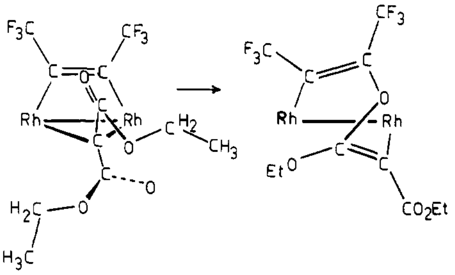
formation of a new C–C bond resulting from interaction between the alkylidene carbon and an alkyne carbon. Some representative examples of the complexes obtained are shown in 5–8. Isolation of the $\mu$-alkylidene–$\mu$-alkyne intermediate was described only in the Os system, and here further conversion to the migration product 7 requires heating in xylene at 135 °C.

The reaction sequence

$$(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)[\mu\text{-}(\eta^2\text{-}CF_3C_2CF_3)] + N_2CR^1R^2 \xrightarrow{-N_2} (\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)[\mu\text{-}(\eta^1\text{-}CF_3C_2CF_3)] \xrightarrow{\text{soln}} (\eta\text{-}C_5H_5)_2Rh_2(CO)[\eta^1,\eta^3\text{-}C(CF_3)C(CF_3)CR^1R^2]$$

is unique among these systems in that a stable $\mu$-alkylidene–$\mu$-alkyne complex can be isolated *and* converted to the $\eta^1,\eta^3$-allyl complex under mild conditions.

The different form of the conversion reaction when $R^1 = R^2 = CO_2Et$ is also unique among these systems. The preference for formation of a new C–O bond rather than a new C–C bond is presumably due to a combination of stereochemical and electronic effects. Consideration of molecular models establishes that the most sterically favored arrangement of the $\mu$-alkylidene ligand orients the ketonic oxygen toward the alkyne (see 9). Retention of two Rh–C bonds in the final product can be attributed to the stabilizing influence of the electron-withdrawing substituents $CF_3$ and $CO_2Et$.



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## Conclusion

The complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ is an excellent model system for investigating the coordination and subsequent reactions of carbenes. The two systems described in this paper represent two different types of behavior. In one, the carbene C is involved in the formation of a new C–C bond via an intramolecular migration reaction. With the other, formation of a new C–O bond involves the carbonyl O of an ester substituent. A number of other systems are currently being investigated to determine the factors affecting the course of these reactions.

**Acknowledgment.** We thank the Australian Research Grants Scheme for financial support and Dr. B. M. Gatehouse for use of X-ray facilities.

**Registry No.** 1, 71844-53-6; **2a**, 84330-33-6; **2b**, 84349-75-7; 3, 92641-70-8; 4, 84330-38-1; $N_2CH_2$, 334-88-3; $N_2C(CO_2Et)_2$, 5256-74-6.

**Supplementary Material Available:** Tables of thermal parameters and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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# Regioselective Pentadienylation of Carbonyl Compounds by Oligosilylated Pentadienylmetals

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Pentadienylation of simple aliphatic ketones or aldehydes by [1,5-bis(trimethylsilyl)pentadienyl]lithium was found to proceed regioselectivity at the $C_3$ atom of the pentadienyl moiety while the reaction with [1,3,5-tris(trimethylsilyl)pentadienyl]lithium preferred addition at the terminal carbon atom, resulting in conjugated trienes through Peterson elimination. A conjugated hexaene was obtained by treating [1,10-bis(trimethylsilyl)-2,4,6,8-octatetraene-1,10-diyl]dilithium with 2,4-dimethyl-3-pentanone via double Peterson elimination. Pentadienylation of $\alpha,\beta$-unsaturated ketones or aldehydes with [1,5-bis(trimethylsilyl)pentadienyl]- or [1,3,5-tris(trimethylsilyl)pentadienyl]lithium occurred selectively in a 1,4 fashion at the $C_3$ atom of pentadienyl moiety. Although the reaction of [1-(trimethylsilyl)pentadienyl]lithium with carbonyl compounds gave a mixture of regioisomers, the selective addition at the $C_3$ atom of pentadienyl group was realized by transmetalation to [5-(trimethylsilyl)-2,4-pentadienyl]magnesium, -boron, and -copper.

## Introduction

Direct allylation or pentadienylation[1] of electrophiles with allylic anions[2] or pentadienyl anions[3] is one of the important fundamental procedures in organic synthesis for elongation of carbon chains. However, the process often suffers a disadvantage that the reaction results in a complex mixture of regioisomers by uncontrolled attack at $\alpha$-, $\gamma$-, or $\epsilon$-positions of the carbanions because the electron

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[1] The addition of the pentadienyl group at its $C_1$, $C_3$, or $C_5$ position may be best described in the term pentadienylation.

[2] (a) Seebach, D.; Geiss, K. H. *J. Organomet. Chem. Libr.* **1976**, *1*, 1. (b) Seyferth, D.; Wursthorn, K. R.; Mammarella, R. E. *J. Org. Chem.* **1977**, *42*, 3104. (c) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (d) Bates, R. B.; Ogle, C. A. "Carbanion Chemistry"; Springer-Verlag: New York, 1983.

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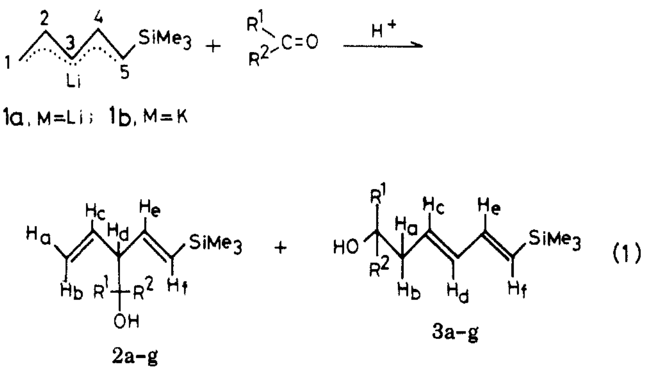
densities on these atoms are nearly identical.[4] To circumvent this, Lewis acid promoted regiocontrolled allylation and dienylmethylation with 2-propenylsilane or 2,4-pentadienylsilane has recently been developed by Sakurai et al.[5,6] and Seyferth et al.[7] A reaction path via a carbocation intermediate is proposed for these reactions.[8]

We have examined the regio- and stereoselective pentadienylation of carbonyl compounds using bulky anionic reagents such as di- and trisilylated pentadienyl metals as alternatives to the carbocations. Our attention is focused on the effective control of the reaction pathway by the steric bulk of $Me_3Si$ group. Regiocontrol by the steric effect of $Me_3Si$ group has been already reported for the addition of [1-(trimethylsilyl)allyl]lithium to ketones[9] and for the trimethylsilylation or alkylation of silylated pentadienyl anions.[10] The present method has an advantage of leaving reactive $Me_3Si$ group(s) in the product which are readily convertible into various functionalities.[11]

As an extension of the present method, transmetalation of the silylated pentadienyllithium reagents to magnesium, boron, or copper derivatives was examined in order to find better reagents for selective reaction where the regio- and stereocontrols are facilitated by the combined effect of the metal and the trimethylsilyl group.

**Regiochemistry in Addition Reaction with Monosilylated Pentadienyl Anions.** The reaction of [(*E*)-1-(trimethylsilyl)pentadienyl]lithium (**1a**) with sterically less hindered aliphatic ketones and aldehydes generally gave a mixture of two regioisomers (**2** and **3**) by competitive attack at the central ($C_3$) and terminal ($C_1$) carbons of the pentadienyl moiety (eq 1). Although the regioselectivity is poor in these cases, all the reactions proceeded stereoselectively to give the *E* or *E,E* isomers. The addition at the $C_5$ position was completely suppressed due to the steric hindrance by the $Me_3Si$ group (Table I). When a bulky ketone such as 2,4-dimethyl-3-pentanone or 3,3-dimethyl-2-butanone was employed as an electrophile, the regioselection was much improved. The addition occurred predominantly at the $C_1$ atom to give upon hydrolysis a single isomeric alcohol, **3d** or **3e**, respectively, of the *E,E* configuration. A similar result has been reported briefly for the reactions with benzophenone or benzaldehyde.[12] The metal exchange of 1 from lithium **1a** to potassium **1b** affected the relative ratio of the products very little. In some favorable cases, the addition of this reagent is reversible and heating the product in solution gave a single isomer. For example, the reaction of **1a** with 3-pentanone at 0 °C gave a 23/77 mixture of **2c** and **3c** upon hydrolysis while isomerization occurred when the reaction mixture was held at 70 °C for 5 h to give products **2c** and **3c** in a ratio of 96/4. Similar behavior has already been reported by Miginiac et al. for the reaction with nonsilylated pentadienyllithium.[13] This procedure is not effective for converting the adducts derived from ethanal or propanal. Only a modest change in product ratio (60/40) was observed in these cases after the mixture was heated to 80 °C for 10 h. Thus, the above procedure has limited application and often causes a significant decrease in yield during heating. Therefore an alternative method is required to perform the selective pentadienylation, especially for the reaction with less bulky ketones and aldehydes.



a, $R^1 = R^2 = CH_3$; b, $R^1\text{-}R^2 = C_5H_{10}$; c, $R^1 = R^2 = C_2H_5$; d, $R^1 = R^2 = i\text{-}C_3H_7$; e, $R^1 = CH_3$, $R^2 = t\text{-}C_4H_9$; f, $R^1 = H$, $R^2 = CH_3$; g, $R^1 = H$, $R^2 = i\text{-}C_3H_7$

Table I. Pentadienylation of Aliphatic Ketones and Aldehydes by Monosilylated Pentadienyl Anions, 1a and 1b

| carbonyl compds | anions | product ratio, % (geometry) 2 | 3 | total yield, % |
|---|---|---|---|---|
| $(CH_3)_2CO$ | 1a | 88 (*E*) (**2a**) | 12 (*E,E*) (**3a**) | 65 |
| $(CH_3)_2CO$ | 1b | 69 (*E*) (**2a**) | 31 (*E,E*) (**3a**) | 60 |
| cyclohexanone | 1a | 62 (*E*) (**2b**) | 38 (*E,E*) (**3b**) | 75 |
| $(C_2H_5)_2CO$ | 1a | 23 (*E*) (**2c**) | 77 (*E,E*) (**3c**) | 78 |
| $(i\text{-}C_3H_7)_2CO$ | 1a | 0 | 100 (*E,E*) (**3d**) | 56 |
| $(i\text{-}C_3H_7)_2CO$ | 1b | 2 (*E*) (**2d**) | 98 (*E,E*) (**3d**) | 39 |
| $t\text{-}C_4H_9(CH_3)CO$ | 1a | 0 | 100 (*E,E*) (**3e**) | 79 |
| $CH_3CHO$ | 1a | 67 (*E*) (**2f**) | 33 (*E,E*) (**3f**) | 78 |
| $i\text{-}C_3H_7CHO$ | 1a | 66 (*E*) (**2g**) | 34 (*E,E*) (**3g**) | 60 |

Table II. Pentadienylation of Aliphatic Ketones and Aldehydes by [1,5-Bis(trimethylsilyl)pentadienyl]lithium (4)

| carbonyl compd | products ratio, % (geometry) 5 | 6 | total yield, % |
|---|---|---|---|
| $(CH_3)_2CO$ | 100 (*E,E*) (**5a**) | 0 | 48 |
| cyclohexanone | 99 (*E,E*) (**5b**) | 1 | 67 |
| $(i\text{-}C_3H_7)_2CO$ | 0 | 99 (*E,E*) (**6**) | 53 |
| $t\text{-}C_4H_9(CH_3)CO$ | 0 | 0 | 0[a] |
| $CH_3CHO$ | 99 (*E,E*) (**5c**) | 1 | 69 |
| $i\text{-}C_3H_7CHO$ | 100 (*E,E*) (**5d**) | 0 | 81 |

[a] Enolization occurred quantitatively.

