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Unusual Cerium(III) Chloride-promoted Reactions of Alkenyl Grignard Reagents or Alkenyl-lithiums with 1,3-Diphenyl-2-propanone: Formation and Trapping of Diorganometallic Species

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Treatment of vinylmagnesium chloride with anhydrous cerium(III) chloride in tetrahydrofuran at −20 °C, followed by reaction with 1,3-diphenyl-2-propanone, afforded (*Z*)-2,7-dibenzyl-1,8-diphenyl-4-octene-2,7-diol and (*Z*)-2,7-dibenzyl-1,8-diphenyl-4,6-octadien-2-ol in 19% and 9% yield, respectively. Isopropenylmagnesium bromide underwent trimerization on treatment with cerium chloride at 20 °C, and the subsequent reaction with the same ketone provided (*Z,Z*)-2,9-dibenzyl-4,5,7-trimethyl-1,10-diphenyl-4,6-decadiene-2,9-diol in 22% yield. Under similar conditions, the reaction of 2-methyl-1-propenylmagnesium bromide provided (*Z*)-2,6-dibenzyl-4-methyl-1,7-diphenyl-3,5-heptadien-2-ol in 7% yield. Vinyl-lithium and isopropenyl-lithium were also subjected to dimerization by the action of cerium chloride, and the generated di-organometallic species were trapped by 1,3-diphenyl-2-propanone.

Keywords: organocerium reagent; Grignard reagent; organolithium reagent; alkenyl organometallic reagents; cerium chloride; coupling reaction; ketone; addition reaction

INTRODUCTION

The Griganrd reaction of carbonyl compounds to yield alcohols is undoubtedly one of the most fundamental and versatile methods for carbon–carbon bond formation (for excellent reviews, see Ref. 1). Despite its enormous synthetic utility, it is also well recognized that the Grignard reaction is often accompanied by so-called abnormal reactions such as enolization, reduction and conjugate addition. In some cases such abnormal reactions prevail over the 'normal addition', resulting in poor yields of desired compounds. Previously, we reported that anhydrous cerium(III) chloride significantly promoted the normal addition reaction of Grignard reagents to carbonyl compounds with remarkable suppression of abnormal reactions.[2] One of the characteristic features of this method is that the reactions are carried out under mild conditions (0 °C through to room temperature) except for alkenyl Grignard reagents. Alkenyl Grignard reagents decompose at around room temperature on contact with cerium chloride, and hence the subsequent reaction with carbonyl compounds results in the formation of a complex mixture, giving no trace or low yield of the corresponding addition products. These reactions, therefore, should be carried out at −78 °C to obtain the normal addition products in satisfactory yields.[2b] A typical example is shown in Scheme 1. Thus, when vinylmagnesium chloride or bromide was mixed with cerium chloride at −78 °C and it was allowed to react with 1,3-diphenyl-2-propanone at the same temperature, the normal addition product, 2-benzyl-1-phenyl-3-buten-2-ol (**1**), was produced in excellent yield. In sharp contrast, when the mixture of the Grignard reagent and cerium chloride was warmed to temperatures higher than −20 °C and then it was reacted with 1,3-diphenyl-2-propanone, no trace of compound **1** was produced.

We have been interested in the latter unusual reaction and have intended to isolate and characterize the reaction products in order to clarify the scope of the reaction. For this purpose, vinylmagnesium chloride and isopropenylmagnesium bromide were selected as the model substrates. At the same time, the corresponding organolith-

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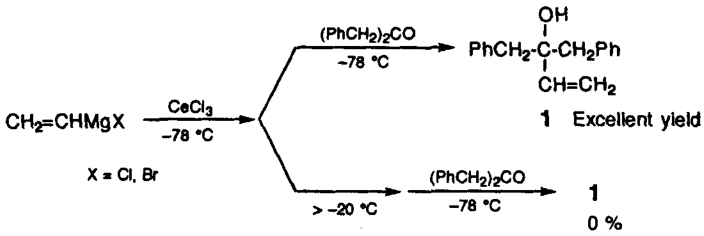


Scheme 1

ium reagents were also employed in order to compare their reactivities with those of the Grignard reagents. In this paper we describe the results of these reactions together with the mechanistic aspects. A preliminary account of the results has appeared.[3]

RESULTS AND DISCUSSION

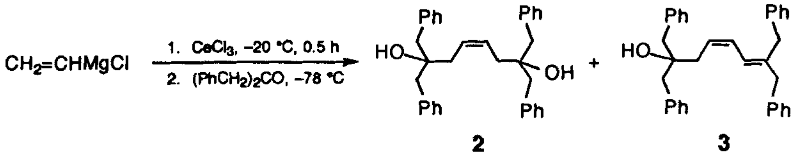
Isolation and characterization of unusual products

