF at 30 °C for 3 h gave pentadienylmagnesium bromide coordinated with two moles of THF as an oily substance. Yield; 90% (9.9 g). The reaction of the resulting THF complex (6.6 g, 30 mmol) with TMEDA (6 ml, 40 mmol) gave TMEDA complex having mp 122 °C quantitatively.

Preparation of Bis(dienyl)magnesium·TMEDA Complexes **2**—**7**. In essentially the same way to the preparation of **1**, crystals of TMEDA complexes of **2**—**7** were prepared. Recrystallization of **4** and **7** were done in a mixture of toluene and pentane (1: 10) at 0 °C.

Crystal Data and Structure Determination of Bis(2,4-dimethylpentadienyl)magnesium·TMEDA. $C_{20}H_{38}N_2Mg$, *F.W.* 330.9, orthorhombic, space group Pbcn (No. 60), (20 °C) $a=10.145(2)$, $b=12.486(2)$, $c=17.587(2)$ Å, $V=2227.8(5)$ Å^3, $D_C=0.987$ g cm^{-3} for $Z=4$; (−60 °C) $a=10.105(6)$, $b=12.325(6)$, $c=17.580(9)$ Å, $V=2189.6(21)$ Å^3, $D_C=1.004$ g cm^{-3} for $Z=4$.

As the crystals are unstable in air, a crystal with suitable size was selected and sealed in a thin-walled glass capillary tube. In spite of the repeated recrystallizations and the very careful sealing only a few crystals were found useful for the X-ray analysis. Preliminary X-ray photographic study determined the corresponding space group as Pbcn (systematic absence of reflections, $0kl$: $k=2n+1$, $h0l$: $l=2n+1$, $hk0$: $h+k=2n+1$).

Unit-cell dimensions and reflection intensities were measured on a Rigaku automated, four-circle diffractometer. Zirconium-filtered Mo $K\alpha$ radiation was used. The θ-2θ scan technique was applied. The scan rate was 4° min^{-1} and the scan range for each reflection was $\Delta 2\theta=(2.0+0.70\tan\theta)°$. Background of 5 s were measured before and after each scan. Intensity data were first collected at 20 °C, but the higher angle reflections were too weak to be observed and the structure determined was not sufficiently accurate. Intensity data were therefore collected again at −60 °C, a total of 1185 (714 non-zero) reflections being observed ($2\theta \leqq 42°$). But the number of unobserved reflections was still large. Low temperature was attained by the gas flow method of liquid nitrogen. However, as the crystal was sealed in the glass-capillaly tube, the deposition of the frost on the glass due to the moisture in air was much easier than the crystal without sealing in the glass capillary. The lowest temperature attained without the frost was only −60 °C. The intensity data were corrected for usual Lorentz and polarization effects but not for absorption [$\mu(\text{Mo } K\alpha)=0.88\ \text{cm}^{-1}$].

Since the space group is Pbcn and four molecules are contained per unit-cell, the molecule must lie on a special position, two-fold axis or center of symmetry.

The structure was solved by the heavy atom method, and refined isotropically by the block-diagonal least-squares procedure (*HBLS V*).[40] The room temperature structure was first determined, but the convergence of the refinement was insufficient ($R=0.185$ for 807 non-zero reflections). The structure was, therefore, refined using the intensity data obtained at −60 °C. After the R value decreased to 0.162, the refinement was carried out anisotropically with unit weight, and the final R value was rather high as 0.135 for 714 non-zero reflections. This limits the accuracy of the result. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography, Vo. IV.[41] Calculations were done on an ACOS series 77 system 700 computer at Osaka University.[42] The final atomic positional and thermal parameters are listed in Table 10.[43]

