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Reaction of Trialkyl(dibromomethyl)silanes or 1,2-Bis(dibromomethyl)benzene with Triorganomanganates. A Facile and Selective Synthesis of Alkenylsilanes and 1,2-Diaryl-1,2-dihydrobenzocyclobutenes

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Treatment of trialkyl(dibromomethyl)silanes with trialkylmanganates, derived from manganese(II) chloride and three molar amounts of Grignard reagents or alkyllithiums, provided (*E*)-1-trialkylsilyl-1-alkenes with high stereoselectivity in good yields. The reaction of trialkyl(dibromomethyl)silanes with alkylmagnesium halides proceeded in the presence of a catalytic amount of manganese(II) chloride. Treatment of 1,2-bis(dibromomethyl)benzene with triphenylmanganate gave 1,2-diphenyl-1,2-dihydrobenzocyclobutene.

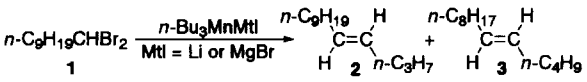
Dialkylcuprate(I)[1] and trialkylzincate[2] have been widely used for organic synthesis. In contrast, much less information is available on the potential utility of a trialkylmanganate-(II).[3,4] Recently we have reported that the reaction of *gem*-dibromocyclopropanes with a trialkylmanganate, followed by treatment with an electrophile, provides dialkylated cyclopropanes.[5] Here, we report that the treatment of *gem*-dibromoalkanes with trialkylmanganate,[6,7] derived from $MnCl_2$ and three molar amounts of RMgX or RLi, affords alkenes and also that the reaction takes place in the presence of a catalytic amount of manganese(II) chloride. In addition we want to report the reaction of 1,2-bis(dibromomethyl)benzene with triarylmanganate or tetraarylmanganate provides 1,2-diarylbenzocyclobutenes, which are useful building blocks for Diels–Alder reaction and are difficult to prepare by other methods.

Results and Discussin

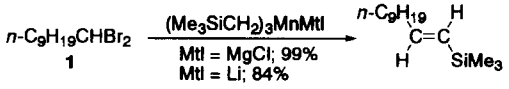
1) Reaction of *gem*-Dibromoalkanes with Trialkylmanganate(II). Treatment of 1,1-dibromodecane **1** with tributylmanganate, generated from $MnCl_2$ and three molar amounts of butyllithium, gave a mixture of 4-tetradecene (**2**, *E*/*Z* = 92/8) and 5-tetradecene (**3**, *E*/*Z* = 92/8) in 95% combined yield (**2**/**3** = 1/1) (Scheme 1). The use of butylmagnesium bromide in place of butyllithium gave the same isomeric mixture **2** and **3** (**2**/**3** = 1/1) in 91% yield. The reaction proved to proceed in the presence of a catalytic amount of manganese(II) chloride. Thus, an addition of a solution of **1** (1.0 mmol) to a THF solution of butylmagnesium bromide (3.0 mmol) and manganese chloride (0.1 mmol) at 0 °C provided **2** and **3** in 83% combined yield.

The reaction was applied to the preparation of alkenylsilanes[8] and the representative results are shown in Table 1 and Scheme 2. Several comments are worth noting. (1) Stoichiometric reaction and catalytic reaction were equally effective for the formation of 1-trialkylsilyl-1-alkenes.[9] (2) (*E*)-Alkenylsilanes were obtained exclusively and no trace of the *Z*-isomer could be detected in the reaction mixture. (3) Among various manganese salts examined, $MnCl_2$, Mn(acac)$_3$, and $Mn_2(CO)_{10}$ proved to be good catalysts. For instance, treatment of *i*-$Pr_3SiCHBr_2$ with ethylmagnesium bromide in the presence of these catalysts gave (*E*)-1-triisopropylsilyl-1-propene in 88, 74, or 85% yield, respectively. (4) Diiodide (*t*-$BuMe_2SiCHI_2$) was as reactive as dibromide **4b** and afforded the 1-*t*-butyldimethylsilyl-1-pentene in 88% yield upon treatment with *n*-Bu_3MnLi. Dichloride (*t*-$BuMe_2SiCHCl_2$) was less reactive than **4b**, and the reaction with *n*-Bu_3MnLi gave the same alkenylsilane in 57% yield after prolonged reaction time (25 °C, 21 h). (5) The reaction of 1,1-dibromodecane **1** with tris(trimethylsilylmethyl)manganate gave 1-trimethylsilyl-1-undecene exclusively and no isomeric allylic silane (1-trimethylsilyl-2-undecene) could be detected (Scheme 2). The hydrogen on the carbon-bearing trimethylsilyl group was eliminated selectively.

We are tempted to assume the following reaction mechanism for the stoichiometric reaction: (1) initial halogen-manganese exchange to give **6**, (2) alkyl migration under

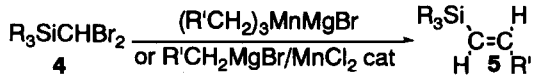


Scheme 1.



Scheme 2.

Table 1. Preparation of (*E*)-1-Trialkylsilyl-1-alkene[a)]



Entry		Substrate	Reagent	Time (h)	Yield (%)
1	**4a**	$Ph_2MeSiCHBr_2$[b)]	Me_3MnMgI	2	89
2	**4a**	$Ph_2MeSiCHBr_2$[b)]	$Et_3MnMgBr$	2	76
3	**4a**	$Ph_2MeSiCHBr_2$[b)]	*n*-Bu_3MnLi	2	95
4	**4a**	$Ph_2MeSiCHBr_2$[b)]	$(PhCH_2)_3MnMgBr$	2	88
5	**4b**	*t*-$BuMe_2SiCHBr_2$	$(Me_3SiCH_2)_3MnMgCl$	1	57
6	**4b**	*t*-$BuMe_2SiCHBr_2$	*n*-$Bu_3MnMgBr$	1	72
7	**4b**	*t*-$BuMe_2SiCHBr_2$	*n*-Bu_3MnLi	1	96
8	**4c**	*i*-$Pr_3SiCHBr_2$	$Et_3MnMgBr$	1	79
9	**4a**	$Ph_2MeSiCHBr_2$[b)]	*n*-$C_4H_9MgBr/MnCl_2$	12	67
10	**4a**	$Ph_2MeSiCHBr_2$[b)]	*n*-$C_{16}H_{33}MgBr/MnCl_2$	12	62
11	**4b**	*t*-$BuMe_2SiCHBr_2$	*n*-$C_4H_9MgBr/MnCl_2$	2	87
12	**4c**	*i*-$Pr_3SiCHBr_2$	$EtMgBr/MnCl_2$	2	88
13	**4c**	*i*-$Pr_3SiCHBr_2$	$MeMgI/MnCl_2$	2	75
14	**4d**	$Me_3SiCHBr_2$	*n*-$C_8H_{17}MgBr/MnCl_2$	2	76
15	**4e**	$(c\text{-}C_6H_{11})_2MeSiCHBr_2$[c)]	*n*-$C_4H_9MgBr/MnCl_2$	2	95

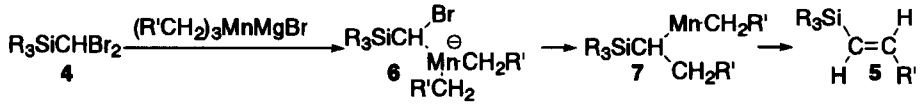
a) Stoichiometric reactions were performed with $R_3SiCHBr_2$ (1.0 mmol) and manganate (1.2 mmol) at 0 °C unless otherwise noted. In the catalytic reactions, Grignard reagent (3.0 mmol), $R_3SiCHBr_2$ (1.0 mmol) and $MnCl_2$ (0.05 mmol) were employed. b) The reactions were performed at 25 °C. c) *c*-C_6H_{11} = cyclohexyl.

Br^- elimination providing **7**, and (3) elimination of Mn and hydrogen at the β-position[10] (Scheme 3).

