The ketal of **3** was obtained in 86% yield (recrystallized from hexane): mp 89.5-90 °C; IR (KBr) ν_{max} 2950, 1450, 1300, 1095, 1055, 920 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.3 (3 H, s), 3.26 (3 H, s), 2.56 (4 H, br s), 2.32 (2 H, br s), 2.1-1.3 (10 H, series of m). Anal. Calcd for $C_{15}H_{22}O$: C, 76.88; H, 9.46. Found: C, 76.33; H, 9.60.

Hydrolysis gave **3** in 96% yield (recrystallized from hexane): mp 160 °C (sublimes), 200 °C dec; IR (KBr) ν_{max} 2925, 1755, 1450, 1120, 690 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 2.76 (4 H, s), 2.48 (2 H, br s), 2.2-1.4 (10 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 214.3, 48.5, 29.5, 27.0, 16.5, 16.2. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.45; H, 8.86.

The ketal of **4** was obtained in 70% yield and recrystallized from dichloromethane-hexane: mp 92 °C; IR (KBr) ν_{max} 3050, 2950, 1440, 1380, 1300, 1060, 690 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.24-6.0 (2 H, m), 5.8-5.5 (2 H, m), 3.38-3.1 (2 H, m), 3.3 (3 H, s), 3.26 (3 H, s), 2.84 (4 H, m), 1.86 (2 H, m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 131.9, 128.7, 113.9, 50.8, 50.4, 41.2, 40.2, 38.5, 33.9. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.07; H, 7.76.

Hydrolysis as above gave **4** in 90% yield (recrystallized from dichloromethane-hexane): mp 165 °C; IR (KBr) ν_{max} 3025, 2950, 1760, 1380, 1130, 690 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.3-6.06 (2 H, m), 5.9-5.64 (2 H, m), 3.44 (2 H, m), 2.94 (4 H, m), 1.74 (2 H, br s); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 213.6, 129.4, 129.1, 43.7, 39.5, 37.3, 28.8. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.52; H, 6.51.

The conversions of **2-4** into the alcohols with LAH and MeLi were carried out in ether under nitrogen at 0 °C. After aqueous workup, drying, and evaporation of solvent, the yields were essentially quantitative. The product ratios were determined by means of ^{1}H NMR experiments on a QE-300 NMR spectrometer operating at 300.15 MHz as described in the text. For the shift reagent studies, a carefully weighed amount of the alcohol or alcohol mixture was dissolved in a known amount of $CDCl_3$, and NMR spectra were measured after additions of various amounts of a $CDCl_3$ solution of $Eu(fod)_3$ of known strength. After each addition, the volume was reduced to the original by applying a vacuum.

The MM2 calculation with energy minimization was carried out with the MACRO Model V.2.5 program developed by C. Still, Department of Chemistry, Columbia University.

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Supplementary Material Available: The derivation of eqs 1 and 2 and ^{13}C NMR spectra of **3** and its ketal (6 pages). Ordering information is given on any current masthead page.

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Highly Selective Trapping of Unsymmetrical Pentadienyl Anions by Silicon and Tin Electrophiles. Marked Contrast between Kinetic and Thermodynamic Control of Product Composition

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The nucleophilic reaction of lithium and potassium salts of five pentadienyl anions bearing sterically and/or coordinatively different groups at their unsymmetrical 2-position toward Me_3SiCl and Me_3SnBr is described. When the anion of the potassium salt was trapped by Me_3SiCl, (*Z*)-4-substituted-pentadienylsilanes were obtained with high selectivity (87-100%). The lithium salt, however, gave a mixture of (*E*)- and (*Z*)-4-substituted-pentadienylsilanes. The coupling reaction proceeds under kinetic control, because the product composition from Si trapping reflected the structure of the parent dienyl anion and the steric interaction between the incoming Me_3Si group and the substituent on the anion. In contrast, when the anion was trapped by Me_3SnBr under the identical conditions, (*Z*)-2-substituted-pentadienyltins were formed with 60-96% selectivity. Only relatively small changes in product composition, as a function of the cation or the substituent on the anion, were observed. These results could be explained by thermodynamic controlling factors, including a 1,5-Me_3Sn shift, and a redistribution of pentadienyl groups under basic conditions.

Introduction

In recent years, much attention has been paid to the chemistry of pentadienylmetals **1**.[2] They can be regarded as both extended analogues of allylmetals **2** and acyclic analogues of cyclopentadienylmetals **3**. The majority are fluxional molecules. The existence of various coordination modes, η^1-, η^3-, and η^5-forms (corresponding to **1a**, **1b**, and **1c**, respectively), and the equilibria among them make extensive exploitation of pentadienylmetal chemistry difficult. Only the simplest pentadienylmetals, or their symmetrically substituted homologues, have been studied in order to avoid complexity.

1a

1b

1c

2a

2b

3

In organic synthesis, main group metal derivatives of pentadienes have been utilized as pentadienyl anions or

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[2] For reviews see: (a) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15-29. (b) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56-62.

0022-3263/91/1956-2011$02.50/0

Table I. Trapping of (2-Substituted-pentadienyl)lithiums and -potassiums by Silicon and Tin Electrophiles[a]