Preparation of Pentadienylaluminium Compounds. Granules of anhydrous aluminium chloride (2.7 g, 20 mmol) was added to the potassium pentadienide (2.1 g, 20 mmol) dissolved in THF (60 ml) at 0 °C with stirring. After refluxing the solution for 30 min, the solution was reduced to *ca.* 30 ml by evaporation and then hexane (50 ml) was added to induce the precipitation of the salt. The supernatant liquid separated by centrifugation was evaporated to dryness and washed with hexane (50 ml) to give potassium tetrakis(pentadienyl) aluminium·THF complex as an oily material. Yield: 92% (7.4 g). ^{1}H-NMR (C_6D_6) $\delta=6.10$, 6.30 (m, 8, CH=), 5.93 (d of t, 4, CH–), 4.90 (d of d, 4, $J=14.0$, *trans* CH_2=), 4.72 (d of d, 4, $J=9.0$, *cis* CH_2=), 3.65 (m, 4, CH_2O of THF), 1.40 (m, 4, CH_2 of THF), 0.16 (d, 8, CH_2).

In the similar manner, the 2:1 reaction of $(CH_3)_2AlCl$ with potassium pentadienide gave potassium dimethyldipentadienylaluminium in 70% yield. No tripentadienylaluminium corresponding to bis(pentadienyl)magnesium was obtained as evidenced by distillation of the whole reaction products in high vacuum. ^{1}H-NMR (C_6D_6) $\delta=6.14$—6.33 (m, 4, CH), 5.60 (d of t, 2, $J=14.0$, CH–CH_2), 4.78, 4.72 (d of d, 8, CH_2=), 3.53 (m, 4, CH_2O of THF), 1.60 (m, 4, CH_2 of THF), 0.90 (d, 4, CH_2), −0.12 (s, 6, CH_3). Hydrolysis of $K[(C_5H_7)_4Al]$

Table 10. Atomic positional and thermal parameters of $Mg(C_7H_{11})_2$·TMEDA
Estimated standard deviations in parentheses.

Atom	X	Y	Z
Mg	0. (0)	0.0790(5)	0.2500(0)
N(1)	0.0508(11)	−0.0535(8)	0.3287(6)
C(1)	0.1745(14)	0.1764(11)	0.2249(7)
C(2)	0.2466(14)	0.1554(10)	0.1541(8)
C(3)	0.2275(14)	0.1999(11)	0.0815(8)
C(4)	0.1295(15)	0.2817(12)	0.0595(8)
C(5)	0.0135(15)	0.3025(14)	0.0955(9)
C(6)	0.3593(15)	0.0707(12)	0.1588(10)
C(7)	0.1657(18)	0.3452(14)	−0.0125(9)
C(8)	−0.004(3)	−0.1527(11)	0.2919(8)
C(9)	0.1948(14)	−0.0640(14)	0.3405(10)
C(10)	−0.0187(19)	−0.0422(13)	0.4029(8)

Atom	*B*(11)	*B*(22)	*B*(33)	*B*(12)	*B*(13)	*B*(23)
Mg	0.0116(7)	0.0061(5)	0.0029(3)	0. (0)	0.0004(8)	0. (0)
N(1)	0.0146(15)	0.0070(9)	0.0032(4)	0.0002(19)	−0.0003(14)	−0.0007(11)
C(1)	0.0154(19)	0.0103(13)	0.0033(6)	−0.011(3)	0.0034(18)	−0.0012(15)
C(2)	0.0111(16)	0.0066(11)	0.0061(7)	−0.005(3)	0.001(2)	−0.0001(15)
C(3)	0.0113(18)	0.0075(11)	0.0056(7)	−0.003(3)	−0.0012(19)	0.0007(16)
C(4)	0.017(3)	0.0101(14)	0.0040(7)	−0.009(3)	−0.006(2)	0.0005(16)
C(5)	0.0113(19)	0.0157(17)	0.0064(8)	0.001(4)	0.003(3)	0.002(3)
C(6)	0.014(2)	0.0107(15)	0.0075(9)	0.012(3)	−0.001(3)	0.002(3)
C(7)	0.024(3)	0.0151(19)	0.0040(7)	0.002(4)	−0.000(3)	0.0048(19)
C(8)	0.035(4)	0.0075(12)	0.0048(7)	0.000(4)	−0.012(4)	0.0001(15)
C(9)	0.0115(19)	0.0144(17)	0.0083(9)	0.002(4)	−0.008(3)	0.005(3)
C(10)	0.027(3)	0.0142(17)	0.0033(6)	0.010(4)	0.008(3)	0.0021(17)

and $K[(C_5H_7)_2(CH_3)_2Al]$ in toluene produced 1,4-pentadiene exclusively (99%) in 98% GC yield. Reaction of acetaldehyde and acetone, followed by hydrolysis gave 1,4-diene derivatives (purity, 99%) in 90% yield in both cases (spectral data of the products are given later in this section).