**Selective Addition of 1,5-Disilylated Pentadienyllithium.** The selective addition of carbonyl compounds at the terminal $C_1$ atom of the pentadienyl group has been achieved recently by Lewis acid-promoted pentadienylation (dienylmethylation) which proceeds through a car-

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(4) (a) Hoffmann, R.; Olofson, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 943. (b) Bushby, R. J.; Patterson, A. S. *J. Organomet. Chem.* **1977**, *132*, 163. (c) Dewar, M. J. S.; Fox, M. A.; Nelson, D. J. *J. Organomet. Chem.* **1980**, *185*, 157.

(5) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. See also: Calas, R.; Dunogues, J.; Deleris, G. *Tetrahedron Lett.* **1976**, 2449.

(6) Hosomi, A.; Saito, M.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 3783.

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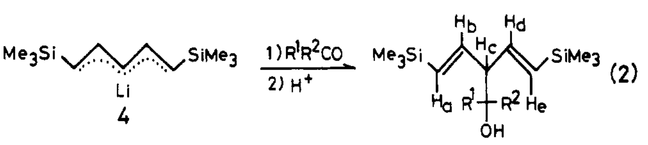
(11) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: New York, 1983. Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: Londom, 1981.

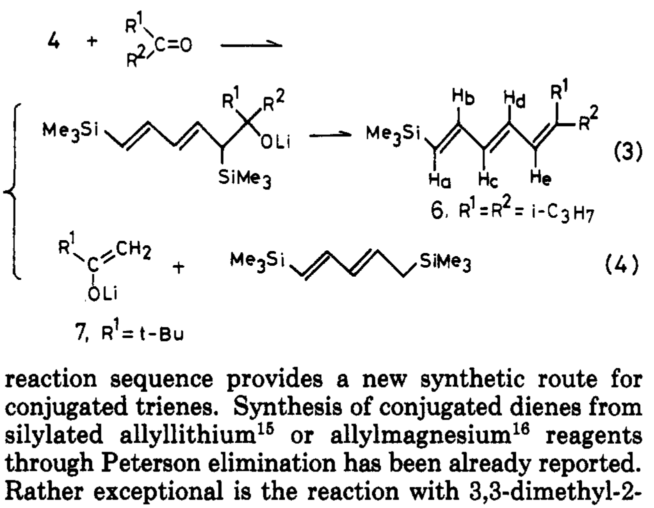
(12) Oppolzer, W.; Burford, S. C.; Marazza, F. *Helv. Chim. Acta* **1980**, *63*, 555.

(13) (a) Gerard, F.; Miginiac, P. *Bull. Soc. Chim. Fr.* **1974**, 2527. (b) See also for reaction mechanism: Ewans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3319.

bocation intermediate.[5,7] However, the selective addition at the central $C_3$ atom has not yet been realized. Our strategy employed here is to control the mode of reaction by the steric effect of $Me_3Si$ groups substituted at the both ends ($C_1$ and $C_5$) of pentadienyl anions. Actually, highly regioselective 1,4-pentadienylation of simple aliphatic ketones and aldehydes (addition at the $C_3$ atom of pentadienyl group) occurred when [(*E*,*E*,*E*,*E*)-1,5-bis(trimethylsilyl)pentadienyl]lithium (4)[10] was allowed to react with acetone, cyclohexanone, acetaldehyde, or isobutanal (eq 2). The results are shown in Table II. Thus, double silylation was found to be effective in directing the attack at the central carbon atom to give isomerically pure alcohols **5a–d** upon hydrolysis of the product. Rather exceptional is the reaction with bulky ketones such as 2,4-dimethyl-3-pentanone that favored the terminal attack over central attack due to the severe steric repulsion between the alkyl group of a ketone and the $C_2$, $C_3$, $C_4$ carbon skeleton of **4**. The species thus formed immediately are converted into conjugated trienes **6** by Peterson elimination[14] (syn elimination of $Me_3SiO^-$) following eq 3. This reaction sequence provides a new synthetic route for conjugated trienes. Synthesis of conjugated dienes from silylated allyllithium[15] or allylmagnesium[16] reagents through Peterson elimination has been already reported. Rather exceptional is the reaction with 3,3-dimethyl-2-butanone in which enolization to give **7** was preferred, releasing the starting compound 1,5-bis(trimethylsilyl)-1,3-pentadiene quantitatively following eq 4. Although the mode of reaction of disilylated pentadienyl anions varies depending on the bulkiness of carbonyl compounds, the selective addition of 1,5-disilylated pentadienyl anion to simple ketones and aldehydes is valuable as a convenient transformation useful for organic synthesis.



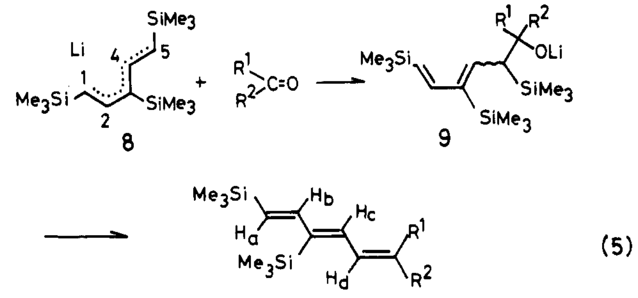
5a, $R^1 = R^2 = CH_3$
b, $R^1$-$R^2$ = $C_5H_{10}$
c, $R^1$ = H, $R^2$ = $CH_3$
d, $R^1$ = H, $R^2$ = *i*-$C_3H_7$



**Conjugated Triene Synthesis with 1,3,5-Trisilylated Pentadienyl Anion.** The metalation of 1,3,5-tris(trimethylsilyl)-1,4-pentadiene gave a versatile reagent, [1,3,5-tris(trimethylsilyl)pentadienyl]lithium (**8**), which affords silylated trienes of potential utility in organic synthesis (eq 5). In contrast to the central carbon attack observed for **4**, this reagent undergoes reaction at its terminal carbon. This reaction sequence has a broad applicability toward a wide variety of carbonyl compounds including less bulky ketones and aldehydes (Table III). Since the trisilylated pentadienyl anion **8** is known to possess the *E*,*E*,*Z*,*E* geometry as its limiting structure,[10] insertion of a ketone at $C_5$ atom of **8** should give rise to a conjugated triene of *E*,*E* configuration via **9** while addition at the $C_1$ atom will afford the *Z*,*E* isomer, if the reaction proceeds with retention of configuration.

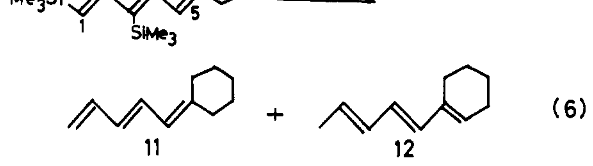
Table III. Conjugated Trienes by the Addition 1,3,5-Trisilylated Pentadienyllithium (8) to Ketones and Aldehydes

| carbonyl compds | purity of 10, % | yield, % |
|---|---|---|
| $(CH_3)_2CO$ | 99 (**10a**) | 83 |
| cyclohexanone | 100 (**10b**) | 65 |
| $(C_2H_5)_2CO$ | 100 (**10c**) | 58 |
| $(i\text{-}C_3H_7)_2CO$ | 0 | 0 |
| $CH_3CHO$ | 99 (**10d**) | 90 |
| $i\text{-}C_3H_7CHO$ | 100 (**10e**) | 82 |



10a, $R^1 = R^2 = CH_3$
b, $R^1$-$R^2$ = $C_5H_7$
c, $R^1 = R^2 = C_2H_5$
d, $R^1$ = H, $R^2$ = $CH_3$
e, $R^1$ = H, $R^2$ = *i*-$C_3H_7$

As a result, the reaction with cyclohexanone or 3-pentanone gave a single isomer of the triene with the *E*,*E* configuration. The configuration was confirmed by the desilylation experiment. Addition of a stoichiometric amount of dry HCl to **10b** resulted in the formation of a nonsilylated triene **11** together with **12** in a 3:1 ratio to indicate that insertion of cyclohexanone to **8** occurred preferentially at the $C_5$ atom (eq 6). The formation of **12** should be the result of isomerization of **11**. When compound **8** was treated with an aldehyde, the Peterson elimination took place nonselectively and gave **10d** and **10e** as a 1:1 mixture of the *E* and *Z* isomers as revealed by the $^1$H NMR spectrum. Diminished stereoselectivity will be due to the competitive syn and anti elimination often observed for the Peterson reaction with aliphatic aldehydes.[14b] A bulky ketone, 3,3-dimethyl-2-butanone, is inert to **8** even at 60 °C.



**1,4 Addition of Silylated Pentadienylmetals to Unsaturated Carbonyl Compounds.** The success in the

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(14) (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. (b) Hurdlik, P. F.; Peterson, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 1464.

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(16) (a) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415. (b) Chan, T. H.; Li, J.-S., *J. Chem. Soc., Chem. Commun.* **1982**, 969.

**Table IV. Pentadienylation of Unsaturated Carbonyl Compounds by Silylated Pentadienyllithium, 1a, 4, and 8**

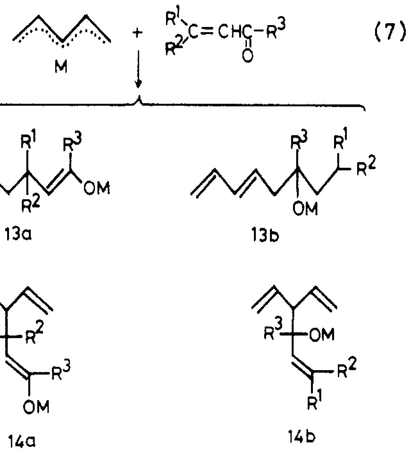
| reagent | carbonyl compd | product ratio, % 15 | product ratio, % 16 | total yield, % |
|---|---|---|---|---|
| 1a | cyclo-2-hexenone | 32 (**15a**) | 68 (**16a**) | 75 |
| 1a | $(CH_3)_2C{=}CHCOCH_3$ | 45 (**15b**) | 55 (**16b**)[a] | 54[b] |
| 1a | $(CH_3)_2C{=}CHCOOC_2H_5$ | 90 (**15c**) | 10 (**16c**) | 78 |
| 4 | cyclo-2-hexenone | 72 (**15d**) | 28 (**16d**) | 78 |
| 4 | $(CH_3)_2C{=}CHCOCH_3$ | 99 (**15e**) | 1 (**16e**) | 87 |
| 4 | $(CH_3)_2C{=}CHCOOC_2H_5$ | 95 (**15f**) | 5 (**16f**) | 80 |
| 8 | cyclo-2-hexenone | 100 (**15g**) | 0 | 75 |

[a] Contains other isomers (45%) other than **16b**. [b] Combined yield of **15b** and **16b**.

regiocontrolled addition of oligosilylated dienyl anions to saturated carbonyl compounds stimulated us to explore the possibility of the selective addition to unsaturated ketones, aldehydes, and esters.