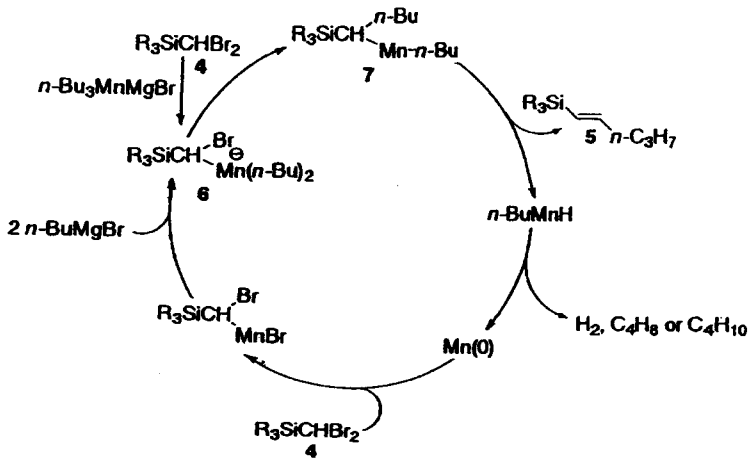
Meanwhile, the reaction mechanism for catalytic pathway could be as follows. Low-valent manganese species Mn(0), generated from *n*-BuMnH, would insert into one of the carbon–bromine bonds to give $R_3SiCH(Br)MnBr$.[11] An attack of two molar amounts of *n*-BuMgBr on $R_3SiCH(Br)MnBr$ regenerates **6** (Scheme 4).[12]

The facility of Mn-H elimination depended on the nature of the substituents on silicon. In the case of trialkylsilyldibromomethane such as **4b**, **4c**, **4d**, and **4e**, elimination took place easily at 0 °C for 2 h. On the other hand, the elimination from $Ph_2MeSiCH(MnEt)Et$, derived from the reaction of **4a** with triethylmanganate, was slow and methyldiphenylpropylsilane was obtained in 17% yield along with alkenylsilane (47%). Thus, the reaction temperature was raised and the reaction mixture of **4a** was stirred at 25 °C for 2 h to suppress the formation of diphenylmethylpropylsilane (< 5%).

Use of cyclopropylmagneseium bromide as a Grignard reagent gave dienylsilanes, which did not have a cyclopropane ring. The reaction of trialkyl(dibromomethyl)silanes with the substituted cyclopropyl Grignard reagents also proceeded effectively to give the corresponding dienylsilanes



Scheme 3.



Scheme 4.

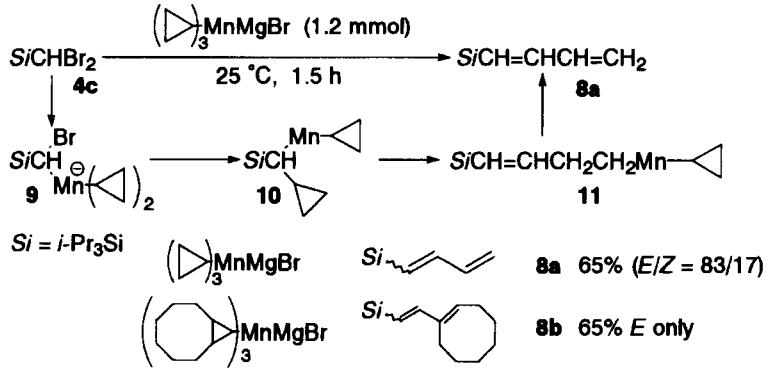
(Scheme 5). The formation of dienylsilanes could be explained as follows: (1) Bromine–manganese exchange followed by cyclopropyl migration under Br^- elimination provided **10** in a similar fashion to the reaction with trialkylmanganate such as n-$Bu_3MnMgBr$; (2) isomerization of **10** into homoallylmanganese **11** under cyclopropane ring cleavage; and (3) β-hydride elimination to give dienylsilane **8a**.

In the reaction of 1,1-dibromodecane with tributylmanganate, two regioisomeric alkenes were produced, as shown in Scheme 1, because of the presence of two types of β-hydrogens. The reaction is not useful for synthetic purposes. However, treatment of dibromoalkane **12**, generated from epoxide and t-butyldimethylsilyldibromomethyllithium,[13] with butylmagnesium bromide in the presence of $MnCl_2$ catalyst gave alkene **13** as a single regioisomer. The coordination of oxygen of the siloxy group to manganese would cause formation of five-membered ring intermediate **14** in which only one type of β-hydrogens is available for *syn*-elimination of Mn-H (Scheme 6).[14]

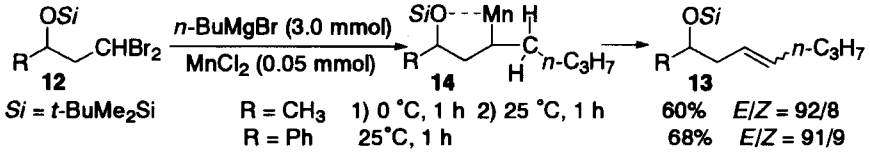
Trialkyl(tribromomethyl)silane, t-$BuMe_2SiCBr_3$ (**15**), afforded alkenylsilane **16** upon treatment with n-BuMgBr under $MnCl_2$ catalysis.[15] Addition of an electrophile such as D_2O, allyl bromide, or benzaldehyde provided the corresponding adducts in good yields. The results supported the conclusion that an intermediary bromoalkene **17** was converted into alkenylmagnesium species **18** through metal-halogen exchange under the reaction conditions (Scheme 7).

2) Reaction of 1,2-Bis(bromomethyl)benzene and 1,2-Bis(dibromomethyl)benzene with Triarylmanganate(II). Next, we examined the reactions of the substrates bearing phenyl group instead of trialkylsilyl moiety. Treatment of dibromomethylbenzene (**19**) with tributylmanganate gave the corresponding styrene derivative **20** only in 9% yield. In contrast, the reaction of **19** with triphenylmanganate proceeded unexpectedly to give 1,1,2,2-tetraphenylethane (**21**) in 76% yield (Scheme 8).

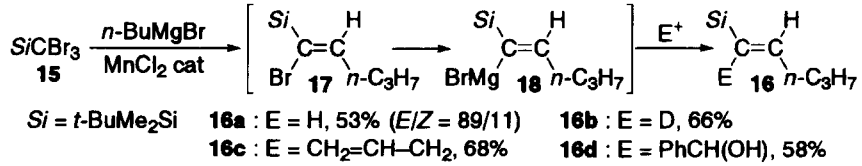
The formation of tetraphenylethane **21** might be explained by the intermolecular coupling of the intermediary manganese species **22** or by reductive elimination from **23**. Then it was anticipated that the reaction of 1,2-bis(dibromomethyl)benzene **24** with triphenylmanganate would provide 1,2-diphenyl-1,2-dihydrobenzocyclobutene (**25a**).[16,17] This was indeed the case and treatment of **24** with various triarylmanganates afforded the corresponding 1,2-dihydrobenzo-



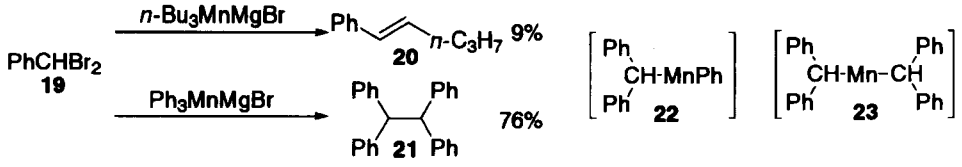
Scheme 5.



Scheme 6.



Scheme 7.

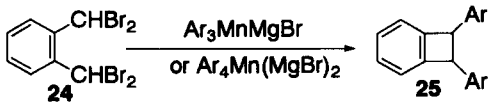


Scheme 8.

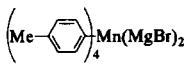
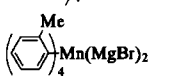
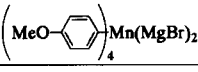
cyclobutene derivatives **25** in moderate to good yields. The results are shown in Table 2.