Dienylation of Carbonyl Compounds with 1—7. To the benzene solution (60 ml) of bis(dienyl)magnesium **1**—**7** (20 mmol) was added acetone (2.9 ml, 40 mmol) dropwise at 5 °C. The reaction mixture was stirred for 2 h at 30 °C and hydrolyzed with 2 mol dm^{-3} HCl at 5 °C. After filtration, benzene fraction was distilled under reduced pressure. The reaction of bis(dienyl)magnesium with acetaldehyde was carried out in the same manner but with diisopropyl ketone at 50 °C for 3 h.

Dienylation of Acetone. *2-Methyl-3-vinyl-4-penten-2-ol from 1*: IR (neat) 3440 (OH), 1638 (C=C), 1015, 915 cm^{-1} ($CH=CH_2$); ^{1}H-NMR ($CDCl_3$) $\delta=5.94$ (d of d of d, 2, CH=), 5.15 (d of d, 2, $J=16.5$, *trans* $CH_2=$), 5.02 (d of d, 2, $J=10.2$, *cis* $CH_2=$), 2.75 (t, 1, $J=8.0$, CH), 1.98 (s, 1, OH), 1.18 (s, 6, CH_3); Found: C, 76.07; H, 11.4%; M$^+-1$, 125. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.1%; M, 126.

trans-*2-Methyl-3-vinyl-4-hexen-2-ol from 2*: IR (neat) 3450, 1635, 990, 912 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=5.71$ (d of d of d, 1, CH), 5.53 (d of d, 1, $J=13.7$ *trans* $CH=CHCH_3$), 5.53 (d of q, 1, CH), 5.12 (d of d, 1, $J=10.3$ *cis* CH_2), 5.07 (d of d, 1, $J=16.5$ *trans* CH_2), 3.14 (d of d, $J=8.1$, CH), 2.09 (s, 1, OH), 1.75 (d, 3, CH_3), 1.15 (s, 6, CH_3).

cis-*2-Methyl-3-vinyl-4-hexen-2-ol from 2*: IR (neat) 3450, 1635, 990, 719 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=5.71$ (d of d of d, 1, CH), 5.53 (d of d, 1, $J=9.2$, *cis* $CH=CHCH_3$), 5.53 (d of q, 1, CH=), 5.08, 5.16 (m, 2, CH_2), 2.72 (d of d, $J=8.0$, CH), 2.09 (s, 1, OH), 1.87 (d, 3, CH_3), 1.15 (s, 6, CH_3).

2,4-Dimethyl-3-vinyl-4-penten-2-ol from 3: IR (neat) 3490, 1635, 1000, 915 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=6.10$ (d of d of d, 1, CH), 5.15 (d of d, 1, $J=10.4$, for *cis* $CH_2=$), 5.02 (d, 2, $J=2.2$, CH_2), 5.00 (d of d, 1, CH_2), 2.75 (d, 1, CH), 1.87 (s, 3, CH_3), 1.73 (s, 1, OH), 1.25 (s, 6, CH_3).

2,3-Dimethyl-3-vinyl-4-penten-2-ol from 4: ^{1}H-NMR ($CDCl_3$) $\delta=5.82$ (d of d, 2, CH), 5.14 (d of d, 2, $J=10.4$ for *cis* CH_2, $J=2.8$ for gem H), 4.99 (d of d, 2, $J=16.5$, *trans* CH_2), 1.73 (s, 1, OH), 1.25 (s, 3, CH_3), 1.24 (s, 6, CH_3); MS, Found: M$^+-1$, 139.