For the addition reaction of group 1A or 2A organometallic compounds with $\alpha,\beta$-unsaturated carbonyl compounds, it is generally recognized that 1,2 addition is kinetically favored but 1,4 addition is thermodynamically preferred. The ratio of 1,2 to 1,4 product also varies, reflecting hardness (ionicity) at the metal site and bulkiness of the electrophiles.[17] In the reaction of [1-(trimethylsilyl)allyl]lithium with $\alpha,\beta$-unsaturated cyclohexenone, 1,2 addition occurs at the less hindered $C_3$ atom of the allyl anions as reported by Magnus.[18] Such a trend has been found also in the reaction of a Grignard reagent with cyclohexenone; i.e., less bulky $CH_3MgBr$ preferred the 1,2 addition but $t$-$C_4H_9MgBr$ favored the 1,4 addition.[19]

The following four reactions are possible for the addition reaction of the pentadienyl anion toward unsaturated carbonyl compounds. In the case of reaction between nonsilylated pentadienyllithium and 4-methyl-3-penten-2-one, a mixture of **13a**, **13b**, and **14a** was obtained in 41:12:47 ratio. To realize the regiocontrolled reaction effected by the steric bulk of $(CH_3)_3Si$ group, we have demonstrated the addition reaction of mono-, di-, and trisilylated pentadienyllithium using cyclo-2-hexen-1-one, 4-methyl-3-penten-2-one, and ethyl 3,3-dimethylacrylate as a representative example of $\alpha,\beta$-unsaturated cyclic ketone, acyclic ketone, and unsaturated ester, respectively. The results of the reactions are shown in the Table IV. The reaction of monosilylated pentadienyllithium **1** with cyclo-2-hexen-1-one or 4-methyl-3-penten-2-one gave a mixture of regioisomer **15a** (**15b**) and **16a** (**16b**) while the reaction with ethyl 3,3-dimethylacrylate gave **15c** with high regioselectivity (eq 8).



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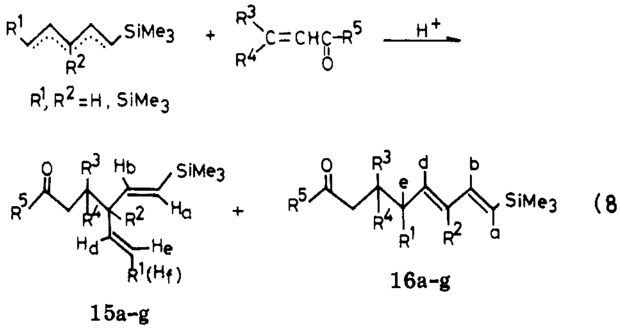

(8)

a, $R^{1-3}$ = H, $R^4$-$R^5$ = $C_3H_6$; b, $R^{1,2}$ = H, $R^{3-5}$ = $CH_3$; c, $R^{1,2}$ = H, $R^{3,4}$ = $CH_3$, $R^5$ = $OC_2H_5$; d, $R^1$ = $Me_3Si$, $R^{2,3}$ = H, $R^4$-$R^5$ = $C_3H_6$; e, $R^1$ = $Me_3Si$, $R^2$ = H, $R^{3-5}$ = $CH_3$; f, $R^1$ = $Me_3Si$, $R^2$ = H, $R^{3,4}$ = $CH_3$, $R^5$ = $OC_2H_5$; g, $R^{1,2}$ = $Me_3Si$, $R^3$ = H, $R^4$-$R^5$ = $C_3H_6$

The regioselection was much improved when a 1,5-disilylated pentadienyl anion **8** was used as a reagent. For example, the 1,4 addition of **8** to a linear unsaturated ketone or ester took place predominantly at the central carbon of **8** to give the adduct **15e,f**. A cyclic ketone, cyclo-2-hexen-1-one, still furnished the 1,4 addition at both the $C_1$ and $C_3$ atoms, but highly selective 1,4 addition to cyclo-2-hexenone at the central carbon of the pentadienyl moiety was eventually accomplished by the use of a bulky 1,3,5-trisilylated pentadienyl anion. Thus, the regiocontrolled 1,4 addition to a variety of unsaturated carbonyl compounds was achieved by introducing two or three trimethylsilyl groups in pentadienyl anions. 1,2 addition to $\alpha,\beta$-unsaturated ketones and esters was completely suppressed in these reactions. Lewis acid ($TiCl_4$) promoted reaction of 4-methyl-3-penten-2-one with ($E$)-2,4-pentadienyltrimethylsilane is known to give a Michael-type adduct (4,4-dimethyl-6,8-nonadien-2-one) as well as a cyclic product in 35/24 ratio at low temperature.[7a]

**A Novel Route for Preparation of Conjugated Polyenes.** A convergent synthesis of functionalized polyenes is of great value especially for the synthesis of natural products such as insect pheromones and insecticides. In order to find additional versatility of silylated pentadienyl anions, we have examined the preparation of conjugated tetraenes and hexaenes starting from 1,3,7,9-decatetraene which is readily obtainable by homocoupling of pentadienylpotassium with CuCl.[3a] The metalation of 1,3,7,9-decatetraene with metallic potassium in THF at 0–30 °C gave a monoanion preferentially (90% yield based on metal) while the metalation with potassium at −20 °C in the presence of a large excess of $NEt_3$ produced a dianion in good yield as a yellow precipitate. The formation of mono- and dianions were confirmed by the successive trimethylsilylation of the product.

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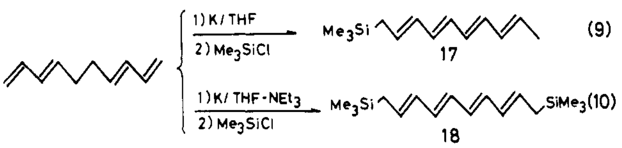
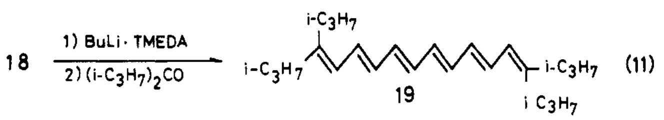
The former gave (*E,E,E,E*)-1-(trimethylsilyl)-2,4,6,8-decatetraene (**17**) in 90% yield and the latter gave (*E,E,E,E*)-1,10-bis(trimethylsilyl)-2,4,6,8-decatetraene (**18**) in ~70% yield. The structure of these tetraenes was confirmed by the $^1H$ and $^{13}C$ NMR spectra (see Experimental Section). The formation of **17** is the result of base-catalyzed isomerization of the 1,3,7,9-decatetraenyl monoanion. Similar base-catalyzed isomerization is well-known.[20] The double metalation could occur prior to the isomerization when the reaction was assisted by weak interaction of a tertiary amine.



17 (9)

18 (10)

The metalation of the resulting silylated tetraene **18** was attempted with BuLi, BuLi/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA), or BuLi/*N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA).[21] The latter two served as good metalating agents and produced a dianion. The resulting 1,10-bis(trimethylsilyl)-2,4,6,8-decatetraenediyldilithium has desired reactivity toward 2,4-dimethyl-3-pentanone and gave the target hexaene **19** in reasonable yield via double Peterson elimination. The electronic spectral pattern of **19** is very close to that of (*E,E,E,E,E,E*)-tetradeca-2,4,6,8,10,12-hexaene.[22] Butyllithium was not suitable as a metalating agent since anionic polymerization of **18** occurred preferentially.



19 (11)

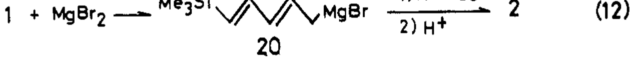
**Selective Addition by Silylated Pentadienyl Compounds of Magnesium, Boron and Copper.** In order to realize the selective addition of a monosilylated pentadienyl group into less bulky ketones or aldehydes, transmetalation of monosilylated pentadienyl anion into σ-bonded groups 2 and 3 metal derivatives has been demonstrated since bis(pentadienyl)magnesium,[23] bis(pentadienyl)beryllium,[24] and bis(pentadienyl)zinc[24] are known to react with simple carbonyl compounds selectively at the $C_3$ atom of pentadienyl group. Effectiveness of pentadienylstannane has also been reported recently.[25] The reactions tested here are addition to simple ketones by silylated pentadienylmagnesium, pentadienylboron, and pentadienylcopper reagents, which are readily available by transmetalation of **1a** or **4**.

[5-(Trimethylsilyl)-2,4-pentadienyl]magnesium bromide (**20**) gave a single product in good yield when it was allowed to react with acetone or isobutanal (Table V). The utility of this reagent lies in its extremely high selectivity and easy handling due to its high thermal stability. Regioselectivity in pentadienylation of 4-methyl-3-penten-2-one was insufficient.

Table V. Pentadienylation by [5-(Trimethylsilyl)pentadienyl]magnesium (**20**), -boron (**21**), and -copper (**22**)

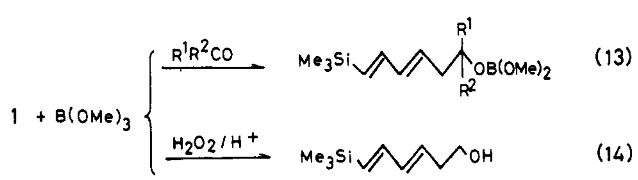
| reagent | carbonyl compd | product ratio, % | | total yield, % |
|---|---|---|---|---|
| | | **2** (**15**) | **3** (**16**) | |
| **20** | $(CH_3)_2CO$ | 97 | 3 | 85 |
| **20** | $i$-$C_3H_7CHO$ | 98 | 2 | 91 |
| **20** | $(CH_3)_2C{=}CHCOCH_3$ | 45 | 55[a] | 40[b] |
| **21** | $(CH_3)_2CO$ | 96 | 4 | 75 |
| **21** | $i$-$C_3H_7CHO$ | 98 | 2 | 72 |
| **21** | $(CH_3)_2C{=}CHCOCH_3$ | 52 | 48[a] | 56[b] |
| **22** | $(CH_3)_2CO$ | 100 | 0 | 88 |
| **22** | $i$-$C_3H_7CHO$ | 100 | 0 | 85 |
| **22** | $(CH_3)_2C{=}CHCOCH_3$ | 76 | 24[a] | 56[b] |

[a] Contains 30–60% of byproducts besides **3** or **16**.
[b] Combined yield of **2** (**15**) and **3** (**16**).