Several comments are worth noting. (1) *Trans*-1,2-diaryl-1,2-dihydrobenzocyclobutenes were obtained preferentially. (2) Tetraphenylmanganate was more effective than triphenylmanganate for the formation of **25** (Entries 1 and 4). (3) The use of 2.2 molar amounts of manganate was essential to obtain the product in moderate yield. When 1.1 or 1.5 molar amounts of the reagents were employed, the yields of the products dramatically decreased. (4) The reaction proved to proceed in the presence of a catalytic amount of manganese(II) chloride. However, the *trans*/*cis* ratio of the product (*trans*/*cis* = 78/22) was inferior to that obtained in the stoichiometric reaction. (5) Lithium triphenylmanganate was not so effective as magnesium triphenylmanganate species.

Table 2. Preparation of 1,2-Diaryl-1,2-dihydrobenzocyclobutene[a)]



24 **25**

Entry	Reagent	Product		(*trans*/*cis*)
1	$Ph_3MnMgBr$	**25a**	52%	(93/7)
2	$Ph_3MnMgBr$[b)]	**25a**	25%	
3	$Ph_3MnMgBr$[c)]	**25a**	35%	
4	$Ph_4Mn(MgBr)_2$	**25a**	60%	(93/7)
5		**25b**	58%	(93/7)
6		**25c**	55%	(89/11)
7		**25d**	64%	(83/17)

a) Reactions were performed with manganese reagent (2.2 mmol) and 1,2-bis(dibromomethyl)benzene (1.0 mmol) at 0 °C unless otherwise noted. b) $Ph_3MnMgBr$ (1.1 mmol) was employed. c) $Ph_3MnMgBr$ (1.5 mmol) was employed.

For instance, the use of triphenylmanganate(II) (Ph_3MnLi), derived from $MnCl_2$ and three molar amounts of phenyllithium, instead of $Ph_3MnMgBr$ gave 1,2-diphenyl-1,2-dihydrobenzocyclobutene (**25a**, *trans*/*cis* = 88/12) in 25% yield.

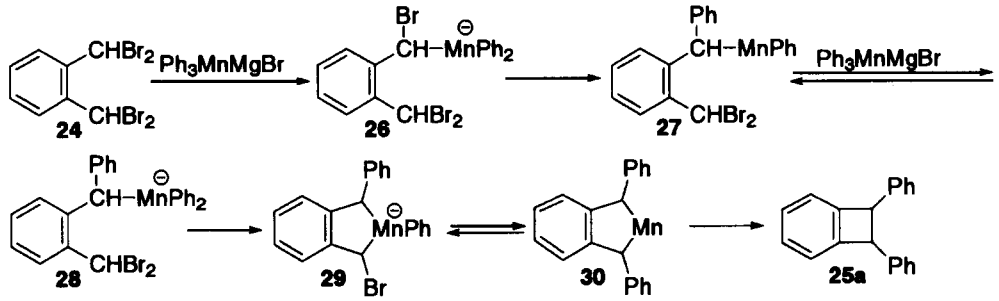
We are tempted to assume the following reaction mechanism for the formation of 1,2-diaryl-1,2-dihydrobenzocyclobutene (Scheme 9): (1) The initial bromine-manganese exchange to afford **26**, (2) phenyl migration from manganese to adjacent carbon under Br^- elimination producing **27**, (3) regeneration of manganate **28** by the migration of the phenyl group from the second triphenyl manganate, (4) the intramolecular exchange between manganese and bromine in **28** to provide **29**, (5) the migration of phenyl group under Br^- elimination providing the manganacyclopentane **30** and (6) reductive elimination of Mn(0) to afford the final product **25a**.

Treatment of 1,2-bis(bromomethyl)benzene (**31**) with triphenylmanganate gave *o*-benzyltoluene (**32**) in 92% yield. The reaction of **31** with triallylmanganate in place of triphenylmanganate proceeded to provide the corresponding allylated product **33** in 68% yield. Moreover quenching these reaction mixtures with D_2O afforded the deuterated compounds **34** and **35**, respectively (Scheme 10). An addition of benzaldehyde before quenching with water gave benzylic alcohol **36** in 85% yield.

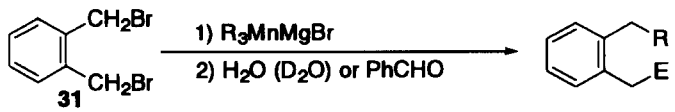
We assume the following reaction mechanism for the formation of **32**—**36**: (1) Exchange between bromine and manganese to afford **37**, which collapses to *o*-quinodimethane **38**[18] under 1,4-elimination; (2) an addition of phenyl moiety or allyl group of second molecule of manganate to **38** affords phenylated or allylated benzylmanganate species **39**; and (3) trapping with electrophiles such as D_2O or benzaldehyde provides the corresponding adducts **32**—**36** (Scheme 11).

Meanwhile, treatment of **31** (1.0 mmol) with tetrabutylmanganate (1.0 mmol) afforded **40** and **41** in 33 and 43% yields, respectively (Scheme 12).

In addition, the use of double amounts of manganate re-

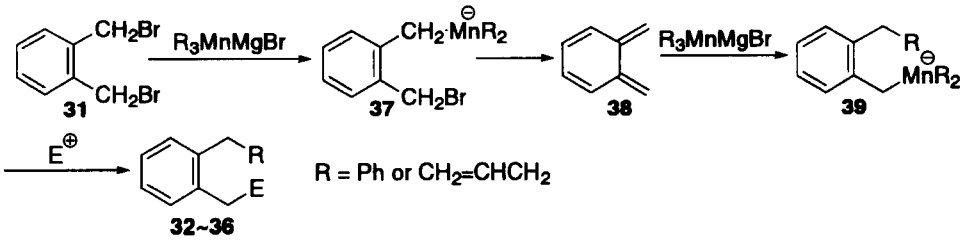


Scheme 9.

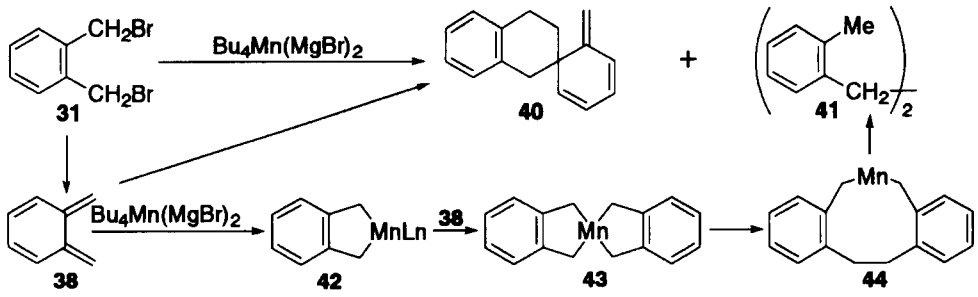


32 R = Ph E = H (92%) **33** R = CH_2=$CHCH_2$ E = H (68%)
34 R = Ph E = D (92%, 100%D) **35** R = CH_2=$CHCH_2$ E = D (68%, 100%D)
36 R = CH_2=$CHCH_2$ E = PhCH(OH) (85%)

Scheme 10.



Scheme 11.



Scheme 12.

sulted in the selective formation of **41** in 23% yield without contamination by **40**. These findings also suggested an intermediacy of *o*-quinodimethane **38**. Dimerization of the quinodimethane would provide **40**. On the other hand, the formation of **41** could be explained as follows. Reaction of *o*-quinodimethane **38** with **42**[19] would afford spiromanganese complex **43**, from which reductive elimination could give manganacyclononane **44**.[20] Aqueous workup could provide **41**. With two molar amounts of manganese compound, only the dimer **41** was obtained in poor yield, as mentioned above. In this case, manganacyclopentane **42** could be a major product but a final product 1,2-dimethylbenzene upon aqueous workup could not be isolated because of its volatility. To make this point clear, we examined the reaction of **45** with two molar amounts of tetrabutylmanganate. A mixture of tetramethyldimethoxybenzene **46** and dimer **47** was obtained in 62 and 20% yield, respectively as we expected. Quenching with D_2O gave the corresponding deuterated compounds **46** *d*-2 and **47** *d*-2 (Scheme 13).

In conclusion: (1) Treatment of trialkyl(dibromomethyl)silanes with trialkylmanganate(II) provided (*E*)-1-trialkylsilyl-1-alkenes with high stereoselectivity in good yields. The reaction also proceeded in a catalytic manner.