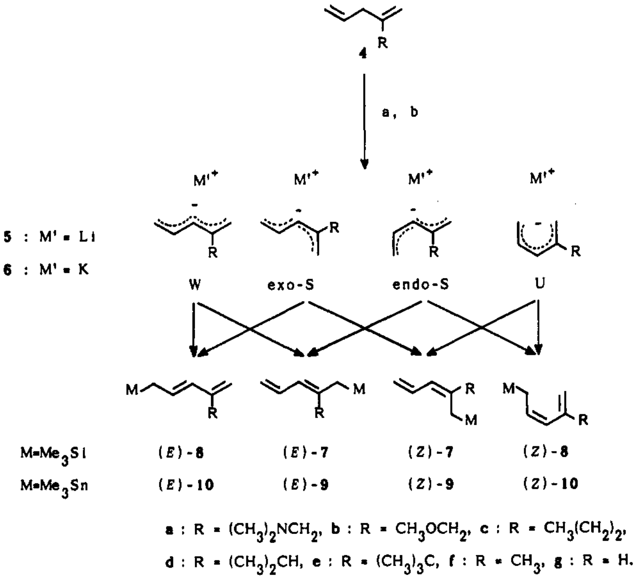
		product distribution, % (total yield, %)[b]											
		M = $SiMe_3$						M = $SnMe_3$					
compd, R	M′	entry	(*E*)-**8**	(*E*)-**7**	(*Z*)-**7**	(*Z*)-**8**		entry	(*E*)-**10**	(*E*)-**9**	(*Z*)-**9**	(*Z*)-**10**	
5a, CH_2NMe_2	Li	1	21	32	20	27	(68)	11	7	8	85	0	(70)
6a, CH_2NMe_2	K	2	1.5	3	1.5	94	(54)	12	6	3	91	0	(65)
5b, CH_2OMe	Li	3	31	3	38	28	(73)	13	7	8	85	0	(70)
6b, CH_2OMe	K	4	3	t[c]	10	87	(43)	14	8	4	88	0	(53)
5c, $(CH_2)_2Me$	Li	5	55	8	18	19	(70)	15	30	14	56	0	(90)
6c, $(CH_2)_2Me$	K	6	0	0	11	89	(77)	16	30	10	60	0	(78)
5d, $CHMe_2$	Li	7	44	0	19	37	(69)	17	25	9	66	0	(65)
6d, $CHMe_2$	K	8	0	0	5	95	(86)	18	7	0	93	0	(80)
5e, CMe_3	Li	9	49	1	1	49	(61)	19	9	5	86	0	(42)
6e, CMe_3	K	10	0	t[c]	0	100	(75)	20	2	2	96	0	(74)
6f, Me	K							21	29	12	59	0	(62)
6f, Me	K							22[d]	10	14	86	0	(53)

[a] The electrophile was added to a solution of the anion (normal addition) at −78 °C in THF, unless otherwise noted. [b] Product distribution and yields were determined by ^1H NMR. [c] Trace amount (<1%). [d] A solution of the anion was added to Me_3SnBr (inverse addition).

their equivalents[2a] to introduce conjugated pentadienyl groups into various electrophiles. If one takes their fluxionality into account, pentadienylmetals with a stable carbon–metal σ-bond are useful reagents. Among them, the silicon and tin derivatives have moderate nucleophilicity due to extended σ–π conjugation. Pentadienyltins have been used for the selective pentadienylation of α,β-unsaturated carbonyl compounds and quinones.[3a–g] Both of the latter are excellent dienophiles, yet pentadienylation occurred without the formation of Diels–Alder adducts.

Under these circumstances, a problem arises as to how the regio- and stereoselective preparation of pentadienylmetal compounds can be controlled. Obviously, the successful application of pentadienylmetals in organic synthesis depends on their isomeric purity, which may influence reactivity and selectivity. This is especially true for compounds **1a**, which possess a stable carbon–metal σ-bond. Such compounds are usually prepared by metal exchange between a pentadienyl alkali metal salt and a halide of less electropositive metal. The situation is more complex in the case of an unsymmetrically substituted pentadienyl anion than in that of an unsubstituted one. In particular, the regioselectivity that might be observed in the electrophilic trapping of a *2-substituted* pentadienyl anion is most interesting, because the steric environments of the terminal carbon atoms would be different due to the location of the substituent.[4]

Scheme I[a]



[a] (a) *n*-BuLi (M′ = Li) or *n*-BuLi/*t*-BuOK (M′ = K); (b) Me_3SiCl (M = Me_3Si) or Me_3SnBr (M = Me_3Sn).

We have already made a preliminary report[4c] on the highly selective stannylation of the 2-(methoxymethyl)pentadienyl anion. Herein, we describe the regio- and stereoselectivity of the trapping of several 2-substituted pentadienyl anions by Me_3SiCl and Me_3SnBr, to give pentadienylsilanes (PDS) and pentadienyltins (PDT), respectively. A marked contrast in the regioselectivity of trapping was observed: kinetically controlled trimethylsilylation preferentially gave 4-substituted pentadienylsilanes, whereas thermodynamically controlled trimethylstannylation preferentially gave 2-substituted pentadienyltins.

Results and Discussion

Two alkali metal cations, Li^+ and K^+, were employed as counterions in the pentadienyl salts. The lithium salts in THF preferentially assume the W and exo-S forms, whereas the potassium salts preferentially assume the U form (Scheme I). These preferences were established by Schlosser et al.[4a] in a study of the trapping of 2-methylpentadienyl anion by $(MeO)_2BF$. The anion conformation would be reflected in the product distribution, as long as the initially formed products did not isomerize.[2a,4b,5]

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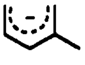
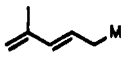
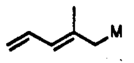
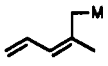
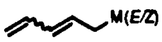
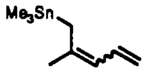
Table II. Effect of Redistribution[a]


6f

K^+ + silicon or tin compound (MX) $\xrightarrow{-78\ °C}$ products

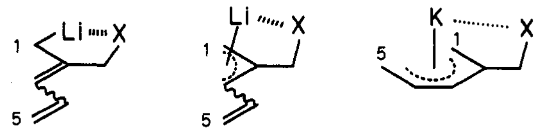
entry	MX (E/Z)	product distribution, %[b]			
					
1	 7g (9/1)	0	0	0	100 (9/1)
2	 9g (8/2)	20	11	31	38 (8/2)
3	 9f (2/8)	30	20	50	
4[c]	9f (2/8)	23	17	30	30 (8/2)

[a] The silane or stannane (MX) was added to 6f (normal addition). [b] Determined by ^1H NMR. [c] Pentadienyllithium 5g was employed instead of 6f.

Second, pentadienyl anions with five different substituents were studied to determine the influences of intramolecular coordination of a polar group with the metal cation and substituent bulkiness on product regio- and stereochemistry. The substituents were (dimethylamino)methyl (Me_2NCH_2), methoxymethyl ($MeOCH_2$), *n*-propyl, isopropyl, and *tert*-butyl groups. The (dimethylamino)methyl and methoxymethyl groups were capable of coordination with the counterion.

The alkali metal salts were prepared by deprotonation of 1,4-dienes 4 with either *n*-BuLi in THF or a *n*-BuLi/*t*-BuOK mixture[6] in hexane. The anion so produced was trapped by the addition of the electrophile, Me_3SiCl or Me_3SnBr, in THF at −78 °C (normal addition). The components of the mixture of silylated or stannylated products were identified by ^1H NMR spectroscopy, by comparison of the values of their proton chemical shifts and coupling constants with those of the unsubstituted compounds **7g** and **9g**. The results are summarized in Table I.