20 (12)

$(CH_3)_3SiCH{=}CHCH{=}CHCH_2B(OCH_3)_2$, prepared from **1** and $B(OCH_3)_3$, was also able to selectively add to acetone or isobutanal at the $C_3$ atom of the pentadienyl moiety. The formation of [5-(trimethylsilyl)-2,4-pentadienyl]dimethoxyboron (**21**) was confirmed by the oxidation with $H_2O_2$/aqueous NaOH which gives rise to $(CH_3)_3SiCH{=}CHCH{=}CHCH_2OH$ in 80% yield. The use of $B(OCH_3)_3$ is superior to $BF(OMe)_2$ or $BF_3 \cdot OEt_2$ with regard to the yield. The latter two systems gave products contaminated by some polymerizates. 1,5-Disilylated pentadienylboron compound was also obtained in the similar manner and the oxidation with $H_2O_2$/aqueous NaOH gave $(CH_3)_3SiCH{=}CHCH{=}CHCH(OH)Si(CH_3)_3$ in 82% yield. However, the resulting 1,5-disilylated pentadienyldimethoxyboron was found to be completely inert toward acetone or 3-pentanone at 0 °C. When the reaction temperature was raised to 40–50 °C, spontaneous polymerization of the pentadienylboron occurred and hence no addition occurred. Thus, disilylated pentadienylboron has no use (as yet) in synthesis.



(13)

(14)

We have also prepared silylated pentadienylcopper to compare the chemical behavior with corresponding magnesium and boron derivatives since organocopper reagents often show the high selectivity. Reactions of pentadienylcopper with saturated esters at low temperature have been reported by Miginiac.[27] Since thermal instability of organocopper in many cases throw obstacles in the handling of the reagent or measurement of the spectrum, phosphine-coordinated copper reagent was used to improve the thermal stability. Phosphine-coordinated alkyl coppers are recently reported.[28] Thus, $Me_3SiCH{=}CHCH{=}$

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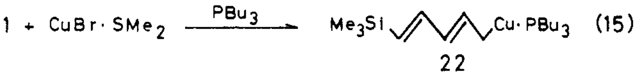
Table VI. $^1$H NMR Parameters of Pentadienylmagnesium Bromide, Pentadienylcopper, and Their Silylated Derivatives[a]

| | chem shift, ppm (coupling const, Hz) | | |
|---|---|---|---|
| | $H_1$ ($H_5$) | $H_2$ ($H_4$) | $H_3$ |
| $C_5H_7MgBr$ | 2.92 ($J_{1,2}$ = 11.3) | 6.50 ($J_{2,3}$ = 11.7) | 5.48 |
| $C_5H_7Cu{\cdot}PBu_3$ | 3.06 ($J_{1,2}$ = 11.5) | 6.11 ($J_{2,3}$ = 11.5) | 4.73 |
| $(Me_3Si)C_5H_6MgBr$<br>**20** | 3.53 ($J_{1,2}$ = 12.1)<br>2.27 ($J_{4,5}$ = 15.2) | 6.35 ($J_{2,3}$ = 11.8)<br>6.41 ($J_{3,4}$ = 11.8) | 5.36 |
| $(Me_3Si)C_5H_6Cu{\cdot}PBu_3$<br>**22** | 3.60 ($J_{1,2}$ = 12.5)<br>2.78 ($J_{4,5}$ = 15.2) | 6.04 ($J_{2,3}$ = 11.5)<br>6.11 ($J_{3,4}$ = 11.6) | 4.62 |
| $(Me_3Si)_2C_5H_5MgBr$<br>**23** | 3.25 ($J_{1,2}$ = 15.0) | 6.58 ($J_{2,3}$ = 12.0) | 5.49 |
| $(Me_3Si)_2C_5H_5Cu{\cdot}PBu_3$<br>**24** | 3.48 ($J_{1,2}$ = 15.5) | 6.21 ($J_{2,3}$ = 11.2) | 4.59 |

[a] Measured at 0 °C in THF-$d_8$. Chemical shift values are calibrated by using the downfield THF peak as the internal standard, assumed to be 3.75 ppm.

$CHCH_2Cu{\cdot}P(C_4H_9)_3$ prepared by the 1:1 reaction of 1 with $CuBr{\cdot}SMe_2$ in the presence of 4 equiv of $PBu_3$ was allowed



(15)

to react with acetone or 1-butanal at 0 °C, and a pure product was obtained. Highly regioselective additions (>95%) occurred at the $C_3$ atom in these cases, but the reaction with 4-methyl-3-penten-2-one is not selective. In conclusion, the regioselectivity observed in the reaction of monosilylated pentadienylmagnesium, -boron, and -copper with acetone or isobutanal is much higher than that of monosilylated pentadienyllithium or -potassium but nearly identical with that of 1,5-disilylated pentadienyl anions. For pentadienylation of α,β-unsaturated ketones, 1,5-disilylated pentadienyllithium is superior to silylated boron and copper derivatives with regard to the regioselectivity and ease of handling of the reagents.

**Structure of Pentadienylcopper in Solution.** The solution of silylated and nonsilylated pentadienylcopper was analyzed by means of NMR since the stabilization with phosphine now allows spectral measurements. The NMR patterns of $C_5H_7Cu{\cdot}PBu_3$, $Me_3SiC_5H_5Cu{\cdot}PBu_3$, and $(Me_3Si)_2C_5H_4Cu{\cdot}PBu_3$ in THF-$d_8$ are very close to those of corresponding magnesium compounds, indicating that rapid 1,3 rearrangement occurs in these systems even at −78 °C (eq 16). The coupling constant of $J_{2,3}$ (11.6–12.0 Hz) observed for $C_5H_7Cu{\cdot}P(C_4H_9)_3$, **20**, and [1,5-bis(trimethylsilyl)pentadienyl]copper (**23**) is nearly equal in magnitude to $J_{2,3}$ (11.0–11.6 Hz) found for (*E,E*)-pentadienyllithium or (*E,E,E,E*)-disilylated pentadienyllithium[3a] which exhibits the "W"-formed structure at low temperature. The magnitude of $J_{2,3}$ for [1,5-bis(trimethylsilyl)pentadienyl]magnesium (**24**) is also identical with the above. The values of $J_{1,2}$ (15.0–15.5 Hz) for the 1,5-disilylated copper compound **23** and magnesium compound **24** indicate that the equilibrium (eq 16) is established with *E,E,E,E* configuration.

(16)

## Experimental Section

**General Remarks.** All operations were conducted with Schlenk techniques under an argon atmosphere. Solvents and carbonyl compounds were distilled after being dried over Na–K alloy and calcium hydride, respectively. Preparations of [1-(trimethylsilyl)pentadienyl]lithium (**1a**), [1-(trimethylsilyl)pentadienyl]potassium (**1b**), [1,5-bis(trimethylsilyl)pentadienyl]lithium (**4**), and [1,3,5-tris(trimethylsilyl)pentadienyl]lithium (**8**) were carried out in the same manner as reported previously.[10] The gas chromatographic analysis and the separation of reaction products were conducted on a Yanaco Model GC3800 gas chromatograph equipped with a column packed with DEGS on Uniport-B (Gaschro Kogyo Co.) or Silicon-DC550 on 60/80 mesh Celite. $^1$H and $^{13}$C NMR spectra were recorded on a Varian XL-100 instrument at 100 and 25.2 MHz, respectively. Electronic spectra were run on a JASCO Model UVIDEC-5A spectrometer and the mass spectra (EI, 70 eV) on a JEOL 01SG-2 spectrometer.

**Reaction of [1-(Trimethylsilyl)pentadienyl]lithium (1a) with Carbonyl Compounds.** To a THF solution (20 mL) of **1a** (0.6 g, 4 mmol) held at −70 °C was added dropwise acetone (0.4 mL, 5 mmol) dissolved in THF (5 mL) with magnetic stirring. The mixture was allowed to warm gradually to 25 °C and stirred for 10 min. After the product was treated with a small portion of aqueous ammonium chloride at 0 °C, the resulting solution was dried over sodium sulfate, filtered, and distilled to obtain a mixture of unsaturated alcohols. Separation of the alcohols into the respective isomers was carried out on a preparative gas chromatograph. Characterization of each alcohol was made in terms of $^1$H NMR and the mass spectra together with elemental analysis. Reaction of **1a** with cyclohexanone, 3-pentanone, 2,4-dimethyl-3-pentanone, 3,3-dimethyl-2-butanone, ethanal, or isobutanal and the characterization of the products were carried out in essentially the same way as described above. Spectral data for the major product in each of these reactions are given below. The subscript of H used for the assignment of proton signals is given in eq 1.

**2-Methyl-3-vinyl-5-(trimethylsilyl)-4-penten-2-ol (2a):** NMR ($CDCl_3$) δ 6.03 (dd, $J_{ef}$ = 19.1 Hz, $J_{de}$ = 7.9 Hz, $H_e$), 5.83 (ddd, $J_{bc}$ = 17.5 Hz, $J_{ac}$ = 9.5 Hz, $J_{cd}$ = 7.9 Hz, $H_c$), 5.68 (d, $H_f$), 5.06 (dd, $H_b$), 5.00 (dd, $H_a$), 2.70 (t, $H_d$), 1.67 (s, OH), 1.10 (s, $CH_3$), 0.00 (s, $SiMe_3$); mass spectrum, *m/e* 198 ($M^+$). Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.98; H, 11.02.

**2-Methyl-7-(trimethylsilyl)-3,5-heptadien-2-ol (3a):** NMR ($CDCl_3$) δ 6.46 (dd, $J_{ef}$ = 17.8 Hz, $J_{de}$ = 10.0 Hz, $H_e$), 5.99 (dd, $J_{cd}$ = 14.8 Hz, $H_d$), 5.73 (dt, $J_{ac}$ = $J_{bc}$ = 8.1 Hz, $H_c$), 5.71 (d, $H_f$), 2.20 (d, $H_a$ and $H_b$), 1.64 (s, OH), 1.16 (s, $CH_3$), 0.00 (s, $Me_3Si$); mass spectrum, *m/e* 198 ($M^+$). Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.73; H, 11.08.

**[1-Vinyl-3-(trimethylsilyl)-2-propenyl]cyclohexan-1-ol (2b):** NMR ($CDCl_3$) δ 5.90 (dd, $J_{ef}$ = 18.3 Hz, $J_{de}$ = 8.0 Hz, $H_e$), 5.80 (ddd, $J_{bc}$ = 17.2 Hz, $J_{ac}$ = 7.3 Hz, $J_{cd}$ = 8.0 Hz, $H_c$), 5.66 (d, $H_f$), 5.06 (dd, $H_a$), 5.01 (dd, $H_b$), 2.68 (t, $H_d$), 1.67 (s, OH), 1.74 (m, $CH_2$, 4 H), 1.45 (m, $CH_2$, 6 H), 0.01 (s, $Me_3Si$); mass spectrum, *m/e* 238 ($M^+$). Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.42; H, 10.97.

