May, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***54***, *1481—1491 (1981)* 1481

Chemistry of Dienyl Anions. IV. Geometry of Pentadienyl Anions in Solution and in the Solid State Determined by Regioselective Trimethylsilylation and NMR

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(Received December 4, 1980)

The configurational analysis of a series of alkyl substituted pentadienyl anions in THF was examined by trimethylsilylation and from the variable temperature ^{1}H- and ^{13}C-NMR spectra. Potassium pentadienide, -2-methylpentadienide or -2,4-dimethylpentadienide produced preferentially (*Z*)-2,4-pentadienyltrimethylsilane or its methyl substituted analogues to indicate that these compounds have the "U"-shaped structure in solution. By contrast, trimethylsilylation of potassium pentadienide and -2-methylpentadienide in the crystalline state produced the (*E*)- and the (*E*),(*Z*)-isomers, respectively, suggesting that the geometry is drastically changed to the "W"- or "S"-shaped by the medium effect. The W-shaped structure of potassium 3-methylpentadienide in THF and in the solid state is exceptional. Geometry of trapped products of potassium cycloheptadienide and -cyclooctadienide is also (*Z*) but the silylation occurred on the central carbon in contrast to the terminal silylation seen for the open-chain pentadienides. Geometry of these dienyl anions determined by NMR below −30 °C was consistent with the result obtained from trimethylsilylation. Superficial conflict between MINDO/3 prediction and the experimental evidence was reasonably reconciled by considering contact ion pairs for potassium pentadienide in THF and more strongly-solvated ion pairs for the lithium analogues.

A study of structures and configurational stabilities of a series of pentadienyl anions is of particular importance since such carbanions are crucial intermediates for base-catalyzed equilibration[1] of diolefins and are valuable organometallic reagents for syntheses.[2] Several theoretical studies on the geometry of open-chain pentadienyl anions are now available. Extended Hückel calculations by Hoffmann and Olofson[3] and CNDO/2 by Bushby *et al.*[4] predict that the horseshoe-like "U"-shaped anion should be preferred over the zigzag-like "W"- or sickle-like "S"-shaped anions. However, Dewar *et al.*[5] recently reported on the basis of MINDO/3 and MNDO calculations that the W-shaped structure is more stable than the U- or S-shaped structure by 2.5—15.5 kJ/mol for pentadienyl, 3-methyl- or 1,3-dimethylhexadienyl anions. Dewar's prediction is in accord with the experimental evidence obtained by NMR which indicates that lithium pentadienide,[6] hexadienide[7] and 2-methylpentadienide in THF, and potassium pentadienide[8] and hexadienide[9] in liquid ammonia exist preferentially as W-shaped anions. However, Schlosser *et al.* recently reported evidence for the U-shaped structure for the first time in the cases of potassium 2-methyl- and 2,4-dimethylpentadienide in THF based on the geometry of 2,4-pentadien-1-ol chemically derived from the anions.[10] Such predominance of the U-shaped structure has also been confirmed by us independently for the parent potassium pentadienide in THF from the hydrolysis data.[11]

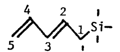
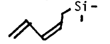
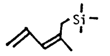
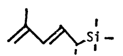
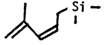
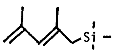
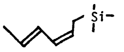
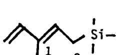
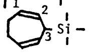
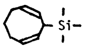
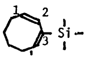
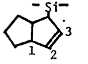
This paper is concerned with 1) the regioselective trimethylsilylation of a series of potassium pentadienide in THF to determine the geometry of the pentadienyl moiety to confirm Dewar's MO prediction and the geometry suggested by Schlosser *et al.*, 2) the direct measurement of the geometry in solution by variable temperature ^{1}H- and ^{13}C-NMR, and 3) the medium (solution *vs.* the solid state) and counter-cation dependence of the geometry of a series of pentadienyl anions. All the experiments were conducted with use of isolated crystalline pentadienyl anions.

Results and Discussion

Chemical Trapping in Solution and in the Solid State. Trimethylsilylation of pentadienyl anions with an equimolar amount of chlorotrimethylsilane can be accomplished with extreme regioselectivity as has been shown in the trimethylsilylation of some nucleophiles.[12] Potassium pentadienide **1**, rubidium pentadienide **2**, and caesium pentadienide **3** in THF at 20 °C gave (*Z*)-2,4-pentadienyltrimethylsilane in 88, 90, and 92% regioselectivity in 95—98% yield and at −40 °C in 96—98% regioselectivity as evidenced by high resolution GC, ^{1}H-NMR (Table 1), IR, MS, and the analytical data (Table 5 in experimental section). Such high regioselectivity has also been found in the protolysis of **1** at 5 °C giving 92—95% of (*Z*)-1,3-pentadiene.[11] No product derived from the electrophilic attack on the central atom is formed in either case. In contrast, lithium pentadienide **4** in THF gave the (*E*)-isomer exclusively (98% yield) at −40 °C. The *Z*/*E* ratio for **1**—**3** (98:2) was determined with a high resolution gas chromatograph equipped with a 45 m capillary column. The resulting products are thermally stable and no isomerization of (*Z*)- to (*E*)-2,4-pentadienyltrimethylsilane or of the (*E*)- to the (*Z*)-isomer occurred by heating to 80 °C for 1 h in THF. The thermal stability permits the isolation of the respective pure isomers (Fig. 1) by distillation or with preparative GC. Sodium pentadienide gave a 7:3 mixture of (*Z*)- and (*E*)-isomers at 30 °C and a 6:4 mixture at −20 °C. Thus, the geometry of trapped products was successfully controlled by changing the counter cation.

If above anions are present as a single torsional isomer and trimethylsilylation occurs equally at both termini (C_1 and C_5), it would yield just one pair of products as shown in Schemes 1 and 2. Based on this postulate, the above results are readily explained

TABLE 1. ^{1}H-NMR CHEMICAL SHIFTS(δ-VALUES) AND COUPLING CONSTANTS(Hz) FOR PENTADIENYLTRIMETHYLSILANES IN $CDCl_3$ AT 30 °C[a)]

