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A Novel C−C Single-Bond Formation Accompanying C−O Bond Cleavage by Use of a Ketone, an Alkylating Reagent, and a Low-Valent Vanadium Complex in the Presence of a Catalytic Amount of Molecular Oxygen

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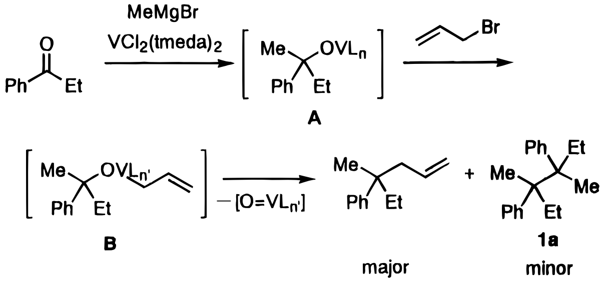
A C−C single-bond-forming reaction from ketones with accompanying C−O bond cleavage mediated by a RMgBr or RLi−vanadium(II)−O_2 system has been accomplished. Different from conventional reductive coupling reactions of ketones such as the McMurry coupling, the present method forms a C−C single (instead of a double) bond and yields a product that contains components derived from the ketone and the alkylating reagent in a one-pot reaction. Collaboration of both a low-valent vanadium(II) species and a higher-valent vanadium species produced from vanadium(II) and a catalytic amount of O_2 effects the abstraction of the oxygen atom from a C−O bond.

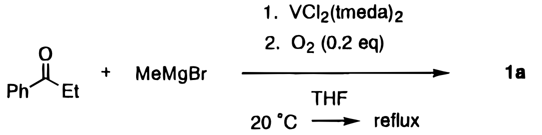
Introduction

New methodologies for C−C bond formation mediated by transition-metal complexes are of considerable interest in the fields of both organic synthesis and organometallic chemistry.[1] The pinacol coupling reaction is one of the most useful C−C bond-forming reactions, based on carbonyl compounds and mediated by low-valent early-transition metals.[2] Although the reductive dehydroxy coupling of alcohols has also proven to be an efficient method for forming C−C bonds,[3,4] examples of this reaction beyond those using low-valent titanium[3] and niobium[4] are rare. Different from the pinacol coupling reactions, the present reaction makes a C−C single bond with accompanying C−O bond cleavage. To remove the oxygen atom from a C−O single bond without accompanying dehydration, the strong oxophilicity of low-valent early-transition metals is utilized.[5]

We have already shown that the oxophilicity and the reducing power of low-valent vanadium complexes can be applied to the construction of asymmetric quaternary carbons from carbonyl compounds (eq 1).[6] We have suggested an alkoxy(allyl)vanadium species **B** as the key intermediate in this reaction. Although the intermediate could not be isolated or detected, its intermediacy was suggested by the increase of the yield of the quaternary carbon compound and the decrease of a byproduct, the coupling product **1a**, under high dilution conditions. During the course of our study for the reaction of the alkoxyvanadium species **A** with an allyl bromide, we have found that the allyl bromide is essential for generation of the coupling product **1a** and it can be displaced by a catalytic amount of molecular oxygen. We describe herein a new C−C single-bond-forming reaction by reductive coupling of carbonyl compounds mediated by a system comprised of MeMgBr, a low-valent vanadium, and a catalytic amount of O_2 (eq 2).[7]



(1)



(2)

Results and Discussion

We have found that a combination of $VCl_2(tmeda)_2$ [tmeda = *N,N,N′,N′*-tetramethylethylenediamine][8] and a catalytic amount of O_2 induces efficiently the reductive dimerization of alcoholates, derived from ketones and an alkylating reagent, with accompanying C−O bond cleavage, to give a coupling product having a C−C single bond. For example, propiophenone was first reacted with methylmagnesium bromide (1.0 equiv) in THF and then treated with $VCl_2(tmeda)_2$ (1.0 equiv) at 20 °C for 1 h. The resulting reaction mixture was heated under reflux in the presence of O_2 (0.2 equiv) to give a coupling product **1a** in 89% isolated yield along with tertiary alcohol **2a** in 11% isolated yield (eq 3). The coupling product **1a** can be considered to be obtained by homocoupling of an intermediate, alkoxyvanadium species **A**, with accompa-

