APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 491–503 (1995)

Yb/TMSBr Promoted Homocoupling Reactions of Aliphatic Ketones, α,β-Unsaturated Ketones and Aliphatic Imines

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A powerful reducing reagent, ytterbium dibromide ($YbBr_2$), was synthesized by a new method using ytterbium metal and trimethylsilyl bromide (TMSBr) in tetrahydrofuran–hexamethylphosphoramide (THF–HMPA). $YbBr_2$, thus formed *in situ*, causes coupling reactions of aliphatic ketones, *α,β*-unsaturated ketones and aliphatic aldimines to give bis-silylated 1,2-diols, 1,6-diketones and 1,2-diamines, respectively, in good yields. In the case of aliphatic ketimines, the corresponding reduced and silylated amines are obtained. In this solvent system, the trialkylsilyl moiety of trialkylsilyl bromide is converted to trialkylsilanes quantitatively. These results show that the Yb/TMSBr reagent generates $YbBr_2$ *in situ* and the $YbBr_2$ thus formed acts as a single-electron reductant for these coupling reactions.

Keywords: lanthanoid metal; *α,β*-unsaturated ketone; aliphatic imine; homocoupling reaction; ytterbium dibromide; 1,2-diol; 1,6-diketone; 1,2-diamine

1 INTRODUCTION

Rapid developments in the application of lanthanoids to organic synthesis have been achieved recently.[1] Particularly, low-valent lanthanoid reagents such as samarium di-iodide (SmI_2) have been widely used in organic reactions as one-electron reductants. We have developed the new lanthanoid reagents for organic synthesis.[2–4] For example, lanthanoid metals such as ytterbium (Yb) serve as powerful reducing agents.[5–13] Yb metal acts as a two-electron reducing agent in the reaction with diaryl ketones to give Yb-oxymetallacycles, which react with various electrophiles at the umpoled carbon atom of the ketones.[14–16]

Pinacol coupling at the 1-position of ketones using low-valent *f*-block transition metals such as samarium(II) [Sm(II)] has been extensively studied and proved to be efficient for C–C bond formation.[17, 18] Oxidative homocoupling at the 2-position of ketones can be achieved by nickel peroxide.[19] In contrast, reductive homocoupling reaction at the 3-position of enones was achieved electrochemically[20] or by reducing reagents such as Hg(Na),[21] Li,[22] organomanganese reagents[23] and Bu_3SnH[24] using *α,β*-unsaturated ketones.

There are many reports on inter- and intramolecular reductive coupling reactions at the 3-position of *α,β*-unsaturated carbonyl compounds. Calas and co-workers reported that the reaction of *α,β*-unsaturated ketones with Mg-TMSCl in HMPA gave Michael adducts of silyl anions along with the 3,3′-coupling adducts.[25] Furthermore, White and Larson depicted formation of the 3,3′-coupling adducts in the reaction of benzylideneacetone with Yb(II)/ammonia (NH_3) in a lower yield.[26] We also detected the 3,3′-coupling adducts as minor products in the reaction of chalcone (1,3-diphenyl-2-propene-1-one) with Yb metal.[5] In the case of *α,β*-unsaturated esters, a cerium(IV) assisted electrochemical reduction[27] and the samarium di-iodide promoted homocoupling reaction[28] are reported.

In continuing studies on exploring lanthanoid mediated reactions, we have investigated the reductive coupling reactions of aliphatic ketones and *α,β*-unsaturated ketones[29] and aliphatic imines[30] using a novel reducing agent, ytterbium metal/trimethylsilyl bromide (Yb/TMSBr) (Eqn [1]). The combination of ytterbium metal with trialkylsilyl bromide generates $YbBr_2$, which has

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CCC 0268–2605/95/050491–13
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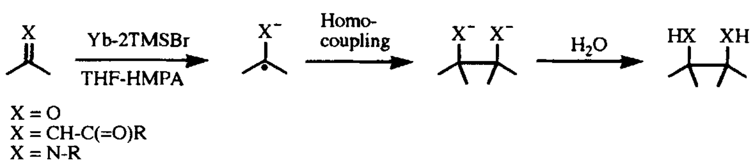
Received 23 June 1994
Accepted 18 July 1994



[1]

a powerful reducing ability. A similar reductive coupling reaction of carbonyl compounds using the TMSCl–NaI–Sm mixed system was also reported, but the active species was not characterized.[31] On the other hand, isolation of divalent ytterbium compounds such as $YbCl_2(THF)_4$ and $Yb(SiPh_3)_2(THF)_4$ were reported,[32] and divalent samarium compounds such as SmI_2,[17] $SmBr_2$,[33,34] $SmCl_2$[35] and $Sm(OTf)_2$[18] (Tf = triflyl, i.e. trifluoromethanesulfonyl) are known and have been applied to the reductive coupling of carbonyl compounds. Although several methods for the synthesis of $YbBr_2$ were developed,[36] there is no report of a simple and easy preparation of $YbBr_2$ for organic synthesis.