(2) The reaction of 1,2-bis(dibromomethyl)benzene with arylmanganate(II) proceeded effectively to give 1,2-diaryl-1,2-dihydrobenzocyclobutene in moderate yields.

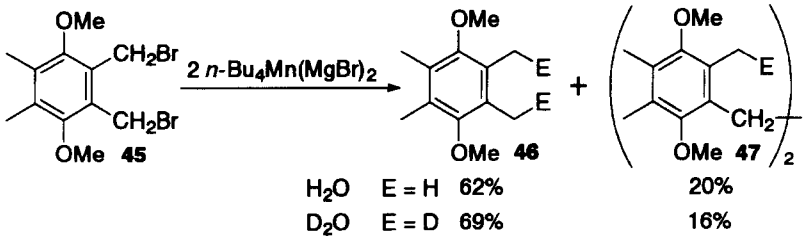
(3) Treatment of 1,2-bis(bromomethyl)benzene with triphenylmanganate(II) or triallylmanganate(II), followed by trapping with electrophile to afford the corresponding adducts.

(4) The reactivity of various manganates could be summarized as follows: (a) Triorganomanganates, derived from manganese(II) chloride and three molar amounts of Grignard reagent, were effective for all reactions described in this paper. (b) Lithium triorganomanganates, R_3MnLi, were as effective as magnesium triorganomanganate, R_3MnMgX, in the reaction of trialkyl(dibromomethyl)silane. However, R_3MnLi was not so effective in the reaction of 1,2-bis(dibromomethyl)benzene. (c) Manganese(II) chloride-catalyzed reaction with Grignard reagent proceeded effectively in the case of trialkyl(dibromomethyl)silanes. In contrast, the use of alkyllithiums instead of Grignard reagents gave no desired products.

Experimental

Distillation of the products was performed using Kugelrohr (Büchi); the boiling points are indicated by the air-bath temperature values without any correction. The boiling points are not described when distillation could not be performed. The NMR spectra (^1H and ^{13}C) were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. The IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Starting Materials. The following starting materials:



Scheme 13.

1,1-dibromodecane (**1**)[21], *t*-butyl(dibromomethyl)dimethylsilane (**4b**),[13,22], dibromomethyltriisopropylsilane (**4c**),[23] dibromomethyltrimethylsilane (**4d**),[24] *t*-butyl(dichloromethyl)dimethylsilane,[13,22] 1,1-dibromo-3-(*t*-butyldimethylsiloxy)butane,[13] 1,1-dibromo-3-(*t*-butyldimethylsiloxy)-3-phenylpropane,[13] 1,1-dibromo-2-(*t*-butyldimethylsiloxy)-2-phenylethane (**48**),[13], and 2,3-bis(bromomethyl)-1,4-dimethoxy-5,6-dimethylbenzene (**45**),[25] were prepared according to the literature. (Dibromomethyl)methyldiphenylsilane (**4a**), dicyclohexyl(dibromomethyl)methylsilane (**4e**), and *t*-butyl(diiodomethyl)dimethylsilane, were prepared in similar fashion.[13]

(Dibromomehtyl)methyldiphenylsilane (4a): IR (neat) 3066, 3046, 2964, 1590, 1489, 1255, 1116, 792, 736, 695, 617 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.85 (s, 3H), 5.52 (s, 1H), 7.34—7.49 (m, 6H), 7.61—7.68 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = −6.00, 32.65, 128.11, 130.43, 132.53, 135.33. Found: C, 45.45; H, 3.94%. Calcd for $C_{14}H_{14}Br_2Si$: C, 45.43; H, 3.81%.

Dicyclohexyl(dibromomethyl)methylsilane (4e): IR (neat) 2920, 2844, 1446, 1251, 890, 847, 779, 615 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.14 (s, 3H), 1.04—1.40 (m, 12H), 1.66—1.84 (m, 10H), 5.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = −8.90, 23.68, 26.76, 27.80, 28.06, 34.23. HRMS Found: *m/z* 380.0157. Calcd for $C_{14}H_{26}Br_2Si$: M, 380.0171.

***t*-Butyl(diiodomethyl)dimethylsilane:** IR (neat) 2952, 2924, 2854, 1470, 1364, 1251, 835, 821, 807, 774 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.27 (s, 6H), 1.05 (s, 9H), 4.54 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = −41.13, −5.03, 18.34, 27.90. HRMS Found: *m/z* 381.9096. Calcd for $C_7H_{16}I_2Si$: M, 381.9112.

Preparation of *t*-Butyldimethyl(tribromomethyl)silane (15).[26] *tert*-Butyl(dibromomethyl)dimethylsilane (**4b**, 5.8 g, 20 mmol), *N*-bromosuccinimide (3.9 g, 22 mmol), and benzoyl peroxide (0.14 g, 0.58 mmol), was refluxed in carbon tetrachloride (30 mL). The mixture was filtered and the filtrate was concentrated in vacuo. Purification of the product by silica-gel column chromatography (hexane) gave **15** (6.8 g) in 98% yield: Mp 111 °C; IR (neat) 1367, 1253, 834, 777, 619 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.40 (s, 6H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$) δ = −5.69, 20.22, 28.39, 42.51. HRMS Found: *m/z* 308.7731. Calcd for $C_3H_6{}^{79}Br_2{}^{81}BrSi$: (M–*t*-Bu), 308.7768.

General Procedure for the Reaction of 1,1-Dibromodecane with Trialkylmanganate. The reaction of 1,1-dibromodecane with tributylmanganate is representative. Manganese(II) chloride (189 mg, 1.5 mmol) was sonicated in tetrahydrofuran (THF, 10 mL) under argon atmosphere for 10 min. Butyllithium (1.5 M hexane solution, 3.0 mL, 4.5 mmol) (1 M = 1 mol dm^{-3}) was added to the suspension of $MnCl_2$ in THF at 0 °C. The mixture turned into a clear brown solution and then, after this was stirred for 20 min at 0 °C, a solution of 1,1-dibromodecane (**1**, 0.30 g, 1.0 mmol) in THF (2 mL) was added at 0 °C and the whole was stirred at 0 °C for 1 h and then at 25 °C for another 1 h. Extractive workup followed by silica-gel column chromatography gave a mixture of 4-tetradecene (**2**, *E*/*Z* = 92/8) and 5-tetradecene (**3**, *E*/*Z* = 92/8) in 95% combined yield (0.19 g, **2**/**3** = 1/1).

(*E*)-1-Trimethylsilyl-1-undecene: IR (neat) 2922, 2850, 1618, 1467, 1248, 988, 864, 836, 701, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.02 (s, 9H), 0.86 (t, *J* = 6.3 Hz, 3H), 1.16—1.42 (m, 14H), 2.07 (dt, *J* = 6.3, 6.3 Hz, 2H), 5.59 (d, *J* = 18.6 Hz, 1H), 6.01 (dt, *J* = 18.6, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −1.29, 14.00, 22.60, 28.63, 29.13, 29.25, 29.44, 29.45, 31.84, 36.68, 129.55, 147.58. Found: C, 74.39; H, 13.62%. Calcd for $C_{14}H_{30}Si$: C, 74.24; H, 13.35%.

General Procedure for the Reaction of Trialkyl(dibromomethyl)silane with Trialkylmanganate. The reaction of *t*-butyl(dibromomethyl)dimethylsilane (**4b**) with tributylmanganate is representative (Entry 6, Table 1). A solution of **4b** (0.29 g, 1.0 mmol) in THF (2 mL) was added to a solution of tributylmanganate generated from $MnCl_2$ (151 mg, 1.2 mmol) and butylmagnesium bromide (3.6 mmol) under argon atmosphere. The resulting mixture was stirred at 0 °C for 1 h. The mixture was poured into water and extracted with hexane. Purification by silica-gel column chromatography gave (*E*)-1-*t*-butyldimethylsilyl-1-pentene (129 mg) in 72% yield: Bp 65 °C (3 Torr, 1 Torr = 133.322 Pa); IR (neat) 2950, 2926, 2854, 1613, 1465, 1248, 1008, 990, 828, 780, 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ = −0.03 (s, 6H), 0.84 (s, 9H), 0.87 (t, *J* = 7.5 Hz, 3H), 1.40 (tq, *J* = 7.5, 7.5 Hz, 2H), 2.08 (dt, *J* = 6.6, 7.5 Hz, 2H), 5.58 (d, *J* = 18.3 Hz, 1H), 6.00 (dt, *J* = 18.3, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −6.18, 13.53, 16.38, 21.89, 26.37, 38.99, 126.96, 148.65. Found: C, 71.42; H, 13.36%. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12%.