Our initial investigation was undertaken with the reaction of vinylmagnesium chloride. The Grignard reagent was added to a suspension of one molar equivalent of cerium chloride in THF at −78 °C, and the suspension was gradually warmed. The color of the suspension changed from pale yellow to brown at about −45 °C and it turned to dark brown at −20 °C. The resulting mixture was cooled to −78 °C, and 1,3-diphenyl-2-propanone (0.33 mol equiv.) was added. From the reaction mixture (*Z*)-2,7-dibenzyl-1,8-diphenyl-4-octene-2,7-diol (**2**) and (*Z*)-2,7-dibenzyl-1,8-diphenyl-4,6-octadien-2-ol (**3**) were isolated in 19% and 9% yields, respectively, based on 1,3-diphenyl-2-propanone (Scheme 2). Allylmagnesium bromide and phenylethynylmagnesium bromide were treated with cerium chloride at room temperature and were then reacted with 1,3-diphenyl-2-propanone in order to compare their reactivities with that of vinylmagnesium chloride. These reactions afforded the corresponding normal addition products in almost quantitative yield. Other lanthanide salts (CeF_3, CeI_3, $Ce(OSO_2CF_3)_3$, $NdCl_3$, $LaCl_3$, and $YbCl_3$) and cerium metal were tested for the reaction under similar conditions. The use of CeI_3, $Ce(OSO_2CF_3)_3$ and $NdCl_3$ instead of $CeCl_3$ afforded almost the same results, whilst the others did not react with vinylmagnesium chloride at room temperature.

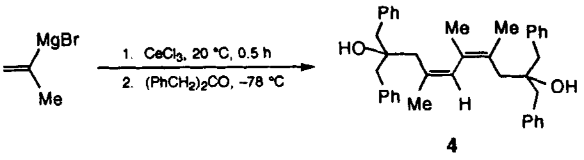
The structure of compound **2** was estimated on the basis of its spectral data and finally unequivocally determined by single-crystal X-ray analysis. The ORTEP drawing of compound **2** is shown in Fig. 1. Similarly, the structure of compound **3** was determined by IR, MS and NMR including nuclear Overhauser enhancement spectroscopy (NOESY).

These results suggest that vinylmagnesium chloride is subjected to dimerization by the action of cerium chloride to generate diorganometallic compounds as the intermediates. In order to confirm the existence of C_4 components as the reactive intermediates, the reaction of vinylmagnesium chloride with cerium chloride was quenched with water. Analysis of the reaction mixture by GC–MS indicated the formation of (*Z*)-2-butene, (*E*)-2-butene, 1-butene, and butane.

In order to study the mechanistic aspects of this unusual coupling reaction of alkenyl Grignard reagents, we investigated the reaction of an α-substituted alkenyl Grignard reagent, isopropenylmagnesium bromide, with cerium chloride. The decomposition of isopropenylmagnesium bromide in the presence of cerium chloride was considerably more sluggish than that of vinylmagnesium chloride. Therefore, isopropenylmagnesium bromide was allowed to react with cerium chloride at 20 °C for 30 min, and then



Scheme 2



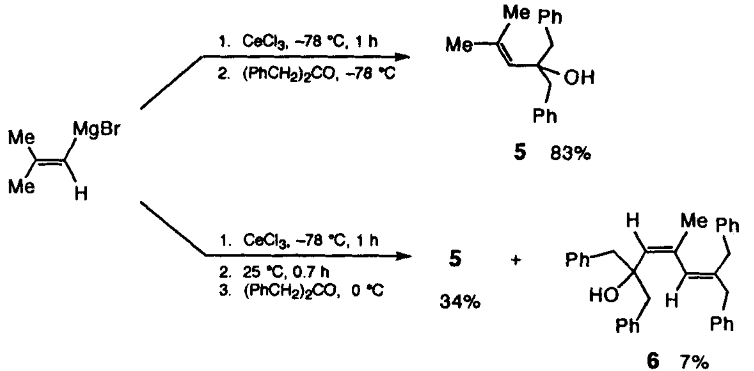
Scheme 3

the mixture was treated with 1,3-diphenyl-2-propanone at −78 °C. From the reaction mixture, a crystalline compound was isolated, although the yield was poor. The structure of the compound was determined to be (*Z*,*Z*)-2,9-dibenzyl-4,5,7-trimethyl-1,10-diphenyl-4,6-decadiene-2,9-diol (**4**) by single-crystal X-ray analysis (Scheme 3). The ORTEP drawing of compound **4** is shown in Fig. 2.

