# Pentadienyl Type Lithium and Potassium Species: The Regioselectivity of their Reactions with Electrophiles

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**Abstract:** Seven structurally distinct pentadienyl type lithium and potassium compounds were screened against a variety of electrophiles in order to assess the regioselectivity of the trapping reactions. Organoborates and analogs thereof (fluorodimethoxyborane) proved to be perfectly regioreliable attacking only unsubstituted terminal positions and thus providing, after oxidation, exclusively primary allylic alcohols. 2,4-Pentadienyllithiums or -potassiums, that carry a methyl group at the 1- or 3-position, exhibit the same extreme regioselectivity towards halotrialkylsilanes or carbon dioxide. Although the unsubstituted parent compounds combine with such electrophiles still preferentially at the terminal position, considerable proportions of branched products are concomitantly formed as well (1/3-attack ratios ranging from 2:1 to > 20:1). Hydroxyalkylating and alkylating reagents such as formaldehyde, oxirane or butyl iodide invariably afford regioisomeric mixtures generally varying in composition between 3:1 and 1:3. The condensation reaction with halotrialkylsilanes appears to follow a concerted ($S_N2$-like) rather than an addition/elimination (ate complex-mediated) mechanism.

**Key words:** diene metalation, superbase chemistry, organometallic mobility, regioselectivity, stereoselectivity

The fascinating stereopreferences and stereodynamics of pentadienyl-type organometallics have been reviewed some years ago.[1] Fundamental facts shall nevertheless be briefly summarized. Whereas 2,4-pentadienyllithium[2] in tetrahydrofuran and 2,4-pentadienylpotassium in liquid ammonia[3] or in paraffinic suspension[4] adopt the zigzag-like outstretched "*W*-form", 2,4-pentadienylpotassium coils up to produce the horseshoe-like "*U*-form" when dissolved in tetrahydrofuran.[5,6] The conformational population of pentadienyls carrying a primary alkyl chain at the 1-position again depends on the nature of the metal and the solvent.[7] In contrast, all 3-methyl-2,4-pentadienyls[4,8] exist in the "*W*-shape" and all 2,4-dimethyl-2,4-pentadienyl[4] in the "*U*-shape" regardless whether combined with lithium or potassium and dissolved in tetrahydrofuran or suspended in hexanes. The third privileged structure, the equally coplanar and hence again optimally resonance-stabilized "*S*-form" has so far been identified only in mobility-restricted cyclic structures.[9,10]

The principal features of the scenario thus being known, numerous details remain to be elucidated. In view of their immense practical importance, the following issues will now be addressed specifically:

- How *regioselectively* do 2,4-pentadienylmetals and 3-methyl-2,4-pentadienylmetals react with a wide variety of electrophiles?
- How *stereoselectively* can the metalation of (*Z*)- and (*E*)-1,4-hexadiene and 2,6-dimethyl-2,5-heptadiene be accomplished?

The stereopreferences of pentadienyl-type organometallics were probed either by NMR spectroscopy[2,3,6,8] or by correlation of the stereocomposition of the reactive intermediates with that of their final, isolable products.[4,5,7,9,10] The latter approach relies on the availability of "well-behaved" electrophiles, such as silanes or boranes, which attack preferentially or exclusively terminal positions of the delocalized area. If, on the contrary, the electrophile becomes attached to the central carbon atom, most if not all stereochemical information inherent in the organometallic intermediate gets lost. Therefore, virtually all trapping studies performed so far employed either chlorotrimethylsilane or fluorodimethoxyborane,[11,12] both electrophiles being reputed to exhibit the required regioselectivity.

As a more systematic investigation has now revealed, the latter assumption is only partially fulfilled. Whereas all halotrialkylsilanes investigated reacted with 2,4-pentadienylpotassium, if suspended in hexanes, almost exclusively at the terminal positions and the 3-substituted isomer was formed only in traces (≤3%), the amount of the latter increased significantly (to 11–44%) whenever tetrahydrofuran was used as the solvent. Carbon dioxide, formaldehyde, oxirane and ethylene sulfate afforded regioisomeric mixtures (**1**, **2**, see Scheme 1) in all solvents (Table 1). In contrast, fluorodimethoxyborane[11,12] and 2-methoxy-1,3,2-dioxa-borolane[13,14] gave only primary derivatives (*Z*-**1** or *E*-**1**) regardless of the reaction medium (Table 1).

A substituent at the 3-position as present in 3-methyl-1,4-pentadienylmetals tends to hinder the approach of an electrophile. After deprotonation of the hydrocarbon precursor with butyllithium in the presence of potassium *tert*-butoxide ("LIC-KOR") in tetrahydrofuran and subsequent interception with silanes or boranes, only the end-on products **3** were found (Scheme 2, Table 2). When oxirane or 1-iodobutane served as the trapping reagents, both the chain-lengthened and the doubly branched regioisomers,

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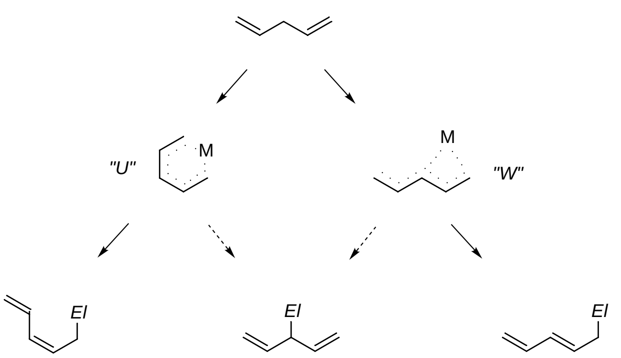


**Z-1** **2** **E-1**

**a** : *El* = Si(CH$_3$)$_3$; **b** : *El* = Si(C$_2$H$_5$)$_3$; **c** : *El* = Si($^i$C$_3$H$_7$)$_3$**d** : *El* = OH;
**e** : *El* = B(OR)$_2$; **f** : *El* = COOH; **g** : *El* = CH$_2$OH; **h** : *El* = CH$_2$CH$_2$OH.