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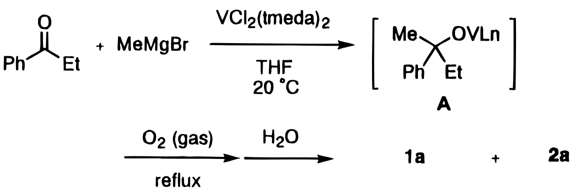


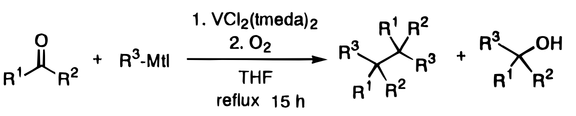
(3)

O_2 (gas)	1a	2a
none	trace	92 %
0.2 equiv	89 %	11 %
under O_2 atmosphere	trace	89 %

nying C−O bond cleavage, while the alcohol **2a** was derived from the hydrolysis of **A** or by the Grignard reaction. A catalytic amount of O_2 is essential for the reductive coupling. Without O_2 (under pure Ar atmosphere), the reductive coupling did not proceed at all, and the tertiary alcohol **2a** was mainly obtained instead. An excessive amount of O_2 also prevented the coupling reaction; under pure O_2 atmosphere only **2a** was obtained.

The representative results of the reductive coupling starting from several ketones are summarized in Table 1. When propiophenone or acetophenone was employed as the starting ketone, the coupling product **1** was obtained in moderate to good yield. Although the facile cleavage of the C−O bond at the benzylic position was observed, aliphatic ketones did not afford the corresponding coupling product at all under similar reaction conditions (Table 1, run 9). When MeMgBr or MeLi was used as an alkylating reagent, no other product besides the coupling product and the tertiary alcohol was obtained. When EtMgBr, C_3H_5MgBr, or ^nBuLi was used as the alkylating reagent, the isolated yield of the coupling product **1** decreased compared to that obtained with MeMgBr. The coupling product derived from propiophenone and PhMgBr was easily transformed into a mixture of 1,1-diphenyl-1-propene and 1,1-diphenylpropane by homolytic cleavage of the C−C bond having four phenyl groups of the initial product (run 6).[9] Although the reactions of run 1 (a combination of propiophenone and MeMgBr) and run 8 (a combination of acetophenone and EtMgBr) should give the same alkoxyvanadium intermediate, the yield of the coupling product in run 8 was very poor compared to that in run 1. The reason for the difference in yield is not clear at the moment.

Table 1. Reductive Coupling Reaction Mediated by a $VCl_2(tmeda)_2$−O_2 System[a]

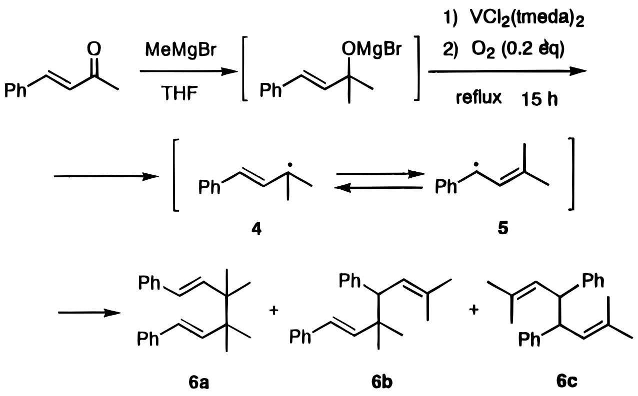


1 2

run	R^1	R^2	R^3-Mtl (alkylating reagent)	products	yield / %[b] 1[c]	yield / %[b] 2
1	Ph	Et	MeMgBr	a	89	11
2			MeLi	a	74	24
3			EtMgBr	b	63	24
4			^nBuLi	c	31[d]	30
5			$CH_2{=}CHCH_2MgBr$	d	58	35
6			PhMgBr	e	0[e]	4
7		Me	MeMgBr	f	84	0
8			EtMgBr	a	37	13
9	$Ph(CH_2)_2$	Me	MeMgBr	g	0	96
10			PhMgBr	h	69	15

[a] Ketone (1.0 equiv), R^3MgBr or R^3Li (1.0 equiv), $VCl_2(tmeda)_2$ (1.0 equiv), and O_2 (0.2 equiv) were employed. [b] Isolated yield. [c] *meso*:*dl* = 1:1. [d] The ratio of the diastereomers was not determined. [e] 1,1-Diphenyl-1-propene (47% isolated yield) and 1,1-diphenylpropane (39% isolated yield) were obtained.