**[5-(Trimethylsilyl)-2,4-pentadienyl]cyclohexan-1-ol (3b):** NMR ($CDCl_3$) δ 6.45 (dd, $J_{ef}$ = 18.2 Hz, $J_{de}$ = 9.5 Hz, $H_e$), 6.07 (dd, $J_{cd}$ = 17.2 Hz, $H_d$), 5.71 (dt, $J_{ac}$ = $J_{bc}$ = 7.5 Hz, $H_c$), 5.69 (d, $H_f$), 2.18 (d, $H_a$ and $H_b$), 1.80 (s, OH), 1.44 (m, $CH_2$, 10 H); mass spectrum, *m/e* 238 ($M^+$). Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.11; H, 11.10.

**3-Ethyl-8-(trimethylsilyl)-5,7-octadien-3-ol (3c):** NMR ($CDCl_3$) δ 6.39 (dd, $J_{ef}$ = 17.0 Hz, $J_{de}$ = 9.0 Hz, $H_e$), 5.99 (dd, $J_{cd}$ = 14.2 Hz, $H_d$), 5.62 (d, $H_f$), 5.59 (dt, $J_{ac}$ = $J_{bc}$ = 7.2 Hz, $H_c$), 2.13 (d, $H_a$ and $H_b$), 1.74 (s, OH), 1.59 (q, $J$ = 7.0 Hz, $CH_2$), 0.78 (t, $CH_3$), −0.05 (s, $Me_3Si$); mass spectrum, *m/e* 226 ($M^+$). Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.98; H, 11.59.

**2-Methyl-3-isopropyl-8-(trimethylsilyl)-5,7-octadien-3-ol (3d):** NMR ($CDCl_3$) δ 6.43 (dd, $J_{ef}$ = 17.5 Hz, $J_{de}$ = 9.8 Hz, $H_e$), 5.95 (dd, $J_{cd}$ = 15.2 Hz, $H_d$), 5.68 (dt, $J_{ac}$ = $J_{bc}$ = 7.9 Hz, $H_c$), 5.64 (d, $H_f$), 2.27 (d, $H_a$ and $H_b$), 1.86 (m, $J$ = 7.1 Hz, CH, 2 H), 1.40

(s, OH), 0.87 (d, CH$_3$, 12 H), −0.02 (s, Me$_3$Si); mass spectrum, *m/e* 254 (M$^+$). Anal. Calcd for C$_{15}$H$_{30}$OSi: C, 70.79; H, 11.88. Found: C, 70.25; H, 11.70.

**2,2,3-Trimethyl-8-(trimethylsilyl)-5,7-octadien-3-ol (3e):** NMR (CDCl$_3$) $\delta$ 6.48 (dd, $J_{ef}$ = 17.2 Hz, $J_{de}$ = 9.8 Hz, H$_e$), 6.17 (dd, $J_{cd}$ = 15.5 Hz, H$_d$), 5.90 (dt, $J_{ac}$ = $J_{bc}$ = 7.9 Hz, H$_c$), 5.68 (d, H$_f$), 2.23 (d, H$_a$ and H$_b$), 1.37 (s, OH), 1.07 (s, CH$_3$), 0.91 (s, *t*-Bu), −0.01 (s, Me$_3$Si); mass spectrum, *m/e* 240 (M$^+$). Anal. Calcd for C$_{14}$H$_{28}$OSi: C, 69.93; H, 11.74. Found: C, 69.91; H, 11.63.

**3-Vinyl-5-(trimethylsilyl)-4-penten-2-ol (2f):** NMR (CDCl$_3$) $\delta$ 5.92 (dd, $J_{ef}$ = 18.2 Hz, $J_{de}$ = 8.5 Hz, H$_e$), 5.90 (ddd, $J_{bc}$ = 16.2 Hz, $J_{ac}$ = 10.0 Hz, $J_{cd}$ = 8.2 Hz, H$_c$), 5.68 (d, H$_f$), 5.04 (dd, H$_b$), 5.02 (dd, H$_a$), 3.68 (q, CH, 1 H), 2.67 (t, H$_d$), 1.68 (s, OH), 1.08 (s, CH$_3$, 3 H), 0.02 (s, Me$_3$Si); mass spectrum, *m/e* 184 (M$^+$). Anal. Calcd for C$_{10}$H$_{20}$OSi: C, 65.15; H, 10.94. Found: C, 65.10; H, 10.87.

**7-(Trimethylsilyl)-4,6-heptadien-2-ol (3f):** NMR (CDCl$_3$) $\delta$ 6.42 (dd, $J_{ef}$ = 17.9 Hz, $J_{de}$ = 9.2 Hz, H$_e$), 6.06 (dd, $J_{cd}$ = 14.1 Hz, H$_d$), 5.70 (d, H$_f$), 5.67 (dt, $J_{ac}$ = $J_{bc}$ = 8.2 Hz, H$_c$), 3.69 (q, $J$ = 6.5 Hz, CH, 1 H), 2.19 (m, H$_a$ and H$_b$), 1.82 (s, OH), 1.10 (d, CH$_3$, 6 H), 0.02 (s, Me$_3$Si); mass spectrum, *m/e* 184 (M$^+$). Anal. Calcd for C$_{10}$H$_{20}$OSi: C, 65.15; H, 10.94. Found: C, 64.85; H, 10.38.

**2-Methyl-4-vinyl-6-(trimethylsilyl)-5-hexen-3-ol (2g):** NMR (CDCl$_3$) $\delta$ 6.04 (dd, $J_{ef}$ = 18.4 Hz, $J_{de}$ = 7.9 Hz, H$_e$), 5.84 (ddd, $J_{bc}$ = 17.2 Hz, $J_{ac}$ = 9.8 Hz, $J_{cd}$ = 8.1 Hz, H$_c$), 5.67 (d, H$_f$), 5.08 (dd, H$_b$), 5.03 (dd, H$_a$), 3.25 (dd, $J$ = 7.8 Hz, H$_d$), 2.89 (m, CH, 1 H), 1.68 (s, OH), 1.67 (m, CH, 1 H), 0.80 (d, $J$ = 7.8 Hz, CH$_3$, 6 H), −0.02 (s, Me$_3$Si); mass spectrum, *m/e* 212 (M$^+$). Anal. Calcd for C$_{12}$H$_{24}$OSi: C, 67.86; H, 11.39. Found: C, 67.70; H, 11.30.

**2-Methyl-8-(trimethylsilyl)-5,7-octadien-3-ol (3g):** NMR (CDCl$_3$) $\delta$ 6.45 (dd, $J_{ef}$ = 18.2 Hz, $J_{de}$ = 9.6 Hz, H$_e$), 6.09 (dd, $J_{cd}$ = 14.2 Hz, H$_d$), 5.70 (d, H$_f$), 5.67 (dt, $J_{ac}$ = $J_{bc}$ = 9.2 Hz, H$_c$), 3.37 (m, CH, 1 H), 2.19 (m, H$_a$ and H$_b$), 1.67 (s, OH), 1.64 (m, CH, 1 H), 0.99 (d, CH$_3$, 6 H), 0.01 (s, Me$_3$Si); mass spectrum, *m/e* 212 (M$^+$). Anal. Calcd for C$_{12}$H$_{24}$OSi: C, 67.86; H, 11.39. Found: C, 67.76; H, 11.28.

**Reaction of [1,5-Bis(trimethylsilyl)pentadienyl]lithium (4) with Carbonyl Compounds.** A rapidly stirred solution of 4 (0.9 g, 4 mmol) in THF (25 mL) was treated with 1.2 equimolar amount of freshly distilled 2-propanone, cyclohexanone, 2,4-dimethyl-3-pentanone, ethanal, or isobutanal (5 mmol) at −78 °C. The mixture was stirred at 20 °C for 10 min and then quenched with 0.1 mol dm$^{-3}$ aqueous HCl (0.5 mL). After usual workup, the following products were obtained from each of the reactions. The subscripts of H and $J$ are given in eq 2. The elemental analysis agreed well with the calculated values.

**2-Methyl-3-[2-(trimethylsilyl)ethenyl]-5-(trimethylsilyl)-4-penten-2-ol (5a):** NMR (CDCl$_3$) $\delta$ 6.01 (dd, $J_{ab}$ = $J_{de}$ = 18.6 Hz, $J_{bc}$ = $J_{cd}$ = 7.9 Hz, H$_b$ and H$_d$), 5.65 (d, H$_a$ and H$_e$), 2.71 (t, H$_c$), 1.62 (s, OH), 1.11 (s, CH$_3$), 0.03 (s, Me$_3$Si); mass spectrum, *m/e* 270 (M$^+$). Anal. Calcd for C$_{14}$H$_{30}$OSi: C, 59.19; H, 11.18. Found: C, 59.18; H, 11.20.

**1-[2-(Trimethylsilyl)ethenyl]-3-(trimethylsilyl)-2-propenylcyclohexan-1-ol (5b):** NMR (CDCl$_3$) $\delta$ 6.03 (dd, $J_{ab}$ = $J_{de}$ = 19.0 Hz, $J_{bc}$ = $J_{cd}$ = 7.6 Hz, H$_b$ and H$_d$), 5.61 (d, H$_a$ and H$_e$), 2.68 (t, H$_c$), 1.69 (s, OH), 1.87 (m, CH$_2$, 4 H), 1.43–1.49 (m, CH$_2$, 6 H), 0.00 (s, Me$_3$Si, 18 H); mass spectrum, *m/e* 311 (M$^+$). Anal. Calcd for C$_{17}$H$_{34}$OSi$_2$: C, 65.73; H, 11.03. Found: C, 65.55; H, 11.05.

**3-[2-(Trimethylsilyl)ethenyl]-5-(trimethylsilyl)-4-penten-2-ol (5c):** NMR (CDCl$_3$) $\delta$ 5.96 (dd, $J_{ab}$ = 18.0 Hz, $J_{bc}$ = 6.9 Hz, H$_b$), 5.93 (dd, $J_{de}$ = 18.0 Hz, $J_{cd}$ = 6.9 Hz, H$_d$), 5.68 (d, H$_a$), 5.65 (d, H$_e$), 3.67 (q, CH, 1 H), 2.70 (dt, $J$ = 6.7 Hz, H$_c$), 1.62 (s, OH), 1.11 (d, $J$ = 6.8 Hz, CH$_3$, 3 H), 0.02 (s, Me$_3$Si); mass spectrum, *m/e* 257 (M$^+$). Anal. Calcd for C$_{13}$H$_{28}$OSi$_2$: C, 60.87; H, 11.02. Found: C, 60.89; H, 11.05.