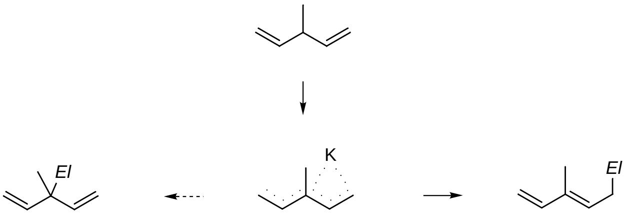
**Scheme 1**

**Table 1** Reaction of 2,4-Pentadienylpotassium in Petroleum Ether and in THF with a Variety of Electrophiles *El*-X: Yields of Trapping Products, γ/α-Ratios of Regioisomers **2** *vs.* **1** and *Z/E*-Composition of Isomers **1**

| Cpd | *El*-X | In PET[a] | | | In THF[b] | | |
|---|---|---|---|---|---|---|---|
| | | Yield (%) | γ/α Ratio | *Z/E* Ratio | Yield (%) | γ/α Ratio | *Z/E* Ratio |
| **a** | $ISi(CH_3)_3$ | 95 | 3:97 | 2:98 | 95 | 46:54 | 98:2 |
| **a** | $BrSi(CH_3)_3$ | 95 | 3:97 | 2:98 | 96 | 41:59 | 98:2 |
| **a** | $ClSi(CH_3)_3$ | 95 | 3:97 | 2:98 | 98 | 24:76 | 98:2[c] |
| **a** | $FSi(CH_3)_3$ | 88 | <1:99 | 5:95 | 95 | 16:84 | 94:6 |
| **b** | $ClSi(C_2H_5)_3$ | 85 | 4:96 | 2:98 | 95 | 15:85 | 98:2 |
| **c** | $ClSi(^iC_3H_7)_3$ | 33 | <1:99 | 11:89 | 97 | <1:99 | 80:20 |
| **d** | $FB(OCH_3)_2$[d] | 43 | <1:99 | 2:98 | 54 | <1:99 | 93:7 |
| **e** | $H_3COB(OR)_2$[e] | 67 | <1:99 | 9:91 | 54 | <1:99 | 95:5 |
| **f** | $CO_2$[f] | 49 | 12:88 | 4:96 | 71 | 38:62 | 98:2 |
| **g** | $OCH_2$[f,g,h,i] | - | - | - | 54 | 50:50 | 97:3 |
| **h** | $O(CH_2)_2$[f,i,j] | 64 | 52:48 | 9:91 | 65 | 91:9 | 98:2[k] |

[a] PET = petroleum ether (in general, hexanes).
[b] THF = tetrahydrofuran.
[c] When the metalation was carried out with *sec*-butyllithium at –75 °C in the absence of potassium *tert*-butoxide, 93% of products were formed in a γ/α-ratio of 12:88 and a *Z/E*-ratio of 5:95.
[d] After the immediately ensuing treatment with alkaline hydrogen peroxide the allyl alcohol was isolated.
[e] B(OR)$_2$ = 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl).
[f] Followed by neutralization at 0 °C.
[g] Formaldehyde as a 0.8 M solution in THF.[15,16,]
[h] When the metalation was carried out with *sec*-butyllithium at –75 °C in the absence of potassium *tert*-butoxide, 42% of products were formed in a γ/α-ratio of 69:31 and a *Z/E*-ratio of 5:95.
[i] The branched γ-product underwent partial isomerization to its conjugated isomer (see Ref.[17]).
[j] O(CH$_2$)$_2$ = oxirane.
[k] Ethylene sulfate (1,3,2-dioxathiolane 2,2-dioxide) instead of oxirane.

**3** and **4**, were obtained (Table 2). The configuration of the end-on products **3** was invariably *E*.



**4** "W" ***E*-3**

**a** : *El* = Si(CH$_3$)$_3$; **b** : *El* = Si(C$_2$H$_5$)$_3$; **d** : *El* = OH; **e** : *El* = B(OR)$_2$;
**f** : *El* = COOH; **h** : *El* = CH$_2$CH$_2$OH; **i** : *El* = C$_4$H$_9$.

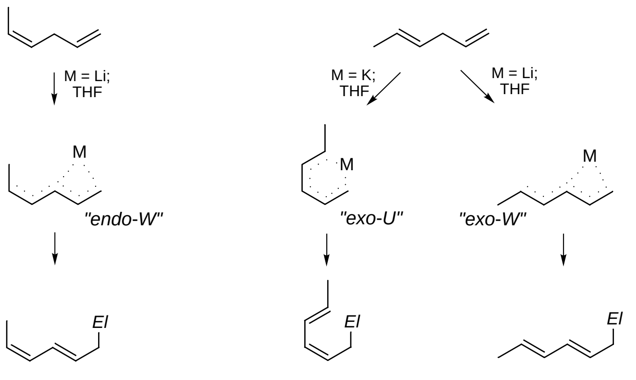
**Scheme 2**

**Table 2** Reaction of 3-Methyl-2,4-pentadienylpotassium in THF with a Series of Electrophiles: Yields of Trapping Products, γ/α-Ratios of Regioisomers **4** *vs.* **3** and *Z/E*-Composition of Isomers **3**

| Compd | *El*-X | Yield (%) | γ/α | (*Z/E*)-**3** |
|---|---|---|---|---|
| **a** | $ClSi(CH_3)_3$ | 86 | <1:99 | >97:3 |
| **b** | $ClSi(C_2H_5)_3$ | 83 | <1:99 | >97:3 |
| **d** | $FB(OCH_3)_2$[a] | 52 | <1:99 | >97:3 |
| **c** | $H_3COB(OR)_2$[b] | 63 | <1:99 | >97:3 |
| **f** | $CO_2$[c] | 73 | <1:99 | >97:3 |
| **h** | $O(CH_2)_2$[c,d] | 73 | 64:36 | >97:3 |
| **i** | $IC_4H_9$ | 67 | 54:46 | >97:3 |

[a] After treatment of the initially formed boronate with alkaline hydrogen peroxide the allyl alcohol was isolated.
[b] B(OR)$_2$ = 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl).
[c] Followed by neutralization at 0 °C.
[d] O(CH$_2$)$_2$ = oxirane.