We report here full details of Yb/TMSBr promoted coupling reactions of cyclic ketones, α,β-unsaturated ketones[29] and aliphatic imines, and isolation and characterization of $YbBr_2$.[30]

2 RESULTS AND DISCUSSION

2.1 Reaction of aliphatic ketones with ytterbium and trimethylsilyl bromide

The coupling reaction of cyclohexanone with the Yb/TMSBr reagent was examined. The reaction was completed within 5 h at room temperature. From this reaction, bis-silylated diol **1** was selectively obtained without the formation of 1,2-diol (Eqn [2]). The results are summarized in Table 1. In this reaction, an equimolar amount of Yb metal and 1.5 equivalents of TMSBr relative to cyclohexanone were needed to attain best yields (entry 8 in Table 1). This reaction did not occur with Yb metal alone (entry 5 in Table 1). The mixed solvent (THF/HMPA = 4 : 1) gave the best result, but THF alone and other nonpolar solvents were not effective. The yield of the coupling products decreased with increasing amounts of HMPA.

1 [2]

Representative results for the homocoupling reactions of cyclic ketones with the Yb/TMSBr reagent using the optimized conditions are summarized in Table 2. As shown in this table, various cyclic ketones were homocoupled smoothly to give the corresponding bis-silylated diols. Six- and five-membered ring ketones are reactive, but seven- and eight-membered ring ketones are less reactive (entries 4 and 5 in Table 2). The reaction of 3-methylcyclohexanone afforded three diastereomers in the ratio of 79 : 15 : 6 according to the ^{13}C NMR analysis (entry 3 in Table 2). Sterically hindered bulky ketones such as adamantanone and menthone were not reactive.

2.2 Reaction of aliphatic α,β-unsaturated ketones with ytterbium and trimethylsilyl bromide

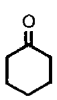
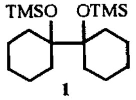
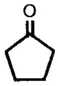
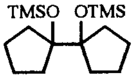
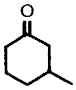
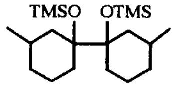
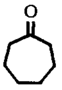
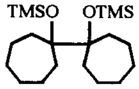
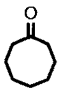
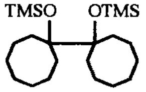
Although aromatic α,β-unsaturated ketones such as chalcone react with Yb metal to give the cyclodimerized adduct along with 3,3′-coupling adducts, aliphatic α,β-unsaturated ketones did not react with Yb metal alone.[5] We have also found that the Yb/TMSBr reagent can cause a

Table 1 Yb/TMSBr promoted coupling of cyclohexanone[a]

Entry	Yb (mmol)	TMSBr (mmol)	Solvent	Yield (%)[b]
1	0	2.0	THF/HMPA (4:1)	0
2	0.25	2.0	THF/HMPA (4:1)	27
3	0.50	2.0	THF/HMPA (4:1)	61
4	1.00	2.0	THF/HMPA (4:1)	93
5	1.00	0	THF/HMPA (4:1)	0
6	1.00	0.5	THF/HMPA (4:1)	50
7	1.00	1.0	THF/HMPA (4:1)	73
8	1.00	1.5	THF/HMPA (4:1)	89
9	1.00	1.5	THF	28
10	1.00	1.5	THF/HMPA (3:2)	43
11	1.00	1.5	THF/HMPA (2:3)	33
12	1.00	1.5	THF/HMPA (1:4)	15
13	1.00	1.5	HMPA	0
14	1.00	1.5	DME	20
15	1.00	1.5	Benzene	0
16	1.00	1.5	Hexane	0

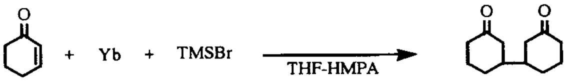
[a] Cyclohexanone (1 mmol), room temp. 5 h.
[b] Isolated yield based on cyclohexanone.