The following five observations were noteworthy. (1) Me_3SiCl reacted preferentially with the anion at the 5-position, i.e., at the terminus farther from the substituent, to give, mainly, 4-substituted-pentadienylsilanes 8 (entries 5–10), whereas Me_3SnBr apparently reacted preferentially at the 1-position, i.e., at the terminus nearer to the substituent, to give, mainly, 2-substituted-pentadienyltins 9 (entries 11–22). (2) With the tin electrophile, *no* (*Z*)-4-substituted-pentadienyl product [(*Z*)-10] was obtained (entries 11–22). (3) The two counterions exhibited intensely different effects on the product distribution in trimethylsilylation. On the other hand, the product distribution among the tin compounds was less affected by the identity of the counterion. (4) The regioselectivity of both trimethylsilylation and trimethylstannylation was enhanced with increasing bulkiness of the substituent on the anion. (5) The presence of substituents—Me_2NCH_2 and $MeOCH_2$—capable of coordination with the counterion increased the proportion of 2-substituted-pentadienyl products, regardless of the electrophile employed. This was in comparison with the *n*-propyl substituent, which exerted almost the same steric effect but was incapable of coordination with the counterion.



11a 11b 11c

Figure 1. Intramolecular complexation.

PDS Formation. Me_3SiCl trapped the pentadienyl anion under kinetic control. Several factors influenced the product distribution. The pentadienylpotassiums selectively (>95%) afforded (*Z*)-PDSs [(*Z*)-7 and (*Z*)-8] without exception, whereas the pentadienyllithiums gave *E*/*Z* mixtures [(*E*)-7 + (*E*)-8: (*Z*)-7 + (*Z*)-8 = 65:35 to 34:66]. When the counterion was K^+, the high *Z* selectivity, regardless of the nature of the substituent, suggested that the anions assumed the U conformation. This result is thus in good agreement with Schlosser's observation.[4a] In contrast, (2-*n*-propylpentadienyl)lithium (**5c**), for example, gave a mixture of silylated products, which suggested that the anion preferentially assumed the W and exo-S conformations. This is also a result similar to that of Schlosser's for (2-methylpentadienyl)lithium (**5f**). However, when the substituent was isopropyl (**5d**) or *tert*-butyl (**5e**), U- and endo-S-shaped anions seemed also to be favored, judging from the increased formation of (*Z*)-8. Thus, the bulkier the substituent became, the more (*Z*)-PDS was formed.

The product distribution as a function of the counterion indicated that *the PDS formation was kinetically controlled*. A scrambling experiment supported this belief. The reaction of unsubstituted PDS **7g** and (2-methylpentadienyl)potassium (**6f**) (entry 1, Table II), showed that PDS, once formed, underwent neither redistribution nor isomerization under basic conditions, although PDT, as will be shown, did both.

The regioselectivity in PDS formation was governed by both the bulkiness and coordinative character of the substituents. The presence of hydrocarbon substituents on the anion contributed to predominant formation of 4-substituted-PDSs. This selectivity can be explained simply in terms of the bulkiness of the substituent. Steric repulsion between the substituent and incoming Me_3SiCl played a major role in the determination of the product distribution.

The effect of the coordinative substituents can be interpreted in terms of intramolecular complexation[7] (Figure

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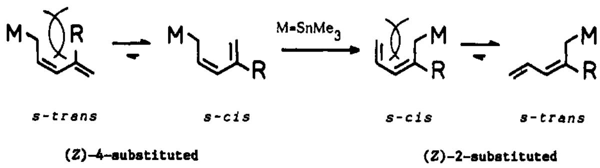
[6] Lochmann, L.; Pospisil, J.; Lim, D. *Tetrahedron Lett.* **1966**, 257–262. Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9. Bahl, J. J.; Bates, R. B.; Gordon, B., III. *J. Org. Chem.* **1979**, *44*, 2290–2291.

Scheme II



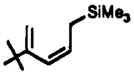
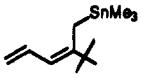
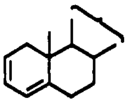
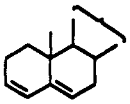
1). Coordination of the nitrogen or oxygen atom of the substituent with Li^+ would increase the contribution of the complexes **11a** (a σ-type complex) and **11b** (a η^3-complex) to the structure of the salt. Because both structures have more negative charge localized at the 1-position than at the 5-position, reaction at the 1-position should increase.

In contrast to Li^+, K^+ as the counterion did not show such a coordinative effect on product distribution (entries 2 and 4, Table I). This could be explained as follows: K^+, a "softer" and larger cation than Li^+, can form the U-shaped η^5-pentadienyl complex **11c**. However, coordination with a polar substituent would have only a very small effect on the shape of the complex, i.e., both the 1- and 5-positions of **11c** would be almost equivalent electronically.[8] Also, the low Lewis acidity of the electrophile, Me_3SiCl, would be reflected by the negligible affinity between the silicon atom and the substituent. Therefore the mere bulkiness of the substituent was the major factor controlling regioselectivity in PDS formation.

PDT Formation. In contrast to Me_3SiCl, Me_3SnBr trapped the pentadienyl anions to give 2-substituted-pentadienyltins **9**. This result would be curious and unexplainable in terms of kinetic control. Another notable phenomenon was that no (*Z*)-**10** was produced. These two observations suggested that isomerization of (*Z*)-**10** to (*Z*)-**9** via a 1,5-shift of the Me_3Sn group may have occurred. Such behavior is well known in cyclopentadienyltin chemistry,[9] as a thermal [1,5] sigmatropic rearrangement. For example, trimethyl(cyclopentadienyl)tin readily undergoes the rearrangement: the activation energy ($\Delta G^{\ddagger}$) is reported to be only 7.1 kcal/mol.[10] The rearrangement of other compounds, such as (*Z*)-triphenyl(pentadienyl)tin ($\Delta G^{\ddagger}$ = 19.4 kcal/mol)[11] and (*Z*)-trichloro(pentadienyl)tin ($\Delta G^{\ddagger}$ < 7.4 kcal/mol),[12] has been reported. Therefore, a Me_3Sn shift in the present situation was very probable,[13] although the attempted detection of (*Z*)-**10** by ^1H NMR, even at low temperatures (<−50 °C), was unsuccessful.