The 1,4-pentadiene derived products **1** were *trans*-isomers when prepared in petroleum ether and *cis*-isomers when prepared in tetrahydrofuran (Table 1). The 3-methyl-1,4-pentadiene derived products **3** had invariably the *E*-configuration (Table 2). We wanted to include in the present study also “5-methyl-2,4-pentadienylmetals” (2,4-hexadienylmetals) which we expected to show, qualitatively at least, the same stereochemical dynamics and preferences as already reported for 2,4-decadienylmetals.[7] This was indeed found to be the case. For well intelligible reasons,[7,18] the internal double bond retained the configuration inherited from its hydrocarbon precursor and the organometallic intermediate generated upon deprotonation with *sec*-butyllithium adopted the “*W*-form”. However, after the interception with standard electrophiles, some 2*Z*,4*Z*-isomer (2*Z*,4*Z*-**5**) was inevitably isolated along with the 2*E*,4*Z*-isomer (2*E*,4*Z*-**5**) in an approximate ratio of 1:12 (Table 3). Since admixtures of the sterically unrealistic “*U*-form” can be ruled out, there must have occurred some leakage to the “*S*-form”. The coexistence of “*S*-forms” offers also the most plausible explanation of why *trans*-1,4-hexadiene after metalation with “LIC-KOR” did not provide the pure 2(*Z*,4*E*)-isomer (2*Z*,4*E*-**5**, *via* the *U*-shaped intermediate) nor after metalation with *sec*-butyllithium, again in tetrahydrofuran, the pure 2*E*,4*E*-isomer (2*E*,4*E*-**5**, *via* the *W*-shaped intermediate) but mutually stereocontaminated materials in approximate ratios of 7:1 and 12:1, respectively (Scheme 3, Table 3).



**2*E*,4*Z*-5** **2*Z*,4*E*-5** **2*E*,4*E*-5**

**a** : *El* = Si(CH$_3$)$_3$; **d** : *El* = OH; **e** : *El* = B(OR)$_2$; **f** : *El* =COOH.

**Scheme 3**

**Table 3** Consecutive Reaction of *cis*- or *trans*-1,4-Hexadiene with Various Metalating Reagents (“rg.”) and Various Electrophiles (*El*-X): Yields and 2*Z*,4*Z*/2*E*,4*Z*- or 2*Z*,4*E*/2*E*,4*E*-Product Ratios Depending on Whether the *cis*-Diene or the *trans*-Diene Served as the Precursor

| Cpd | *El*-X | *cis*-Diene rg.: LIS[a] | | *trans*-Diene rg.: LIC-KOR[b] | | rg.: LIS[a] | |
|---|---|---|---|---|---|---|---|
| | | Yield (%) | Product Ratio | Yield (%) | Product Ratio | Yield (%) | Product Ratio |
| **a** | ClSi(CH$_3$) $_3$ | 59 | 10:90 | 72 | 91:9 | 57 | 12:88 |
| **d** | FB(OCH$_3$)$_2$[c] | 41 | 9:91 | 53 | 92:8 | 45 | 12:88 |
| **e** | H$_3$COB(OR)$_2$[d] | 60 | 8:92 | 63 | 96:4 | 65 | 18:82 |
| **f** | CO$_2$[e] | 18 | 6:94 | 16 | 92:8 | 17 | 16:84 |

[a] LIS = *sec*-butyllithium.

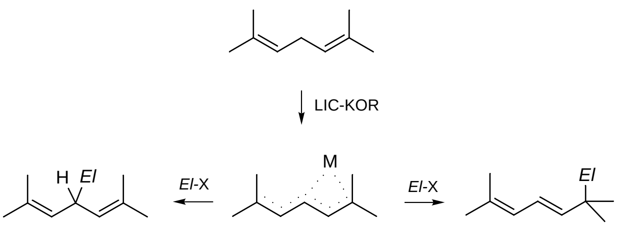
[b] LIC-KOR = “superbasic” 1:1 mixture of butyllithium (“LIC”) and tassium *tert*-butoxide (“KOR”).

[c] After the immediately ensuing treatment with alkaline hydrogen per ide the allyl alcohol was isolated.

[d] B(OR)$_2$ = 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl).

[e] After neutralization at 0 °C, the carboxylic acid was obtained.

The metalation of 5-methyl-1,4-hexadiene with *sec*-butyllithium or superbasic mixed metal reagent followed by treatment with chlorotrimethylsilane invariably produced stereomixtures suggesting the coexistence of a “*W*-conformer” and an “*S*-conformer”.[19] On the contrary, a neat “*W*-structure” can be attributed to the organometallic species generated by metalation of 2,6-dimethyl-2,5-heptadiene with “LIC-KOR” in tetrahydrofuran. Although its condensation with chlorotrimethylsilane mainly takes place at the 4-position (51% of isomer **6**) and only to a small extent (6%) at the 2-position, the exclusive *trans*-configuration of the latter isomer **7** has been unequivocally established (Scheme 4).



**6** *"W"* ***E*-7**

**Scheme 4**

To our knowledge, fluorotrimethylsilane (see Table 1) has never been used before as a trapping agent for polar organometallic species. It proved to be far less reactive than the heavier halotrimethylsilanes. For example, when chlorotrimethylsilane was added to a solution of 2,4-pentadienylpotassium in tetrahydrofuran kept at –75 °C, the characteristic red color disappeared in the course of a few seconds while a steep temperature rise indicated an exothermal process. In contrast, fluorotrimethylsilane was found to be inert at –75 °C and to react only slowly at –50 °C. Judging on this basis, the relative chloride/fluoride rates $k_{Cl}/k_F$ must be situated between 10 and 100, thus falling in the same range which is typical for bimolecular nucleophilic substitutions ($S_N2$).[20,21] In contrast, one would expect to encounter reversed ratios if a nucleophilic addition/nucleofugal elimination mechanism featuring an ate complex[22,23] intermediate were operative. 4-Fluoronitrobenzene undergoes irreversible nucleophilic aromatic substitutions up to 400 times faster than the chloro analog does.[24–26]

For laboratory routine and abbreviations, see previous publications emanating from this laboratory (e.g., Ref.[27]). $^1$H NMR spectra were recorded of solutions in CDCl$_3$ at 400 MHz.