2,4-Dimethyl-3-isopropenyl-4-penten-2-ol from 5: IR (neat) 3500, 1643, 1020, 890 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=4.91$ (d, 4, $J=2.9$, CH_2), 2.54 (s, 1, CH), 2.24 (s, 1, OH), 1.72 (s, 6, CH_3), 1.16 (s, 6, CH_3); Found: C, 77.9; H, 11.5%; M$^+-1$, 153. Calcd for $C_{10}H_{18}O$; C, 77.86; H, 11.76%; M, 154.

2-(2,6-Cycloheptadienyl)-2-propanol from 6: ^{1}H-NMR ($CDCl_3$) $\delta=5.81$ (d of t, 2, $J=12.2$, $CH_2CH=$), 5.68 (d of d, 2, CH), 3.20 (d of d, 1, CH), 2.27 (m, 4, CH_2), 1.52 (s, 1, OH), 1.27 (s, 6, CH_3).

2-(2,7-Cyclooctadienyl)-2-propanol from 7: IR (neat) 3510, 1638, 1075 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=5.90$ (d of d, 2, $J=12.2$, CH), 5.49 (d of t, 2, CH), 3.30 (d of d, 1, $J=6.6$, CH), 2.18 (m, 4, CH_2), 2.00 (s, 1, OH), 1.35 (m, 2, CH_2), 1.16 (s, 6, CH_3); Found: C, 79.46; H, 10.92%; M$^+-1$, 165. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91%; M, 166.

Dienylation of Acetaldehyde. *3-Vinyl-4-penten-2-ol from 1*: IR (neat) 3380, 1637, 999, 915 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=5.89$ (d of d of d, 2, CH), 5.15 (d of d, 2, $J=10.0$, CH_2), 5.03 (d of d, 2, $J=16.2$, CH_2), 3.76 (d of d, 1, $J=6.0$, $C\underline{H}$-CH_3), 2.82 (bt, 1, CH), 1.98 (s, 1, OH), 1.20 (d, 3, $J=6.2$, CH_3); MS, Found: M$^+-1$, 111.

1-(2,7-Cyclooctadienyl)ethanol from 7: IR (neat) 3420, 1635, 1070 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=5.65$ (d of t, 2, CH), 5.62 (d of d, 2, $J=11.8$, CH), 3.82 (d of q, 1, CH), 3.25 (bt, $J=6.5$, CH), 2.30 (m, 4, CH_2), 1.98 (s, 1, OH), 1.47 (m, 2, CH_2), 1.20 (d, 3, $J=6.8$, CH_3); MS, Found: M$^+-1$, 151.

Dienylation of Diisopropyl Ketone. *2-Methyl-3-isopropyl-5,7-octadien-3-ol from 1*: IR (neat) 3500, 1640, 1605, 988, 830, 784 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=6.35$ (d of d of d, 1, CH), 5.95 (d of t, 1, $J=15.5$, CH), 5.92 (d of d, 1, $J=9.5$, CH), 5.12 (d of d, 1, $J=16.5$, *trans* $CH_2=CH$), 5.02 (d of d, 1, $J=10.2$, *cis* $CH_2=CH$), 2.38 (d, 2, $J=7.0$, CH_2), 1.88 [m, 2, $C\underline{H}(CH_3)_2$], 1.30 (s, 1, OH), 0.98 (d, 12, $J=7.3$, CH_3); Found: C, 78.85; H, 12.25%; M$^+-1$, 181. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%; M, 182.

2-Methyl-3-isopropyl-5,7-nonadien-3-ol from 2: IR (neat) 3500, 988, 950 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=6.12$ (d of d, 1, $J=15.5$, CH), 5.90 (d of d, 1, $J=15.6$, $C\underline{H}=CHCH_2$), 5.52 (d of q, 1, CH), 5.48 (d of t, 1, CH), 2.30 (d, 2, $J=7.5$, CH_2), 1.92 [m, 2, $C\underline{H}(CH_3)_2$], 1.73 (d, 3, $J=6.5$, CH_3), 1.40 (s, 1, OH), 0.95 (d, 12, $J=7.5$, CH_3).