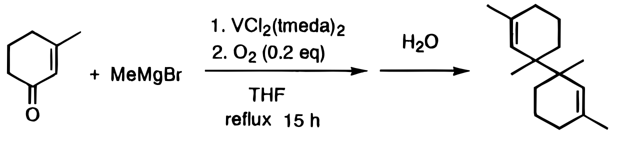
Scheme 1



100 % (**6a** : **6b** : **6c** = 8 : 54 : 38)

Although it is known that a low-valent titanium[3] or niobium[4] is capable of carrying out the reductive coupling of allyl or benzyl alcohol, neither is effective in our system for the cleavage of the C−O bond of the alcoholates. When a low-valent titanium or niobium was employed instead of a low-valent vanadium in our system, only a tertiary alcohol and/or its dehydrated product was mainly obtained.

The cleavage of the C−O bond at the allylic position also proceeded similarly. For example, reaction of 3-methyl-2-cyclohexen-1-one with MeMgBr, $VCl_2(tmeda)_2$, and O_2 successively afforded the coupling product **3** (*meso*:*dl* = 60:40 or *vice versa*) in 80% isolated yield (eq 4).



(4)

3 80 %
(*dl* : *meso* = 60 : 40 or *vice versa*)

When benzalacetone was employed as the starting carbonyl compound, the coupling product was obtained quantitatively but as a mixture of regioisomers (**6a**:**6b**:**6c** = 8:54:38) by ^1H NMR (Scheme 1). These regioisomers were produced by homo- or heterocoupling of the two kinds of radical species, **4** and **5**, which were generated as an equilibrium mixture by the homolytic cleavage of the C−O bond of the intermediate alkoxyvanadium species. The ratio of the regioisomers reflects the relative stability between the benzylic allylic radical **5** and the allylic tertiary radical **4**. In the absence of O_2, the coupling reaction did not proceed, and only the tertiary alcohol, 1,1-dimethyl cinnamyl alcohol, generated by the 1,2-addition of methyl group to benzalacetone, was obtained after hydrolysis of the reaction mixture. This result indicated that the allylic rearrangement of the vanadium or magnesium alcoholate did not occur.

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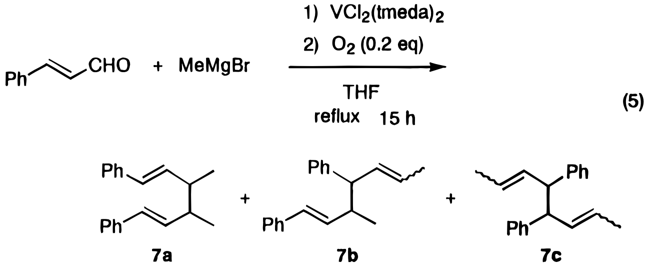
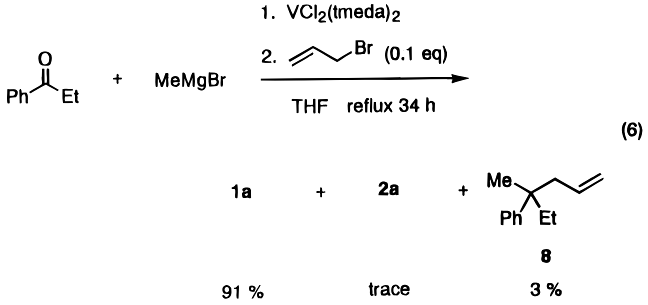
Elimination of an oxovanadium species from the alkoxyvanadium intermediates was the key step in this C−C single-bond formation. When an aliphatic or an aromatic aldehyde such as benzaldehyde or 1-phenylpropanal was used as a starting carbonyl compound, the C−O bond of the intermediate alkoxyvanadium was not cleaved. When *trans*-cinnamaldehyde, an α,*β*-unsaturated aldehyde, was used as a starting carbonyl compound, however, the corresponding coupling products **7** were easily obtained as a mixture of regioisomers (eq 5).