Starting Materials and Reagents: 1,4-Pentadiene, 3-methyl-1,4-pentadiene and *cis*-1,4-hexadiene are commercial. *trans*-1,4-Hexadiene[28] and 2,7-dimethyl-2,6-heptadiene[29] were prepared according to literature procedures. The same holds for the reagents fluorodimethoxyborane[11,12] and 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and the solution of formaldehyde in tetrahydrofuran.[15,16]

### Metalation and Trapping Reactions; General Procedures

a) At 0 °C, BuLi (25 mmol) in hexanes (15 mL) and the diene (25 mmol) were added to a suspension of potassium *tert*-butoxide (2.8 g, 25 mmol) in hexanes (25 mL). After 20 min of vigorous stirring at 0 °C, the electrophile (25 mmol) was added to the mixture at –75 °C or the latter was poured onto an excess of freshly crushed dry ice. If the reagent was a trialkylhalosilane or 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, the precipitate formed was removed by filtration or centrifugation and the product isolated by distillation. The alcoholates and carboxylates obtained in reactions with formaldehyde, oxirane or carbon dioxide were neutralized with a slight excess of HCl in $Et_2O$[24] before the workup continued as described above. The dimethyl boronates resulting from the treatment with fluorodimethoxyborane were oxidized with 35% aq $H_2O_2$ in alkaline medium[11] to afford allylic alcohols, which were extracted with $Et_2O$ and distilled. The composition of crude reaction mixtures was always checked by gas chromatography using calibrated reference compounds ("internal standards") for the assessment of yields. To make acids more volatile, they had beforehand been converted into their methyl esters by exhaustive treatment with ethereal diazomethane.

b) If the reaction between the dienyl type organopotassium compound and the electrophilic reagent was to be performed in homogeneous solution, the metalation was carried out as described in the preceding paragraph. Then the hexanes were stripped off under reduced presure. At 75 °C, precooled THF (125 mL) was added, followed 20 min later, still at –75 °C, by the electrophile.

c) If the organolithium derivative was to be generated in THF, the hydrocarbon (25 mmol) was dissolved in this solvent (125 mL) and was treated with *sec*-BuLi (25 mmol) for 1 h at –50 °C. The electrophile (25 mmol) was added at –75 °C.

### Products Derived from 1,4-Pentadiene

(*Z*)- and (*E*)-Trimethyl-2,4-pentadienylsilane (*Z*- and *E*-**1a**),[30] trimethyl-(1-vinyl-2-propenyl)silane (**2a**),[31] (*Z*)[32]- and (*E*)[33]-2,4-pentadien-1-ol (*Z*- and *E*-**1e**), (Z)[34]- and (*E*)[35]-3,5-hexadien-1-ol (*Z*- and *E*-**1g**), 2-vinyl-3-buten-1-ol (**2g**),[36] (*Z*)[37]- and (*E*)[38]-4,6-heptadien-1-ol (*Z*- and *E*-**1h**), 3-vinyl-4-penten-1-ol[37,39] and methyl (*E*)-3,5-hexadienoate[40] (**2h**) have been reported previously.

### (*Z*)-Triethyl-2,4-pentadienylsilane (*Z*-1b)

Purified by preparative gas chromatography (2 m, 10% SE-30, 125 °C); bp 90–91 °C/12 mmHg; $n_D^{20}$ 1.4786.

$^1$H NMR: δ = 6.63 (1 H, ddd, *J* = 16.9, 11.0, 10.4 Hz), 5.93 (1 H, t, *J* = 10.8 Hz), 5.52 (1 H, q, *J* = 9.4 Hz), 5.13 (1 H, d, *J* = 16.5 Hz), 5.03 (1 H, d, *J* = 9.7 Hz), 1.69 (2 H, d, *J* = 8.9 Hz), 0.96 (9 H, s), 0.55 (6 H, q, *J* = 7.7 Hz).

MS: *m/z* = 183 (100, $M^+$ + 1), 182, (9, $M^+$), 132 (64), 115 (73), 104 (32), 87 (97).

Anal. Calcd for $C_{11}H_{22}Si$ (182.4): C, 72.44; H, 12.16. Found: C, 72.39; H, 12.10.

### (*E*)-Triethyl-2,4-pentadienylsilane (*E*-1b)

Purified by preparative gas chromatography (2 m, 10% SE-30, 125 °C); bp 90–91 °C/12 mmHg; $n_D^{20}$ 1.4792.

$^1$H NMR: δ = 6.29 (1 H, dt, *J* = 17.1, 10.2 Hz), 5.94 (1 H, dd, *J* = 15.1, 10.2 Hz), 5.72 (1 H, dt, *J* = 15.1, 8.3 Hz), 4.98 (1 H, d, *J* = 17.1 Hz), 4.84 (1 H, d, *J* = 10.2 Hz), 1.57 (2 H, d, *J* = 8.3 Hz), 0.93 (9 H, t, *J* = 8.0 Hz), 0.53 (6 H, q, *J* = 8.0 Hz).

Anal. Calcd for $C_{11}H_{22}Si$ (182.4): C, 72.44; H, 12.16. Found C, 72.02; H, 11.90.

### Triethyl-(1-vinyl-2-propenyl)silane (2b)

Separated from the isomers *Z*-**1b** or *E*-**1b** by preparative gas chromatography (2 m, 10% SE-30, 125 °C); bp 88–89 °C/12 mmHg; $n_D^{20}$ 1.4718.

$^1$H NMR: δ = 5.92 (2 H, ddd, *J* = 17.2, 9.6, 8.5 Hz), 4.9 (4 H, m), 2.66 (1 H, t, *J* = 8.3 Hz), 0.97 (9 H, t, *J* = 7.7 Hz), 0.59 (6 H, q, *J* = 7.7 Hz).

MS: *m/z* = 183 (84, $M^+$ + H), 132 (81), 115 (85), 104 (34), 87 (100).

Anal. Calcd for $C_{11}H_{22}Si$ (182.4): C, 72.44; H, 12.16. Found: C, 72.54; H, 12.03.

### (*Z*)-Triisopropyl-2,4-pentadienylsilane (*Z*-1c)

Colorless liquid; bp 119–120 °C/12 mmHg; $n_D^{20}$ 1.4641.