Furthermore, that rearrangement occurred is reasonable from conformational considerations (Scheme II). (*Z*)-4-Substituted-PDTs appear to prefer the s-cis conformation rather than the s-trans conformation because of the steric effect of the substituent. The UV data summarized in Table III showed a small molar absorptivity (ε) for (*Z*)-**8e** (a model for (*Z*)-**10e**), which indicates a contribution from an s-cis-diene chromophore.[14] An s-cis conformation is necessary for the rearrangement to occur, and a preference for that conformation should reduce the activation energy required. On the other hand, (*Z*)-2-substituted-PDTs probably prefer the s-trans conformation. The large ε value displayed by (*Z*)-**9e** supports this interpretation.[14] Thus, a reverse Me_3Sn shift did not occur, and mainly (*Z*)-2-substituted-PDT [(*Z*)-**9**] was produced.

Table III. UV Data for (*Z*)-8e, (*Z*)-9e, and Related Conjugated Dienes

compound	λ_{max}, nm (ε)	conformation
 (*Z*)-**8e**	228.5 (5000)[a]	s-cis
 (*Z*)-**9e**	262.0 (15 300)[a]	s-trans
	256.5 (8000)[a,c]	s-cis
	217.0 (20 900)[a,c]	s-trans
	275.0 (6300)[b,c]	s-cis
	235.0 (23 000)[b,c]	s-trans

[a] In *n*-hexane solution. [b] In ethanol solution. [c] Value cited in ref 14b.

If the product distribution were determined only by kinetic factors and a [1,5] rearrangement of the initially formed product, the phenomena described in point 3 above would be unexplainable, because the differences in the product distribution of the tin compounds as a function of the counterion would be too small. However, PDTs did undergo redistribution with (2-methylpentadienyl)potassium (**6f**) (Table II). Enriched trimethyl(2-methylpentadienyl)tin (**9f**)[15] and **6f** afforded a regioisomeric mixture of **9f** and **10f** (entry 3), in which the distribution of products was similar to that of the normal coupling reaction (entry 21, Table I). Moreover, that redistribution occurred is substantiated by the results shown in entry 2, where trimethyl(pentadienyl)tin (**9g**) and **6f** were em-

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[7] Horvath, R. F.; Chan, T. H. *J. Org. Chem.* **1989**, *54*, 317–327. Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356–363. Fitt, J. J.; Gschwend, H. W. *J. Org. Chem.* **1981**, *46*, 3349–3352. Biellmann, J.-F.; Ducep, J.-B. *Org. React. (N.Y.)* **1981**, *27*, 1–332. Still, W. C.; Macdonald, T. L. *J. Org. Chem.* **1976**, *41*, 3620–3622; *J. Am. Chem. Soc.* **1974**, *96*, 5561–5563.

[8] The intensity of the coordination of a "hard" base, nitrogen or oxygen, with a "softer" acid, K^+, would be expected to be less than that with to a "harder" acid, Li^+. It is known that the affinity of an ethereal oxygen atom for an alkali metal cation increases as the size of the cation decreases.[4b]

[9] For reviews on the fluxionality of cyclopentadienyl systems, see: Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187–217. Mironov, V. A.; Fedorovich, A. D.; Akhrem, A. A. *Russ. Chem. Rev.* **1981**, *50*, 666–681. Jutzi, P. *Chem. Rev.* **1986**, *86*, 983–996. Mann, B. E. *Chem. Soc. Rev.* **1986**, *15*, 167–187.

[10] Luzikov, Y. N.; Sergeyev, N. M.; Ustynyuk, Y. A. *J. Organomet. Chem.* **1974**, *65*, 303–310.

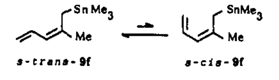
[11] Hails, M. J.; Mann, B. E.; Spencer, C. M. *J. Chem. Soc., Dalton Trans.* **1983**, 729–732.

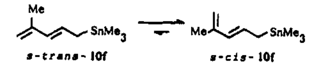
[12] Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *Tetrahedron* **1989**, *45*, 1067–1078.

[13] 1,5-Shifts of other metals in open pentadienyl systems have been also reported: see ref 3p.

[14] (a) Cais, M. *The Chemistry of Alkenes*: Patai, S., Ed.; Interscience: New York, 1964; Chapter 12. (b) Gillam, A. E.; Stern, E. S. *An Introduction of Electronic Absorption Spectroscopy in Organic Chemistry*; Edward Arnold: London, 1954; pp 93–125.

[15] The regioisomeric purity of **9f** was increased by the removal of **10f** as a Diels–Alder adduct with maleic anhydride. (See Experimental Section.) A 1,3-disubstituted-butadiene such as **10f** probably assumes the s-cis conformer much more readily than a 1,1-disubstituted-butadiene such as **9f**, which would probably favor the s-trans conformation. Therefore, only **10f** undergoes a facile Diels–Alder reaction. (a) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537–562. (b) Bachman, G. B.; Goebel, C. G. *J. Am. Chem. Soc.* **1942**, *64*, 787–789.





ployed to a similar experiment. Partial exchange of the pentadienyl moieties gave not only **9g** but also **9f** and **10f**.[16] Also PDT **9f** similarly exchanged pentadienyl moieties with pentadienyllithium (**5g**) (entry 4). It thus could be demonstrated that PDTs do isomerize by redistribution to produce a mixture of products *strongly influenced by thermodynamic factors,* although the substituent and the counterion may vary the contribution of thermodynamic and kinetic factors.

Thermodynamic effects can also explain the phenomena mentioned in points 4 and 5 above. The decreased bulkiness of the substituent might possibly reduce the relative thermodynamic stability of (*Z*)-**9**, the substituent of which is trans to the terminal vinyl group. For example, when the substituent was a less bulky methyl group, the regioisomeric purity of the products was decreased by redistribution (entry 21, Table I; entries 3 and 4, Table II), which required an excess of anion. In contrast, the proportion of (*Z*)-**9f** was much increased (entry 22, Table I) when the anion was trapped under conditions where an excess of electrophile existed, i.e., when anion **6f** was added to Me$_3$SnBr ("inverse addition") to suppress the redistribution and to intensify the effect of the 1,5-shift of Me$_3$Sn.