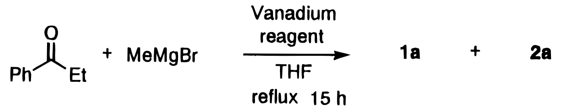
74 % (**7a** : **7b** : **7c** = 20 : 65 : 15)

To clarify the effect of the added O_2,[10,11] other initiators for this deoxygenative coupling reaction were also examined. In the course of our study on the deoxygenative allylation of ketones mediated by a combination of a vanadium(II) complex and allyl bromide, we found that a coupling product similar to **1a** was obtained as a byproduct. Thus, at first, a catalytic amount of allyl bromide (0.1 equiv) instead of O_2 in eq 3 was added after the formation of alkoxyvanadium **A**. The same coupling product **1a** was obtained in 91% isolated yield along with a small amount of the allylation product **8** and the alcohol **2a** (eq 6). As the amount of allyl bromide increased, the yield of the coupling product **1a** decreased gradually with an increase in the amount of **8**. With 4.0 equiv of allyl bromide, **1a** was obtained in 50% isolated yield along with **8** in 46% isolated yield.



We have reported that higher-valent alkoxy(allyl)vanadium species **B** (probably a tetravalent complex) obtained by oxidative addition of allyl bromide to alkoxyvanadium(II) species **A** is postulated as a key intermediate for the deoxyallylation. That is, the role of a catalytic amount of allyl bromide in the coupling reaction is the production of a catalytic amount of the higher-valent vanadium species **B** from alkoxyvanadium(II) species **A** by the oxidative addition. A small amount of a higher-valent vanadium complex may be the real initiator and essential for the reaction.

Table 2. Several Vanadium Species Mediated Reductive Coupling Reactions[a]



run	vanadium reagent	yield[b]/% 1a[c]	2a
1	$VCl_3(thf)_3$	58	22
2	$VCl_3(thf)_3 + 0.2O_2$	56	22
3	VCl_4	0	26[d]
4	$VCl_4 + 0.2O_2$	0	58[d]
5	$VCl_2(tmeda)_2 + 0.2VCl_3(thf)_3$	91	6
6	$VCl_2(tmeda)_2 + 0.2VCl_4$	88	2

[a] Propiophenone (1.0 equiv), MeMgBr (1.0 equiv), and vanadium species (1.0 equiv) were employed. [b] Isolated yield. [c] *meso*:*dl* = 1:1. [d] Mixtures of 2-phenyl-1-butene and 2-phenyl-2-butene were obtained in 20% (run 3) and 23% (run 4) isolated yield, respectively.

To get information about the above assumption, we examined the effect of several higher-valent vanadium species on the coupling reaction (Table 2). When a vanadium(III) complex, $VCl_3(thf)_3$,[12] was employed instead of the $VCl_2(tmeda)_2$−O_2 system, the coupling reaction also occurred to some extent, but the isolated yield of the coupling product **1a** was much lower (run 1 of Table 2 vs. run 1 of Table 1). Addition of O_2 into the $VCl_3(thf)_3$ system did not affect the result seriously (Table 1, run 2). In a system employing a vanadium(IV) complex, the VCl_4 or VCl_4−O_2 system, the *β*-elimination of the oxometal species from the alkoxycomplexes occurred instead of the coupling reaction (Table 1, runs 3 and 4). It was found that the vanadium(III) or vanadium(IV) species had a similar effect to that of O_2 or allyl bromide. A combination system, $VCl_2(tmeda)_2$−a catalytic amount of $VCl_3(thf)_3$ or VCl_4, afforded the coupling product **1a** in good isolated yield just as the $VCl_2(tmeda)_2$−O_2 system did (Table 1, runs 5 and 6). In the $VCl_2(tmeda)_2$−O_2 system, a catalytic amount of a vanadium(III) or a vanadium(IV) species[13] should be produced, and their collaboration[14] with a low-valent vanadium(II) complex having higher reduction power and oxophilicity[15−17] would induce the C−O bond cleavage to promote the coupling reaction. The unsuccessful coupling reaction in pure O_2 atmosphere indicated that the vanadium(II) species is requisite for the present deoxygenative