$^1$H NMR: δ = 6.71 (1 H, ddd, *J* = 16.7, 11.3, 10.2 Hz), 5.92 (1 H, t, *J* = 10.9 Hz), 5.60 (1 H, qm, *J* = 9.5 Hz), 5.14 (1 H, d, *J* = 17.1 Hz), 5.05 (1 H, dm, *J* = 10.1 Hz), 1.76 (2 H, d, *J* = 8.4 Hz), 1.05 (18 H, d, *J* = 2.6 Hz).

MS: *m/z* (%) = 225 (100, $M^+$ + H), 174 (92), 157 (23), 87 (33), 76 (31), 73 (66).

Anal. Calcd for $C_{14}H_{28}Si$ (224.5): C, 74.91; H, 12.57. Found: C, 74.91; H, 12.15.

### (*E*)-Triisopropyl-2,4-pentadienylsilane (*E*-1c)

Colorless liquid; bp 119–120 °C/12 mmHg; $n_D^{20}$ 1.4648.

$^1$H NMR: δ = 6.30 (1 H, dt, *J* = 16.7, 10.1 Hz), 6.00 (1 H, dd, *J* = 15.1, 10.4 Hz), 5.00 (1 H, dm, *J* = 17.0 Hz), 4.85 (1 H, dm, *J* = 10.1 Hz), 1.67 (2 H, d, *J* = 7.9 Hz), 1.05 (18 H, d, *J* = 2.6 Hz).

MS: *m/z* (%) = 225 (100, $M^+$ + H), 174 (72), 87 (21), 76 (31), 73 (52).

Anal. Calcd for $C_{14}H_{28}Si$ (224.5): C, 74.91; H, 12.57. Found: C, 74.66; H, 12.31.

### (*Z*)-4,4,5,5-Tetramethyl-2-(2,4-pentadienyl)-1,3,2-dioxaborolane (*Z*-1d)

Colorless liquid; bp 102–104 °C/35 mmHg; $n_D^{20}$ 1.4582.

$^1$H NMR: δ = 6.64 (1 H, dt, *J* = 16.4, 10.3 Hz), 6.02 (1 H, t, *J* = 10.4 Hz), 5.58 (1 H, q, *J* = 8.7 Hz), 5.16 (1 H, d, *J* = 16.1 Hz), 5.07 (1 H, d, *J* = 9.8 Hz), 1.84 (2 H, d, *J* = 7.0 Hz), 1.26 (12 H, s).

MS: *m/z* (%) = 194 (81, $M^+$), 179 (23), 136 (20), 95 (100), 83 (56).

Anal. Calcd for $C_{11}H_{19}BO_2$ (194.1): C, 68.08; H, 9.87. Found C, 67.79; H, 9.59.

### (*E*)-4,4,5,5-Tetramethyl-2-(2,4-pentadienyl)-1,3,2-dioxaborolane (*E*-1d)

Colorless liquid; bp 102–104 °C/32 mmHg; $n_D^{20}$ 1.4577.

$^1$H NMR: δ = 6.30 (1 H, dt, *J* = 16.9, 10.5 Hz), 6.04 (1 H, dd, *J* = 15.0, 10.2 Hz), 5.75 (1 H, dt, *J* = 14.9, 7.3 Hz), 5.02 (1 H, d, *J* = 16.9 Hz), 4.90 (1 H, d, *J* = 10.0 Hz), 1.75 (2 H, d, *J* 7.5 Hz), 1.24 (12 H, s).

MS: *m/z* (%) = 194 (100, $M^+$), 179 (11), 136 (34), 84 (45).

Anal. Calcd for $C_{11}H_{19}BO_2$ (194.1): C, 68.08; H, 9.87. Found: C, 67.74; H, 9.82.

### Methyl (*Z*)-3,5-Hexadienoate (*Z*-1f)

After alkaline extraction of the corresponding acid, neutralization, re-extraction into $Et_2O$, treatment with ethereal diazomethane and purification by preparative gas chromatography (2 m, 10% C-20M, 125 °C); bp 50–52 °C/12 mmHg; $n_D^{20}$ 1.4314.

$^1$H NMR: δ = 5.95 (2 H, ddd, *J* = 16.9, 10.3, 7.4 Hz), 5.20 (2 H, d, *J* = 10.2 Hz), 5.18 (2 H, d, *J* = 17.1 Hz), 3.76 (1 H, t, *J* = 7.5 Hz), 3.72 (3 H, s).

MS: *m*/*z* (%) = 126 (36, $M^+$), 111 (12), 95 (19), 84 (100).

Anal. Calcd for $C_7H_{10}O_2$ (126.2): C, 66.65; H, 7.99. Found: C, 66.91; H, 8.01.

### Methyl 2-Vinyl-3-butenoate (2f)

Workup and gas chromatographic isolation as described in the preceding paragraph; colorless liquid; bp 54–55 °C/12 mmHg; $n_D^{20}$ 1.4911.

$^1$H NMR: δ = 6.56 (1 H, ddd, *J* = 16.6, 11.2, 10.3 Hz), 6.17 (1 H, t, *J* = 7.0 Hz), 5.62 (1 H, dt, *J* = 10.7, 7.1 Hz), 5.28 (1 H, d, *J* = 16.6 Hz), 5.20 (1 H, d, *J* = 9.6 Hz), 3.70 (3 H, s), 3.24 (2 H, d, *J* = 7.5 Hz).

MS: *m*/*z* (%) = 144 (74, $M^+ + NH_4$), 126 (33, $M^+$), 85 (100).

Anal. Calcd for $C_7H_{10}O_2$ (126.2): C, 66.65; H, 7.99. Found: C, 67.00; H, 7.84.

### Products Derived from 3-Methyl-1,4-pentadiene

(*E*)-3-Methyl-2,4-pentadien-1-ol,[41] 3-methyl-3-vinyl-4-penten-1-ol[42] and (*E*)-3-methyl-1,3-nonadiene[43] have been reported previously. Therefore, these compounds were only characterized by their physical constants (bp, $n_D^{20}$), their $^1$H and $^{13}$C nuclear magnetic resonances and mass spectra.[44]

### (*E*)-Trimethyl-(3-methyl-2,4-pentadienyl)silane (*E*-3a)

Configurational assignment on the basis of $^1$H,$^1$H-NOESY; colorless liquid; bp 59–60 °C/8 mmHg; $n_D^{20}$ 1.4706.