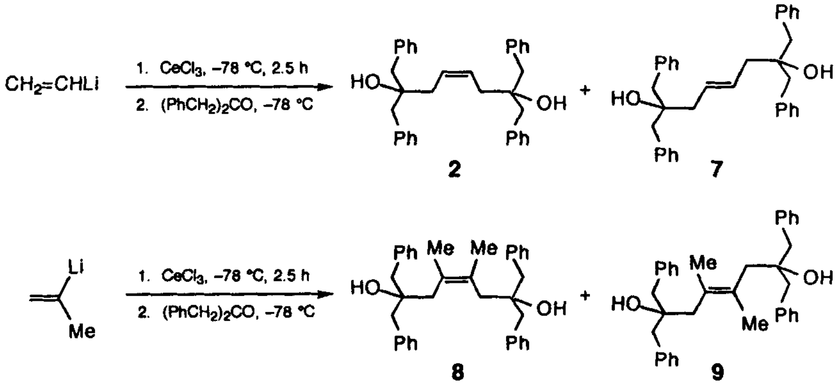
It is noted that the product **4** involves three components of the original Grignard reagent unit. This result can be explained by assuming that the Grignard reagent undergoes trimerization by the action of cerium chloride involving formation of diorganometallic species.

Another interesting result was obtained in the reaction of 2-methyl-1-propenylmagnesium bromide, as is illustrated in Scheme 4. When the mixture of the Grignard reagent and cerium chloride was kept at −78 °C and then it was allowed to react with 1,3-diphenyl-2-propanone, 2-benzyl-4-methyl-1-phenyl-3-penten-2-ol (**5**) was obtained in 83% yield. On the other hand, when the mixture of the Grignard reagent and cerium chloride was warmed to 25 °C, (*Z*)-2,6-dibenzyl-4-methyl-1,7-diphenyl-3,5-heptadien-2-ol (**6**) was isolated in 7% yield. The structure of compound **6** was determined by IR, MS and NMR inlcuding nuclear Overhauser effect (NOE) experiments.

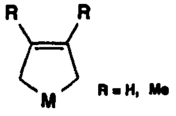
Our attention next turned to the reactions of alkenyl-lithiums with anhydrous cerium chloride. First, vinyl-lithium was treated with cerium chloride. In this case, the color of the mixture turned to dark brown even at −78 °C, and the subsequent reaction with 1,3-diphenyl-2-propanone provided diols **2** and **7** in 11% and 21% yields, respectively. Under similar conditions, isopropenyl-lithium was converted to compounds



Scheme 4



Scheme 5



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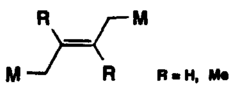

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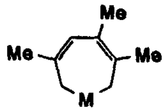

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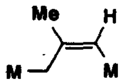

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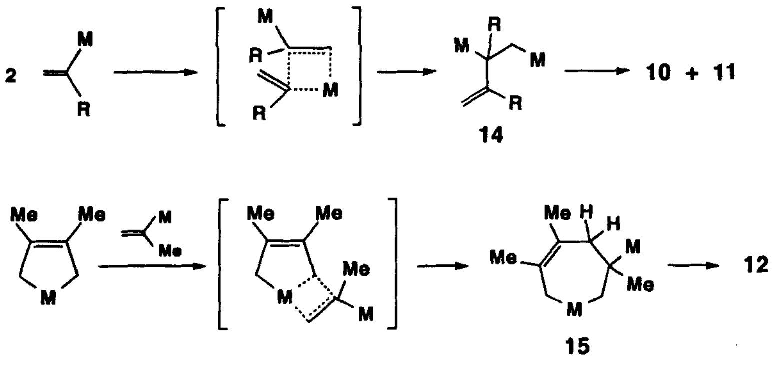
8 and 9 in 7% and 14% yields, respectively (Scheme 5). When vinyl- and isopropenyllithiums were treated with cerium chloride at −30 °C, only (*Z*)-isomers, 2 and 8, were isolated in 16% and 12% yield, respectively. No traces of (*E*)-isomers, 7 and 9, were produced under these conditions.

Although many carbonyl addition reactions of alkenylcerium reagents have been reported, this type of unusual reaction is unprecedented.[4]

Mechanistic aspects

The formation of the unusual products, **2**–**4** and **6**–**9**, can be interpreted by assuming the existence of diorganometallic species **10**–**13** as the reactive intermediates.

Although the precise mechanism for the generation of these diorganometallic species has not yet been clarified, we tentatively propose the dimerization and trimerization pathways depicted in Scheme 6. Thus, the reaction might involve carbometallation of the carbon–carbon double bond to generate diorganometallic species **14** which might isomerize to **10** and **11**. It is also assumed that diorganometallic species **12** is formed via *β*-hydrogen elimination of an intermediate **15**.



Scheme 6

EXPERIMENTAL

General

Infrared spectra were recorded on a Hitachi-IR 215 spectrophotometer. ^{1}H NMR spectral data were recorded on a JEOL JNM-FX-270 (at 270 MHz), JEOL JNM-GSX-400 (at 400 MHz) or JEOL JNM-GSX-500 (at 500 MHz) spectrometer. ^{13}C NMR spectra were obtained on JEOL JNM-GX-270 (68 MHz), JEOL JNM-GSX-400 (100 MHz) or JEOL JNM-GSX-500 (126 MHz) spectrometers. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in δ units, and coupling constants are given in cycles per second (Hertz). Mass spectra were measured with JEOL HMS-HX-110 (EI) and JEOL JMS-DX 300 (FD and FAB) instruments. Gas chromatographic analyses were carried out on a VZ-7 column. GC–MS spectra were obtained with a Shimadzu QP-1000. Microanalyses were performed on a Perkin–Elmer 240B at the Chemical Analysis Center of Chiba University.