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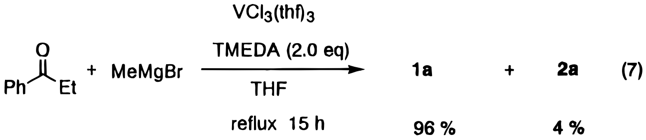
coupling. It has been reported that reaction of $VCl_3(thf)_3$ with RMgBr gave the vanadium(II) and vanadium(IV) species by disproportionation.[18] Thus, in the $VCl_3(thf)_3$ system (Table 2, run 1), some vanadium(II) species would be also produced by disproportionation of the vanadium(III) species, and the coupling product **1a** was obtained in 58% isolated yield.

TMEDA also plays an important role in the deoxygenative coupling reaction. For example, when $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$[19] was employed as another vanadium(II) species instead of $VCl_2(tmeda)_2$, the coupling product **1a** was not obtained and the alcohol **2a** was obtained in 59% isolated yield. Of course, when only TMEDA (without vanadium) instead of $VCl_2(tmeda)_2$ was employed, the cleavage of the C−O bond did not proceed at all. One of the reasons for this difference could be that $VCl_2(tmeda)_2$ is soluble in THF, whereas $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ is not sufficiently soluble. Surprisingly, when a combination of vanadium(III) complex, $VCl_3(thf)_3$, and 2.0 equiv of TMEDA was employed instead of the $VCl_2(tmeda)_2/O_2$ system, the coupling reaction occurred smoothly and the coupling product **1a** was obtained in 96% isolated yield along with the alcohol in 4% yield, which was a similar result to the $VCl_2(tmeda)_2-O_2$ system (eq 7). The combination of a vanadium(II) species and a higher-valent vanadium species prepared by disproportionation of the trivalent alkoxyvanadium species derived from $VCl_3(thf)_3$ and the magnesium alcoholate in the presence of TMEDA should be very effective for the deoxygenative coupling reaction.



Experimental Section

All manipulations were conducted under argon atmosphere with standard Schlenk methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used after distillation. THF was distilled from sodium benzophenone ketyl under argon prior to use. TMEDA was distilled from calcium hydride under argon prior to use. $VCl_2(tmeda)_2$,[8] $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$,[19] and $VCl_3(thf)_3$[12] were prepared according to published procedures. VCl_4 was obtained from a commercial supplier (Aldrich) and was used without further purification. The melting points are uncorrected.

General Procedure for the Reductive Coupling Reaction. To a solution of propiophenone (1.0 mmol) in THF (5.0 mL) was added a THF solution of MeMgBr (1 mol/L, 1.2 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 20 °C, a blue solution of $VCl_2(tmeda)_2$ (1.0 mmol) in THF (10 mL) was added at 20 °C, and then O_2 gas (5.0 mL) was introduced into the reaction mixture by syringe. The resulting dark purple solution was refluxed for 15 h. Aqueous NaOH solution (1 mol/L, 3 mL) was added, and the mixture was stirred at 20 °C for an additional 1 h. The precipitated brown solid was removed by filtration and washed with ethyl acetate. The combined filtrate and washings were dried over $MgSO_4$ and concentrated in vacuo. The residual oily materials were purified by column chromatography on silica gel to afford the coupling product and the alcohol. The ratio of the diastereomers (*dl*:*meso*) of the coupling product was determined by ^1H NMR.