Table 2 Yb/TMSBr promoted coupling of cyclic ketones[a]

Entry	Ketone	Product	Yield (%)[b]
1		 **1**	89
2		 **2**	62[c]
3		 **3**	57 (79:15:6)[d]
4		 **4**	31[c]
5		 **5**	39

[a] Ketone (2 mmol), Yb (2 mmol), TMSBr (3 mmol), THF (4 cm^3)–HMPA (1 cm^3), room temp. 5 h.
[b] Isolated yield based on the ketone.
[c] Reaction time 15 h.
[d] Diastereomer ratio was determined by ^{13}C NMR.

3,3′-coupling reaction of aliphatic α,β-unsaturated ketones to give 1,6-diketones. The combination of various halosilanes with Yb metal and solvent effect were examined in the reaction of 2-cyclohexenone (Eqn [3] and Table 3). One can see that, of the trimethylsilyl halides, trimethylsilyl bromide was the best for this coupling reaction to afford 1,6-diketone **6** in 90% yield (entry 2 in Table 3). Nondonor solvents resulted in a lower yield. In the case of THF as sole solvent, a higher reaction temperature or longer reaction time was required (entries 2 and 7 in Table 3). As is the case for the reaction of cyclic ketones, this reaction also required THF–HMPA (4:1) as a mixed solvent to attain high yields (entry 4 in Table 3).



6

[3]

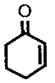
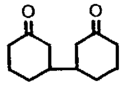
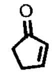
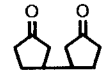
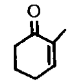
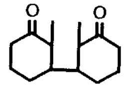
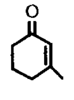
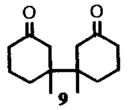
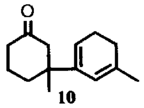
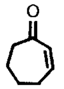
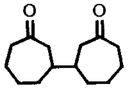
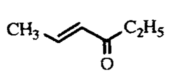
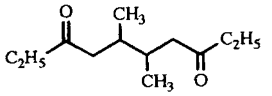
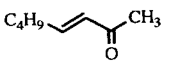
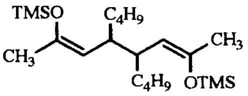
Representative results for the homocoupling reaction of α,β-unsaturated ketones are listed in Table 4. Both cyclic and acyclic enones undergo coupling. Although electrochemical coupling of enol acetates is reported to be nonstereoselective to give a DL/*meso* = 1:1 mixture,[37] the present coupling reaction of 2-methyl- or 3-methyl-2-cyclohexenones with the Yb/TMSBr reagent gives a single diastereomer (entries 3 and 4 in Table 4). But the reaction of other enones is not stereoselective and gives two diastereomers (DL/*meso* = 1:1). Samarium (Sm) metal was less reactive than Yb metal, and affords the 1,6-diketone **8** in lower yields (46% yield, 52% recovery) as compared with entry 3 in Table 4. Small amounts of saturated ketones were also formed, along with 1,6-diketones (entries 3 and 6 in Table 4). In the case of 3-methylcyclohexenone, 1,3′-coupling

Table 3 Yb/TMSBr promoted coupling of 2-cyclohexenone[a]

Entry	TMSX (2 mmol)	Solvent (3 cm^3)	Temperature	Time (h)	Yield (%)[b]
1	TMSCl	THF	Reflux	3	32
2	TMSBr	THF	Reflux	3	90
3	TMSI	THF	Reflux	3	5
4	TMSBr	THF/HMPA (4:1)	R.t.[c]	17	92
5	TMSBr	n-Hexane	R.t.	17	40
6	TMSBr	Benzene	R.t.	17	40
7	TMSBr	THF	R.t.	17	85
8	TMSBr	DME	R.t.	17	79
9	TMSBr	Diglyme	R.t.	17	68

[a] 2-Cyclohexenone (1 mmol)m, Yb (1 mmol).
[b] GC yield based on 2-cyclohexenone.
[c] R.t., Room temperature.

Table 4 Yb/TMSBr promoted reaction of α,β-unsaturated ketones[a]

Entry	Ketone	Conditions[b] (time/h)	Products and yield (%)[c]	
1		A(17) B (3)		**6** 92[d] **6** 90[d]
2		A (40) B (4)		**7** 45[d] **7** 68[d]
3		B (8)		**8** 92[c]
4		A (17) B (17)	 **9**  **10**	**9** 68, **10** 30 **9** 32, **10** 60
5		A (6) B (12)		**11** 46[e] **11** 46[e]
6		A (72)		**12** 67[c,f]
7		A (10)		**13** 66[c,g]

[a] Ketone (1 mmol), Yb (1 mmol), TMSBr (2 mmol).