All experiments were carried out under an atmosphere of dry argon. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 F_{254}, 0.25 mm) were used. The products were purified by preparative TLC on silica gel (Wakogel B–5F).

Cerium chloride, lanthanum chloride, neodymium chloride and ytterbium chloride were purchased from Wako Pure Chemicals Ltd. Cerium fluoride was purchased from Nippon Yttrium Co. Ltd. Cerium triflate was provided by Seimi Chemical Co. Ltd. Cerium iodide was prepared *in situ* by the reaction of cerium metal with iodine in THF. The following Grignard reagents were pre-

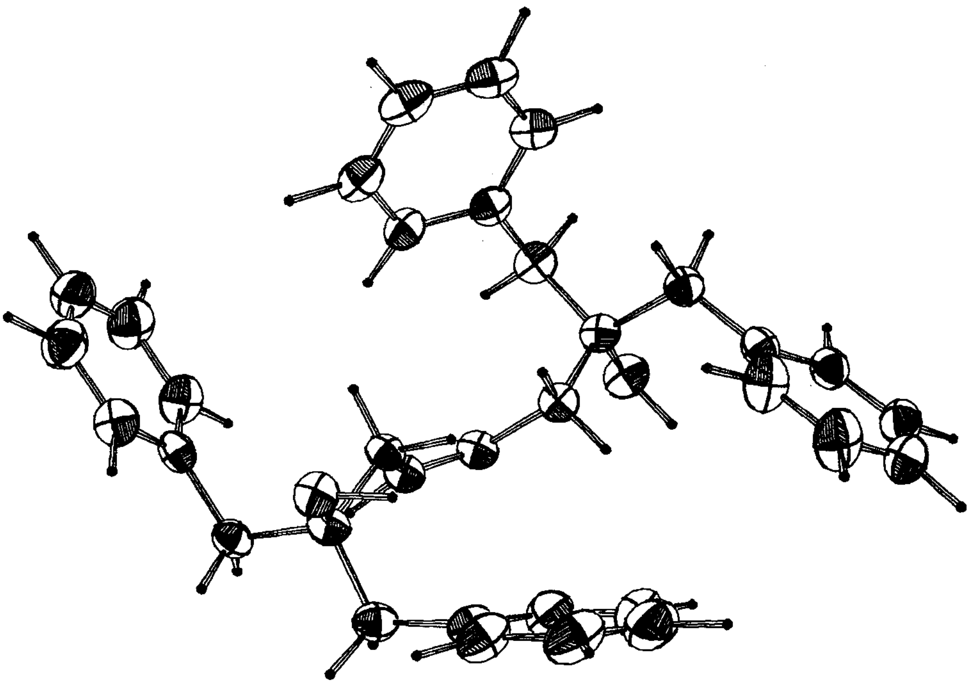


Figure 1 ORTEP drawing of (*Z*)-2,7-dibenzyl-1,8-diphenyl-4-octene-2,7-diol (**2**).

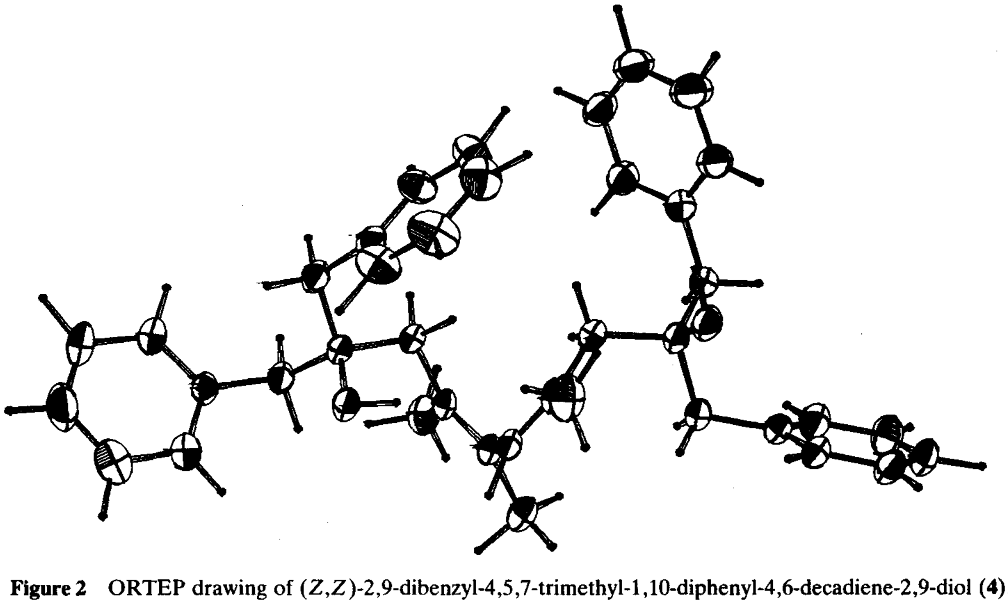


Figure 2 ORTEP drawing of (*Z*,*Z*)-2,9-dibenzyl-4,5,7-trimethyl-1,10-diphenyl-4,6-decadiene-2,9-diol (**4**).