The coordinative effects of nitrogen and oxygen atom (entries 11–14, Table I) contributed significantly not only to the anion structure but also to the product PDT distribution. In entries 11 and 13 (Li$^+$ as the counterion), *intramolecular coordination of the substituent to a Lewis acid* (the tin atom[17]) seemed to contribute to the high regioselectivity observed, because the 1,5-shift of Me$_3$Sn alone would result in the production of only 47–66% (estimated from entries 1 and 3, Table I) of (*Z*)-**9**. Moreover, **9b** was formed much more selectively than **9c**, which bears an *n*-propyl group incapable of coordination with the cation.

Conclusion. Thus, both kinetically controlled products (4-substituted-pentadienylsilanes (*E*)- and (*Z*)-**8**) and thermodynamically controlled products (2-substituted-pentadienyltins (*E*)- and (*Z*)-**9**) could be obtained with high selectivity (≥89%) by controlling anion conformation and synthetic procedures (entries 2, 4, 6, 8, 10, 11, 13, 18, 20, and 22, Table I). This marked contrast in behavior was striking because silicon and tin are both group 14 elements. In the former instance, steric and conformational effects in the anions controlled product selectivity. In the latter, the ease of isomerization of PDTs by way of a [1,5]-Me$_3$Sn shift and by redistribution largely affected selectivity. This behavior can be considered to arise from the differences in carbon–metal bond properties, such as bond energy and bond length.

The synthetic importance of the results should be stressed. Here described is what appears to be the first instance where a [1,5] metal shift (or fluxionality) of pentadienylmetals was utilized synthetically. It permitted the selective formation of (*Z*)-**9**. Furthermore, pentadienylmetal reagents of high isomeric purity should prove to be useful synthons for the introduction of a pentadienyl group into organic molecules. Some of such PDTs have already been applied in organic synthesis.[3f,g]

In summary, methodology for the selective synthesis of certain pentadienylmetal compounds has been provided. It may prove possible to apply this methodology in the synthesis of other pentadienylmetals.

Experimental Section

General. NMR spectra were recorded with JEOL JNM-PS100 and JNM-FX400 spectrometers. Chemical shifts are reported in ppm relative to Me$_4$Si (δ 0.00) or CHCl$_3$ (δ 7.26). Coupling constants (*J*) are reported in hertz. IR spectra were recorded with a JASCO IRA-1 spectrometer. UV spectra were recorded with a Shimadzu UV-160 spectrometer. Ultrasonic irradiation was applied with a Branson Model B-220 (output power: 100 W) instrument. Tetrahydrofuran (THF) was distilled from benzophenone ketyl and was stored over sodium wire. Hexane was distilled from phosphorus pentoxide and was stored over 4A molecular sieves. All other solvents were used after simple distillation. As a usual workup procedure, organic extracts were washed with water and brine and dried (MgSO$_4$), and the solvent was evaporated in vacuo.

Synthesis of 2-Substituted-1,4-pentadienes. 2-[(Dimethylamino)methyl]-1,4-pentadiene (4a). To a suspension of zinc powder (16.38 g, 0.25 mol) in THF (100 mL) containing a small amount of iodine was added allyl bromide (21.6 mL, 0.25 mol) drop-by-drop over 30 min under nitrogen with external ultrasonic irradiation. The resulting solution of allylzinc bromide was added drop-by-drop to a mixture of propargyl alcohol (5.8 mL, 0.1 mol), THF (50 mL), and 2 g of CuI under nitrogen with ultrasonic irradiation. After addition was complete, ultrasonic irradiation was continued for another hour, to afford a green suspension. The suspension was then cautiously poured into ice/water, and the solid was dissolved by addition of concentrated aqueous HCl. The two liquid layers were separated and the aqueous layer was extracted with ether. The combined organic layers were washed throughly with aqueous ammonia and then were subjected to the usual workup. The residue was distilled to give 2-(hydroxymethyl)-1,4-pentadiene (6.75 g, 68.8 mmol, 69%) as a colorless liquid: bp 57–60 °C (17 mmHg) [lit. bp 84 °C (25 mmHg),[18] 54–56 °C (12 mmHg)[19]]; ^{1}H NMR (CCl$_4$) δ 2.79 (d, 2 H, *J* = 7), 2.91 (s, 1 H), 3.99 (s, 2 H), 4.84–5.12 (m, 4 H), 5.80 (ddt, 1 H, *J* = 18, 10, 7); IR (neat) 3330, 3100, 3000, 2920, 1820, 1640 cm^{-1}.

To a solution of the dienol (2.08 g, 21.2 mmol) and pyridine (0.5 mL) in hexane (20 mL) was added PBr$_3$ (0.9 mL) in hexane (3 mL) drop-by-drop at −10 °C. After the mixture was stirred for 2 h, ice/water was added. After separation of the two liquid layers, the organic layer was washed with saturated aqueous NaHCO$_3$ and then was treated as usual to give 2-(bromomethyl)-1,4-pentadiene (2.29 g, 14.2 mmol, 67%).

A mixture of the bromide (1.61 g, 10 mmol), pentane (8 mL), and 50% aqueous Me$_2$NH (10 mL) was vigorously stirred for 1 h at 0 °C. After addition of 10% aqueous NaOH, the mixture was extracted with ether. The extract was dried (Na$_2$SO$_4$) and concentrated. The residue was distilled to give **4a** as a colorless liquid (0.670 g, 5.35 mmol, 54%): bp 73–76 °C (100 mmHg) (Kugelrohr); ^{1}H NMR (CCl$_4$) δ 2.12 (s, 6 H), 2.80 (br s, 2 H), 2.83 (br d, 2 H, *J* = 7), 4.87 (s, 1 H), 4.93 (s, 1 H), 5.07 (d, 1 H, *J* = 10), 5.09 (d, 1 H, *J* = 16), 5.84 (ddt, 1 H, *J* = 16, 10, 7); IR (neat) 3080, 2970, 2930, 2800, 2750, 2710, 1820, 1635 cm^{-1}.