2,5-Dimethyl-3-isopropyl-5,7-octadien-3-ol from 3: IR (neat) 3510, 1644, 1610, 995, 898 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=6.45$ (d of d of d, 1, CH), 6.01 (d, 1, $J=10.2$, CH), 5.12 (d of d, 1, $J=16.7$, $CH_2=$), 5.00 (d of d, 1, $J=10.2$, $CH_2=CH$), 2.28 (s, 2, CH_2), 1.89 (m, 2, $C\underline{H}$-CH_3), 1.59 (s, 1, OH), 0.98 (d, 12, CH_3).

2,7-Dimethyl-3-isopropyl-5,7-octadien-3-ol from3 : IR (neat) 3510, 1640, 905 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=6.20$ (d, 1, $J=15.2$, CH), 5.74 (d of t, 1, CH), 4.88 (d, 2, $CH_2=$), 2.34 (d, 2, $J=8.4$, CH_2), 1.89 (m, 2, $C\underline{H}$-CH_3), 1.59 (s, 1, OH), 0.98 (d of d, 12, $J=7.0$ and 2.8, CH_3).

2,6-Dimethyl-3-isopropyl-5,7-octadien-3-ol from 4: IR (neat) 3500, 1640, 1608, 990, 894 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=6.43$ (d of d, 1, CH), 5.64 (t, 1, CH), 5.13 (d of d, 1, $J=17.0$, $CH_2=CH$), 4.99 (d of d, 1, $J=10.8$, $CH_2=CH$), 2.42 (d, 2, $J=7.8$, CH_2), 1.89 (m, 2, $C\underline{H}CH_3$), 1.78 (s, 3, CH_3), 1.28 (s, 1, OH), 0.97 (d, 12, $J=7.5$ and 2.8, CH_3); MS, Found: M$^+-1$, 195.

2,5,7-Trimethyl-3-isopropyl-5,7-octadien-3-ol from 5: IR (neat) 3570, 1635, 894 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=5.81$ (s, 1, CH), 5.01, 4.85 (d, 2, $J=2.5$, $CH_2=$), 2.33 (s, 2, CH_2), 1.98, 1.85 (two s, 6, CH_3), 1.93 (m, 2, $C\underline{H}$-CH_3), 1.35 (s, 1, OH), 0.98 (d, 12, CH_3); Found: C, 79.95; H, 12.25%; M$^+-1$, 209. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46%; M, 210.

3-(2,6-Cycloheptadienyl)-2,4-dimethyl-3-pentanol from 6: IR (neat) 3510, 1665, 1641 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=6.10$ (d of d, 2, $J=11.5$, CH), 5.56 (d of t, 2, CH), 3.20 (bt, 1, CH), 2.30 (m, 4, CH_2), 1.90 (m, 2, CH), 1.60 (s, 1, OH), 1.00 (d, 12, CH_3); Found: C, 80.71; H, 11.60%; M$^+-1$, 207. Calcd for $C_{14}H_{24}O$: C, 80.70; H, 11.62%; M, 208.

3-(2,7-Cyclooctadienyl)-2,4-dimethyl-3-pentanol from 7: IR (neat) 3370, 1658, 1080 cm^{-1}; PMR ($CDCl_3$) $\delta=5.3$—5.8 (m, 4, CH), 3.58 (t, 1, CH), 2.38 (m, 4, CH_2), 2.30 (s, 1, OH), 1.90 (m, 2, CH), 1.40 (m, 2, CH_2), 1.00 (d, 12, CH_3).