pared according to procedures in the literature and their concentrations were determined by titration: vinylmagnesium chloride,[5] vinylmagnesium bromide,[6] isopropenylmagnesium bromide,[7] phenylethynylmagnesium bromide[8] and allylmagnesium bromide.[9] Vinyl-lithium[10] and isopropenyl-lithium[11] were prepared by known procedures. Other simple chemicals were purchased and were used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon prior to use.

2-Benzyl-1-phenyl-3-buten-2-ol (1)

This compound was obtained in almost quantitative yield according to the procedure described in the literature.[2b] Colorless oil. ^1H NMR (270 MHz) ($CDCl_3$) δ 1.54 (s, 1H, exchangeable with D_2O), 2.90 (s, 4H), 4.91 (dd, $J = 17.2$ Hz, $J = 1.3$ Hz, 1H), 5.01 (dd, $J = 10.7$ Hz, $J = 1.3$ Hz, 1H), 5.94 (dd, $J = 17.2$ Hz, $J = 10.7$ Hz, 1H), 7.10–7.35 (m, 10H). IR (neat): ν 3520, 3000, 2890, 1485, 925, 770, 705 cm^{-1}.

(*Z*)-2,7-Dibenzyl-1,8-diphenyl-4-octene-2,7-diol (2) and (*Z*)-2,7-dibenzyl-1,8-diphenyl-4,6-octadien-2-ol (3)

In a 30-ml two necked flask, 792 mg (3 mmol) of $CeCl_3 \cdot H_2O$ was completely dried *in vacuo* by stirring at 130–140 °C for 3 h. While the flask was still hot, argon gas was introduced and the flask was then cooled in an ice bath. Dry THF (6 ml) was added all at once with vigorous stirring. The ice bath was removed and the suspension was well stirred overnight under argon at room temperature. To this was added vinylmagnesium chloride (2 ml of 1.5 M THF solution) with vigorous stirring at −78 °C. The temperature of the mixture was elevated to −20 °C, whereupon its color turned to dark brown. After 30 min, the mixture was cooled to −78 °C and 210 mg (1 mmol) of 1,3-diphenyl-2-propanone was added. The mixture was stirred for an additional 30 min and then quenched by 5 ml of 1 M HCl. The organic layer was separated and the aqueous layer was extracted three times with ether. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was subjected to preparative TLC to give the compounds (*Z*)-2,7-dibenzyl-1,8-diphenyl-4-octene-2,7-diol (**2**) (45.7 mg, 19%) and (*Z*)-2,7-dibenzyl-1,8-diphenyl-4,6-octadien-2-ol (**3**) (19.5 mg, 9%).

Compound **2**: m.p. 115.0–115.5 °C (from hexane). ^1H NMR (500 MHz) ($CDCl_3$): δ 1.59 (br s, 2H), 1.98 (d, $J = 4.8$ Hz, 4H), 2.75 (d, $J = 13.7$ Hz, 4H), 2.76 (d, $J = 13.7$ Hz, 4H), 5.76 (t, $J = 4.8$ Hz, 2H), 7.17–7.33 (m, 20H). ^{13}C NMR (68 MHz) ($CDCl_3$): δ 36.4, 45.7, 74.4, 126.5, 127.8, 128.2, 130.8, 137.2. IR (KBr): 3400, 3000, 2880, 1580, 1480, 1440 cm^{-1}. Analysis: calcd for $C_{34}H_{36}O_2$: C, 85.67; H, 7.61. Found: C, 85.71; H, 7.70%.

Compound **3**: colorless oil. ^1H NMR (500 MHz) ($CDCl_3$) δ 1.54 (s, 1 H), 2.28 (d, $J = 7.4$ Hz, 2H), 2.85 (s, 4 H), 3.24 (s, 2 H), 3.42 (s, 2 H) 5.64 (dt, $J = 7.4$ Hz, 11.0 Hz, 1H), 6.11 (d, $J = 11.6$ Hz, 1H), 6.56 (dd, $J = 11.0$ Hz, 11.6 Hz, 1H), 7.18–7.31 (m, 20H). ^{13}C NMR (100 MHz) ($CDCl_3$): δ 35.4, 36.3, 43.4, 45.7, 74.6, 123.2, 126.1, 126.2, 126.4, 126.5, 127.1, 128.2, 128.3, 128.4, 128.7, 129.1, 130.8, 137.2, 139.5, 141.3. IR (neat) 3400, 3020, 2900, 1600, 1500, 1455 cm^{-1}. Analysis: calcd for $C_{34}H_{34}O$: C, 89.04; H, 7.47. Found: C, 89.03; H, 7.62%.