**2-Methyl-4-[2-(trimethylsilyl)ethenyl]-6-(trimethylsilyl)-5-hexen-3-ol (5d):** NMR (CDCl$_3$) $\delta$ 5.97 (dd, $J_{ab}$ = 18.5 Hz, $J_{bc}$ = 7.0 Hz, H$_b$), 5.94 (dd, $J_{de}$ = 18.5 Hz, $J_{cd}$ = 7.0 Hz, H$_d$), 5.69 (d, H$_a$), 5.64 (d, H$_e$), 3.69 (m, CH, 1 H), 2.69 (m, H$_c$), 1.60 (m, CH, 1 H), 0.85 (d, CH$_3$, 6 H), 1.71 (s, OH), 0.10 (s, Me$_3$Si), 0.05 (s, Me$_3$Si); mass spectrum, *m/e* 285 (M$^+$). Anal. Calcd for C$_{15}$H$_{32}$OSi$_2$: C, 63.33; H, 11.33. Found: C, 63.15, H, 11.33.

**1-(Trimethylsilyl)-6-isopropyl-7-methyl-1,3,5-octatriene (6):** NMR (CDCl$_3$) $\delta$ 6.55 (dd, $J_{ab}$ = 18.0 Hz, $J_{bc}$ = 9.4 Hz, H$_b$), 6.52 (dd, $J_{de}$ = 10.2 Hz, H$_d$), 6.08 (d, H$_e$), 5.82 (dd, $J_{cd}$ = 14.8 Hz, H$_c$), 5.78 (d, H$_a$), 2.96 (m, CH, 1 H), 2.36 (m, $J$ = 6.9 Hz, CH, 1 H), 1.04 (d, CH$_3$, 6 H), 1.02 (d, CH$_3$, 6 H), 0.02 (s, Me$_3$Si); mass spectrum, *m/e* 237 (M$^+$); UV (hexane) 265, 275, 286, 297 nm. Anal. Calcd for C$_{15}$H$_{28}$Si: C, 76.19; H, 11.94. Found: C, 76.17; H, 11.87.

**Reaction of [1,3,5-Tris(trimethylsilyl)pentadienyl]lithium (8) with Carbonyl Compounds.** The reaction was carried out in essentially the same manner as described for the reaction of 1 with acetone. The following conjugated trienes were isolated by distillation in vacuo.

**1,3-Bis(trimethylsilyl)-6-methyl-1,3,5-heptatriene (10a):** IR (neat) 2955, 2900, 2880, 1626, 1576, 1244, 986, 867, 837, 743, 695 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 7.00 (d, $J_{ab}$ = 18.9 Hz, H$_b$), 6.51 (d, $J_{cd}$ = 11.2 Hz, H$_c$), 6.28 (d, H$_d$), 5.77 (d, H$_a$), 1.79 (s, CH$_3$, 6 H), 0.11 (s, Me$_3$Si), 0.05 (s, Me$_3$Si); mass spectrum, *m/e* (relative intensity), 224 (M$^+$, 5), 225 (M$^+$ + 1, 2), 226 (M$^+$ + 2, 1); UV (hexane) 262, 288, 298 nm. Anal. Calcd for C$_{14}$H$_{28}$Si$_2$: C, 66.58; H, 11.18. Found: C, 66.28; H, 11.23.

**[3,5-Bis(trimethylsilyl)-2,4-pentadienylidene]cyclohexane (10b):** IR (neat) 2955, 2925, 2900, 2855, 1625, 1576, 1446, 1244, 986, 866, 837, 755, 743, 695 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 7.04 (d, $J_{ab}$ = 19.1 Hz, H$_b$), 6.61 (d, $J_{cd}$ = 11.4 Hz, H$_c$), 6.26 (d, H$_d$), 5.80 (d, H$_a$), 2.20, 2.35 (m, CH$_2$, 4 H), 1.56 (m, CH$_2$, 6 H), 0.12 (s, Me$_3$Si), 0.08 (s, Me$_3$Si); mass spectrum, *m/e* (relative intensity) 292 (M$^+$, 5), 293 (M$^+$ + 1, 2), 294 (M$^+$ + 2, 1); UV (hexane) 257, 289, 298 nm. Anal. Calcd for C$_{17}$H$_{32}$Si$_2$: C, 69.78; H, 11.02. Found: C, 69.46; H, 11.03.

**1,3-Bis(trimethylsilyl)-6-ethyl-1,3,5-octatriene (10c):** IR (neat) 2960, 2895, 2875, 1628, 1576, 1247, 985, 867, 837, 740, 694 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 7.05 (d, $J_{ab}$ = 19.0 Hz, H$_b$), 6.62 (d, $J_{cd}$ = 10.3 Hz, H$_c$), 6.31 (d, H$_d$), 5.82 (d, H$_c$), 2.24 (q, $J$ = 7.5 Hz, CH$_2$, 2 H), 2.15 (q, $J$ = 7.5 Hz, CH$_2$, 2 H), 1.06 (t, CH$_3$, 3 H), 1.04 (t, CH$_3$, 3 H), 0.10 (s, Me$_3$Si), 0.04 (s, Me$_3$Si); mass spectrum, *m/e* (relative intensity) 280 (M$^+$, 6), 281 (M$^+$ + 1, 2), 282 (M$^+$ + 2, 1); UV (hexane) 266, 289, 299 nm. Anal. Calcd for C$_{16}$H$_{32}$Si$_2$: C, 68.49; H, 11.51. Found: C, 68.43; H, 11.47.

**1,3-Bis(trimethylsilyl)-1,3,5-heptatriene (10d) (*E,E,E* isomer):** IR (neat) 2960, 2900, 2860, 1620, 1578, 1244, 985, 866, 836, 750, 695 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 7.02 (d, $J_{ab}$ = 18.9 Hz, H$_b$), 6.54 (dd, $J_{cd}$ = 10.3 Hz, $J_{de}$ = 16.0 Hz, H$_d$), 6.62 (d, H$_c$), 5.87 (d, H$_a$), 5.85 (dq, $J$ = 6.7 Hz, CH), 1.82 (d, CH$_3$, 3 H), 0.09 (s, Me$_3$Si), 0.02 (s, Me$_3$Si); mass spectrum *m/e* (relative intensity) 238 (M$^+$, 6), 239 (M$^+$ + 1, 2), 240 (M$^+$ + 2, 1); UV (hexane) 286, 297 nm. Anal. Calcd for C$_{13}$H$_{26}$Si$_2$: C, 65.46; H, 10.99. Found: C, 65.48; H, 10.99.

**1,3-Bis(trimethylsilyl)-7-methyl-1,3,5-octatriene (10e) (*E,E,E* isomer):** IR (neat) 2955, 2900, 2840, 1644, 1576, 1244, 1001, 864, 837, 755, 695 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 7.04 (d, $J_{ab}$ = 18.2 Hz, H$_b$), 6.62 (d, $J_{cd}$ = 10.3 Hz, H$_c$), 6.30 (dd, $J$ = 15.6 Hz, H$_d$), 5.83 (d, H$_a$), 5.76 (dd, CH, 1 H), 1.64 (m, CH, 1 H), 0.99 (d, CH$_3$, 6 H), 0.08 (s, Me$_3$Si), 0.00 (s, Me$_3$Si); mass spectrum, *m/e* (relative intensity) 266 (M$^+$, 6), 267 (M$^+$ + 1, 3), 268 (M$^+$ + 2, 1); UV (hexane) 265, 288, 298 nm. Anal. Calcd for C$_{15}$H$_{30}$Si$_2$: C, 67.58; H, 11.34. Found: 67.45; H, 11.56.

**Desilylation of 10b.** [3,5-Bis(trimethylsilyl)-2,4-pentadienylidene]cyclohexane (1.1 mL, 3 mmol) was added to an acetonitrile solution (6 mL) of dry HCl (1.9 mmol) at −20 °C. The mixture was stirred at 0 °C for 30 min and poured into aqueous ammonium chloride. Extraction with ether followed by distillation (125 °C/1 mmHg) gave a conjugated triene 11 (68%) together its isomer 12 (32%) in 45% combined yield.

**2,4-Pentadienylidenecyclohexane (11).** $^1$H NMR (CDCl$_3$) $\delta$ 6.60 (ddd, $J$ = 11.5 Hz, CH), 5.97 (dd, $J$ = 16.1 Hz, CH), 5.94 (dd, CH), 5.04 (dd, =CH$_2$, trans), 4.91 (dd, =CH$_2$, cis), 2.2–2.3 (m, CH$_2$), 1.56 (m, CH$_2$); mass spectrum, *m/e* 148 (M$^+$). Calcd for C$_{11}$H$_{16}$ 148.

**1,3-Pentadienyl-1-cyclohexene:** $^1$H NMR (CDCl$_3$) $\delta$ 6.08 (m, CH=CH, 3 H), 5.70 (m, CH$_3$CH and CH$_2$CH), 2.12 (m, CH$_2$), 1.61 (d, CH$_3$), 1.56 (m, CH$_3$); mass spectrum, *m/e* 148 (M$^+$). Anal. Calcd for C$_{11}$H$_{16}$: C, 89.12; H, 10.88. Found: C, 89.01; H, 10.87.

**Reaction of Silylated Pentadienyl Anions with Unsaturated Carbonyl Compounds.** The reaction of 1, 4, or 8 with cyclo-2-hexenone, 4-methyl-3-penten-2-one, or ethyl 3,3-dimethylacrylate was carried out in the similar manner as described for the reaction with acetone. The isomers of the addition products were separated on a preparative gas chromatograph.

**3-(3-(Trimethylsilyl)-1-vinyl-2-propenyl)cyclohexanone (15a):** $^1$H NMR (CDCl$_3$) 5.85 (dd, $J_{ab}$ = 18.5 Hz, $J_{bc}$ = 6.4 Hz,

$H_b$), 5.72 (ddd, $J_{cd}$ = 6.5 Hz, $J_{de}$ = 11.3 Hz, $J_{df}$ = 16.8 Hz, $H_d$), 5.58 (d, $H_a$), 4.96 (dd, $H_e$), 4.89 (dd, $H_f$), 2.58 (m, $H_c$), 2.16–2.36 (m, $CH_2$ and CH, 5 H), 1.64–1.92 (m, $CH_2$, 4H), −0.05 (s, $Me_3Si$); mass spectrum, *m/e* 236 ($M^+$). Anal. Calcd for $C_{14}H_{24}OSi$: C, 72.12; H, 10.23. Found: C, 72.05, H, 10.22.

**3-(5-Trimethyl-2,4-pentadienyl)cyclohexanone (16a):** $^1H$ NMR ($CDCl_3$) $\delta$ 6.48 (dd, $J_{ab}$ = 18.6 Hz, $J_{bc}$ = 9.3 Hz, $H_b$), 6.09 (dd, $J_{cd}$ = 14.7 Hz, $H_c$), 5.73 (dt, $J_{de}$ = 7.7 Hz, $H_d$), 5.71 (d, $H_a$), 2.29 (m, $CH_2$, 2 H), 1.96 (m, $CH_2$, 4 H), 1.72 (m, C H, 1 H), 1.64 (m, $CH_2$, 4 H), −0.05 (s, $Me_3Si$); mass spectrum, *m/e* (calcd) for $C_{14}H_{24}OSi$ 236.4, *m/e* (measd) 236 ($M^+$).