Thermal Cracking of Pentadienylmagnesium·THF Complexes. Bis(pentadienyl)magnesium·THF complex (4.0 g) dissolved in toluene (50 ml) which contains 5 mol equivalent of THF was heated to 120 °C for 3 h in a sealed tube, gray precipitates of degradation products being formed. Resulting mixture was hydrolyzed with 2 mol dm^{-3} HCl and the toluene soluble fraction was distilled. The ratio of 6,8-nonadien-1-ol to 5-vinyl-6-hepten-1-ol was 3 : 7. Yield, 40%. In the same way, thermal cracking of pentadienylmagnesium bromide·THF complex was carried out at 130 °C for 4 h, the same products being obtained in a 7 : 3 ratio in 60% yield.

6,8-Nonadien-1-ol: IR (neat) 3450, 1642, 1605, 987, 905 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=6.5$—6.6 (m, 2, CH), 5.62 (d of t, 1, $J=15.5$, CH), 5.00, 5.12 (m, 2, $CH_2=$), 3.68 (t, 2, CH_2), 2.16 (d of t, 2, CH_2), 2.20 (s, 1, OH), 1.45 (m, 6, CH_2); M$^+$, 140. Calcd for $C_9H_{16}O$: M, 140.

5-Vinyl-6-hepten-1-ol: IR (neat) 3500, 1635, 995, 912 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=5.78$ (m, 2, CH), 5.00 (d of d, 2, $J=10.2$, *cis* CH_2=CH), 4.95 (d of d, 2, $J=17.2$, *trans* CH_2=CH), 3.62 (bt, 2, $J=6.9$, CH_2), 2.69 (m, 1, $J=9.2$, CH), 2.35 (s, 1, OH), 1.44 (m, 6, CH_2); Found: C, 77.85; H, 10.91%; M^+-1, 139. Calcd for $C_9H_{15}O$: C, 77.66; H, 10.85%; M, 140.

Thermal Cracking of Bis(hexadienyl)magnesium·oxepane Compound. Oxepane complex of bis(hexadienyl)magnesium was prepared by 2: 1 reaction of THF free potassium hexadienide (2.4 g, 20 mmol) with magnesium bromide (1.8 g, 10 mmol) in oxepane (30 ml). After evaporation of oxepane in vacuum, oxepane complex was extracted from the residue with diethyl ether (100 ml). Bis(hexadienyl)magnesium·oxepane complex was obtained as an oily substance by evaporation of diethyl ether. Thermal craking was carried out in toluene at 120 °C for 5 h after the addition of 10 mol equivalent of oxepane. Yield, 40%.

8,10-Dodecadien-1-ol: IR (neat) 3510, 1640, 1602, 987, 910 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=6.4$—6.5 (m, 2, CH), 5.50 (d of t, 1, $J=16.0$, CH), 5.40 (d of q, 1, $J=15.5$, CH), 3.68 (bt, 2, $J=6.9$, CH_2), 2.10 (d of t, 2, CH_2), 2.20 (s, 1, OH), 1.68 (d, 3, CH_3), 1.49 (m, 10, CH_2), M^+-1, 181. Calcd for $C_{12}H_{22}O$: M, 182.

7-Vinyl-8-decen-1-ol: IR (neat) 3505, 1636, 995, 911 cm^{-1}; ^{1}H-MNR ($CDCl_3$) $\delta=5.81$ (m, 1, CH), 5.62 (d of d, 1, $J=15.2$, CH), 5.50 (d of q, 1, CH), 5.00 (m, 2, CH_2), 3.65 (bt, 2, CH_2), 2.75 (m, 1, CH), 1.65 (d, 2, CH_3), 1.49—1.52 (m, 10, CH_2); Found: C, 79.53; H, 12.05%; M^+-1, 181. Calcd for $C_{12}H_{22}O$: C, 79.04; H, 12.18%; M, 182.

Preparation of Trienes: Catalysts, MCl_2 (η^5-C_5H_5)$_2$ (M=Ti, Zr, Nb, 2 mol%) or CuCl (0.12 g, 5 mol% to magnesium compounds), was added to the diethyl ether solution (100 ml) of pentadienylmagnesium bromide·2THF (7.9 g, 25 mmol) cooled to 0 °C and then 3-bromopropene (3.5 ml, 40 mmol) was added dropwise with vigorous stirring. The mixture was stirred for 20 h at 0 °C, then warmed to 30 °C for 1 h and quenched with 2 mol dm^{-3} HCl. Diethyl ether fraction was distilled. Typical yield: 90% based on 3-bromopropene.