$^1$H NMR: δ = 6.40 (1 H, dd, *J* = 17.2, 10.7 Hz), 5.58 (1 H, t, *J* = 9.0 Hz), 4.99 (1 H, d, *J* = 17.2 Hz), 4.84 (1 H, d, *J* = 10.7 Hz), 1.69 (3 H, s), 1.60 (2 H, d, *J* = 9.0 Hz), 0.01 (9 H, s).

Anal. Calcd for $C_9H_{18}Si$ (154.3): C, 70.04; H, 11.76. Found: C, 70.48; H, 11.76.

### (*E*)-Triethyl-(3-methyl-2,4-pentadienyl)silane (*E*-3b)

Colorless liquid; bp 108–110 °C/8 mmHg; $n_D^{20}$ 1.4826.

$^1$H NMR: δ = 6.38 (1 H, dd, *J* = 17.4, 10.7 Hz), 5.58 (1 H, t, *J* = 8.9 Hz), 4.98 (1 H, d, *J* = 17.4 Hz), 4.84 (1 H, d, *J* = 10.7 Hz), 1.72 (3 H, s), 1.63 (2 H, d, *J* = 8.9 Hz), 0.95 (9 H, t, *J* = 7.9 Hz), 0.54 (6 H, q, *J* = 7.9 Hz).

Anal. Calcd for $C_{12}H_{24}Si$ (196.4): C, 73.38; H, 12.32. Found: C, 72.80; H, 12.02.

### (*E*)-4,4,5,5-Tetramethyl-2-(3-methyl-2,4-pentadienyl)-1,3,2-dioxaborolane (*E*-3e)

Colorless liquid; bp 100–102 °C/13 mmHg; $n_D^{20}$ 1.4648.

$^1$H NMR: δ = 6.38 (1 H, dd, *J* = 17.0, 10.4 Hz), 5.62 (1 H, t, *J* = 7.8 Hz), 5.02 (1 H, d, *J* = 17.0 Hz), 4.86 (1 H, d, *J* = 10.4 Hz), 1.76 (2 H, d, *J* = 7.8 Hz), 1.70 (3 H, s), 1.22 (12 H, s).

MS: *m*/*z* (%) = 209 (89, $M^+ + H$), 208 (61, $M^+$), 151 (22), 108 (95), 85 (100).

Anal. Calcd for $C_{12}H_{21}BO_2$ (208.1): C, 68.08; H, 9.87. Found: C, 67.82; H, 9.87.

### (*E*)-4-Methyl-3,5-hexadienoic Acid (*E*-3f)

Configurational assignment on the basis of $^1$H, $^1$H-NOESY; monoclinal colorless crystals; mp 32–33 °C; bp 108–110 °C/0.2 mmHg.

$^1$H NMR: δ = 6.43 (1 H, dd, *J* = 17.5, 10.6 Hz), 5.66 (1 H, t, *J* = 7.2 Hz), 5.20 (1 H, d, *J* = 17.5 Hz), 5.05 (1 H, d, *J* = 10.6 Hz), 3.26 (2 H, d, *J* = 7.2 Hz), 1.78 (3 H, s).

MS: *m*/*z* (%) = 126 (36, $M^+$), 111 (12), 84 (100).

Anal. Calcd for $C_7H_{10}O_2$ (126.2): C, 66.65; H, 7.99. Found: C, 66.61; H, 7.87.

### (*E*)-5-Methyl-4,6-heptadien-1-ol (*E*-3h)

Separated by preparative gas chromatography (2 m, 10% C-20M, 150 °C) from a 2:1 mixture, which contained the regioisomer **4h**[42] as the major component; colorless liquid; bp 108–110 °C/5 mmHg; $n_D^{20}$ 1.4429.

$^1$H NMR: δ = 6.38 (1 H, dd, *J* = 17.0, 10.3 Hz), 5.51 (1 H, t, *J* = 7.0 Hz), 5.11 (1 H, d, *J* = 17.0 Hz), 4.94 (1 H, d, *J* = 10.3 Hz), 3.67 (2 H, d, *J* = 6.2 Hz), 2.24 (2 H, q, *J* = 7.0 Hz), 1.76 (3 H, s), 1.68 (2 H, pent, *J* = 6.2 Hz), 1.38 (1 H, s).

MS: m/z (%) = 126 (15, $M^+$), 109 (12), 93 (100), 79 (53).

Anal. Calcd for $C_8H_{14}O$ (126.2): C, 76.14; H, 11.18. Found: C, 76.36; H, 10.99.

### 3-Methyl-3-vinyl-1-heptene (4i)

Separated by preparative gas chromatography (2 m, 5% C-20M, 125 °C) from a 1:1 mixture containing also the regioisomer *E*-**3i**;[43] colorless liquid; bp 143–145 °C/12 mmHg; $n_D^{20}$ 1.4476.

$^1$H NMR: δ = 5.81 (2 H, dd, *J* = 17.0, 10.0 Hz), 4.99 (2 H, d, *J* = 10.0 Hz), 4.97 (2 H, d, *J* = 17.0 Hz), 1.3 (6 H, m), 1.09 (3 H, s), 0.90 (3 H, t, *J* = 7.1 Hz).

Anal. Calcd for $C_{10}H_{18}$ (138.3): C, 86.88; H, 13.12. Found: C, 86.92; H, 12.81.

### 5-Methyl-5-vinyl-6-hepten-1-ol

By product formed in 12% yield upon trapping of the 3-methyl-2,4-pentadienylpotassium intermediate with fluorodimethoxyboron along with (*E*)-3-methyl-2,4-pentadien-1-ol[41] (52%); separation by preparative gas chromatography (2 m, 10% C-20M, 150 °C); colorless liquid; bp 88–90 °C/0.5 mmHg; $n_D^{20}$ 1.4820.

$^1$H NMR: δ = 5.80 (2 H, dd, *J* = 17.5, 10.9 Hz), 5.00 (2 H, d, *J* = 11.4 Hz), 4.97 (2 H, d, *J* = 18.0 Hz), 3.64 (2 H, t, *J* = 6.6 Hz), 1.55 (2 H, pent, *J* = 7.0 Hz), 1.4 (4 H, m), 1.10 (3 H, s).

MS: *m*/*z* (%) = 121 (3), 107 (9), 95 (20), 82 (199).