Entry	Anion	Products	C_1-H(J_{12})	C_2-H(J_{23})	C_3-H(J_{34})	C_4-H	C_5-H(J_{45})	
Si-1	**1**		1.48 (d, 7.8)	5.63 (d of t, 15.2)	5.73 (d of d, 10.0)	6.25 (d of d of d)	4.93(trans, 16.2) 4.79(cis, 10.1)	−0.09 (CH_3-Si)
Si-2	**1**		1.61 (d, 8.6)	5.47 (d of d, 10.4)	5.91 (d of d, 10.3)	6.54 (d of d of d)	5.08(trans, 16.2) 4.95(cis, 10.4)	−0.04 (CH_3-Si)
Si-3	**5**		1.67(S)	—	5.75 (d, 10.8)	6.42 (d of d of d)	4.95(trans, 16.5) 4.84(cis, 10.4)	0.00(CH_3-Si) 1.74(CH_3)
Si-4	**5**		1.51 (d, 7.6)	5.61 (d of t, 15.0)	5.98 (d)	—	4.87(gem, 1.8) 4.80	−0.03(CH_3-Si) 1.80(CH_3)
Si-5	**5**		1.71 (d, 8.8)	5.40 (d of t, 11.3)	5.74 (d)	—	4.87 4.84	−0.01(CH_3-Si) 1.86(CH_3)
Si-6	**6**		1.79(S)	—	5.50(S)	—	4.80 4.70	1.71(CH_3) 1.79(CH_3)
Si-7	**7**		1.57 (d, 8.8)	5.30 (d of t, 9.8)	5.82 (d of d, 10.2)	6.17 (d of d)	5.59 (d of q, 14.5)	1.72(CH_3, 7.0) −0.05(CH_3-Si)
Si-8	**8**		1.56 (d, 8.6)	5.53 (t, 8.6)		6.34 (d of d)	4.96(trans, 16.9) 4.79(cis, 10.7)	−0.02(CH_3-Si) 1.66(CH_3)
Si-9	**9**		5.66 (d of t, 11.1)	5.45 (d of d, 5.8)	2.50 (t)	5.45 (d of d)	5.67 (d of t, 11.7)	0.03(CH_3-Si) 2.22(J_{18}=3.8, CH_2)
Si-10	**10**		5.19 (d of t, 11.4)	5.67 (d of d, 4.1)	2.28 (d of d)	5.67 (d of d, 11.4)	5.19 (d of t)	0.00(CH_2-Si) 1.21(J_{18}=6.5, CH_2) 2.37(J_{78}=8.1, CH_2)
			5.48 (d of t, 10.8)	5.77(d)	—	5.05 (d, 5.0)	2.10(m)	1.49(CH_2) 0.06(CH_3-Si)
			2.08(m)	6.14 (d, 7.0)	6.00 (d, 7.0)	2.15(m)	2.08(m)	1.44(CH_2) 0.18(CH_3-Si)

a) $CHCl_3$ was used as an internal standard(assuming to be 7.20 ppm downfield from TMS).

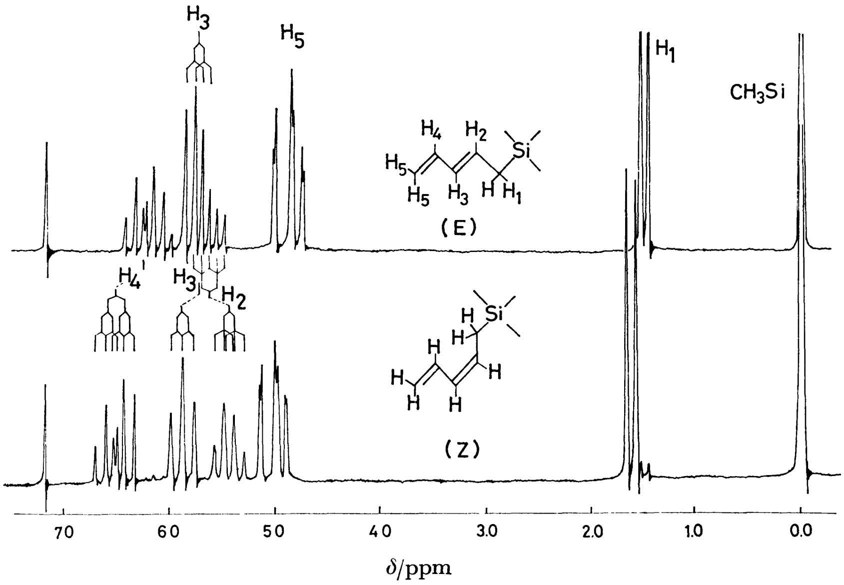
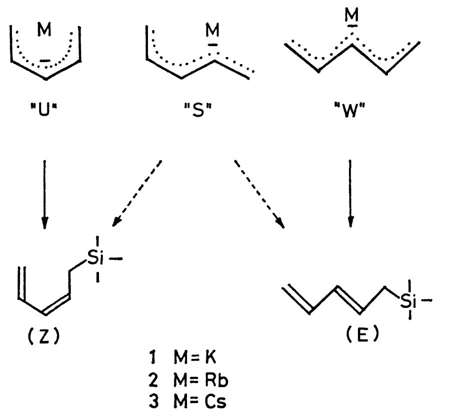
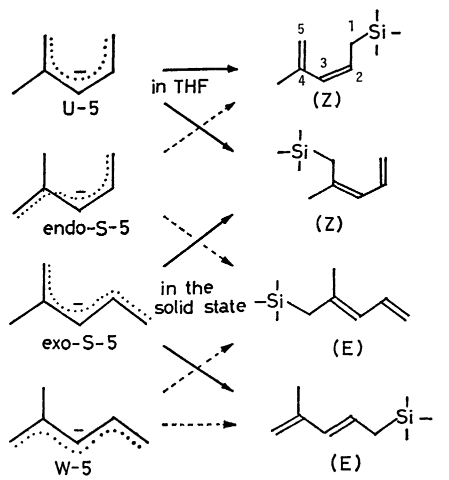


Fig. 1. ^{1}H-NMR spectra (100 MHz, in $CDCl_3$) of (Z)- and (E)-2,4-pentadienyltrimethylsilane prepared from **1** in THF and in the solid state.

by regarding the U-shaped structure for **1**—**3** in solution and the W-shaped structure for **4**. The S-shaped anion should produce a Z/E mixture. To rationalize this assumption, the chemical trapping of an unsymmetrical pentadienyl anion, potassium 2-methylpentadienide **5**, was examined in THF at −20 °C using pure single crystals of **5**. Indeed, a 11:9 mixture of (Z)-4-methyl-2,4-pentadienyltrimethylsilane and (Z)-2-methyl-2,4-pentadienyltrimethylsilane was obtained to indicate the presence of a single torsional isomer with the U-shaped structure. The configuration of the former was determined from the proton-proton coupling constant (described later) observed in the ^{1}H-NMR spectrum (100 MHz) and by the measurement of NOE for the latter. This behavior corresponds well to dimethoxyboration-oxidation sequence of **5** in THF at −78 °C reported by Schlosser which gave (Z)-4-methyl-2,4-pentadien-1-ol (41%) and (Z)-2-methyl-2,4-pentadien-1-ol (22%) implying the U-shaped structure in THF.[10a)] If the anion **5** assumes the *endo-S-*, *exo-S-*, or W-structure, (E)-2-methyl- or (E)-4-methyl-2,4-pentadienyltrimethylsilane should be accompanied. Ex-



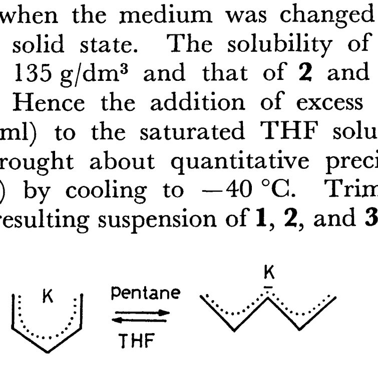
Scheme 1.



Scheme 2.

change of the counter cation to lithium changed the geometry of the product; *i.e.*, successive treatment of 2-methyl-1,4-pentadiene with *s*-butyllithium in THF, fluorodimethoxyborane and alkaline hydrogen peroxide has been reported to produce both 4-methyl- and 2-methyl-2,4-pentadien-1-ol.[13)] The formation of (*E*)-isomer favored over (*Z*)-isomer consistent with the trimethylsilylation of **4**. Based on these facts, one can conclude the structure of **1**, **2**, **3**, and **5** in solution to be the U-shaped and **4** to be the W-shaped structure in solution. The S-shape may be, thus, excluded for **1**—**5**.