2-(Methoxymethyl)-1,4-pentadiene (4b). To a suspension of powdered KOH (7.5 g) in dimethyl sulfoxide (DMSO, 20 mL)/dimethylformamide (DMF, 20 mL) were successively added 2-(hydroxymethyl)-1,4-pentadiene (2.94 g, 30 mmol) and methyl iodide (3 mL, 48 mmol) at −15 °C with vigorous stirring. After 1 h, the mixture was poured into ice/5% aqueous HCl and was extracted with pentane. The extract was worked up as used to afford **4b** as a colorless liquid (2.77 g, 24.7 mmol, 82%): bp 108–112 °C (Kugelrohr); ^{1}H NMR (CCl$_4$) δ 2.76 (d, 2 H, *J* = 7), 3.25 (s, 3 H), 3.78 (s, 2 H), 4.88–5.10 (m, 4 H), 5.80 (ddt, 1 H, *J* = 17, 9, 7); IR (neat) 3100, 3000, 2940, 2830, 1820, 1640 cm^{-1}.

2-*tert*-Butyl-1,4-pentadiene (4e). To a THF solution (50 mL) of lithium diisopropylamide [prepared from diisopropylamine (7.7 mL, 55 mmol) and *n*-BuLi (1.4 M in hexane, 35.7 mL, 50 mmol)]

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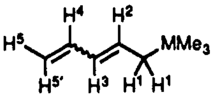
[16] The redistribution seems to occur in a manner similar to the metal exchange between an organotin compound and an alkyllithium. See: Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths; London, 1987; Chapter 9 and references cited therein.

[17] For recent examples, see: Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Siro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606–4610, and references cited therein.

[18] Duboudin, J. G.; Jousseaume, B. *J. Organomet. Chem.* **1979**, *168*, 1–11.

[19] Frangin, Y.; Gaudemar, M. *J. Organomet. Chem.* **1977**, *142*, 9–22.

Table IV. NMR Data of Pentadienylsilanes and -tins[a]



(*E*)-7	R	MMe_3	H^1	H^2	H^3	H^4	H^5	$H^{5'}$	R	
a	CH_2NMe_2		1.78	–	5.95 (10.1)	6.59 (16.5, 10.5)	5.04 (10.6, 1.5)	5.14 (16.5, 1.5)	2.16 (6 H)	2.81 (2 H)
b	CH_2OMe			–		6.62 (16.8, 11.0)				
c	$(CH_2)_2Me$			–		6.56 (16.8, 11.0)				
e	CMe_3			–		6.57				
g	H[c]	0.00	1.51 (8.8)	5.69 (15.1, 8.8)	5.91 (15.1, 10.3)	6.28 (16.9, 10.3, 10.3)	4.84 (10.3, 1.8)	4.98 (16.9, 1.8)	–	

(*Z*)-7	R	MMe_3	H^1	H^2	H^3	H^4	H^5	$H^{5'}$	R	
a	CH_2NMe_2		1.78	–	5.88 (10.5)	6.47 (16.5, 10.5)	4.95 (10.5, 1.5)	5.07 (16.5, 1.5)	2.15 (6 H)	2.75 (2 H)
b	CH_2OMe	0.01	1.70	–	5.98 (11.0)	6.48 (16.8, 11.0, 10.4)	5.02 (10.4, 1.8)	5.13 (16.8, 1.8)	3.29 (3 H)	3.81 (2 H)
c	$(CH_2)_2Me$		1.68	–	5.77 (11.0)	6.45 (16.8, 11.0, 10.4)	4.88 (10.4, 1.8)	5.01 (16.8, 1.8)	1.97 (2 H, t, 7.3)	
d	$CHMe_2$		1.71	–	5.78 (11.0)	6.45 (16.8, 11.0, 10.1)	4.89 (10.1, 2.1)	5.02 (16.8, 2.1)	1.04 (6 H, d, 7.0)	2.09 (1 H, septet, 7.0)
e	CMe_3			–		6.43				
g	H[c]	0.00	1.64 (9.9)	5.49 (10.3, 9.9)	5.92 (10.3, 10.2)	6.57 (16.9, 10.3, 10.2)	5.00 (10.3, 1.8)	5.11 (16.9, 1.8)	–	

(*E*)-8	R	MMe_3	H^1	H^2	H^3	H^5		R		
a	CH_2NMe_2		1.52 (7.0)	5.94 (15.8, 7.0)	5.88 (15.8)	4.88	4.93 (2.1)	2.96 (2 H)		
b	CH_2OMe	0.03	1.53 (7.9)	5.81 (16.2, 7.9)	5.91 (16.2)	4.96	4.99	3.31 (3 H)	4.05 (2 H)	
c	$(CH_2)_2Me$	0.01	1.53 (8.2)	5.70 (15.7, 8.2)	5.91 (15.7)	4.75	4.80 (2.1)	0.92 (3 H, t, 7.6)	1.49 (2 H, m)	2.15 (2 H, t, 7.6)
d	$CHMe_2$	0.01	1.53 (7.9)	5.74 (15.9, 7.9)	5.86 (15.9)	4.74	4.78	1.07 (6 H, d, 6.7)	2.54 (1 H, septet, 6.7)	
e	CMe_3	0.02	1.52 (7.3)	5.84 (15.0, 7.3)	5.91 (15.0)	4.66	4.89	1.07 (9 H)		

(*Z*)-8	R	MMe_3	H^1	H^2	H^3	H^5		R		
a	CH_2NMe_2	0.03	1.77 (8.9, 1.5)	5.60 (11.9, 8.9)	5.75 (11.9, 1.2)	5.01	5.09	2.17 (6 H)	2.87 (2 H)	
b	CH_2OMe	0.03	1.75 (8.9, 1.2)	5.59 (11.6, 8.9)	5.71 (11.6, 1.2)	5.07	5.18	3.32 (3 H)	3.91 (2 H)	
c	$(CH_2)_2Me$	0.03	1.73 (8.9, 1.5)	5.50 (11.6, 8.9)	5.68 (11.6, 1.5)	4.86	4.92	0.89 (3 H, t, 6.7)	1.44 (2 H, sextet, 6.7)	2.06 (2 H, t, 6.7)
d	$CHMe_2$	0.02	1.70 (8.9, 1.5)	5.55 (11.6, 8.9)	5.73 (11.6, 1.5)	4.79	4.92	1.02 (6 H, d, 6.7)	2.28 (1 H, septet, 6.7)	
e	CMe_3	0.03	1.66 (8.5, 1.5)	5.56 (11.6, 8.5)	5.92 (11.6, 1.5)	4.73	5.00	1.06 (9 H)		