Physical data for methyldiphenyl(2-phenylethenyl)silane[27] and 1-triisopropylsilyl-1,3-butadiene (**8a**)[28] were identical with those reported in literature.

(*E*)-1-Methyldiphenylsilylpropene: IR (neat) 3064, 3044, 2952, 2906, 1619, 1428, 1250, 1111, 984, 789, 732, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.60 (s, 3H), 1.89 (dd, *J* = 6.0, 1.5 Hz, 3H), 5.98 (dq, *J* = 18.3, 1.5 Hz, 1H), 6.18 (dq, *J* = 18.3, 6.3 Hz, 1H), 7.30—7.40 (m, 6H), 7.48—7.56 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = −3.90, 22.72, 127.13, 127.83, 129.21, 134.90, 137.14, 146.42. Found: C, 80.77; H, 7.76%. Calcd for $C_{16}H_{18}Si$: C, 80.61; H, 7.61%.

(*E*)-1-Methyldiphenylsilyl-1-pentene: Bp 200 °C (0.5 Torr); IR (neat) 3064, 3046, 2954, 2924, 1616, 1429, 1250, 1112, 992, 790, 731, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.58 (d, 3H), 0.90 (t, *J* = 7.5 Hz, 3H), 1.44 (tq, *J* = 7.2, 7.2 Hz, 2H), 2.16 (dt, *J* = 6.3, 7.2 Hz, 2H), 5.93 (d, *J* = 18.6 Hz, 1H), 6.14 (dt, *J* = 18.6, 6.3 Hz, 1H), 7.29—7.37 (m, 6H), 7.47—7.54 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = −3.80, 13.57, 21.64, 38.90, 125.39, 127.82, 129.17, 134.81, 137.27, 151.53. Found: C, 81.13; H, 8.50%. Calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32%.

(*E*)-1-*t*-Butyldimethylsilyl-2-trimethylsilylethene: Bp 73 °C (1 Torr); IR (neat) 2950, 2928, 2854, 1471, 1464, 1248, 1174, 1011, 867, 826, 758, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.00 (s, 6H), 0.04 (s, 9H), 0.84 (s, 9H), 6.54 (d, *J* = 22.5 Hz, 1H), 6.61 (d, *J* = 22.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −6.63, −1.69, 16.42, 26.40, 148.00, 152.73. Found: C, 61.30; H, 12.47%. Calcd for $C_{11}H_{26}Si_2$: C, 61.59; H, 12.22%.

(*E*)-1-Triisopropylsilylpropene: Bp 64 °C (1 Torr); IR (neat) 2848, 1619, 1461, 1384, 1368, 1245, 1070, 1013, 988, 882, 748, 636 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.98—1.04 (m, 21H), 1.83 (dd, *J* = 6.3, 1.5 Hz, 3H), 5.51 (dq, *J* = 18.9, 1.5 Hz, 1H), 6.07 (dq, *J* = 18.9, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 10.58, 18.35, 18.56, 125.37, 144.26. Found: C, 72.42; H, 13.00%. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21%.

1-[2-(Triisopropylsilyl)ethenyl]cyclooctene (8b): IR (neat) 2920, 2848, 1629, 1585, 1466, 988, 882, 786, 772 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.00—1.18 (m, 21H), 1.28—1.60 (m, 8H), 2.18—2.27 (m, 2H), 2.40—2.46 (m, 2H), 5.63 (d, *J* = 19.5 Hz, 1H), 5.74 (t, *J* = 8.1 Hz, 1H), 5.50 (d, *J* = 19.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 10.88, 18.61, 23.51, 25.90, 26.91, 27.21, 28.59, 30.29, 118.93, 133.23, 141.20, 148.68. HRMS Found: *m/z* 292.2599. Calcd for $C_{19}H_{36}Si$: M, 292.2586.

General Procedure for Manganese(II) Chloride-Catalyzed Reaction of Trialkyl(dibromomethyl)silane with Grignard Reagent. Preparation of (*E*)-1-triisopropylsilyl-1-propene is representative. A solution of (dibromomethyl)triisopropylsilane

(**4c**, 0.33 g, 1.0 mmol) in THF (2 mL) was added to a THF solution of ethylmagnesium bromide (3.0 mmol) and manganese(II) chloride (6 mg, 0.05 mmol) at 0 °C under argon atmosphere. The mixture was stirred for 2 h at 0 °C. Extractive workup (hexane, H_2O) followed by silica-gel column purification provided (*E*)-1-triisopropylsilylpropene in 88% yield.

(*E*)-1-Methyldiphenylsilyl-1-heptadecene: IR (neat) 3064, 3044, 2922, 2850, 1615, 1466, 1428, 1250, 1112, 991, 789, 731, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.59 (s, 3H), 0.87 (t, J = 6.9 Hz, 3H), 1.19—1.33 (m, 24H), 1.35—1.48 (m, 2H), 2.18 (dt, J = 6.3, 6.3 Hz, 2H), 5.93 (d, J = 18.3 Hz, 1H), 6.15 (dt, J = 18.3, 6.3 Hz, 1H), 7.30—7.39 (m, 6H), 7.49—7.55 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = −3.81, 14.02, 22.60, 28.47, 29.13, 29.28, 29.41, 29.58, 29.62, 31.85, 36.85, 125.08, 127.82, 129.17, 134.91, 137.27, 151.83. Found: C, 82.60; H, 10.45%. Calcd for $C_{30}H_{46}Si$: C,82.88; H, 10.66%.

Triisopropylsilylethene: Bp 76 °C (5 Torr); IR (neat) 2938, 2862, 1466, 1408, 1384, 1368, 1012, 949, 882, 698, 668, 634 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.99—1.08 (m, 21H), 5.63—5.76 (m, 1H), 5.95—6.08 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 10.51, 19.44, 133.32, 134.43. Found: C, 61.30; H, 12.47%. HRMS Found: *m/z* 184.1647. Calcd for $C_{11}H_{24}Si$: M, 184.1648.

(*E*)-1-Trimethylsilyl-1-nonene: Bp 50 °C (0.5 Torr); IR (neat) 2952, 2924, 2850, 1618, 1467, 1248, 987, 865, 837, 701, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.20 (s, 9H), 0.86 (t, J = 7.2 Hz, 3H), 1.18—1.42 (m, 10H), 2.07 (dt, J = 6.3, 6.9 Hz, 2H), 5.59 (d, J = 18.6 Hz, 1H), 6.00 (dt, J = 18.6, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −1.30, 13.97, 22.56, 28.63, 29.09, 31.75, 36.67, 129.55, 147.57. Found: C, 72.54; H, 13.37%. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21%.

(*E*)-1-Dicyclohexylmethylsilyl-1-pentene: IR (neat) 2912, 2844, 1616, 1447, 1247, 1098, 992, 910, 889, 847, 820, 773 cm^{-1}; ^1H NMR ($CDCl_3$) δ = −0.11 (s, 3H), 0.62—0.73 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H), 0.92—1.28 (m, 12H), 1.39 (tq, J = 7.2, 7.2 Hz, 2H), 1.50—1.76 (m, 8H), 2.07 (dt, J = 6.3, 7.2 Hz, 2H), 5.48 (d, J = 18.3 Hz, 1H), 5.95 (dt, J = 18.3, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −9.58, 13.49, 21.91, 23.45, 27.00, 27.65, 27.77, 28.16, 28.29, 39.06, 125.44, 148.87. HRMS Found: *m/z* 278.2434. Calcd for $C_{18}H_{34}Si$: M, 278.2431.