A drastic change in geometry of the trapped products was found when the medium was changed from solution to the solid state. The solubility of **1** in THF at 40 °C is 135 g/dm^3 and that of **2** and **3** is lower than that. Hence the addition of excess pentane or octane (10 ml) to the saturated THF solution (1 ml) at 40 °C brought about quantitative precipitation of **1**—**3** (90%) by cooling to −40 °C. Trimethylsilylation of the resulting suspension of **1**, **2**, and **3** in pentane surprisingly produced (*E*)-2,4-pentadienyltrimethylsilane exclusively (98% GC yield) in 84, 90, and 92% regioselectivity at 0 °C and in 93—95% regioselectivity (~95% yield) at −70 °C in sharp contrast to the reaction in solution which gave the (*Z*)-isomer. THF-free pentadienyl anions of **1** and **2**, which were prepared by heating crystals to 80 °C *in vacuo*,[11a)] are sparingly soluble in hydrocarbons and showed an extreme regioselectivity in silylation (99% in pentane at 0 °C). Lithium compound **4** or its TMEDA complex **4′** suspended in pentane at 0 °C also produced the (*E*)-isomer exclusively (97%) in line with the reaction in solution. No medium effect was observed for the lithium analogue. These results clearly indicate the W-shaped structure for **1**—**4** and **4′** in the crystalline state but the S-shape can not be ruled out distinctly from this experiment. Dialkoxyboration-oxidation of **1** in hexane (in the solid state reaction) also produced (*E*)-pentadien-1-ol exclusively,[10b)] whereas it was recently found to give (*Z*)-isomer in good yield by reaction in THF solution in agreement with our result.[15c)] Thus, the frequently experienced poor reproducibility on the (*Z*)/(*E*)-ratio has now solved by introducing the concept of the medium effect.



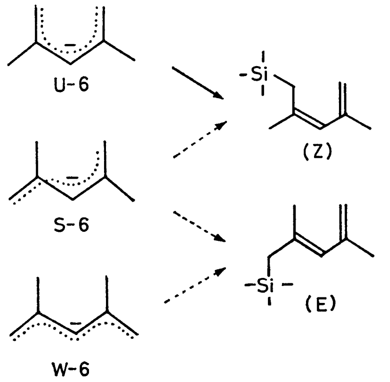
U-1
(in solution)

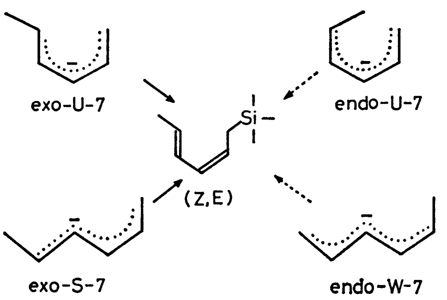
W-1
(in the solid state)

The similar medium effect was found also for **5**, which gave (*E*)-4-methyl-2,4-pentadienyltrimethylsilane (48%), (*Z*)-4-methyl-2,4-pentadienyltrimethylsilane (12%), and (*Z*)-2-methyl-2,4-pentadienyltrimethylsilane (40%) in the solid state reaction in pentane (THF coordinated to **5** was removed previously at 80 °C *in vacuo*). No contamination of (*E*)-2-methyl-2,4-pentadienyltrimethylsilane was detected in each isolated products. This shows that **5** has predominantly the *exo*-S-shaped structure in the crystalline state. The *exo*-S/U-ratio is calculated to be 78/22 if the U-**5** species in the solid state is postulated to give (*Z*)-4-methyl- and (*Z*)-2-methyl-2,4-pentadienyltrimethylsilane in 11/9 ratio as was observed in trimethylsilylation in solution. Protolysis of **5** with water producing a *ca.* 1:1 mixture of (*Z*)-2-methyl- and 4-methylpentadiene in both media[11)] gave little information on the configuration.

The steric repulsion between the two methyl groups on the 2,4-dimethylpentadienyl anions will lead to the U- or S-shaped structure since planar W-form is sterically hindered for this anion. Indeed, (*Z*)-2,4-dimethyl-2,4-pentadienyltrimethylsilane was identified as the almost exclusive product (97% regioselectivity, 96% yield) from potassium 2,4-dimethylpentadienide **6** both in solution and in the solid state suggesting the presence of the U-shaped single torsional isomer. The geometry was determined by the NOE experiment. The U-shaped structure have recently been confirmed also by Schlosser *et al.* by dialkoxyboration-oxidation of **6** in THF which results in the exclusive production of (*Z*)-2,4-dimethylpentadien-1-ol.[10)]

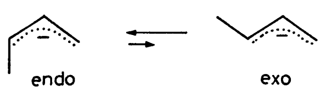
The trapped product of potassium hexadienide **7** also comprises one isomer, (2*Z*,4*E*)-2,4-hexadienyltrimethylsilane (92%) independent of the medium (solution and the solid state) and hexadiene precursor [1,3-hexadiene, 1,4-hexadiene, (*E*,*E*)-2,4-hexadiene and (*E*,*Z*)-2,4-hexadiene]. This result suggests the con-

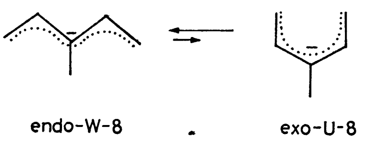




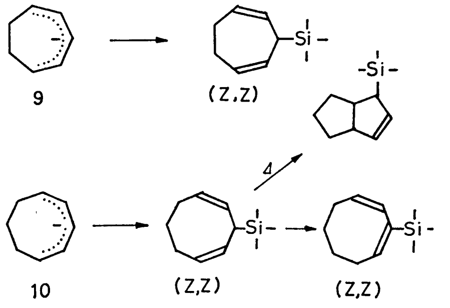
figuration of **7** to be either *exo*-U- or *exo*-S-shaped or their mixture. The value of the proton-proton coupling constant of J_{45}, 14.5 Hz, observed in ^{1}H-NMR (described later) evidently excludes the endo-W-form which had been considered for lithium derivative[7)] or **7** in liquid ammonia.[9)] The planar *endo*-U-shape seems implausible for steric reasons. The most striking feature of this reaction lies in the predominant attack of chlorotrimethylsilane on the primary carbon end (at C_1). Electrophilic attack on the secondary carbon (C_5 attached to CH_3 group) which should give 1-methyl-2,4-pentadienyltrimethylsilane was absent. This regioselectivity is valuable for organic syntheses[33a)] and an insect pheromone was recently prepared utilizing this type of reagent.[14)]

The geometry of 3-alkylpentadienyl anions seems exceptional. For example, potassium 3-methylpentadienide **8** in solution and in the solid state gave (*E*)-3-methylpentadienyltrimethylsilane (in 92—95% regioselectivity) by trimethylsilylation and (*E*)-3-methyl-1,3-pentadiene exclusively (97—99%) by hydrolysis in THF at −30 °C. Their structures were confirmed by the lack of NOE and the reaction with maleic anhydride.[11)] Thus, only **8** gave the (*E*)-isomer contrary to the behavior of other open-chain dienyl anions (**1**—**3**, **5**—**7**) in solution. The difference in geometry may be correlated to the strong preference of allylic potassium for the endo configuration over the exo configuration.[15)]





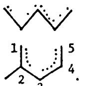
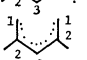
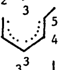
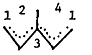
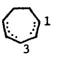
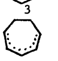
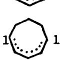
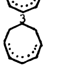
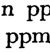
The mode of reaction of pentadienyl anions in a cyclic skeleton, *e.g.*, cycloheptadienyl or cyclooctadienyl anions, is known to be different from that of linear pentadienyl anions.[11,16)] The former showed a clear predominance of the electrophilic attack on the central carbon while the latter underwent attack on the terminal carbons reflecting higher charge on C_3-atom as confirmed by the ^{1}H-NMR (described later). Trimethylsilylation of potassium cycloheptadienide **9** in solution occurred only at the central carbon as expected and pure (*Z*,*Z*)-2,6-cycloheptadienyltrimethylsilane was obtained in high yield (99%). Potassium cyclooctadienide **10** behaved similarly to **9** but the isomerization of (*Z*,*Z*)-2,7-cyclooctadienyltrimethylsilane into (*Z*,*Z*)-1,7-cyclooctadienyl derivative was rapid in THF at 40 °C presumably due to the base catalysis. Isomerization of isolated (*Z*,*Z*)-2,7-cyclooctadienyltrimethylsilane to (*Z*)-bicyclo[3.3.0]-oct-3-en-2-yltrimethylsilane by electrocyclization[17)] was also observed by heating to 200 °C in a column of gas chromatograph (typical percent conversion, 30—40%).