Anal. Calcd for $C_{10}H_{18}O$ (154.3): C, 77.87; H, 11.76. Found: C, 77.87; H, 11.64.

### Products Derived from *cis*-1,4-Hexadiene

(2*E*,4*Z*)-(2,4-Hexadienyl)trimethylsilane[31,45] (2*E*,4*Z*-**5a**) and (2*E*,4*Z*)-2,4-hexadien-1-ol[46] (2*E*,4*Z*-**5b**) are known compounds. They were identified on basis of their physical constants (bp, $n_D^{20}$), $^1$H NMR and mass spectra.[44]

### (2*E*,4*Z*)-2-(2,4-Hexadienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2*E*,4*Z*-5e)

Colorless liquid; isolated by distillation; (2*E*,4*Z*/2*E*,4*Z*) ratio 8:92; bp 98–100 °C/12 mmHg; $n_D^{20}$ 1.4672; 3.1 g (60%).

$^1$H NMR: δ = 6.32 (1 H, dd, *J* = 14.7, 10.7 Hz), 5.98 (1 H, t, *J* = 10.6 Hz), 5.71 (1 H, dt, *J* = 14.7, 7.3 Hz), 5.32 (1 H, dq, *J* = 10.6, 7.0 Hz), 1.78 (2 H, d, *J* = 7.3 Hz), 1.72 (3 H, d, *J* = 7.0 Hz), 1.25 (12 H, s).

MS: *m*/*z* (%) = 208 (100, $M^+$), 109 (56), 81 (68).

Anal. Calcd for $C_{12}H_{21}BO_2$ (208.1): C, 68.08; H, 9.87. Found: C, 67.97; H, 10.01.

### Methyl (3*E*,5*Z*)-3,5-Heptadienoate (3*E*,5*Z*-5f’)

After treatment of the extracted and neutralized carboxylic acids with diazomethane; main component (18%) in a 45:40:15 mixture containing two further regioisomers (see below); separation of the colorless liquid by preparative gas chromatography (2 m, 10% C-20M, 125 °C); (3*Z*,5*Z*/3*Z*,5*E*) ratio 6:94; bp 78–80 °C/12 mmHg; $n_D^{20}$ 1.4722.

$^1$H NMR: δ = 6.45 (1 H, dd, *J* = 15.2, 10.9 Hz), 6.01 (1 H, t, *J* = 10.9 Hz), 5.73 (1 H, dt, *J* = 15.2, 7.2 Hz), 5.49 (1 H, dq, 10.9, 7.2 Hz), 3.70 (3 H, s), 3.16 (2 H, d, *J* = 7.2 Hz), 1.75 (3 H, d, *J* = 7.2 Hz).

Anal. Calcd for $C_8H_{12}O_2$ (140.2): C, 68.54; H, 8.63. Found: C, 68.74; H, 8.86.

### Methyl (*E*)-2-Methyl-3,5-hexadienoate

Workup and gas chromatographic separation as described in the preceding paragraph; 16%; colorless liquid; bp 71–72 °C/12 mmHg; $n_D^{20}$ 1.4735.

$^1$H NMR: δ = 6.32 (1 H, dt, *J* = 16.9, 10.1 Hz), 6.13 (1 H, dd, *J* = 15.1, 10.7 Hz), 5.77 (1 H, dd, *J* = 15.1, 8.0 Hz), 5.19 (1 H, d, *J* = 16.9 Hz), 5.08 (1 H, d, *J* = 10.1 Hz), 3.69 (3 H, s), 3.20 (1 H, quint, *J* = 7.0 Hz), 1.29 (3 H, d, *J* = 7.0 Hz).

MS: *m*/*z* = 158 (68, M$^+$ + NH$_4$), 140 (22, M$^+$), 81 (100), 79 (18).

Anal. Calcd for $C_8H_{12}O_2$ (140.2): C, 68.54; H, 8.63. Found: C, 68.78; H, 8.45.

### Methyl (*Z*)-2-Vinyl-3-pentenoate

Workup and gas chromatographic separation as described above (see 3*E*,5*Z*-**5d**); 6%; colorless liquid; bp 72–74 °C/12 mmHg; $n_D^{20}$ 1.4749.

$^1$H NMR: δ = 5.94 (1 H, ddd, *J* = 17.0, 10.0, 6.9 Hz), 5.70 (1 H, dq, *J* = 10.6, 6.6 Hz), 5.55 (1 H, dd, *J* = 10.6, 9.1 Hz), 5.17 (1 H, d, *J* = 16.9 Hz), 5.15 (1 H, d, *J* = 10.2 Hz), 4.07 (1 H, dd, *J* = 9.1, 6.9 Hz), 3.71 (3 H, s), 1.68 (3 H, d, *J* = 6.0 Hz).

MS: *m*/*z* (%) = 158 (43, M$^+$ + NH$_4$), 140 (12, M$^+$), 81 (100), 79 (19).

Anal. Calcd for $C_8H_{12}O_2$ (140.2): C, 68.54; H, 8.63. Found: C, 68.79; H, 8.34.

### Products Derived from *trans*-1,4-Hexadiene: Metalation with Butyllithium and Potassium *tert*-Butoxide; (2*Z*,4*E*)-2-(2,4-Hexadienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2*Z*,4*E*-5e)

Isolated by distillation; (2*Z*,4*E*/2*E*,4*E*) ratio 96:4; colorless liquid; bp 100–101 °C/12 mmHg; $n_D^{20}$ 1.4709.

$^1$H NMR: δ = 6.32 (1 H, dd, *J* = 14.6, 10.8 Hz), 5.96 (1 H, t, *J* = 10.8 Hz), 5.66 (1 H, dq, *J* = 14.6, 6.7 Hz), 5.42 (1 H, dt, *J* = 10.8, 7.8 Hz), 1.82 (2 H, d, *J* = 7.8 Hz), 1.78 (3 H, d, *J* = 6.7 Hz), 1.26 (12 H, s).

MS: *m*/*z* (%) = 209 (27, M$^+$ + H), 208 (100), 109 (68), 81 (44).

Anal. Calcd for $C_{12}H_{21}BO_2$ (208.1): C, 68.08; H, 9.87. Found: C, 68.23; H, 9.58.