3,4-Dimethyl-3,4-diphenylhexane (1a).[20] A mixture of two diastereomers (*dl*:*meso* = 50:50); $R_f = 0.27$ (hexane) mp 55−57 °C; ^1H NMR (C_6D_6) δ 0.62 (t, $J = 7.6$ Hz, 6H), 1.20 [s, 3H, (*dl*)], 1.23[s, 3H, (*meso*)], 1.30−1.48 (m, 2H), 1.47−1.58 [m, 1H, (*meso*)], 1.95−2.13 [m, 1H, (*dl*)], 2.05−2.23 (m, 1H), 6.85−7.23 (m, 10H).

3,4-Diethyl-3,4-diphenylhexane (1b):[20b] $R_f = 0.27$ (hexane); mp 42−44 °C; ^1H NMR ($CDCl_3$) δ 0.66 (t, $J = 7.2$ Hz, 12H), 2.00 (q, $J = 7.2$ Hz, 8H), 6.93−7.01(m, 4H), 7.03−7.14 (m, 6H).

5,6-Diethyl-5,6-diphenyldecane (1c). A ratio of two diastereomers (*dl*:*meso*) could not be determined due to a poorly resolved signals of both isomers: $R_f = 0.45$ (hexane); ^1H NMR ($CDCl_3$) δ 0.64 [t, $J = 7.3$ Hz, 6H (*dl* or *meso*)], 0.65 [t, $J = 7.3$ Hz, 6H (*meso* or *dl*)], 0.81 (t, $J = 7.3$ Hz, 6H), 0.76−0.89 (m, 2H), 0.92−1.07 (m, 2H), 1.15−1.27 (m, 4H), 1.87−2.02 (m, 8H), 6.92−6.96 (m, 4H), 7.11−7.24 (m, 6H); MS (EI) *m/z* 175 $[M^+ - C_6H_5C(C_2H_5)C_4H_9]$; IR (neat) 3130, 3100, 2950, 2920, 2860, 1940, 1800, 1740, 1590, 1490, 1460, 1440, 1380, 1330, 1250, 1070, 1030, 970, 910, 840, 790, 750, 700 cm^{-1}. Anal. Calcd for $C_{26}H_{38}$: C, 89.07; H, 10.93. Found: C, 89.39; H, 10.96.

4,5-Diethyl-4,5-diphenylocta-1,7-diene (1d). A mixture of two diastereomers (*dl*:*meso* = 50:50) was obtained: $R_f = 0.24$ (hexane); ^1H NMR ($CDCl_3$) δ 0.67 [t, $J = 7.4$ Hz, 6H (*dl* or *meso*)], 0.72 [t, $J = 7.4$ Hz, 6H (*meso* or *dl*)], 1.91−2.17 [m, 3H], 2.10−2.31 (m, 1H), 2.55−2.97 (m, 4H), 4.79−4.98 [m, 4H (*dl* or *meso*)], 4.95−5.14 [m, 4H (*meso* or *dl*)], 5.52−5.68 [m, 2H (*dl* or *meso*)], 5.68−5.84 [m, 2H (*meso* or *dl*)], 6.66−7.02 (m, 4H), 6.97−7.11 (m, 6H); MS (EI) *m/z* 318 (M^+); IR (neat) 3070, 2975, 2940, 2890, 1640, 1600, 1500, 1460, 1440, 1420, 1400, 1390, 1080, 1040, 1000, 915, 770, 705 cm^{-1}. Anal. Calcd for $C_{24}H_{30}$: C, 90.51; H, 9.49. Found: C, 90.73; H, 9.25.

1,1-Diphenylprop-1-ene:[21] $R_f = 0.28$ (hexane); ^1H NMR ($CDCl_3$) δ 1.74 (d, $J = 7.1$ Hz, 3H), 6.15 (q, $J = 7.1$ Hz, 1H), 7.15−7.38 (m, 10H).

1,1-Diphenylpropane:[22] $R_f = 0.22$ (hexane); ^1H NMR ($CDCl_3$) δ 0.89 (t, $J = 7.3$ Hz, 3H), 2.06 (dt, $J = 7.8$, 7.3 Hz, 2H), 3.77 (t, $J = 7.8$ Hz, 1H), 7.10−7.28 (m, 10H).