Determination of geometry of **1** in liquid ammonia by trimethylsilylation was unsuccessful due to the predominant production of 1,1,1,3,3,3-hexamethyldisilazane. To confirm the geometry of pentadienyldimethoxyborane, which was postulated by Schlosser *et al.* as the intermediate in dialkoxyboration-oxidation of **1**, we attempted its isolation by distillation but the borane compounds were thermally too unstable to permit the isolation and were converted to polymeric substances above 0 °C.

Direct Measurement of the Geometry in Solution by ^{1}H-NMR. The variable ^{1}H-NMR spectra (Table 2) were measured in THF-d_8 to obtain direct evidence for the configuration of above-mentioned anions and to confirm the geometry determined by the regioselective trimethylsilylation and hydrolysis. Lithium pentadienide **4** and its TMEDA complex, which were obtained by direct metalation of 1,4-pentadiene with metallic Li[11)] or butyllithium[7)] in THF, are fluxional at room temperature but the rotation around the C_1–C_2(C_4–C_5) and C_2–C_3(C_3–C_4) bonds was frozen by lowering the temperature below −70 °C (Fig. 2). The proton-proton coupling constant of J_{23}(J_{34}), 11.9—12.0 Hz observed for **4** (THF complex) and the TMEDA complex at −90 °C is essentialy the same as that reported by Bates *et al.*[6)] indicating the presence of the W-shaped single torsional isomer. The coupling constant for allylic lithium compounds

TABLE 2. ^{1}H-NMR CHEMICAL SHIFTS(δ-VALUES) AND COUPLING CONSTANTS(Hz) OF POTASSIUM PENTADIENIDES IN THF-d_8 AT -40 °C AND RELATED COMPOUNDS$^{a)}$

	Geometry	Counter cation	C_1-H(J_{12})	C_2-H(J_{23})	C_3-H(J_{34})	C_4-H	C_5-H(J_{45})	Others
1		K	3.47(trans, 16.1) 3.55(cis, 10.6)	6.23 (d of d of d, 8.7)	3.55(t)	—	—	
2		Rb	3.40(trans, 16.4) 3.58(cis, 10.5)	6.15 (d of d of d, 8.7)	3.50(t)	—	—	
3		Cs	3.38(trans, 16.4) 3.59(cis, 10.5)	6.12 (d of d of d, 8.7)	3.50(t)	—	—	
4		Li	3.04(trans, 15.5) 2.68(cis, 9.1)	6.13 (d of d of d, 11.5)	4.35(t)	—	—	
1		K$^{b)}$	3.01(trans, 15.1) 2.58(cis, 9.0)	6.13 (d of d of d, 11.5)	4.35(t)	—	—	
5		K	3.39(gem, 3.0) 3.26(gem, 3.0)	—	3.59 (d, 9.0)	6.18 (d of d of d)	3.53(trans, 17.1) 3.50(cis, 11.1)	1.92(CH_3)
6		K	3.32(d, gem, 2.6)	—	3.46 (q, J_{13}=1.3)	—	3.54 (d, gem, 1.9)	1.96(CH_3) 1.98(CH_3)
7		K	3.39(d, 15.2) 3.26(d, 10.0)	6.21 (d of d of d, 8.6)	3.41 (d of d, 8.3)	6.05 (d of d)	4.13 (d of q, 8.7)	1.93 (d, 6.2, CH_3)
7		K$^{b)}$	3.01(trans, 15.1) 2.45(cis, 10.0)	6.09 (d of d of d, 11.5)	4.07 (d, 11.5)	5.84 (d of d)	3.07 (d of q, 8.7)	1.58 (d, CH_3)
8		K	2.90(trans, 15.8) 2.87(cis, 10.0)	6.20 (d of d)	—	—	—	1.57 (s, CH_3)
9		K	3.90(d of t, 9.2)	5.86(d of d, 7.8)	3.39(t)	—	—	2.53 (m, CH_2)
9		K$^{b)}$	3.51(d of t, 9.4)	5.67(d of d, 7.8)	3.14(t)	—	—	2.53 (m, CH_2)
10		K	3.10(d of q, 8.9)	5.87(d of d, 7.2)	2.64(t)	—	—	3.10(m ,CH_2) 1.11(q, 6.0)
10		K$^{b)}$	2.61(d of q, 9.3)	5.65(d of d, 7.0)	2.33(t)	—	—	3.11(m, 7.8) 2.15(m, 5.9)

a) In ppm downfield from external TMS in THF-d_8(calibrated using the downfield THF peak, assumed to be 3.75 ppm). Data were collected at 100 MHz from the decoupled spectra. b) Data in liquid ammonia by Kloosterziel *et al.* (Refs. 8, 9, and 20).

is known to be 6.5—7.5 Hz for cis-inner bond,[16] 11.5—12.0 Hz for trans-inner bond, 9—10 Hz for cis-outer bond, and 16—17 Hz for trans-outer bonds. The values increased by exchanging the cation to potassium; cis-inner bond 8.3—9.1 Hz,[18] trans-inner bond 13 Hz,[18] cis-outer bond 9—10 Hz, and trans-outer bond 16—17 Hz. The increased value may be due to the increased C_1–C_2–C_3 angle derived from the electrostatic effect of the larger ionic radius of potassium.

Based on these data, the geometry of a series of potassium dienides was analyzed. The NMR signals of the protons on $C_1(C_5)$ and C_3 of parent anion **1** heavily overlapped with each other and therefore the correct coupling constant was measured utilizing potassium 1,1,5,5-tetradeuterated pentadienide[2b] in THF-d_8 (Fig. 3). The value of J_{23} was found for the first time to be 9.1 Hz at 60 °C and was frozen out to give 8.7 Hz below -30 °C. This value clearly shows the cis-relationship of the two protons on the C_2–C_3 and C_3–C_4 bonds. The geometry of **1** in ethereal solution was thus shown to be U-shaped in accord with the chemical trapping experiment. The rotation around the outer bonds, C_1–C_2(C_4–C_5), is very slow even at 60 °C as evidenced by the coupling constant, J_{12}(trans)$=$15.9 Hz, J_{12}(cis)$=$10.0 Hz. The values are 16.1 and 9.9 Hz at -30 °C. The high barrier for rotation around the C_1–C_2 (estimated to be $>$25 kcal/mol by Schlosser[10c]) and C_2–C_3 bonds may account for the small temperature dependence of the coupling constant variation ΔJ_{12} (0.2 Hz) and ΔJ_{23} (0.4 Hz). Such high rotational barriers have recently been reported also for allylic potassium compounds.[18] The behavior of rubidium and caesium derivatives is similar to **1** but their coupling constants at 38 °C are a little smaller; J_{23}=8.9 Hz for **2** and 8.7 Hz for **3**. Therefore the rotational barrier around the C_2–C_3 bond in the pentadienyl anion was estimated to increase with the ionic radius of the alkali counter ion, $\mathrm{Li}<\mathrm{Na}\ll\mathrm{K}<\mathrm{Rb}\simeq\mathrm{Cs}$ in line with the order observed for allylic anion system,[19] though the line-shape analysis is required to obtain the exact value, ΔG. The spectra of **1** obtained from (Z)-, (E)-1,3-pentadiene or 1,4-pentadiene were the same with each other irrespective of the geometry of starting dienes.