2-*t*-Butyldimethylsiloxy-4-octene: IR (neat) 2956, 2926, 2894, 1464, 1377, 1362, 1255, 1129, 1082, 1005, 970, 835, 773, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.02 (s, 6H), 0.83—0.90 (m, 12H), 1.09 (d, J = 6.3 Hz, 3H), 1.35 (tq, J = 7.2, 7.2 Hz, 2H), 1.95 (dt, J = 7.2, 7.2 Hz, 2H), 1.90—2.20 (m, 2H), 3.76 (tq, J = 6.3, 6.3 Hz, 1H), 5.30—5.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = −4.84, −4.70, 13.59, 18.09, 22.51, 23.31, 25.80, 34.73, 43.02, 68.93, 127.08, 132.59. Found: C, 69.35; H, 12.70%. Calcd for $C_{14}H_{30}SiO$: C, 69.35; H, 12.47%.

1-*t*-Butyldimethylsiloxy-1-phenyl-3-heptene: Bp 164 °C (0.5 Torr); IR (neat) 3024, 2954, 2926, 2854, 1472, 1464, 1454, 1362, 1256, 1091, 1068, 1006, 968, 939, 836, 775, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ = −0.15 (s, 3H), 0.00 (s, 3H), 0.84 (t, J = 7.5 Hz, 3H), 0.86 (s, 9H), 1.32 (tq, J = 7.5, 7.5 Hz, 2H), 1.87—1.96 (m, 2H), 2.22—2.43 (m, 2H), 4.58—4.64 (m, 1H), 5.29—5.46 (m, 2H), 7.16—7.23 (m, 1H), 7.25—7.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = −5.02, −4.79, 13.56, 18.16, 22.46, 25.78, 34.70, 43.30, 75.55, 126.05, 126.73, 126.88, 127.99, 132.95, 145.55. Found: C, 75.12; H, 10.64%. Calcd for $C_{19}H_{32}SiO$: C, 74.93; H, 10.59%.

General Procedure for the Reaction of Trialkyltribromomethylsilane with Grignard Reagent in the Presence of a Catalytic Amount of $MnCl_2$ Followed by Addition of Electrophile. Preparation of 1-*t*-butyldimethylsilyl-1-phenyl-2-hexen-1-ol (**16d**) is representative. Butylmagnesium bromide (0.95 M, ether solution, 4.2 ml, 4.0 mmol) was added to a suspension of $MnCl_2$ (6 mg, 0.05 mmol) in THF (10 mL) at 0 °C under argon atmosphere. After this was stirred for 20 min at 0 °C, a solution of **15** (0.37 g, 1.0 mmol) in THF (2 mL) was added. The mixture was stirred for 1 h at 0 °C and then for 30 min at 25 °C. The mixture was cooled to 0 °C and benzaldehyde (0.16 ml, 1.6 mmol) was added dropwise. The whole was stirred for 15 min at 0 °C and then for 30 min at 25 °C. Extractive workup followed by silica-gel column purification provided **16d** in 58% yield: IR (neat) 3470, 3058, 3020, 2952, 2926, 2854, 1604, 1493, 1463, 1449, 1361, 1249, 1010, 917, 824, 767, 749, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ = −0.10 (s, 3H), 0.04 (s, 3H), 0.88 (s, 9H), 0.89 (t, J = 7.5 Hz, 3H), 1.32—1.52 (m, 2H), 1.81 (d, J = 4.8 Hz, 1H), 2.02—2.26 (m, 2H), 5.75 (d, J = 4.8 Hz, 1H), 6.00 (t, J = 7.5 Hz, 1H), 7.19—7.26 (m, 1H), 7.28—7.40 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = −4.61, −3.95, 13.74, 17.12, 22.54, 27.09, 31.74, 72.58, 126.16, 126.77, 128.17, 141.70, 143.88, 145.29. Found: C, 74.64; H, 10.48%. Calcd for $C_{18}H_{30}OSi$: C, 74.42; H, 10.41%.

(*E*)-1-*t*-Butyldimethylsilyl-1-deuterio-1-pentene (16b): IR (neat) 2952, 2924, 2852, 1605, 1464, 1248, 1007, 990, 968, 823, 807, 775, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ = −0.02 (s, 6H), 0.84 (s, 9H), 0.87 (t, J = 7.5 Hz, 3H), 1.40 (tq, J = 7.5, 7.5 Hz, 2H), 2.08 (dt, J = 6.6, 7.5 Hz, 2H), 5.99 (dt, J = 6.6, 3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −6.21, 13.51, 16.35, 21.83, 26.34, 38.88, 126.50 (t, J = 24 Hz), 148.59. HRMS Found: *m/z* 185.1714. Calcd for $C_{11}H_{23}DSi$: M, 185.1711.

(*E*)-4-*t*-Butyldimethylsilyl-1,4-octadiene (16c): IR (neat) 2952, 2924, 2854, 1636, 1609, 1463, 1248, 1030, 1007, 993, 908, 825, 767, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.01 (s, 6H), 0.84 (s, 9H), 0.89 (t, J = 7.2 Hz, 3H), 1.39 (tq, J = 7.2, 7.2 Hz, 2H), 2.06 (dt, J = 7.2, 7.2 Hz, 2H), 2.88 (d, J = 6.0 Hz, 2H), 4.88—4.99 (m, 2H), 5.71 (ddt, J = 16.8, 10.2, 6.0 Hz, 1H), 5.82 (t, J = 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −6.03, 13.79, 17.17, 22.48, 26.80, 30.79, 34.43, 114.27, 135.30, 137.43, 144.37. HRMS Found: *m/z* 224.1945. Calcd for $C_{14}H_{28}Si$: M, 224.1960.

General Procedure for the Reaction of 1,2-Bis(dibromomethyl)benzene (24) with Arylmanganate. The reaction of 1,2-bis(dibromomethyl)benzene with tetraphenylmanganate is representative (Entry 4, Table 2). A THF solution of **24** (0.42 g, 1.0 mmol) was added to a solution of $Ph_4Mn(MgBr)_2$, generated from $MnCl_2$ (277 mg, 2.2 mmol) and phenylmagnesium bromide (8.8 mmol) at 0 °C under argon atmosphere. After 10 min, the reaction was quenched with water. Extractive workup followed by silica-gel column chromatography gave 1,2-diphenyl-1,2-dihydrobenzocyclobutene (**25a**, *trans*/*cis* = 93/7) in 60% yield.

Physical data for **25a** were identical with those reported in the literature.[17]

1,2-Bis(*p*-methylphenyl)-1,2-dihydrobenzocyclobutene (25b, *trans*/*cis* = 93/7): IR (hexachlorobutadiene) 3025, 1514, 1459, 792, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.16 (s, 0.42H), 2.35 (s, 5.58H), 4.40 (s, 1.86H), 5.13 (s, 0.14H), 6.77—6.87 (m, 0.28H), 7.12—7.20 (m, 8H), 7.22—7.26 (m, 1.86H), 7.33—7.37 (m, 1.86H); ^{13}C NMR ($CDCl_3$) major product δ = 20.99, 58.39, 123.55, 126.92, 128.02, 129.31, 136.36, 139.02, 146.27. Found: C, 92.80; H, 7.08%. Calcd for $C_{12}H_{20}$: C, 92.91; H, 7.09%.

1,2-Bis(*o*-methylphenyl)-1,2-dihydrobenzocyclobutene (25c, *trans*/*cis* = 89/11): IR (neat) 3062, 3016, 2948, 2922, 2856, 1603, 1490, 1460, 1380, 753, 732, 719 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.18 (s, 5.34H), 2.28 (s, 0.66H), 4.65 (s, 1.78H), 5.40 (s, 0.22H), 6.81—6.86 (m, 0.44H), 6.91—6.96 (m, 0.44H), 7.16—7.26 (m, 9.12H), 7.30—7.38 (m, 2H); ^{13}C NMR ($CDCl_3$) major product δ = 19.66, 55.13, 123.54, 126.22, 126.24, 126.69, 127.91, 130.26, 135.74,

140.58, 146.26. HRMS Found: *m/z* 284.1547. Calcd for $C_{22}H_{20}$: M, 284.1566.