**4,4-Dimethyl-5-vinyl-7-(trimethylsilyl)-6-hepten-2-one (15b):** $^1H$ NMR ($CDCl_3$) $\delta$ 5.86 (dd, $J_{ab}$ = 18.3 Hz, $J_{bc}$ = 7.5 Hz, $H_b$), 5.72 (ddd, $J_{de}$ = 17.0 Hz, $J_{df}$ = 7.3 Hz, $J_{cd}$ = 7.7 Hz, $H_d$), 5.65 (d, $H_a$), 5.06 (dd, $H_e$), 5.01 (dd, $H_f$), 2.72 (dd, $H_c$), 2.19 (s, $CH_2$), 1.88 (s, $CH_3$), 0.87 (s, $CH_3$), −0.06 (s, $Me_3Si$); mass spectrum, *m/e* 238 ($M^+$). Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.39; H, 10.78.

**9-(Trimethylsilyl)-4,4-dimethyl-6,8-nonadien-2-one (16b):** $^1H$ NMR ($CDCl_3$) 6.46 (dd, $J_{ab}$ = 18.2 Hz, $J_{bc}$ = 9.5 Hz, $H_b$), 6.07 (dd, $J_{cd}$ = 16.8 Hz, $H_c$), 5.73 (dt, $J_{de}$ = 8.0 Hz, $H_d$), 5.70 (d, $H_a$), 2.29 (s, $CH_2$, $H_e$), 2.12 (m, $CH_2$), 1.87 (s, $CH_3$), 0.92 (s, $CH_3$), −0.03 (s, $Me_3Si$); mass spectrum, *m/e* 238 ($M^+$). Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.34; H, 10.87.

**Ethyl 3,3-dimethyl-4-vinyl-6-(trimethylsilyl)-5-hexenoate (15c):** $^1H$ NMR ($CDCl_3$) $\delta$ 5.92 (dd, $J_{ab}$ = 18.2 Hz, $J_{bc}$ = 7.7 Hz, $H_b$), 5.74 (ddd, $J_{cd}$ = 7.8 Hz, $J_{de}$ = 17.2 Hz, $J_{df}$ = 9.7 Hz, $H_d$), 4.97 (dd, $J_{ef}$ = 4.0 Hz, $H_e$), 4.92 (dd, $H_f$), 4.01 (q, *J* = 7.0 Hz, $CH_2O$), 2.66 (dd, $H_c$), 2.12 (s, $CH_2$, 2 H), 1.15 (t, $CH_3$, 3 H), 0.92 (s, $CH_3$, 6 H), −0.03 (s, $Me_3Si$); mass spectrum, *m/e* 268 ($M^+$). Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 60.75; H, 9.52. Found: C, 60.73; H, 9.51.

**3-[1-[2-(Trimethylsilyl)ethenyl]-3-(trimethylsilyl)-2-propenyl]cyclohexanone (15d):** $^1H$ NMR ($CDCl_3$) $\delta$ 5.81 (dd, $J_{ab}$ = $J_{de}$ = 18.7 Hz, $J_{bc}$ = $J_{cd}$ = 7.8 Hz, $H_b$ and $H_d$), 5.54 (d, $H_a$ and $H_e$), 2.60 (ddd, *J* = 7.8 Hz, CH, 1 H), 2.22 (m, $CH_2$, 4 H), 1.72–1.40 (m, $CH_2$, 4 H), −0.04 (s, $Me_3Si$), 18 H); mass spectrum, *m/e* 309 ($M^+$). Anal. Calcd for $C_{17}H_{32}OSi_2$: C, 66.16; H, 10.45. Found: C, 66.15; H, 10.45.

**4,4-Dimethyl-5-[2-(trimethylsilyl)ethenyl]-7-(trimethylsilyl)-6-hepten-2-one (15e):** $^1H$ NMR ($CDCl_3$) $\delta$ 5.88 (dd, $J_{ab}$ = $J_{de}$ = 18.1 Hz, $J_{bc}$ = $J_{cd}$ = 7.6 Hz, $H_b$ and $H_d$), 5.48 (d, $H_a$ and $H_e$), 2.76 (t, $H_c$), 2.18 (s, $CH_2$, 2 H), 1.88 (s, $CH_3$, 3 H), 0.87 (s, $CH_3$, 6 H), −0.07 (s, $Me_3Si$); mass spectrum, *m/e* (calcd) for $C_{17}H_{34}OSi_2$ 310.6, *m/e* (measd) 311 ($M^+$).

**Ethyl 3,3-dimethyl-4-[2-(trimethylsilyl)ethenyl]-6-(trimethylsilyl)-5-hexenoate (15f):** $^1H$ NMR ($CDCl_3$) $\delta$ 5.90 (dd, $J_{ab}$ = $J_{de}$ = 18.8 Hz, $J_{bc}$ = $J_{cd}$ = 8.0 Hz, $H_b$ and $H_d$), 5.49 (d, $H_a$ and $H_e$), 3.96 (q, $CH_2$, 2 H), 2.65 (t, $H_c$), 2.06 (s, $CH_2$, 2 H), 1.08 (t, $CH_3$, 3 H), 0.85 (s, $CH_3$, 6 H), −0.07 (s, $Me_3Si$); mass spectrum, *m/e* 341 ($M^+$). Anal. Calcd for $C_{18}H_{36}O_2Si_2$: C, 63.47; H, 10.65. Found: C, 63.45; H, 10.66.

**3-[1-(Trimethylsilyl)-1-[2-(trimethylsilyl)ethenyl]-3-(trimethylsilyl)-2-propenyl]cyclohexanone (15g):** $^1H$ NMR ($CDCl_3$) $\delta$ 6.12 (d, $J_{ab}$ = 19.1 Hz, $H_b$), 6.09 (d, $J_{de}$ = 19.1 Hz, $H_d$), 5.52 (d, $H_a$), 5.49 (d, $H_e$), 2.16–2.32 (m, $CH_2$ and CH, 5 H), 1.45–1.79 (m, $CH_2$, 4 H), 0.01 (s, $Me_3Si$, 18 H), −0.07 (s, $Me_3Si$, 9 H); mass spectrum, *m/e* 381 ($M^+$). Anal. Calcd for $C_{20}H_{40}OSi_3$: C, 63.31; H, 10.59. Found: C, 63.15; H, 10.82.

**Preparation of 1-(Trimethylsilyl)-2,4,6,8-decatetraene (17).** To a vigorously stirred suspension of potassium sand (0.8 g, 20 mmol) in THF (10 mL) was added 1,3,7,9-decatetraene (3.4 mL, 20 mmol) at −40 °C. The mixture was stirred at 0 °C for 5 h and then at 25 °C for 5 h. After the removal of THF by trap-to-trap distillation, the residue was washed with dry pentane (25 mL) at −40 °C to give decatetraenylpotassium as a viscous orange semisolid in 35% yield. The monoanion (5 mmol) was dissolved in THF (10 mL) and was allowed to react with chlorotrimethylsilane (5 mmol) at 0 °C. Distillation of the product in vacuo followed by recrystallization from pentane at −78 °C gave 1-(trimethylsilyl)-2,4,6,8-decatetraene in 72% yield based on the monoanion: bp 140 °C (0.1 mmHg), mp −5 °C; NMR ($CDCl_3$) $\delta$ 5.99 (m, CH, 6 H), 5.72 (dq, *J* = 15.0 Hz, CH, 1 H), 5.63 (dt, *J* = 14.8 Hz, CH, 1 H), 1.52 (d, $CH_2$), −0.05 (s, $Me_3Si$); mass spectrum, *m/e* (relative intensity), 206 ($M^+$, 14), 207 ($M^+$ + 1, 4), 208 ($M^+$ + 2, 2), 73 ($Me_3Si$, 100). Anal. Calcd for $C_{13}H_{22}Si$: C, 76.65; H, 10.74. Found: C, 76.35; H, 10.70.

**Preparation of 1,10-Bis(trimethylsilyl)-2,4,6,8-decatetraene (18).** To a vigorously stirred suspension of potassium sand (1.0 g, 25 mmol) in a mixture of triethylamine (30 mL) and THF (2 mL) was dropwise added 1,3,7,9-decatetraene (2 mL, 12 mmol) at 0 °C. Stirring was continued at 0 °C for 3 h and then at 25 °C for 10 h to result in the precipitation of 2,4,6,8-decatetraen-1,10-diyldipotassium as a red-brown solid. The solid was separated from the soluble fraction with a centrifuge using a specially designed two-necked glass tube fitted with two rubber septums and washed with 1:2 THF–$NEt_3$ (5 mL) to give the pure dianion in 20–30% yield. Chlorotrimethylsilane (6 mL, 5 mmol) was dropwise added to a THF suspension (15 mL) of 2,4,6,8-decatetraen-1,10-diyldipotassium (0.8 g, 4 mmol) at 0 °C, and stirring was continued for 1 h. Distillation of the product gave 1,10-bis(trimethylsilyl)-2,4,6,8-decatetraene in 90% yield: mp 69 °C; IR (neat) 3002, 2955, 2895, 1630, 1395, 1245, 1098, 1003, 858, 843, 600, 554 $cm^{-1}$; HMR ($CDCl_3$) $\delta$ 6.04, 6.08 (m, CH, 4 H), 6.02 (m, CH, 2 H), 5.62 (dt, *J* = 15.8 Hz, CH, 2 H), 1.54 (d, $CH_2$, 4 H), −0.01 (s, $Me_3Si$, 18 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 134.1, 132.9, 131.6, 131.4, 131.3, 25.9, 0.0; UV (THF) 325, 311, 297, 285, 273 nm; mass spectrum, *m/e* (relative intensity), 278 ($M^+$, 15), 279 ($M^+$ + 1, 6), 280 ($M^+$ + 2, 2), 73 ($Me_3Si$, 100). Anal. Calcd for $C_{16}H_{30}Si_2$: C, 68.98; H, 10.85. Found: C, 68.85; H, 10.89.

**Preparation of a Conjugated Hexaene (19).** *N,N,N′,N′*-Tetramethylethylenediamine (0.6 mL, 4 mmol) was added to a solution of *n*-butyllithium (3.0 mmol) in hexane (4 mL), and the mixture was stirred for 10 min at 25 °C. To the resulting solution was dropwise added 1,10-bis(trimethylsilyl)-2,4,6,8-decatetraene (0.5 mL, 1.5 mmol) at 0 °C, and stirring was continued for 1 h at 25 °C. The solution turned deep red. A solution of 2,4-dimethyl-3-pentanone (0.3 mL, 2 mmol) in hexane (3 mL) then was added with stirring at −70 °C. The mixture was allowed to warm to 25 °C in 10 min, and aqueous ammonium chloride was added. The organic layer was distilled (120 °C (10 torr)) to give 2,15-dimethyl-3,14-diisopropylhexadeca-3,5,7,9,11,13-hexaene (19) in 25% yield: UV (THF) 324, 338, 359, 394 nm; $^1H$ NMR ($CDCl_3$) $\delta$ 6.22 (m, CH═CH, 10 H), 2.36, 2.92 (m, CH, 4 H), 1.03, 1.01 (d, $CH_3$, 24 H): mass spectrum, *m/e* 326 ($M^+$). Anal. Calcd for $C_{24}H_{38}$: C, 88.27; H, 11.73. Found: C, 88.27; H, 11.71.