Potassium hexadienide **7** was prepared from (E,E)-2,4-hexadiene, (E)-1,4-hexadiene, (E)-1,3-hexadiene and/or (Z)-1,3-hexadiene. All of these were heated to 70 °C for 30 min. The ^{1}H-NMR spectra of resulting anions **7** were the same independent of the geometry of the starting dienes and show the presence of two isomers in every cases; *exo*-U-shaped and presumably *exo*-S-shaped anions in 4:1 ratio. The predominant species was readily assigned to be *exo*-U-shaped from the chemical shift and the coupling constant obtained from the decoupled spectra (Table 2). The proton signals of minor species was too weak to make an assignment. However, the extreme stereoselec-

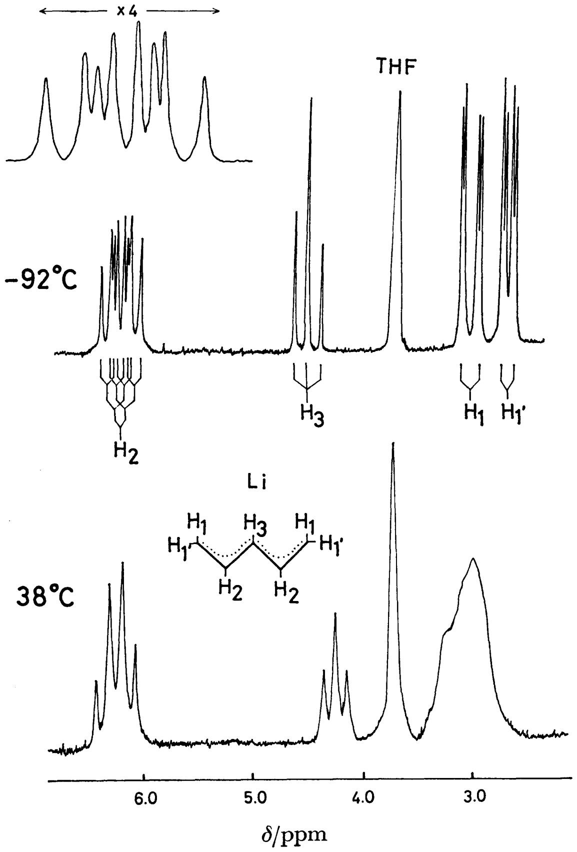


Fig. 2. Variable temperature ^{1}H-NMR spectra (100 MHz) of lithium pentadienide **4** in THF-d_8.

tivity observed in trapped products strongly suggests the presence of the *exo*-S-shaped anion as the minor species because only this isomer (except for the above *exo*-U) can provide (Z,E)-2,4-hexadienyltrimethylsilane. The ^{1}H-NMR spectrum of 2-methylpentadienyl anion **5** gave only partial information on the geometry. That is, J_{34} is 8.7 Hz below -30 °C. This value suggests the U- or *endo*-S-shaped structure for **5** and excludes the W- and *exo*-S-shape. However, we can reasonably suggest the U-shaped structure for **5** because of the result of chemical trapping experiments.

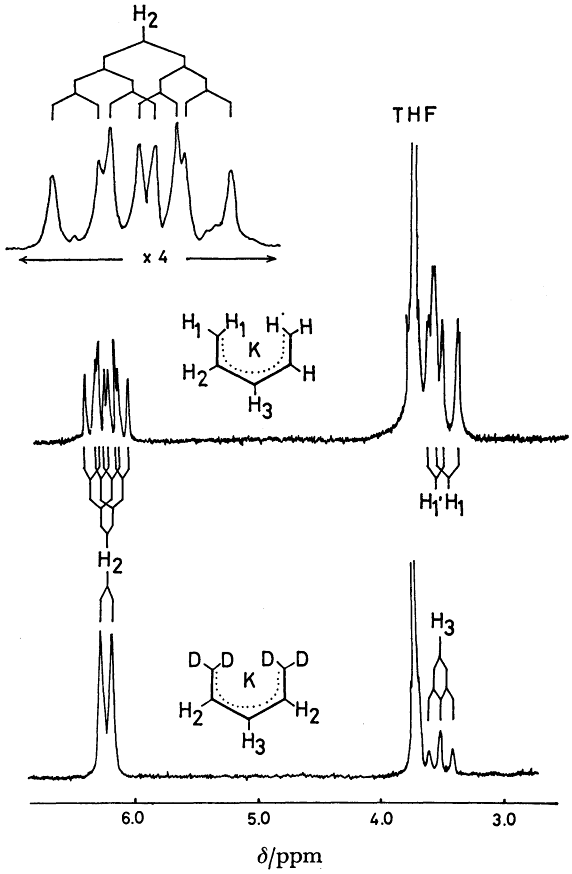


Fig. 3. ^{1}H-NMR spectra (100 MHz) of potassium pentadienide **1** and potassium 1,1,5,5-tetradeuterated pentadienide in THF-d_8 at -60 °C.

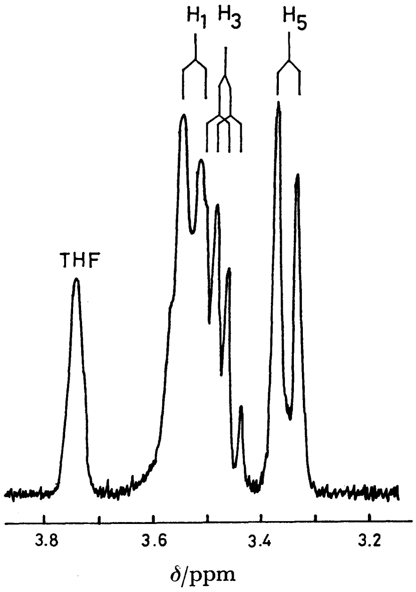
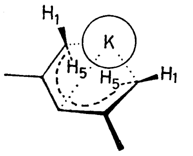
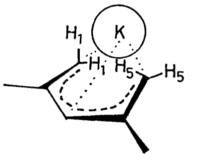


Fig. 4. ^{1}H-NMR spectra (100 MHz) of potassium 2,4-dimethylpentadienide **6** in THF-d_8 at -40 °C.