1,2-Bis(*p*-methoxylphenyl)-1,2-dihydrobenzocyclobutene (25d, *trans/cis* = 83/17): IR (neat) 2994, 2948, 2926, 1611, 1510, 1458, 1302, 1248, 1175, 1036, 825, 809, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.67 (s,1.02H), 3.79 (s, 4.98H), 4.35 (s, 1.16H), 5.10 (s, 0.34H), 6.58 (d, J = 9.0 Hz, 0.68H), 6.82 (d, J = 9.0 Hz, 0.68H), 6.83—6.90 (m, 3.32H), 7.15—7.27 (m, 5.32H), 7.31—7.37 (m, 2H); ^{13}C NMR ($CDCl_3$) major product δ = 55.21, 58.18, 113.97, 123.52, 127.99, 128.04, 134.19, 146.37, 158.55. HRMS Found: *m/z* 316.1460. Calcd for $C_{22}H_{20}O_2$: M, 316.1463.

General Procedure for the Reaction of 1,2-Bis(bromomethyl)benzene (31) with Triphenylmanganate or Triallylmanganate Followed by Addition of Electrophile. Preparation of 1-(3-butenyl)-2-(deuteriomethyl)benzene (**35**) is representive. A THF solution of **31** (0.26 g, 1.0 mmol) was added at 0 °C to a solution of triallylmanganate, generated from $MnCl_2$ (277 mg, 2,2 mmol) and allylmagnesium bromide (6.3 mmol), and the resulting mixture was stirred for 2.5 h at 0 °C. The reaction was quenched with D_2O. Extraction with ethyl acetate (20 mL×3), followed by silica-gel column purification, gave **35** in 66% yield: IR (neat) 3070, 3014, 2928, 2862, 1641, 1493, 1455, 994, 911, 751 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.27—2.37 (m, 4H), 2.65—2.72 (m, 2H), 5.00 (d, J = 10.2 Hz, 1H), 5.07 (d, J = 17.1 Hz, 1H), 5.90 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 7.08—7.17 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 18.90 (t, J = 19.4 Hz), 32.63, 34.22, 114.85, 125.97, 126.02, 128.85, 130.20, 135.93, 138.36, 140.13. Found: C, 89.94; H, 10.16%. Calcd for $C_{11}H_{13}D$: C, 89.73; H, 10.27%.

1-(3-Butenyl)-2-methylbenzene (33): IR (neat) 3064, 3014, 2930, 2862, 1641, 1493, 1461, 995, 911, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.27—2.37 (m, 5H), 2.65—2.72 (m, 2H), 5.00 (d, J = 10.2 Hz, 1H), 5.07 (d, J = 17.1 Hz, 1H), 5.90 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 7.08—7.17 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 19.17, 32.62, 34.21, 114.85, 125.97, 126.02, 128.84, 130.20, 135.94, 138.35, 140.11. Found: C, 90.23; H, 9.91%. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65%.

1-Benzyl-2-(deuteriomethyl)benzene (34): IR (neat) 3056, 3022, 1599, 1493, 1483, 1453, 736, 722, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.22 (t, J = 1.8 Hz, 2H), 3.99 (s, 2H), 7.07—7.31 (m, 9H); ^{13}C NMR ($CDCl_3$) δ = 19.28 (t, J = 19.4 Hz), 39.35, 125.98, 126.05, 126.51, 128.45, 128.81, 130.01, 130.34, 136.67, 139.01, 140.47. HRMS Found: *m/z* 183.1159. Calcd for $C_{14}H_{13}D$: M, 183.1159.

2-[2-(3-Butenyl)phenyl]-1-phenylethanol (36): IR (neat) 3364, 3060, 3022, 2924, 1640, 1604, 1493, 1453, 1044, 1027, 997, 911, 754, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.93 (d, J = 2.7 Hz, 1H), 2.26—2.38 (m, 2H), 2.68—2.77 (m, 2H), 3.02—3.08 (m, 2H), 4.88—4.94 (m, 1H), 5.00 (d, J = 10.2 Hz, 1H), 5.05 (d, J = 16.8 Hz, 1H), 5.87 (ddt, J = 16.8, 10.2, 6.3 Hz, 1H), 7.15—7.22 (m, 4H), 7.27—7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 31.90, 34.99, 42.66, 74.91, 115.02, 125.80, 126.15, 126.87, 127.66, 128.49, 129.50, 130.55, 135.84, 138.13, 140.59, 144.13. Found: C, 85.84; H, 8.18%. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99%.

General Procedure for the Reaction of 31 with *n*-$Bu_4Mn(MgBr)_2$. The reaction of **31** with *n*-$Bu_4Mn(MgBr)_2$ is representive. Butylmagnesium bromide (4.4 mmol) was added to a suspension of $MnCl_2$ (1.1 mmol) in THF (10 mL) at 0 °C under argon atmosphere. After this was stirred for 20 min at 0 °C, a solution of **31** (0.26 g, 1.0 mmol) in THF (2 mL) was added and the whole was stirred for 10 h at 0 °C. The reaction was quenched with water and extracted with ethyl acetate (20 mL×3). Purification by silica-gel column chromatography afforded a mixture of **40** and **41**.

Physical data for **40**[29], **41**[30] and **46**[31] were identical with those reported in the literature.

1,2-Bis(deuteriomethyl)-3,6-dimethoxy-4,5-dimethylbenzene (46*d*-2): IR (nujol) 1401, 1272, 1236, 1085, 1049, 1019 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.16 (t, J = 2.1 Hz, 4H), 2.18 (s, 6H), 3.64 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 12.17 (t, J = 19.4 Hz), 12.43, 60.07, 127.68, 152.87. HRMS Found: *m/z* 196.1413. Calcd for $C_{12}H_{16}D_2O_2$: M, 196.1432.

1,2-Bis(2,5-dimethoxy-3,4,6-trimethylphenyl)ethane (47): IR (nujol) 1273, 1167, 1085, 1055, 1007, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.21 (s, 6H), 2.22 (s, 6H), 2.37 (s, 6H), 2.76 (s, 4H), 3.68 (s, 6H), 3.73 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 11.75, 12.60, 12.77, 28.13, 60.05, 60.82, 127.69, 128.03, 128.52, 132.16, 153.22. HRMS Found: *m/z* 386.2478. Calcd for $C_{24}H_{34}O_4$: M, 386.2457.

1,2-Bis[2-(deuteriomethyl)-3,6-dimethoxy-4,5-dimethylphenyl]ethane (47*d*-2): IR (nujol) 1294, 1087, 1007, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.21 (s, 6H), 2.22 (s, 6H), 2.36 (t, J = 2.4 Hz, 4H), 2.76 (s, 4H), 3.68 (s, 6H), 3.73 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 11.77 (t, J = 39 Hz), 12.61, 12.78, 28.15, 60.06, 60.82, 127.67, 128.05, 128.53, 132.18, 153.23. HRMS Found: *m/z* 388.2595. Calcd for $C_{24}H_{32}D_2O_4$: M, 388.2582.

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References

1 a) R. J. K. Taylor, "Organocopper Reagents, A Practical Approach," Oxford University Press, Oxford (1994). b) B. H. Lipshutz and S. Sengupta, *Org. React.*, **41**, 135 (1992). c) B. H. Lipshutz, in "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, New York (1991), Vol. 1, Chap. 1.4, p. 107. d) B. H. Lipshutz, in "Encyclopedia of Inorganic Chemistry," ed by R. B. King, Wiley, New York (1994). e) Y. Yamamoto, *Angew. Chem., Int. Ed. Engl.*, **25**, 947 (1986). f) E. Nakamura, *Synlett*, **1991**, 539. g) P. Knochel and R. D. Singer, *Chem. Rev.*, **93**, 2117 (1993).