3-Vinyl-1,5-hexadiene: IR (neat) 1650, 1635 cm^{-1}; ^{1}H-NMR ($CDCl_3$) $\delta=5.84$ (d of d of d, 2, CH), 5.80 (d of d of d, 1, CH), 5.02 (d of d, 2, $J=10.2$, CH_2=CH), 4.98 (d of d, 2, $J=16.0$, CH_2=CH), 5.01, 4.98 (m, 2, CH_2=), 2.83 (m, 1, $J=6.2$, $C\underline{H}CH_2$), 2.21 (d of d, 2, $J=6.4$, $C\underline{H_2}$CH=); M^+, 108. Calcd for C_8H_{12}: M, 108.

1,3,7-Octatriene: IR (neat) 1645, 1604, 1004, 900 cm^{-1}; PMR ($CDCl_3$) $\delta=6.4$—6.5 (m, 2, CH), 5.80 (m, 1, CH), 5.69 (d of t, 1, $J=16.0$, CH), 5.10, 4.98 (d of d, 2, CH_2), 5.05, 4.98 (d of d, 2, CH_2), 2.19 (m, 4, CH_2); MS, Found: M^+, 108.

References

1) a) L. Miginiac, *Tetrahedron Lett.*, **1976**, 3083; b) F. Barbot and Ph. Miginiac, *J. Organomet. Chem.*, **145**, 269 (1978); c) F. Derguini-Boumechal, R. Lorne, and G. Linstrumelle, *Tetrahedron Lett.*, **1977**, 1181; d) H. Lehmkuhl and D. Reiner, *J. Organomet. Chem.*, **57**, 29 (1973); e) H. Lehmkuhl, D. Reiner, D. Henneberg, and G. Schrith, *J. Organomet. Chem.*, **57**, 49 (1973); f) H. Lehmkuhl, D. Reiner, J. Brandt, and G. S. Schroth, *J. Organomet. Chem.*, **57**, 39 (1903).

2) a) M. Tomoi and H. Kakiuchi, *Polym. J.*, **5**, 195 (1973); b) E. W. Duck, D. Grant, A. V. Butcher, and D. G. Timms, *Eur. Polym. J.*, **10**, 77 (1974); c) B. Dobbs, R. Jackson, J. N. Gaitskell, R. F. Gray, G. Lynch, D. T. Thompson, and R. Whyman, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1429 (1976).

3) a) T. Cohen and I. Cristea, *J. Am. Chem. Soc.*, **98**, 748 (1976); b) L. Farady, L. Bencze, and L. Marko, *J. Organomet. Chem.*, **10**, 505 (1967); c) S. Akutagawa and S. Otsuka, *J. Am. Chem. Soc.*, **97**, 6870 (1975).

4) a) C. W. Spangler, *Tetrahedron*, **32**, 2681 (1976); b) F. Gerard and Ph. Miginiac, *J. Organomet. Chem.*, **155**, 271 (1978); c) F. Gerard and Ph. Miginiac, *C. R. Acad. Sci., Ser. B*, **273**, 674 (1971).

5) R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.*, **88**, 943 (1966).

6) R. J. Bushby and A. S. Patterson, *J. Organomet. Chem.*, **132**, 163 (1977).

7) a) H. Yasuda, Y. Ohnuma, and A. Nakamura, *Bull. Chem. Soc. Jpn.*, **52**, 2036 (1979); b) H. Yasuda, T. Narita, and H. Tani, *Tetrahedron Lett.*, **1973**, 2443.

8) D. A. Hutchison, K. R. Beck, R. A. Benkeser, and J. B. Grutzner, *J. Am. Chem. Soc.*, **95**, 7075 (1973).

9) a) K. 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**, 586 (1978).

10) G. Weber, W. Saenger, F. Vogtle, and H. Sieger, *Angew. Chem., Int. Ed.*, **18**, 226 (1979).