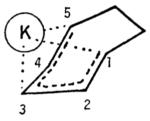
The chemical trapping of potassium 2,4-dimethylpentadienide **6** clearly shows the presence of the U-shaped single torsinal isomer in solution. However, the chemical shift difference was observed between the two terminal proton signals in ^{1}H-NMR below 10 °C (Fig. 4). The double doublet assigned to H-3 is caused by the H_1–H_3 coupling and H_5–H_3 coupling, not the CH_3–H_3 coupling, as evidenced from the decoupled spectrum. Supposition of the S-shaped structure which may explain the NMR data is in conflict with chemical trapping data. Hence, the deformed out-of-plane U-shaped or the following helicene-like U-shaped structure[15c)] is suggested by Schlosser for this observation, although they are indistinguishable by ^{1}H-NMR or chemical trapping experiments. The spectra simulation with a high resolution spectrometer will be required for further discussions.

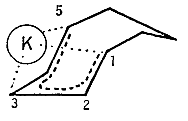




The ^{1}H-NMR spectrum of **8** also gave little information on the geometry but the presence of the single torsional isomer with the W-shaped structure is proposed based on the excellent stereospecificity observed in trimethylsilylation and hydrolysis in addition to the chemical shift values. The proton-proton coupling for the outer bonds (C_1–C_2 and C_4–C_5) is frozen below −30 °C and the spectral pattern was unchanged within 2 Hz on lowering the temperature to −90 °C. The ^{13}C-NMR spectral data at −40 °C (Table 3) also supports the presence of **8** as the single torsional isomer, W- or U-shaped anion. If rapid 1,3-rearrangement occurs exceeding the NMR time scale, a mixture of the (*Z*)- and the (*E*)-isomer should be formed chemically contrary to the fact. Thus, the extreme preference of the endo-W form is considered for **8**.

The coupling constants observed for **9** and **10** in THF-d_8 are essentially the same as those in liquid ammonia reported by Kloosterziel.[20] The plane defined by C_2–C_3–C_4 should never be coplanar to the plane made by C_1–C_2–C_4 or C_2–C_4–C_5 to relieve the ring strain.[21] Therefore, the decreased coupling constant of $J_{2,3}$ (6.8—7.0 Hz) for **9** and **10** compared to the value of $J_{2,3}$ (8.3—9.1 Hz) for open-chain dienylpotassium compounds may be rationalized in terms of the deviation of dihedral angle H_2–C_2–C_3–H_3 from zero to *ca.* 20° calculated by the Karplus equation. The smaller δ-values of H_3 of **9** and **10** as compared with that of **1**—**8** of the open-chain structure might be ascribed to both a larger electron-repelling effect of the CH_2 group bound to pentadienide termini and a larger torsion around the C_2–C_3 (and C_3–C_4) bond of **9** and **10** as Kloosterziel already suggested.[20]





Configurational Studies on Potassium Pentadienides by ^{13}C-NMR. ^{13}C-NMR chemical shifts provide the best measure of the electron density in many delocalized carbanions[22] and have been successfully employed to distinguish the geometry of the isomers considered for some lithium pentadienides.[5,23] ^{13}C-NMR parameters will be useful for configurational analysis of the present potassium derivatives since their rotational barriers around terminal- and inner-bonds is higher than those for lithium derivatives as mentioned above. The spectra of **1**—**3**, **6**, **8**—**10** (Table 3) clearly shows the presence of a single torsional isomer with a symmetric structure, U- or W-form, because the chemical shift value of C-1 or C-2 are equal to that of C-5 or C-4, respectively. The W-shaped structure can be ruled out from the chemical trapping experiments and the ^{1}H-NMR spectral data. The chemical shift of C-1 of **6** is equal to that of C-5 and hence the deformed out-of-plane U-shaped structure seems more probable than the helicene-like U-shaped one. In the case of **7**, two species were detected in agreement with ^{1}H-NMR measurement and the major species is assigned to the *exo*-U-shaped anion.

It is noteworthy that sodium pentadienide show a simple averaged NMR spectrum with three signals assignable to $C_1(C_5)$, $C_2(C_4)$, and C_3 (half-width of the signal is 1.1 ppm) at 20—50 °C but those were split into several peaks (the half-width, 0.2 ppm) by lowering the temperature below −40 °C. One of the best explanation for this is to consider the presence of a 4:1 mixture of S- and U-shaped anions at −40 °C, because this ratio is consistent to the *Z*/*E* ratio (42/58) of 1,3-pentadiene obtained by hydrolysis of sodium pentadienide in THF at −40 °C.

On the basis of the chemical shift data, one can conclude that the electron density on C-3 of potassium

TABLE 3. ^{13}C-NMR CHEMICAL SHIFTS OF POTASSIUM PENTADIENIDES AND RELATED COMPOUNDS IN TETRAHYDROFURAN-d_8 AT −40 °C[a)]

Dienyl anions	C-1	C-2	C-3	C-4	C-5	Others
1 (K)	79.2	137.8	79.6	137.8	79.2	
2 (Rb)	80.5	138.7	80.8	138.7	80.5	
3 (Cs)	81.9	139.6	82.6	139.6	81.9	
(Na) 20 °C	77.7	138.0	77.7	138.0	77.7	
−40 °C	77.4	137.7	77.8 78.4	142.3	77.8	
4 (Li)[c)]	66.2	143.8	86.9	143.8	66.2	
5 (K)	76.9	144.6	80.6	136.5	80.3	28.6(CH_3)
6 (K)	77.4	144.5	83.4	144.5	77.4	28.8(CH_3)
7 (K)[b)]	77.8	144.4	85.4	141.4	95.4	27.1(CH_3)
7′(Li)[c)]	56.7	143.6	81.4	137.3	85.7	
8 (K)	68.7	143.2	85.6	143.2	68.7	12.3(CH_3)
8′(Li)[d)]	64.2	146.9	92.1	146.9	64.2	10.2
9 (K)	95.3	133.9	76.2	133.9	95.3	37.2(C-6, C-7)
9′(Li)[d)]	98.9	134.5	71.3	134.5	98.9	35.6(C-6, C-7)
10 (K)	90.8	138.6	70.7	139.1	90.8	16.5(C-7) 29.3(C-6, C-8)

a) In ppm downfield from external TMS in THF-d_8(calibrated using the high-field THF peak, assumed to be 25.8 ppm). Peak assignments were made in part from an off-resonance decoupled spectrum. b) Major species (*exo*-U). c) Data of W. T. Ford *et al.*(Ref. 7). d) Data of R. B. Bates *et al.*(Ref. 16).

pentadienides (**1**, **5**, **6**, **9**, and **10**) is close to or higher than those on C-1 and C-5, while higher electron density lies on C-1 and C-5 for lithium derivatives (**4**, **8′**). That is, the latter has stronger sp^3 character on the terminal carbons than the former in THF.

Electronic Spectral Studies on Pentadienyl Anions. Acyclic and cyclic potassium pentadienides (except 3-alkylpentadienyl anions) have, thus, been revealed to assume the "U"-shaped structure in THF. The remaining problems to be solved are why potassium pentadienide **1** in liquid ammonia and lithium pentadienide **4** in THF assume the "W"-shape whereas **1** in THF assumes the "U"-shape. The geometry of potassium hexadienide **7** in liquid ammonia and lithium hexadienide (*exo*-W) is also different from **7** in THF (*exo*-U).