2,3-Dimethyl-2,3-diphenylbutane (1f):[23] $R_f = 0.36$ (hexane); mp 115−116 °C (lit.[23] mp 118−119 °C); ^1H NMR ($CDCl_3$) δ 1.31 (s, 12H), 7.04−7.18 (m, 10H).

3,4-Dimethyl-1,3,4,6-tetraphenylhexane (1h). A mixture of two diastereomers (*dl*:*meso* = 50:50); $R_f = 0.13$ (hexane); mp 47−48 °C; ^1H NMR ($CDCl_3$) δ 1.34 [s, 6H (*dl* or *meso*)], 1.41 [s, 6H (*meso* or *dl*)], 1.79−1.99 (m, 2H), 2.05−2.21 (m, 2H), 2.27−2.48 (m, 4H), 6.95−7.24 (m, 20H); MS (EI) *m/z* 209 $[M^+ - C_6H_5(CH_2)_2CCH_3C_6H_5]$; IR (neat) 3087, 3059, 3024, 2960, 2880, 1945, 1870, 1802, 1654, 1602, 1541, 1496, 1453, 1442, 1375, 1270, 1156, 1117, 1065, 1030, 909, 844, 789, 766, 752, 727, 700, 669, 637, 563, 527, 498 cm^{-1}. Anal. Calcd for $C_{32}H_{34}$: C, 91.81; H, 8.19. Found: C, 91.69; H, 8.09.

1,3-Dimethyl-3-(1,3-dimethyl-2-cyclohexen-1-yl)cyclohex-1-ene (3).[24] The ratio of the diastereomers (*dl*:*meso* = 60:40 or vice versa) was determined by ^1H NMR: $R_f = 0.71$ (hexane); ^1H NMR ($CDCl_3$) δ 0.89 [s, 6H (*dl* or *meso*)], 0.89 [s, 6H (*meso* or *dl*)], 1.20−1.88 (m, 12H), 1.65 (s, 6H), 5.26 [bs, 2H (*dl* or *meso*)], 5.29 [bs, 2H (*meso* or *dl*)].

3,3,4,4-Tetramethyl-1,6-diphenylhexa-1,5-diene (6a), 3,3,6-Trimethyl-1,4-diphenylhepta-1,5-diene (6b), and 2,7-Dimethyl-4,5-diphenylocta-2,6-diene (6c). The isomers could not be separated, and their ratio was determined by ^1H NMR analysis (**6a**:**6b**:**6c** = 5:53:42). A ratio of the two diastereomers of **6c** could not be determined: $R_f = 0.46$ (hexane:AcOEt = 10:1); ^1H NMR ($CDCl_3$) δ 1.09 (s, 3H, **6b**),

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1.16 (s, 3H, **6b**), 1.19 (s, 12H, **6a**), 1.45 (d, $J = 1.5$ Hz, 3H, **6c**), 1.58 (d, $J = 1.2$ Hz, 3H, **6c**), 1.60 (d, $J = 1.2$ Hz, 3H, **6c**), 1.64 (d, $J = 1.2$ Hz, 3H, **6b**), 1.76 (d, $J = 1.2$ Hz, 3H, **6c**), 1.78 (d, $J = 1.5$ Hz, 3H, **6b**), 3.44 (d, $J = 10.1$ Hz, 1H, **6b**), 3.76−3.81 (m, 2H, **6c**), 5.34−5.38 (m, 1H, **6c**), 5.48−5.52 (m, 1H, **6c**), 5.64−5.69 (m, 1H, **6b**), 6.25 (d, $J = 16.1$ Hz, 1H, **6b**), 6.31 (d, $J = 16.1$ Hz, 1H, **6b**), 6.39 (d, $J = 15.3$ Hz, 2H, **6a**), 6.43 (d, $J = 15.3$ Hz, 2H, **6a**), 7.20−7.43 (m, 10H **6a** + 10H **6b** + 10H **6c**); MS (CI) m/z 291 ($M^+ + H$), 145 ($M^+ - C_6H_5C_5H_8$); IR (neat, a mixture of **6a**:**6b**:**6c** = 5:53:42) 3060, 3026, 2965, 2925, 1735, 1600, 1494, 1449, 1382, 1261, 1073, 1030, 973, 902, 861, 795, 747, 698, 510 cm^{-1}. Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 91.22; H, 9.01.