(*E*)-9	R	MMe_3	H^1	H^2	H^3	H^4	H^5	$H^{5'}$	R	
a	CH_2NMe_2			–		6.59 (16.8, 11.0)			2.81	
b	CH_2OMe	0.09	1.85	–	5.84 (11.3)	6.57 (16.8, 11.3, 10.4)	4.88 (10.4)	5.01 (16.8)	3.27 (3 H)	3.95 (2 H)
c	$(CH_2)_2Me$	0.10		–	5.73 (11.3)	6.54 (16.8, 11.3, 9.8)	4.80 (9.8, 2.1)	4.94 (16.8, 2.1)		
d	$CHMe_2$	0.10		–		6.56 (16.8, 11.0)				
e	CMe_3		1.78	–		6.61 (16.8, 10.5)				
f	Me	0.10	1.83	–	5.73 (11)	6.52 (16, 11, 10)	4.81 (10)	4.95 (16)	1.72 (3 H; 14[b])	
g	H[d]	0.11 (51.0, 53.4)[b]	1.81 (7.6; 68[b])	5.84 (15.0, 7.6)	5.91 (15.0, 9.2)	6.28 (17.1, 10.1, 9.2)	4.79 (10.1, 1.8)	4.94 (17.1, 1.8)	–	

(*Z*)-9	R	MMe_3	H^1	H^2	H^3	H^4	H^5	$H^{5'}$	R		
a	CH_2NMe_2	0.09 (53.4, 51.0)[b]	1.98 (70)[b]	–	5.75 (11.0)	6.49 (16.8, 11.0, 10.4)	4.94 (10.4, 2.1)	5.06 (16.8, 2.1)	2.15 (6 H)	2.70 (2 H; 10.4[b])	
b	CH_2OMe	0.09 (53.4, 51.0)[b]	1.91 (68)[b]	–	5.83 (10.5)	6.47 (16.4, 10.5, 10.2)	4.99 (10.2, 2.0)	5.11 (16.4, 2.0)	3.28 (3 H)	3.77 (2 H; 11[b])	
c	$(CH_2)_2Me$	0.10 (53.1, 50.7)[b]	1.91 (69)[b]	–	5.63 (11.0)	6.44 (16.8, 11.0, 10.1)	4.85 (10.1, 2.1)	4.98 (16.8, 2.1)	0.90 (3 H, t, 7.3)	1.47 (2 H, sextet, 7.3)	1.93 (2 H, t, 6.7)
d	$CHMe_2$	0.10 (53.1, 50.7)[b]	1.91 (70)[b]	–	5.68 (11.0)	6.44 (16.8, 11.0, 10.1)	4.88 (10.1, 2.1)	5.01 (16.8, 2.1)	1.03 (6 H, d, 6.7)	2.13 (1 H, septet, 6.7)	
e	CMe_3	0.11 (52.5, 50.1)[b]	1.94 (71, 68)[b]	–	5.77 (11.0)	6.38 (16.8, 10.7, 10.4)	4.93 (10.4, 2.1)	5.05 (16.8, 2.1)	1.07 (9 H)		
f	Me	0.11 (53.4, 51.0)[b]	1.91 (69)[b]	–	5.64 (11.0)	6.45 (16.8, 11.0, 10.4)	4.84 (10.4, 2.1)	4.98 (16.8, 2.1)	1.72 (3 H; 14[b])		
g	H[d]	0.12 (53.4, 50.9)[b]	1.92 (9.5; 68[b])	5.64 (10.7, 9.5)	5.79 (11.0, 10.7)	6.58 (15.9, 11.0, 10.4)	4.96 (10.4, 2.4)	5.08 (15.9, 2.4)	–		

(*E*)-10	R	MMe_3	H^1	H^2	H^3	H^5		R	
a	CH_2NMe_2	0.09		6.10 (15.3, 9)	5.88 (15.3)			2.94 (2 H)	
b	CH_2OMe	0.09 (53)[b]	1.81 (8.5; 67[b])	5.98 (15.6, 8.5)	5.88 (15.6)	4.92	4.93	3.30 (3 H)	4.03 (2 H)
c	$(CH_2)_2Me$	0.10	1.80 (7.3)	5.85 (15.3, 7.3)	5.90 (15.3)	4.70	4.75 (2.1)	2.13 (2 H, t, 7.3)	

Table IV (Continued)

(*E*)-10	R	MMe_3	H^1	H^2	H^3	H^5		R
d	$CHMe_2$	0.10	1.83 (7.0)	5.92 (15.1, 7.0)	5.85 (15.1)	4.70	4.75 (2.1)	1.06 (6 H, d, 7.0)
e	CMe_3	0.11	1.81 (8.5)	6.01 (15.9, 8.5)	5.87 (15.9)	4.62 (2.1)	4.87	1.08 (9 H)
f	Me		1.82 (7.4)	5.81 (15, 7)	6.00 (15)	4.73	4.71	1.80 (3 H)

[a] Chemical shifts and coupling constants (in parentheses) were those of an isomeric mixture in $CDCl_3$ solution. A blank space means that the value could not be determined due to overlap of signals. [b] The Sn, H coupling constant. [c] Value cited in ref 3i. [d] Value cited in ref 3b.

was added methyl 3,3-dimethylbutyrate (7.4 mL, 50 mmol) drop-by-drop at −78 °C under nitrogen with stirring. After 1 h, a mixture of allyl bromide (4.8 mL, 55 mmol) and hexamethylphosphoramide (HMPA, 2.9 mL, 15 mmol)[20] was added at −78 °C. The solution was stirred for an additional 2 h, then was poured into water, and extracted with ether. The extract was treated as usual, after first washing with diluted aqueous HCl, to afford methyl 2-*tert*-butyl-4-pentenoate.

A THF solution (20 mL) of the ester was added drop-by-drop to a suspension of $LiAlH_4$ (1.5 g, 39.5 mmol) and THF (20 mL) at 0 °C under nitrogen. After overnight stirring, the mixture was added to ice/water, and the resulting precipitate was decomposed with concentrated aqueous HCl. After extraction with ether, the organic layer was worked up as usual to give the alcohol.