One of the key factors controlling the geometry is the solvation. It is generally accepted that organolithium compounds having carbanion with extensive charge delocalization exist as solvent-separated ion pairs in THF as evidenced by the strong bathochromic shift (24—44 nm) of the absorption maximum in polar solvents.[23–27] The sodium and higher analogues exist as contact ion pairs even in the polar solvents (the absorption maximum appears at shorter wavelength compared to that of the solvent-separated lithium compounds). Similar red shifts are also known for sodium naphthalenide and sodium benzophenone ketyl.[28] However, such cation dependence is observable only when the anion species have extensive π-electron systems; *e.g.*, diphenyl- and triphenylmethyl anions,[23] 1,1-diphenylhexyllithium,[24] diphenyl- and triphenylallylic anions,[25] 9-fluorenyl and the substituted fluorenyl anions.[26] The electronic spectra of organoalkali compounds without extensive negative charge delocalization are less sensitive to solvent polarity as was found for benzylic-,[22] allylic metals,[23] mono- or dianions of polystyrene, polybutadiene and polyisoprene.[29] Kinetic studies are sometimes more useful for these systems to detect the solvent-separated ion pairs.[30] Higher negative charge delocalization seems possible on the pentadienyl moiety compared to the allylic moiety mentioned above. If the π-electron system existing in pentadienyl group is sufficient for the extensive charge delocalization, lithium pentadienide **4** should show the bathochromic shift. The absorption maxima for **1**—**4** and the sodium analogue in THF (Table 4), indeed, appeared at longer wavelength than that of allylic anions (310—320 nm in THF and benzene).[31] However, the absorption maximum of **4** was observed at shorter wavelength than that of **1**—**3**, in line with the spectra of solvent less-sensitive allylic systems in which the wavelength for the absorption maxima increased with an increase of the radius of counter cations. The absorption maximum (355 nm) for **4** in hexane at 20 °C is nearly equal to that in THF. Therefore, the π-electron system existing in the pentadienyl group is concluded to be insufficient to compose the stable solvent-separated ion pairs. Other methods are required to evaluate the solvent-affinity by THF.

TABLE 4. ELECTRONIC ABSORPTION SPECTRAL DATA FOR **1**—**4** IN THF

Dienyl anions	λ_{max}/nm (ε)
4 (Li)	358 (5400)
(Na)[a]	365 (5700)
1 (K)	376 (6200)
2 (Rb)	377 (6000)
3 (Cs)	379 (5800)

a) Sodium pentadienide. All the spectra were measured at 20 °C.

Effect of Solvent-affinity on the Geometry of Pentadienyl Anions. To estimate the approximate strength of the solvation by THF to pentadienyl metals, the ease in dissociation of THF was examined on heating the respective 1:1 THF complexes[11] *in vacuo.* The Rb and Cs complexes readily release the THF molecule (>90%) on heating the crystals at 60 °C/1 mmHg[†] for 15 min, K complex at 80 °C/1 mmHg for 30 min (80% of THF was released as evidenced by GC of the hydrolyzate of octane suspension) while lithium and sodium complexes give off no THF even heating them at 120 °C/0.1 mmHg for 2 h. The weak interaction of THF to **1**, **2**, and **3** was also confirmed by washing the crystals of *ca.* 1:1 THF complexes of **1**—**3** (1 g) in excess of pentane (40 ml) four times at 30 °C, which resulted in the release of 70, 90, and 93% of THF, respectively. Lithium derivative **4** gives off no THF again and sodium derivative 10—20% of THF under the same conditions. This behavior clearly indicates that the solvent-affinity increases as size of the cation decreases, Li>Na≫K>Rb≃Cs. Therefore, we can reasonably explain the solution structure of lithium pentadienide by strongly-solvated ion pairs and potassium and higher alkali metal analogues by contact ion pairs. This inference was also supported by ^{1}H-NMR of **1**—**3** which show the significant low-field shift of the $C_1(C_5)$-proton signals by 0.4—0.9 ppm and high-field shift of C_3-proton by 0.8 ppm compared to the corresponding signals of lithium derivative **4** in THF. A similar high-field shifts (0.18 ppm) of the terminal proton signals caused by the solvation is known for lithium 1,3-diphenylpropenide.[25] The anion **1** in liquid ammonia should also exist as strongly solvated or solvent-separated ion pairs because its ^{1}H-NMR data (chemical shifts and coupling constants, see Table 2) correspond well to that of **4** in THF. Thus, combination of chemical trapping, NMR data and the solvent-affinity will lead to the very important conclusion; *i.e.*, pentadienyl anions which exist as strongly-solvated ion pairs assume the "W"-shaped structure consistent to the MNDO prediction,[5] whereas potassium and the higher alkali metal pentadienides, which will exist as contact ion pairs, favor the "U"-shaped structure. Geometry of the pentadienyl anion in the solid state is probably controlled by the mode of packing in the crystal lattice rather than the solvation effect. The lattice energy would cancel the small difference in net stabilization energy calculated for the three geometries. The X-ray analysis of **1** and **2** with good single crystals confirmed absence of the solvation and the presence of THF molecule at the interstitial po-

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[†] 1 mm Hg≈133.322 Pa.

sition but the intensity data were insufficient to warrant definite conclusion on the geometry in the crystalline state.32)

In contrast to pentadienyl anion, bis(2,4-pentadienyl)metal compounds of Be, Mg, and Zn prefer the (*E*)- over the (*Z*)-structure.2) This behavior is ascribable to their fluxional properties which permit the rearrangement of (*Z*)- to thermally more stable (*E*)-configuration by 1,3- or 1,5-shift. The facile control of the geometry by changing the medium or exchanging the cation will be valuable for organic synthesis. For example, the Lewis acid catalyzed regioselective addition of carbonyl compounds to 2,4-pentadienyltrimethylsilane has been recently reported.33) The reaction of 2,4-pentadienyltrimethylsilane with lithium amide is also useful for introduction of substituents to the pentadienyl group.34)

Experimental

Potassium pentadienide used at the present work were prepared by the procedure previously reported.11) Metallic rubidium (99.9% purity) and caesium (99.9%) used for the direct metalation of 1,3-dienes were purchased from Mitsuwa Pure Chem. Tetrahydrofuran-d_8 (99%, Merck Co.) and chloroform-d_1 (99.8%, Merck Co.) were dried over Na/K alloy and calcium hydride, respectively, and distilled before use. Starting dienes were purchased from Aldrich Chemicals or prepared using the reactions previously described.2,11) Potassium pentadienide-1,1,5,5-d_4 was prepared starting from 1,4-pentadiene-1,1,5,5-d_4.2b) GC analysis was made with a Hitachi Model 163 gas chromatograph using a capillary column (45 m) OV-1, CW-45, or HB-2000 and the separation of the reaction products was done with a Varian-Aerograph Model 700 gas chromatograph using a column (4 m) packed with Silicone DC-550. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian XL-100 instrument with a VFT-100-620L pulse Fourier transform accessory with the use of a sealed tube. NOE was measured using the tube sealed at 10^{-1} mmHg at 63 K after the solution was degassed (15—20% of NOE was observed in $CDCl_3$ and 20—25% in acetone-d_6). IR spectra were recorded on a Hitachi EPI-2 spectrometer. The absorption spectra were run on a JASCO Model UVIDEC-5A spectrometer. Elemental analysis for trimethylsilyl derivatives were carried out using a capillary with a Yanagimoto Model MT-2-CHN analyzer. The mass spectrum was recorded on a JEOL JNS-01SG-2 spectrometer. All the procedures were carried out in an argon atmosphere using the high vacuum technique.