### Methyl (3*Z*,5*E*)-3,5-Heptadienoate (3*Z*,5*E*-5f’)

After carboxylation of the organometallic intermediate, by extraction and treatment of the resulting 3:2 mixture of acids with diazomethane; main component (minor component: see directly below) 24%; separation by preparative gas chromatography (2 m, 5% C-20M, 125 °C), (3*Z*,5*E*/3*E*,5*E*) ratio 92:8; bp 75–77 °C/12 mmHg; $n_D^{20}$ 1.4776.

$^1$H NMR: δ = 6.26 (1 H, dd, *J* = 14.8, 10.8 Hz), 6.11 (1 H, t, *J* = 10.8 Hz), 5.77 (1 H, dq, 14.8, 6.9 Hz), 5.44 (1 H, dt, *J* = 10.8, 7.4 Hz), 3.70 (3 H, s), 3.22 (2 H, d, *J* = 7.4 Hz), 1.79 (3 H, d, *J* = 6.9 Hz).

MS: *m*/*z* (%) = 158 (100, M$^+$ + NH$_4$), 141 (74), 81 (85), 79 (21).

Anal. Calcd for $C_8H_{12}O_2$ (140.2): C, 68.54; H, 8.63. Found: C, 68.57; H, 8.32.

### Methyl (*E*)-2-Vinyl-3-pentenoate

Workup and gas chromatographic separation as described in the preceding paragraph; 16%; bp 71–72 °C/12 mmHg; $n_D^{20}$ 1.4735.

$^1$H NMR: δ = 5.94 (1 H, ddd, *J* = 16.6, 10.4, 7.4 Hz), 5.58 (2 H, m), 5.16 (1 H, d, *J* = 10.4 Hz), 5.14 (1 H, d, *J* = 16.6 Hz), 3.71 (3 H, s), 1.71 (3 H, s).

Anal. Calcd for $C_8H_{12}O_2$ (140.2): C, 68.54; H, 8.63. Found: C, 68.75; H, 8.73.

### Products Derived From *trans*-2,4-Hexadiene: Metalation with *sec*-Butyllithium; (2*E*,4*E*)-2-(2,4-Hexadienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2*E*,4*E*-5c)

Isolated by distillation; (2*Z*,4*E*/2*E*,4*E*) ratio 18:82; bp 104–105 °C/12 mmHg; $n_D^{20}$ 1.4611; 3.4 g (65%).

$^1$H NMR: δ = 6.07 (1 H, dd, *J* = 14.1, 10.3 Hz), 5.99 (1 H, dd, *J* = 14.2, 10.3 Hz), 5.57 (2 H, dt, *J* = 14.2, 8.1 Hz), 5.49 (1 H, dt, *J* = 14.1, 6.6 Hz), 1.73 (2 H, d, *J* = 8.1 Hz), 1.71 (3 H, d, *J* = 6.6 Hz), 1.24 (12 H, s).

MS: *m*/*z* (%) = 209 (31, M$^+$ + H), 208 (100), 109 (77), 84 (88), 81 (79).

Anal. Calcd for $C_{12}H_{21}BO_2$ (208.1): C, 68.08; H, 9.87. Found: C, 67.92; H, 9.76.

### Methyl (3*E*,5*E*)-3,5-Heptadienoate (2*E*,4*E*-5e)

Obtained as the main component (17%) of a 56:30:14 regioisomeric mixture along with methyl (*E*)-2-vinyl-3-pentenoate (see above; 9.3%) and methyl (*E*)-2-methyl-3,5-hexadienoate (see above; 4.3%), separated by preparative gas chromatography (2 m, 5% C-20M, 125 °C); (3*Z*,5*E*/3*E*,5*E*) ratio 16:84; bp 75–76 °C/12 mmHg; $n_D^{20}$ 1.4750.

$^1$H NMR: δ = 6.10 (1 H, dd, *J* = 14.1, 10.2 Hz), 6.03 (1 H, dd, *J* = 14.2, 10.2 Hz), 5.66 (1 H, dq, *J* = 14.2, 7.1 Hz), 5.61 (1 H, dt, 14.1, 7.4 Hz), 3.69 (3 H, s), 3.10 (2 H, d, *J* = 7.4 Hz), 1.75 (3 H, d, *J* = 7.1 Hz).

MS: *m*/*z* (%) = 158 (74, M$^+$ + NH$_4$), 141 (52), 140 (36), 81 (100), 80 (33).

Anal. Calcd for $C_8H_{12}O_2$ (140.2): C, 68.54; H, 8.63. Found: C, 68.75; H, 8.82.

### Products Derived From 2,6-Dimethyl-2,5-heptadiene Trimethyl[3-methyl-1-(2-methyl-1-propenyl)-2-butenyl]silane (6)

Major component (51%) of a 89:11 regioisomeric mixture (for the minor part, see below), separation by preparative gas chromatography (2 m, 5% SE-30, 125 °C); bp 104–106 °C/20 mmHg; $n_D^{20}$ 1.4599.

$^1$H NMR: δ = 5.06 (2 H, d, *J* = 10.6 Hz), 2.78 (1 H, t, *J* = 10.6 Hz), 1.72 (6 H, s), 1.61 (6 H, s), –0.04 (9 H, s).

MS: *m*/*z* (%) = 196 (3, M$^+$), 122 (38), 107 (48), 73 (100).

Anal. Calcd for $C_{12}H_{24}Si$ (196.4): C, 73.38; H, 12.32. Found: C, 73.29; H, 12.24.

### (*E*)-Trimethyl-(1,1,5-trimethyl-2,4-hexadienyl)silane (*E*-7)

Minor component (6%) as mentioned in the preceding paragraph: (*Z*/*E*) < 2:98; bp 114–115 °C/12 mmHg; $n_D^{20}$ 1.4438.

$^1$H NMR: δ = 5.98 (1 H, dd, *J* = 15.4, 10.6 Hz), 5.82 (1 H, d, *J* = 10.6 Hz), 5.62 (1 H, d, *J* = 15.4 Hz), 1.76 (3 H, s), 1.75 (3 H, s), 1.03 (6 H, s), –0.03 (9 H, s).

Anal. Calcd for $C_{12}H_{24}Si$ (196.4): C, 73.38; H, 12.32. Found: C, 73.26; H, 12.25.

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