11) a) Y. Nakano, K. Natsukawa, H. Yasuda, and H. Tani, *Tetrahedron Lett.*, **1972**, 2833; b) K. Fujita, Ph. D. Thesis, Osaka University, 1974.

12) a) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, **1967**, 205; b) R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson. G. D. Forsythe, D. A. Mc Combs, and A. S. Roth, *J. Am. Chem. Soc.*, **95**, 926 (1973); c) G. J. Heiszwolf, J. A. A. Van Drunen, and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **88**, 1377 (1969).

13) H. Kloosterziel and E. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **88**, 1373 (1969).

14) E. A. Baude, *Chem. Ind. (London)*, **1974**, 1557.

15) N. L. Allinger and J. T. Sprauge, *Tetrahedron*, **29**, 3811 (1973).

16) F. Zuccarello, G. Buenmi, and G. Favini, *J. Mol. Struct.*, **18**, 295 (1973).

17) N. L. Allinger, J.F. Viskocil, Jr., U. Burkert, and Y. Yuh, *Tetrahedron*, **32**, 33 (1976).

18) F. A. L. Anet and I. Yavari, *Tetrahedron Lett.*, **1975**, 1567.

19) W. T. Ford and M. Newcombs, *J. Am. Chem. Soc.*, **96**, 309 (1976).

20) H. Yasuda and H. Tani, *Tetrahedron Lett.*, **1975**, 11.

21) a) C. L. Liotta and H. D. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974); b) G. W. Gokel, *Synthesis*, **1976**, 168.

22) L. J. Guggenberger and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 5344 (1964).

23) J. Toney and G. Stucky, *Chem. Commun.*, **1967**, 1168.

24) J. Toney and G. Stucky, *J. Organomet. Chem.*, **28**, 5 (1971).

25) E. Weiss, *J. Organomet. Chem.*, **4**, 101 (1965).

26) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 5825 (1964).

27) C. Johnson, J. Toney, and G. D. Stucky, *J. Organomet. Chem.*, **40**, C11 (1972).

28) J. D. Brooks, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7346 (1972).

29) T. Holm, *Acta Chem. Scand., ser B*, **30**, 985 (1976).

30) a) W. Roelofs, A. Comeaw, A. Hill, and G. Milicevic, *Science*, **174**, 297 (1971); b) C. Descoins and C. A. Henrick, *Tetrahedron Lett.*, **1972**, 2999.

31) M. Sumitani, K. Kanemitsuya, H. Yasuda, and H. Tani, *Bull. Chem. Soc. Jpn.*, **51**, 1511 (1978).

32) a) H. J. Kablitz and G. Wilke, *J. Organomet. Chem.*, **51**, 241 (1973); b) S. Takahashi, T. Shibano, and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **41**, 454 (1968); c) K. Takahashi, G. Hata, and A. Miyake, *Bull. Chem. Soc. Jpn.*, **46**, 600 (1973).

33) A. F. Reid, P. C. Wailes, *Aust. J. Chem.*, **19**, 309 (1966).

34) J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Am. Chem. Soc.*, **98**, 6529 (1976).

35) F. W. Siegert and H. J. L. Meijer, *J. Organomet. Chem.*, **23**, 177 (1970).

36) J. Meisenheimer, *Chem. Ber.*, **61**, 720 (1928).

37) J. Meisenheimer, *Justus Liebigs Ann. Chem.*, **397**, 286 (1913).

38) F. Wagner, M. T. Mocella, M. J. Daniello, Jr., A. H. J. Wang, and E. K. Barefield, *J. Am. Chem. Soc.*, **96**, 2625 (1974).

39) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

40) T. Ashida, The University Crystallographic Computing System-Osaka, The Computation Center, Osaka University, 1973, pp. 55-61.

42) "International Table for X-Ray Crystallography," Kynoch Press, Birmingham, (1974), Vol. IV, pp. 71—98.

43) A list of observed and calculated structure factors are kept as Document No. 8016 at the Chemical Society of Japan.