2 a) M. Isobe, S. Kondo, N. Nagasawa, and T. Goto, *Chem. Lett.*, **1977**, 679. b) D. Seebach and W. Langer, *Helv. Chim. Acta*, **62**, 1701 and 1710 (1979). c) T. Harada, T. Katsuhira, K. Hattori and A. Oku, *J. Org. Chem.*, **58**, 2958 (1993). d) T. Harada, T. Katsuhira, D. Hara, Y. Kotani, K. Maejima, R. Kaji, and A. Oku, *J. Org. Chem.*, **58**, 4897 (1993). e) T. Harada, H. Wada, and A. Oku, *J. Org. Chem.*, **60**, 5370 (1995). f) T. Harada, M. Chiba, and A. Oku, *J. Org. Chem.*, **64**, 8210 (1999).

3 J.-F. Normant and G. Cahiez, "Organomanganous Reagents," in "Modern Synthetic Methods," ed by R. Scheffold, Otto Salle Verlag GmbH & Co, Frankfurt am Main (1983), Vol. 3, p. 173.

4 K. Oshima, *J. Organomet. Chem.*, **575**, 1 (1999); H. Shinokubo and K. Oshima, *J. Synth. Org. Chem. Jpn.*, **57**, 13 (1999).

5 R. Inoue, H. Shinokubo, and K. Oshima, *Tetrahedron Lett.*, **37**, 5377 (1996); E. J. Corey and G. H. Posner, *Tetrahedron Lett.*, **1970**, 315; T. Kauffmann, *Angew. Chem., Int. Ed. Engl.*, **35**, 386 (1996); H. Kakiya, R. Inoue, H. Shinokubo, and K. Oshima, *Tetrahedron*, **56**, 2131 (2000).

6 The reaction of 1,1-dibromoalkanes with trialkylzincate has been reported. T. Harada, Y. Kotani, T. Katsuhira, and A. Oku, *Tetrahedron Lett.*, **32**, 1573 (1991).

7 A part of work has been reported in a communication: H. Kakiya, R. Inoue, H. Shinokubo, and K. Oshima, *Tetrahedron Lett.*, **38**, 3275 (1997).

8 Preparation of alkenylsilane: E. W. Colvin, "Silicon in Organic Synthesis," Butterworth and Co. Ltd., London (1981), p. 79; W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin (1983), p. 79.

9 Treatment of i-$Pr_3SiCHBr_2$ with butyllithium in the presence of a catalytic amount of $MnCl_2$ gave complex mixture which contained small amounts of alkenylsilane.

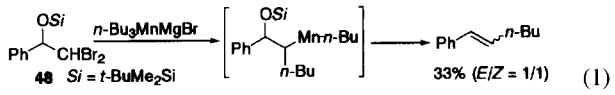
10 Decomposition of the dialkylmanganese species has been reported to proceed by α,β-elimination of a hydro-manganese species. H. Tamura and J. Kochi, *J. Organomet. Chem.*, **29**, 111 (1971). They mentioned that secondary alkyl manganese has decomposed much more easily than primary one.

11 Oxidative insertion of manganese into organic halides has been reported. T. Hiyama, M. Obayashi, and A. Nakamura, *Organometallics*, **1**, 1249 (1982); S.-H. Kim, M. V. Hansen, and R. D. Rieke, *Tetrahedron Lett.*, **37**, 2197 (1996); A. Fürstner and H. Brunner, *Tetrahedron Lett.*, **37**, 7009 (1996); K. Takai, T. Ueda, T. Hayashi, and T. Moriwake, *Tetrahedron Lett.*, **37**, 7049 (1996).

12 Tetraalkylmanganates such as n-$Bu_4Mn(MgBr)_2$ or $R_3SiCH(Br)Mn(n\text{-}Bu)_3(MgBr)_2$ might play a critical role instead of triorganomanganates (n-$Bu_3MnMgBr$ or **6**). In fact, treatment of **4b** with n-$Bu_4Mn(MgBr)_2$ afforded the corresponding alkenylsilane in 66% yield.

13 H. Shinokubo, K. Miura, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **52**, 503 (1996).

14 β-Siloxydibromo compound such as $PhCH(OSi\text{-}t\text{-}BuMe_2)CHBr_2$ (**48**), derived from the reaction of benzaldehyde with t-butyldimethylsilyldibromomethyllithium,[13] gave 1-phenyl-1-hexene via the elimination of Mn-$OSiMe_2$-t-Bu instead of elimination of the Mn-H unit (Eq. 1).



(1)

15 The reaction of **15** with stoichiometric amount of n-$Bu_3MnMgBr$ afforded 1-t-butyldimethylsilyl-1-bromo-1-pentene (**17**) in 55% yield.

16 I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970); M. P. Cava and D. P. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956); H. Finkelstein, *Ber. Dtsch. Chem. Ges.*, **43**, 1528 (1910).

17 L. A. Carpino, *J. Am. Chem. Soc.*, **84**, 2196 (1962); F. R. Jensen and W. E. Coleman, *J. Am. Chem. Soc.*, **80**, 6149 (1958); Y. Takahashi and J. K. Kochi, *Chem. Ber.*, **121**, 253 (1988); W. Baker, J. F. W. McOmie, and D. R. Preston, *J. Chem. Soc.*, **1961**, 2971; G. Quinkert, K. Optitz, W. W. Wiersdorff, and J. Weinlichi, *Tetrahedron Lett.*, **27**, 1863 (1963).

18 a) J. L. Charlton and M. M. Alauddin, *Tetrahedron*, **43**, 2873 (1987). b) J. L. Segura and N. Martin, *Chem. Rev.*, **99**, 3199 (1999). c) Y. Ito, K. Yonezawa, and T. Saegusa, *J. Org. Chem.*, **39**, 2769 (1974). d) H. Nozaki and R. Noyori, *Tetrahedron*, **22**, 2163 (1966). e) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961); B. H. Han and P. Boudjouk, *J. Org. Chem.*, **47**, 751 (1982). f) S. Inaba, R. M. Wehmeyer, M. W. Forkner, and R. D. Rieke, *J. Org. Chem.*, **53**, 339 (1988). g) D. Stephan, A. Gorgues, and A. Le Coq, *Tetrahedron Lett.*, **25**, 5649 (1984). h) H. Sano, H. Ohtsuka, and T. Migita, *J. Am. Chem. Soc.*, **110**, 2014 (1988).

19 The formation of **42** could be as follows. The reaction of **38** with n-$Bu_4Mn(MgBr)_2$ would provide Mn(IV) species which could be converted into Mn(II) by reductive elimination of n-Bu–n-Bu.

20 Triphenylmangante and triallylmanganate were more reactive than trialkykmanganate. Treatment of alkynes with allylmagnesium bromide in the presence of a catalytic amount of manganese (II) chloride gave allylated products. K. Okada, K. Oshima, and K. Utimoto, *J. Am. Chem. Soc.*, **118**, 6076 (1996); J. Tang, K. Okada, H. Shinokubo, and K. Oshima, *Tetrahedron*, **53**, 5061 (1997).

21 T. Takeda, R. Sasaki, A. Nakamura, S. Yamauchi, and T. Fujiwara, *Synlett*, **1996**, 273.

22 J. Villieras, C. Bacquet, and J. F. Normant, *Bull. Soc. Chim. Fr.*, **1975**, 1797.

23 H. Shinokubo, K. Miura, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **34**, 1951 (1993).

24 K. Yoon and D. Y. Son, *J. Organomet. Chem.*, **545—546**, 185 (1997).

25 J. Kang, G. Hilmersson, J. Santamaría, and J. Rebek, Jr., *J. Am. Chem. Soc.*, **120**, 3650 (1998).

26 D. Seyferth, R. L. Lambert, and E. M. Hamson, *J. Organomet. Chem.*, **24**, 647 (1970).

27 C.-H. Jun and R. H. Crabtree, *J. Organomet. Chem.*, **447**, 177 (1993).

28 T. P. Meagher, L. Yet, C. -N. Hsiao, and H. Schechter, *J. Org. Chem.*, **63**, 4181 (1998).

29 a) Y. Ito, M. Nakatsuka, and T. Saegusa, *J. Am. Chem. Soc.*, **104**, 7609 (1982). b) L. A. Errede, *J. Am. Chem. Soc.*, **83**, 949 (1961).

30 D. J. Brickwood, W. D. Ollis, J. S. Stephanatou, and J. F. Stoddart, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 1398.

31 R. Rathore, E. Bosch, and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2*, **1994**, 1157.