3,4-Dimethyl-1,6-diphenylhexa-1,5-diene (7a), 3-Methyl-1,4-diphenylhepta-1,5-diene (7b), and 4,5-Diphenylocta-2,6-diene (7c). The isomers could not be separated, and their ratio was determined by ^{1}H NMR analysis (**7a**:**7b**:**7c** = 26:65:9). A ratio of diastereomers or stereoisomers of **7b** and **7c** could not be determined: $R_f = 0.29$ (hexane); ^{1}H NMR ($CDCl_3$) δ 1.00 [t, $J = 6.9$ Hz, 3H, **7b** (one isomer)], 1.12−1.16 [m, 6H **7a** + 3H **7b** (another isomer)], 1.46−1.51 (m, 6H **7c**), 1.61−1.72 (m, 3H **7b**), 2.29−2.47 (m, 2H **7a**), 2.60−2.71 (m, 1H **7b**), 3.18 [dd, $J = 14.6$, 8.2 Hz, 1H **7b** (one isomer)], 3.50−3.60 [m, 1H **7b** (another isomer) + 1H **7c**], 3.91−3.92 (m, 1H **7c**), 5.20−5.80 (m, 2H **7b** + 4H **7c**), 5.97−6.44 (m, 4H **7a** + 2H **7b**), 7.14−7.40 (m, 10H **7a** + 10H **7b** + 10H **7c**); HRMS (EI) m/z calcd for $C_{20}H_{22}$ (M^+) 262.1721, found 262.1708; IR (neat, a mixture of **7a**:**7b**:**7c** = 26:65:9) 3081, 3060, 3025, 2963, 2925, 2873, 1994, 1872, 1800, 1650, 1599, 1493, 1449, 1373, 1072, 1029, 964, 909, 841, 747, 694, 528 cm^{-1}

Allyl Bromide-Promoted Reductive Coupling Reaction (Eq 6). To a solution of propiophenone (1.1 mmol) in THF (6.5 mL) was added a THF solution of MeMgBr (1 mol/L, 1.2 mmol) at 0 °C. After the reaction mixture was stirred for 4 h at 20 °C, a blue solution of $VCl_2(tmeda)_2$ (1.1 mmol) in THF (24 mL) was added at 20 °C. Immediately, the color of the reaction mixture changed to green. To this was added allyl bromide (0.12 mmol) at 20 °C, and then the resulting dark brown solution was refluxed for 34 h. Aqueous NaOH solution (1 mol/L, 3 mL) was added, and the mixture was stirred at 20 °C for an additional 1 h. The precipitated brown solid was removed by filtration and washed with ethyl acetate. The combined filtrate and washings were dried over $MgSO_4$ and concentrated in vacuo. The residual oily materials were purified by column chromatography on silica gel to afford the coupling product **1a** in 91% yield along with the asymmetric carbon product **8** in 3% yield and a trace of alcohol **2a**.

Typical Procedure for the Reductive Coupling Reaction Using Several Vanadium Species (Table 2). To a solution of propiophenone (1.1 mmol) in THF (6.0 mL) was added a THF solution of MeMgBr (1 mol/L, 1.2 mmol) at 0 °C. After the reaction mixture was stirred for 5 h at 20 °C, a blue solution of $VCl_2(tmeda)_2$ (1.1 mmol) in THF (16 mL) was added at 20 °C. Immediately, the color of the reaction mixture changed to green. To the reaction mixture was added a red solution of $VCl_3(thf)_3$ (0.22 mmol) in THF (5.5 mL) at 20 °C, and then the resulting dark purple solution was refluxed for 15 h. Aqueous NaOH solution (1 mol/L, 3 mL) was added, and the mixture was stirred at 20 °C for an additional 1 h. The precipitated brown solid was removed by filtration and washed with ethyl acetate. The combined filtrate and washings were dried over $MgSO_4$ and concentrated in vacuo. The residual oily materials were purified by column chromatography on silica gel to afford the coupling product **1a** in 91% yield and alcohol **2a** in 6% yield.

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