The alcohol was transformed to the *p*-toluenesulfonate with pyridine (8.1 mL) and *p*-toluenesulfonyl chloride (14.25 g, 75 mmol) in $CHCl_3$ (50 mL) at 0 °C.[21]

A DMF solution (30 mL) of the sulfonate (13.08 g, 44.1 mmol) was added to a suspension of NaI (16.52 g) and DMF (60 mL). The suspension was stirred for 5 h at 55 °C. Then, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 9.2 mL) was added and stirring was continued for 3 h at 85 °C.[22] The mixture was then poured into water and was extracted with pentane. The extract was washed (diluted aqueous HCl and saturated aqueous $NaHCO_3$) and was then treated as usual. Most of the pentane was removed by fractional distillation at atmospheric pressure. Residual pentane was evaporated under reduced pressure. Distillation gave 3.91 g (31.5 mmol, 63% from methyl dimethylbutyrate) of **4e**: bp 114–118 °C (Kugelrohr); ^1H NMR (CCl_4) δ 1.08 (s, 9 H), 2.79 (br d, 2 H, J = 7), 4.65 (br s, 1 H), 4.85 (s, 1 H), 4.91–5.03 (m, 2 H), 5.77 (ddt, 1 H, J = 17, 9, 7); IR (neat) 3080, 2960, 2900, 2860, 1820, 1640 cm^{-1}.

2-*n*-Propyl-1,4-pentadiene (4c) was prepared in 33% yield from methyl valerate (50 mmol) in a manner similar to that for **4e**: bp 106–110 °C (Kugelrohr); ^1H NMR (CCl_4) δ 1.00 (t, 3 H, J = 7), 1.51 (sextet, 2 H, J = 7), 1.96 (br t, 2 H, J = 7), 2.81 (br d, 2 H, J = 6), 4.56 (m, 2 H), 5.01–5.16 (m, 2 H), 5.77 (ddt, 1 H, J = 15, 8, 6); IR (neat) 3080, 2950, 2920, 2860, 1820, 1640 cm^{-1}.

2-Isopropyl-1,4-pentadiene (4d) was prepared in 41% yield from methyl isovalerate (50 mmol) in a manner similar to that for **4e**: bp 103–106 °C (Kugelrohr); ^1H NMR (CCl_4) δ 0.97 (d, 6 H, J = 7), 2.34 (septet, 1 H, J = 7), 2.83 (br d, 2 H, J = 7), 4.73 (m, 1 H), 4.82 (br s, 1 H), 5.03–5.17 (m, 2 H), 5.85 (ddt, 1 H, J = 16, 8.5, 7); IR (neat) 3090, 2960, 2920, 2870, 1820, 1640 cm^{-1}.

Preparation of Pentadienyllithiums 5a–e and Their Trap by Me_3SiCl or Me_3SnBr. Normal Addition. To a THF solution (5 mL) of 1,4-pentadiene (**4**; 1 mmol) was added *n*-BuLi (1.4 M in hexane, 0.75 mL) at −78 °C under nitrogen. The stirred mixture was warmed gradually to 0 °C over 1 h. A deep red color developed. The solution was cooled again to −78 °C, and Me_3SiCl or Me_3SnBr (1 mmol) in THF (1 mL) was added. The red color disappeared immediately. After 30 min, the reaction mixture was quenched with water. Extraction with ether and the usual workup followed. The product mixture was analyzed by ^1H NMR to determine the product ratio and the yield. 1,2-Dichloroethane or benzene was used in as the internal standard.

NMR data for compounds **7–10** are summarized in Table IV.

Preparation of Pentadienylpotassiums 6a–e. To a suspension of *t*-BuOK (112 mg, 1 mmol) in hexane (or pentane) was added *n*-BuLi (1.4 M in hexane, 0.75 mL) at 0 °C under nitrogen. The 1,4-pentadiene (**4**, 1 mmol) was added to the mixture after 5 min at 0 °C. A brownish yellow precipitate soon formed. The solvent was evaporated under reduced pressure. After dry nitrogen was introduced into the reaction vessel, THF (5 mL) was added to dissolve the precipitated solid. The resulting deep red solution was cooled to −78 °C. Silylation or stannylation and product analysis were then performed as described above.

Inverse Addition. A solution of anion **5** or **6**, prepared as described above, was cooled to −78 °C and was added to a cold (−78 °C) solution of Me_3SnBr (1.2 mmol) in THF (3 mL) under nitrogen by cannula. Workup and product analysis were performed as before.

Redistribution Reaction. The redistribution by **6f** is typical. Thus, to a THF solution (5 mL) of (2-methylpentadienyl)potassium (**6f**) [prepared from a mixture of 2- and 4-methyl-1,3-pentadienes[23] (1 mmol) and a mixture of *n*-BuLi (1 mmol) and *t*-BuOK (1 mmol), in a manner similar to the preparation of **6a–e**] was added a silane (**7g**) or stannane (**9f** or **9g**) (1 mmol) at −78 °C under nitrogen. After 1 h of stirring at −78 °C, the reaction mixture was worked up as described above. The product ratio was determined by ^1H NMR.

Enrichment of 2-Substituted-PDT. The enrichment of **9f** was typical. Thus, a mixture of **9f** and **10f** [(*Z*)-**9f**:(*E*)-**9f**:(*E*)-**10f** = 56:14:30] (3.16 g, 12.9 mmol), prepared by the normal addition method, was stirred with maleic anhydride (1.26 g, 12.9 mmol) and ether (25 mL) at 0 °C for 2 h. Forty milliliters of 10% aqueous NaOH was added, and the mixture was shaken vigorously for 1 h at 0 °C. After separation of the two liquid layers, the organic layer was treated as usual to give **9f** (8.90 mmol, 69%) of high regioisomeric purity [(*Z*)-**9f**:(*E*)-**9f**:(*E*)-**10f** = 79:18:3]: bp 90 °C (17 mmHg) (Kugelrohr). In a similar manner, **9b** and **9d** were enriched. **9b**: bp 110–115 °C (20 mmHg) (Kugelrohr). **9d**: bp 51 °C (0.6 mmHg).

[(Methoxymethyl)pentadienyl]tins 9b and 10b were separated by careful preparative TLC on silica gel (hexane containing 0.2–0.5% of diethyl ether) into three regio- and stereoisomers, (*E*)-**9b**, (*Z*)-**9b**, and (*E*)-**10b**. (The R_f values of the compounds decreased in that order.)

Supplementary Material Available: ^1H NMR spectra of compounds **4** and **7–10** (17 pages). Ordering information is given on any current masthead page.

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[23] The methylpentadiene mixture was prepared by the distillation of 2-methyl-2,4-pentanediol in the presence of a catalytic amount of HBr.[15b]