X-ray crystallographic analysis of compound 2

A well-shaped monoclinic crystal of **2** was obtained by recrystallization from hexane: $C_{34}H_{36}O_2$; space group $P2_1/a$; $Z = 4$; $D = 1.161$ g cm^{-3}; cell constants $a = 21.780(24)$ Å, $b = 11.094(21)$ Å, $c = 11.030(11)$ Å, $\beta = 92.6787(84)°$; $V = 2727.6$ Å^3. Lattice constants and intensity data for **1** were measured using graphite-monochromated Cu Kα radiation on a Rigaku AFC-5 diffractometer. A total of 3273 unique reflections with $F_0 > 3\sigma(F_0)$ were obtained using the ω–2θ scanning method with a 2θ scan speed of 4° min^{-1} to 120°. The structure was solved by the UNICS-III system (Computer Library of University of Tokyo) based on direct methods. Approximate positions for all hydrogen atoms were found in subsequent difference Fourier syntheses. Final refinement cycles utilizing anisotropic thermal parameters for all nonhydrogen atoms resulted in $R = 0.0577$.

(*Z,Z*)-2,9-Dibenzyl-4,5,7-trimethyl-1,10-diphenyl-4,6-decadiene-2,9-diol (4)

Isopropenylmagnesium bromide (1.3 M in THF, 2.3 ml) was added to a suspension of cerium chloride (3 mmol) prepared by the procedure described above, at 0 °C. The temperature of the mixture was elevated to 20 °C, whereupon its color turned to dark brown. After 30 min, the mixture was cooled to −78 °C and 210 mg (1 mmol) of 1,3-diphenyl-2-propanone was added and the reaction mixture was worked up by the same procedure described above. The crude products were purified by preparative TLC (ethyl acetate/hexane = 1 : 15) to give 59.6 mg (22%) of white crystals: m.p. 138 °C (from hexane). ^1H NMR (500 MHz) ($CDCl_3$): δ 1.54 (s, 2H), 1.57 (s, 3H), 1.70 (d, $J = 1.1$ Hz, 3H), 1.73 (s, 3H), 1.96 (s, 2H), 2.10 (s, 2H), 2.58 (d, $J = 13.5$ Hz, 2H), 2.62 (d, $J = 13.5$ Hz, 2H), 2.73 (d, $J = 13.5$ Hz, 2H), 2.75 (d, $J = 13.5$ Hz, 2H), 5.68 (s, 1H), 7.16–7.30 (m, 20H). ^{13}C NMR (68 MHz) ($CDCl_3$): δ 19.4, 20.7, 25.6, 42.3, 44.7, 46.4, 74.6, 75.5, 126.2, 126.3, 128.0, 128.3, 130.8, 131.2, 131.6, 132.9, 137.6, 137.7. IR (KBr): ν 3500, 3000, 2900, 1600, 1500 cm^{-1}. FDMS: *m/z* 544 (M^+). Analysis: calcd for $C_{39}H_{44}O_2$: C, 85.99; H 8.14. Found: C, 86.04; H, 8.23%.

X-ray crystallographic analysis of compound 4

A well-shaped monoclinic crystal of **4** was obtained by recrystallization from hexane: $C_{39}H_{44}O_2$; space group $P2_1/n$; $Z = 4$; $D = 1.082$ g cm^{-3}; cell constants $a = 15.026(16)$ Å, $b = 19.348(17)$ Å, $c = 11.039(19)$ Å, $\beta = 91.905(12)°$; $V = 3207.4$ Å^3. Lattice constants and intensity data for **2** were measured using graphite-monochromated Cu Kα radiation on a Rigaku AFC-5 diffractometer. A total of 3753 unique reflections with $F_0 > 3\sigma(F_0)$ were obtained using the ω–2θ scanning method with a 2θ scan speed of 4° min^{-1} to 120°. The structure was solved by the UNICS-III system (Computer Library of University of Tokyo) based on direct methods. Approximate positions for all hydrogen atoms were found in subsequent difference Fourier syntheses. Final refinement cycles utilizing anisotropic thermal parameters for all nonhydrogen atoms resulted in $R = 0.0701$.