Trimethylsilylation of Pentadienyl Anions in THF. A typical experiment is as follows. To a THF solution (100 ml) of **1** (0.5 g, 4.7 mmol) in a Schlenk tube was added dropwise a THF solution (5 ml) of chlorotrimethylsilane (0.6 ml, 4.9 mmol) over a 30 min period under the magnetic

TABLE 5. IR, MS, AND ANALYTICAL DATA FOR PENTADIENYLTRIMETHYLSILANE

Entry	IR(Neat) $\tilde{\nu}$/cm^{-1}			Mass$^{a)}$ (Relative intensity)	Found(%)		Calcd(%)	
	C=C	CH=CH	C-Si		C	H	C	H
Si-1	1638	995 897 797	1246, 1149 852, 839	140(M, 15), 141(M+1, 4) 142(M+2, 1)	68.58	11.50	68.49	11.48
Si-2	1641	1000 892	1246, 1152 850, 839	140(M, 19), 14(M+1, 11) 142(M+2, 4)	68.50	11.49	68.49	11.42
Si-3	1639	988 896	1246, 1152 862, 836	154(M, 25), 155(M+1, 4) 156(M+2, 2)	70.03	11.58	70.04	11.76
Si-4	1638	1036 962	1245, 1150 860, 835	154(M, 12), 155(M+1, 6) 156(M+2, 3)	70.04	11.76	70.04	11.76
Si-5	1636	1000 987 944	1245, 1150 860, 837 756, 702	154(M, 14), 155(M+1, 5) 156(M+2, 1)	70.00	11.61	70.04	11.76
Si-6	1638	1016 882	1256, 1164 866, 839	168(M, 20), 169(M+1, 4) 170(M+2, 1)	71.13	11.90	71.34	11.99
Si-7	1646	978 942 816	1245, 1149 899, 758 705	154(M, 17), 155(M+1, 7) 156(M+2, 5)	69.93	11.42	70.04	11.76
Si-8	1636	1082 989 885	1257, 1245 1149, 855 840, 760	154(M, 18), 155(M+1, 2) 156(M+2, 1)	70.03	11.58	70.04	11.76
Si-9	1644	896 791 751	1205, 837	166(M, 10), 167(M+1, 7) 168(M+2, 1)	71.87	10.92	72.21	10.91
Si-10	1640	909 882 756	1248, 842	180(M, 15), 181(M+1, 8) 182(M+2, 2)	73.20	11.10	73.25	11.18

a) Relative intensity assuming the fragment of $(CH_3)_3Si$ as 100. Spectrum was recorded at 70 eV.

stirring at −40 °C). A rapid addition of chlorotrimethylsilane should be avoided or it causes the production of 3-trimethylsilyl-1,4-pentadiene in <20% yield. The solution changes from orange to colorless near the equivalence point precipitating the salt. The mixture was stirred at −40 °C for 30 min and then at 0 °C for 1 h. After condensing the solution to 10 ml by evaporation, pentane (20 ml) was added for the complete precipitation of the salt. The resulting salt was separated by centrifugation with the use of a two-necked glass tube fitted with rubber stoppers protected with a plastic cover. The precipitate was washed with two portions of pentane (20 ml) for extraction of the products. After the removal of pentane and THF from the combined solution by evaporation, the remaining (*Z*)-pentadienyltrimethylsilane was separated by distillation (143 °C/760 mmHg. GC yield 98% and isolated yield 70—75%). A series of trimethylsilylated compounds was isolated in the similar manner. Trimethylsilylated products from **5**, **6**, and **9** were distilled at 45 °C/6 mmHg, 55 °C/4 mmHg and 75 °C/0.5 mmHg, respectively. When the product comprises isomers, they were separated into the respective isomers with a preparative GC. The geometries and structures of the isolated isomers were analyzed by ^{1}H-NMR (Table 1) and IR, MS, and the elemental analysis (Table 5).

Trimethylsilylation of Pentadienyl Anions in the Solid State. Solubility of potassium pentadienide **1** for THF is relatively small; 135 g/dm^3 at 40 °C, 27 g/dm^3 at 0 °C and that of rubidium and caesium derivatives, **2** and **3**, at 40 °C are 10.5 and 18.5 g/dm^3, respectively. Lithium and sodium derivatives are freely soluble in THF at 0 °C. The addition of pentane or octane (40 ml) to the THF solution (5 ml) of **1**, **2**, and **3** (7.5 mmol for **1**) saturated at 60 °C resulted in the quantitative precipitation (90—92%) of the crystals by cooling the mixture below −40 °C. To the resulting suspension of **1**, **2** or **3** (7.5 mmol) was added dropwise chlorotrimethylsilane (1 ml, 7.7 mmol) in pentane (5 ml) at −70 °C for undergoing the solid state reaction. After continuing the vigorous magnetic stirring for 1 h, the salt was removed by centrifugation at room temperature and trimethylsilylated compounds were isolated by distillation. A typical isolated yield, 85% (GC Yield, 99%). The regioselectivity in reactions of **1**, **2**, and **3** to give the (*E*)-isomer was 93, 95, and 95% respectively. THF-free pentadienyl anions **1**—**3** which were prepared by heating their THF complexes at 80 °C/0.1 mmHg for 40 min were completely insoluble in pentane, benzene or diethyl ether. To a suspension of THF-free compounds **1**—**3** (10 mmol) in pentane (40 ml) was added at −40 °C chlorotrimethylsilane (1.3 ml, 11 mmol) dissolved in pentane (5 ml). The mixture was stirred for 2 h at 0 °C. Thus, (*E*)-2,4-pentadienyltrimethylsilane was produced quantitatively (GC Yield, >98%) and was isolated by distillation (Yield, 90%, regioselectivity, 99%). Great care is necessary in handling the THF-free pentadienyl anions because of their flammability in the air. THF complexes of sodium- and lithium pentadienide **4** were also insoluble in pentane below −40 °C and the solid state reactions were carried out in the same procedure as described for **1**—**3**. The regioselectivity in trimethylsilylation of a series of pentadienyl anions in solution and in the solid state, the (*Z*)/(*E*) ratio of the major products and total yields were summarized in Table 6.

TABLE 6. RESULTS OF TRIMETHYLSILYLATION OF PENTADIENYL ANIONS IN SOLUTION$^{a)}$ AND IN THE SOLID STATE$^{b)}$

Anions	Trimethylsilylation at		(*Z*)/(*E*) ratio of the products	Total yield/%$^{c)}$
	$C_1(C_5)$/%	C_3/%		
1	98	2	94/6	97
1$^{b)}$	99	1	1/99	95
2	97	3	98/2	98
2$^{b)}$	99	1	7/93	92
3	98	2	98/2	95
3$^{b)}$	97	3	4/96	92
4	100	0	1/99	98
4$^{b)}$	95	5	5/95	98
5	99	1	99/1	90
5$^{b)}$	98	2	52/48	92
6	97	3	95/5	96
6$^{b)}$	95	5	92/8	92
7	99	1	96/4$^{d)}$	90
8	93	7	5/95$^{e)}$	99
9	2	98	99/1	99
10	3	97	99/1	71

a) The reaction of pentadienyl anions(4.5 mmol) in THF(100 ml) with $(CH_3)_3SiCl$ was carried out at −40 °C. b) Trimethylsilylation of THF-free pentadienyl anions(10 mmol) was done in pentane(30 ml) at 0 °C. c) GC yield. d) Ratio of (2*Z*,4*E*)-isomer to other isomers. e) Ratio of (*Z*)-isomer to other isomers.

We are grateful to Prof. M. Schlosser, Universite de Lausanne, and Prof. D. E. Bergbreiter, Texas A & M University for their valuable discussions. The financial support of this work by the Kurata Science Foundation is gratefully acknowledged.

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