**Preparation and Reaction of [5-(Trimethylsilyl)-2,4-pentadienyl]magnesium Bromide (20).** Transmetalation of [1-(trimethylsilyl)pentadienyl]lithium (1a) to a magnesium compound was carried out by the same procedure as reported for preparation of a series of pentadienylmagnesium compounds.[23] A THF solution (10 mL) of **1a** (0.6 g, 4 mmol) was added to a THF solution (10 mL) of anhydrous magnesium bromide (0.7 g, 4 mmol) over a 1-h period at 0 °C under magnetic stirring. The orange color of the solution turned to pale-yellow when stirring was continued for 1 h at 25 °C. A solution of acetone, isobutanal, or 4,4-dimethyl-3-buten-2-one (4 mmol) in THF (5 mL) was added to the resulting solution at 0 °C, and the mixture was stirred for 1 h at 25 °C. The solution was evaporated to dryness, and diethyl ether (30 mL) was added. Treatment of the ether solution with 1 mol $dm^{-3}$ aqueous HCl followed by filtration and distillation gave an alcohol, **2a, 2g** or **15b**, in 92, 94, or 35% yield, respectively.

**Reaction of [5-(Trimethylsilyl)-2,4-pentadienyl]dimethoxyboron (21).** To a solution of [1-(trimethylsilyl)pentadienyl]lithium (**1a**; 0.6 g, 4 mmol) in THF (20 mL) was added freshly distilled trimethylborate (0.4 mL, 4 mmol) at −78 °C. The mixture was allowed to warm to 10 °C and held there for 5 min to complete the transmetalation. (Stirring at 20 °C longer than 30 min results in significant decrease in the product yield due to spontaneous polymerization.) After the solution was cooled to −78 °C, acetone, isobutanal, or 4,4-dimethyl-3-buten-2-one (4 mmol) was added, and the solution was stirred at 0 °C for 2 h. Treatment of the solution with acetic acid gave **2a, 2g**, or **15b** in 70, 81, or 42% yield, respectively.

**Preparation and Reaction of [5-(Trimethylsilyl)-2,4-pentadienyl]copper (22).** A mixture of CuBr·$Me_2S$ (0.8 g, 4 mmol) and tributylphosphine (4.0 g, 16 mmol) was dissolved in THF (40 mL) at room temperature to give a colorless solution. [1-(Trimethylsilyl)pentadienyl]lithium (**1a**; 3 mmol) in THF (10 mL) was added to the solution at −78 °C, and the mixture was stirred for 1 h at 0 °C. The color of the solution turned to pale yellow. Raising the temperature over 20 °C must be avoided because the copper complex immediately decomposed to a mixture of

1,3,7,9-decatetraene (90%), 6-vinyl-1,3,7-octatriene (10%), and THF-insoluble, black cluster compounds. The addition of a small excess of $CuBr{\cdot}Me_2S$ and a large excess of tributylphosphine with respect to **1a** is essential for a successful selective addition reaction with carbonyl compounds as described in the text. Acetone, isobutanal, or 4-methyl-3-penten-2-one (3 mmol) then was added to the solution at −78 °C, and the mixture was stirred at 10 °C for 2 h. After the mixture was quenched with aqueous HCl, the product was distilled.

**Registry No.** **1a**, 75150-96-8; **1b**, 83573-32-4; **2a**, 93531-53-4; **2b**, 75135-87-4; **2c**, 93531-54-5; **2d**, 93531-55-6; **2f**, 93531-56-7; **2g**, 93531-57-8; **3a**, 93531-58-9; **3b**, 75135-84-1; **3c**, 93531-59-0; **3d**, 93531-60-3; **3e**, 93531-61-4; **3f**, 93531-62-5; **3g**, 93531-63-6; **4**, 83573-33-5; **5a**, 93531-64-7; **5b**, 93531-65-8; **5c**, 93531-67-0; **5d**, 93531-68-1; **6**, 93531-66-9; **7**, 34865-75-3; **8**, 93531-69-2; **10a**, 93531-70-5; **10b**, 93531-71-6; **10c**, 93564-62-6; **10d**, 93531-72-7; **10e**, 93531-73-8; **11**, 93531-91-0; **12**, 93531-92-1; **15a**, 93531-74-9; **15b**, 93531-75-0; **15c**, 93531-76-1; **15d**, 93531-77-2; **15e**, 93531-78-3; **15f**, 93531-79-4; **15g**, 93531-80-7; **16a**, 93531-81-8; **16b**, 93531-82-9; **16c**, 93531-83-0; **16d**, 93531-84-1; **16e**, 93531-85-2; **16f**, 93531-86-3; **17**, 93531-97-6; **18**, 93531-94-3; **19**, 93531-96-5; **20**, 93531-87-4; **21**, 93531-88-5; **22**, 93531-50-1; **23**, 93531-90-9; **24**, 93531-52-3; $C_5H_7CuPBu_3$, 93531-51-2; $(C_2H_5)_2CO$, 96-22-0; $(i\text{-}C_3H_7)_2CO$, 565-80-0; $t\text{-}C_4H_9(CH_3)CO$, 75-97-8; $CH_3CHO$, 75-07-0; $i\text{-}C_3H_7CHO$, 78-84-2; $(CH_3)_2C{=}CHCOCH_3$, 141-79-7; $(CH_3)_2C{=}CHCOOC_2H_5$, 638-10-8; $C_5H_8MgBr$, 93531-89-6; $(CH_3)_2CO$, 67-64-1; HCl, 7647-01-0; cyclohexanone, 108-94-1; cyclohex-2-enone, 930-68-7; 1,3,7,9-decatetraene, 32509-35-6; 2,4,6,8-decatetraenyl potassium, 93531-93-2; 2,4,6,8-decatraen-1,10-diyldipotassium, 93531-95-4; 6-vinyl-1,3,7-octatriene, 33629-84-4; acetic acid, 64-19-7; (*E,E*)-1,3-pentadien-1,5-diylbis(trimethylsilane), 83573-51-7.

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# Reactions of the Cationic Rhenium Aryldiazenido Complexes $[(\eta\text{-}C_5H_5)Re(CO)_2(N_2Ar)]^+$ and $[(\eta\text{-}C_5Me_5)Re(CO)_2(N_2Ar)]^+$. Monocarbonyl Derivatives with Halide, Isocyanate, Carbamoyl (Carboxamido), and Alkoxycarbonyl Ligands

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Reactions of the dicarbonylrhenium aryldiazenido cations $[CpRe(CO)_2(N_2Ar)]^+$ (1) and $[Cp^*Re(CO)_2(N_2Ar)]^+$ (2) (Cp = $\eta\text{-}C_5H_5$, Cp* = $\eta\text{-}C_5Me_5$, Ar = aryl) with some nucleophiles are described, leading to monocarbonyl aryldiazenido complexes of the general type $CpReX(CO)(N_2Ar)$ and $Cp^*ReX(CO)(N_2Ar)$, with X = Cl, Br, I, NCO, $CO_2R$ (R = alkyl), $CONH_2$, CONHMe, and $CONMe_2$. Some examples of analogous reactions of the manganese complex $[MeCpMn(CO)_2(N_2Ar)]^+$ (MeCp = $\eta\text{-}C_5H_4Me$) are also included. Solid-state or solution reactions of 1 or 2 with alkali halides are quite dependent on the experimental conditions, the halide, and the $\eta^5$-arene. Under appropriate conditions all examples of $CpReX(CO)(N_2Ar)$ and $Cp^*ReX(CO)(N_2Ar)$ with X = Cl, Br, or I can be isolated, but $CpRe(CO)_2(N_2)$, $CpRe(CO)_2X_2$ (X = Br, I), and $Cp^*Re(CO)_2X_2$ (X = Br, I) may also be formed. The isocyanate complexes $CpRe(NCO)(CO)(N_2Ar)$ and $Cp^*Re(NCO)(CO)(N_2Ar)$ are formed from 1 or 2 with $NCO^-$, $N_3^-$, or $N_2H_4$. Alkoxycarbonyl complexes $CpRe(CO_2R)(CO)(N_2Ar)$ and $Cp^*Re(CO_2R)(CO)(N_2Ar)$ are formed by using $OMe^-$ or $[HB(OCHMe_2)_3]^-$ and carbamoyl complexes $CpRe(CONR_2)(CO)(N_2Ar)$ or $Cp^*Re(CONR_2)(CO)(N_2Ar)$ ($R_2$ = $H_2$, HMe, $Me_2$) by using $NH_3$, $MeNH_2$, or $Me_2NH$. Where similar manganese complexes form, they are generally much less stable than the rhenium ones, and the tendency to form the dinitrogen complex $MeCpMn(CO)_2(N_2)$ in the manganese reactions is much greater.

## Introduction

In previous publications we described the synthesis of the cyclopentadienyl[1] (Cp = $\eta\text{-}C_5H_5$) and pentamethylcyclopentadienyl[2] (Cp* = $\eta\text{-}C_5Me_5$), rhenium aryldiazenido complexes $[CpRe(CO)_2(N_2Ar)][BF_4]$ (1) and $[Cp^*Re(CO)_2(N_2Ar)][BF_4]$ (2) (Ar = aryl). These cations display a rich chemistry, and thus far we have concentrated on reactions by which the aryldiazenido ligand in 1 is transformed into aryldiazene, arylhydrazido(2−), arylhydrazido(1−), and dinitrogen analogues[1,3] and on the remarkably stable hydroxycarbonyl and carboxylate complexes of the type $CpRe(CO)(N_2Ar)(COOH)$ and $[CpRe(CO)(N_2Ar)(CO_2)]^-$ (Cp = Cp or Cp*) formed by $OH^-$ attack at a CO group in compounds 1 and 2.[2,4] The latter are examples of a wider range of monocarbonyl derivatives of the type $CpReX(CO)(N_2Ar)$ and $Cp^*ReX(CO)(N_2Ar)$ that may be accessed from the dicarbonyl cations 1 and 2. Some of these are now described in this paper for X = Cl, Br, I, NCO, COOR (R = alkyl), $CONMe_2$, CONHMe, and $CONH_2$. The hydrides $CpReH(CO)(N_2Ar)$ and $Cp^*ReH(CO)(N_2Ar)$ have been discussed elsewhere.[2,4] Some examples of corresponding compounds synthesized from the (methylcyclopentadienyl)manganese complex $[MeCpMn(CO)_2(N_2Ar)][BF_4]$ (3) (MeCp = $\eta\text{-}C_5H_4Me$)[5] are also included here. The reaction of 3 with alkali halides to give the dinitrogen complex $MeCpMn(CO)_2(N_2)$ has been described previously.[5]

## Results

**(a) Halides.** A remarkable solid-state reaction was observed to occur when $[Cp^*Re(CO)_2(N_2Ar)][BF_4]$ (2, Ar

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