2-Benzyl-4-methyl-1-phenyl-3-penten-2-ol (5)

This compound was obtained in 83% yield by the reaction of 1,3-diphenyl-2-propanone with 2-methyl-1-propenylmagnesium bromide in the presence of cerium(III) chloride at −78 °C.[2b] Colorless oil. ^{1}H NMR (270 MHz) ($CDCl_3$): δ 1.52 (d, $J = 1.3$ Hz, 3H), 1.54 (s, 1H, exchangeable with D_2O), 1.63 (d, $J = 1.3$ Hz, 3H), 2.89 (s, 4H), 5.21 (m, 1H), 7.15–7.35 (m, 10H). IR (neat): ν 3520, 2990, 2870, 1480, 1440, 755, 705 cm^{-1}.

(*Z*)-2,6-Dibenzyl-4-methyl-1,7-diphenyl-3,5-heptadien-2-ol (6)

2-Methyl-1-propenylmagnesium bromide (12.5 ml of 0.48 M THF solution) was added with vigorous stirring to a suspension of ceriunm chloride (6 mmol) in THF (24 ml) at −78 °C. The suspension was warmed to 25 °C, kept for 1 h at the same temperature, and cooled to 0 °C. To this suspension was added a solution of 1,3-diphenyl-2-propanone (420 mg, 2 mmol) in THF (3 ml). After 30 min the reaction was quenched with saturated NH_4Cl solution and the products were extracted with ethyl acetate. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residual oil was subjected to preparative TLC (ethyl acetate/hexane = 1 : 10) to give 2-benzyl-4-methyl-1-phenyl-3-penten-2-ol (**5**) (190 mg, 34%) and (*Z*)-2,6-dibenzyl-4-methyl-1,7-diphenyl-3,5-heptadien-2-ol (**6**) (30 mg, 7%). Compound **6** was recrystallized from methanol to give colorless needles: m.p. 93.5–94.5 °C. ^{1}H NMR (270 MHz) ($CDCl_3$): δ 1.65 (s, 3H), 2.67 (s, 2H), 2.70 (s, 1H, exchangeable with D_2O), 2.81 (d, $J = 12.9$ Hz, 2H), 2.90 (d, $J = 12.9$ Hz, 2H), 2.95 (s, 2H), 5.11 (br, s, 1H), 5.31 (br, s, 1H), 6.88–6.91 (m, 4H), 7.10–7.30 (m, 16H). ^{13}C NMR (126 MHz) ($CDCl_3$): δ 25.8, 36.0, 41.8, 48.5, 77.3, 125.8, 126.11, 126.15, 127.0, 127.7, 128.2, 128.3, 128.8, 129.0, 130.6, 130.9, 132.9, 137.6, 139.1, 139.3, 141.2. FABMS: *m/z* 457 ($M - 1$) (2%), 441 (19%) 367 (81%), 154 (53%), 91 (100%). IR (KBr): 3510, 2890, 1490, 1450, 765, 710 cm^{-1}. Analysis: calcd for $C_{34}H_{34}O$: C, 89.04; H, 7.47. Found: C, 88.75; H, 7.44%.

Reaction of 1,3-diphenyl-2-propanone with alkenyllithiums in the presence of $CeCl_3$

An alkenyl-lithium (3 mmol), which was prepared by the reaction of vinyl bromide or isopropenyl bromide with *t*-butyl-lithium, was added to a suspension of cerium chloride (3 mmol) in THF (15 ml) at −78 °C. The color of the mixture turned to dark brown. After 2.5 h, 210 mg (1 mmol) of 1,3-diphenyl-2-propanone was added and the reaction mixture was worked up by the same procedure described above.

Isolation of (*E*)-2,7-dibenzyl-1,8-diphenyl-4-octene-2,7-diol (7) and compound 2

A crude product was obtained by preparative TLC (ethyl acetate/hexane = 1 : 5) and it was recrystallized from hexane to give (*E*)-2,7-dibenzyl-1,8-diphenyl-4-octene-2,7-diol (**7**) (49.6 mg, 21%): m.p. 160.5–161.0 °C. ^{1}H NMR (500 MHz) ($CDCl_3$): δ 1.53 (s, 2H), 2.13–2.20 (m, 4H), 2.80

(s, 8H), 5.54–5.61 (m, 2H), 7.23–7.32 (m, 20H). ^{13}C NMR (126 MHz) ($CDCl_3$): δ 42.1, 45.7, 74.0, 126.5, 128.2, 129.8, 130.8, 137.3. IR (KBr) 3500, 3000, 2900, 1500, 1440 cm^{-1}. Analysis: calcd for $C_{34}H_{36}O_2$: C, 85.67; H, 7.61. Found: C, 85.51; H, 7.60%. Compound **2** (27.0 mg, 11%) was obtained from the mother solution.

Isolation of (*Z*)-2,7-dibenzyl-4,5-dimethyl-1,8-diphenyl-4-octene-2,7-diol (8) and (*E*)-2,7-dibenzyl-4,5-dimethyl-1,8-diphenyl-4-octene-2,7-diol (9)

A crude product was purified by preparative TLC (ethyl acetate/hexane = 1 : 15). The collected solid was recrystallized from hexane to give 34.8 mg (14%) of compound **9**. The mother solution was concentrated and the residue was purified by preparative TLC (benzene). The solid was recrystallized from hexane to give compound **8** (16.8 mg, 7%) as white crystals.

Compound **8**: m.p. 170.0–171.5 °C. ^{1}H NMR (400 MHz) ($CDCl_3$): δ 1.51 (s, 2H), 1.79 (s, 6H), 2.11 (s, 4H), 2.51 (d, j = 13.5 Hz, 4H), 2.61 (d, J = 13.5 Hz, 4H), 7.16–7.32 (m, 20H). ^{13}C NMR (100 MHz) ($CDCl_3$): δ 21.8, 43.8, 46.3, 74.6, 126.3, 128.0, 130.1, 130.9, 137.8. IR (KBr): 3500, 3000, 2900, 1600, 1490, 1440 cm^{-1}. Analysis: calcd for $C_{36}H_{40}O_2$: C, 85.67: H, 7.99. Found: C, 85.83; H, 8.00%.

Compound **9**: m.p. 171.0–172.0 °C. ^{1}H NMR (500 MHz) ($CDCl_3$): δ 1.54 (s, 2H), 1.63 (s, 6H), 2.30 (s, 4H), 2.72 (d, J = 13.7 Hz, 4H), 2.86 (d, J = 13.5 Hz, 4H), 7.21–7.34 (m, 20H). ^{13}C NMR (126 MHz) ($CDCl_3$): δ 22.0, 44.0, 46.6, 75.2, 126.4, 128.1, 139.9, 130.9, 137.6. IR (KBr): 3550, 3000, 2900, 1600, 1500, 1450 cm^{-1}). Analysis: calcd for $C_{36}H_{40}O_2$: C, 85.67: H, 7.99. Found: C, 85.83; H, 8.19%.

Compound **9** was identical with the compound prepared by the reaction of diethyl (*E*)-2,3-dimethylbutenedioate with benzylmagnesium bromide (4 mol equiv.) in the presence of anhydrous cerium chloride.

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Note Supplementary crystallographic data may be obtained from the authors.

REFERENCES

1. (a) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954; (b) J. S. Thayer, *Adv. Organomet. Chem.*, **13**, 1 (1975); (c) J. C. Stowell, *Carbanions in Organic Synthesis*, Wiley, New York, 1979; (d) E. Negishi, *Organometallics in Organic Synthesis*, Vol. 1, Wiley, New York, 1980; (e) B. J. Wakefield, in: *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., and Abel, E. W. (eds), Pergamon, Oxford, 1982, Vol. 7, Chapter 44.
2. (a) T. Imamoto, N. Takiyama and K. Nakamura, *Tetrahedron Lett.* **26**, 4763 (1985); (b) T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima and Y. Kamiya, *J. Am. Chem. Soc.* **111**, 4392 (1989); (c) T. Imamoto, *Pure Appl. Chem.* **62**, 747 (1990); (d) T. Imamoto, in: *Comprehensive Organic Synthesis*, B. M. Trost, I. Fleming and S. L. Schreiber (eds). Pergamon, Oxford, 1991, vol. 1, Chapter 1.8. 1991, Vol. 1, Chapter 1.8; (e) T. Imamoto, *Lanthanides in Organic Synthesis*, Academic Press, New York, 1994, and references cited therein.
3. T. Imamoto, T. Hatajima and K. Ogata, *Tetrahedron Lett.* **32**, 2787 (1991).
4. (a) K. Suzuki, T. Ohkuma and G. Tsuchihashi, *Tetrahedron Lett.* **26**, 861 (1985); (b) L. A. Paquette, D. T. Derussy and J. C. Gallucci, *J. Org. Chem. 54*, 2278 (1989); (c) L. A. Paquette, D. T. DeRussy, T. Vandenheste and R. D. Rogers, *J. Am. Chem. Soc.* **112**, 5562 (1990); (d) L. A. Paquette, J. L. Romine, H.-S. Lin and J. Wright, *J. Am. Chem. Soc.* **112**, 9284 (1990), and references cited therein.
5. H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg and E. H. Miller, *J. Org. Chem.* **22**, 1602 (1957).
6. D. Seyferth, *Organic Syntheses*, Wiley, New York, 1963, Collect. Vol. IV, p. 258.
7. J. W. Scott, F. T. Bizzarro, D. R. Parrish and G. Saucy, *Helv. Chim. Acta* **59**, 290 (1976).
8. J. W. Kroeger and J. A. Nieuwland, *J. Am. Chem. Soc.* **58**, 1861 (1936).
9. M. S. Kharasch and C. F. Fucks, *J. Org. Chem.* **9**, 359 (1944).
10. H. Neumann and D. Seebach, *Tetrahedron Lett.* 1976, 4839.
11. B. M. Trost and J. L. Stanton, *J. Am. Chem. Soc.* **97**, 4018 (1975).