[b] Condition A: THF (2.4 cm^3)–HMPA (0.6 cm^3), room temp. Condition B: THF (3 cm^3), reflux.

[c] GLC yield based on ketones.

[d] The DL: *meso* ratio (1 : 1) was determined by ^{13}C NMR.

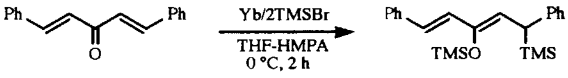
[e] 2-Methylcyclohexanone (6%) was also formed.

[f] 3-Hexanone (25%) was also formed.

[g] (2*Z*,6*Z*)- and (2*E*,6*Z*)-adducts (3 : 1) were formed.

takes place, followed by dehydration to give the 3-(5′-methylcyclohexa-1′,5′-dienyl)-3-methylcyclohexanone (**10**) along with 1,6-diketone **9** (entry 4 in Table 4). The reaction of acyclic enone afforded the bis-silyl enol ether **13** as the corresponding 1,6-diketone (entry 7 in Table 4). Separation of the products by Medium Pressure Liquid Chromatography (MPLC) (SiO_2) gave (2*Z*,6*Z*)- and (2*E*,6*Z*)-isomers in the ratio of 3 : 1. The geometry of the double bond of each isomer was determined by NMR analyses. Each isomer contains two diastereomers (DL/*meso*) in the ratio of 3 : 2, according to the ^{13}C NMR analysis.

The reactions of dibenzylideneacetone and *N*,*N*-dimethylacrylamide with Yb/TMSBr resulted in the formation of 1,4-adducts **14** and **15** derived from the addition of silyl radical species (Eqns [4] and [5]).

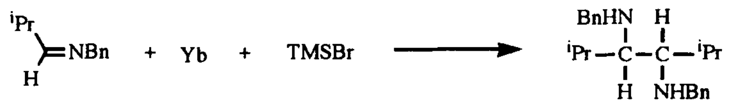


[4]

[5]

2.3 Reaction of aliphatic imines with ytterbium and trimethylsilyl bromide

The growing importance of 1,2-diamines as bidentate ligands of transition-metal catalysis and chiral templates for organic synthesis, and as biologically and medicinally active compounds, has led to the development of new synthetic methods for their preparation.[38–40] We reported the reaction of aromatic aldimines with ytterbium



16

[6]

metal to give the homocoupling adducts, 1,2-diamines.[10] Unfortunately, the reaction of aliphatic aldimines with Yb metal did not occur because of their lower reactivities to the reductant Yb. Furthermore, Imamoto and Nishimura reported that aliphatic aldimines did not undergo reductive coupling and reduction, even with the use of SmI_2.[41] The development of powerful reducing reagents is required to accomplish C–C bond formation via coupling of aliphatic imines.

The reductive coupling reaction of aliphatic imines with the Yb/TMSBr reagent was examined. Reaction of Yb metal and TMSBr with *N*-isobutylidenebenzylamine gave the corresponding homocoupling adduct, *N*,*N'*-dibenzyl-1,2-di-isopropyl-1,2-ethylenediamine (**16**) as a single diastereomer (Eqn [6]). These results are summarized in Table 5. Addition of a polar solvent such as HMPA is also effective for this reaction. The mixed solvent (THF/HMPA = 4 : 1) gives the best result (entry 3 in Table 5), but THF alone and other nonpolar solvents give inferior results. Two roles of HMPA can be envisaged; one is to increase the ease with which an electron transfers from Yb and the other is to stabilize the Yb(II) species by coordination.[5–13] Two-fold quantities of TMSBr relative to Yb metal and to starting imine are required in this reaction.

Representative results for the reaction of aliphatic imines with Yb metal (1 equiv.) and TMSBr (2 equiv.) are summarized in Table 6. In the case of *N*-cyclohexylmethylidenebenzylamine, two diastereomers (DL/*meso*) for diamine **18** were formed in the ratio of 63 : 37 according to ^{13}C NMR analysis. In these reactions, aliphatic aldimines were selectively coupled to give the corresponding symmetric 1,2-diamines in good yields (entries 1–3 in Table 6). Aliphatic ketimines did not undergo reductive coupling because of their steric hindrance on the imine carbon, but suffered reduction of C–N double bond to give the hydrogenated amines **20** and **22**, and α-silylated monoamines **19** and **21** under these conditions (entries 4 and 5 in Table 6).

Table 5 Yb/TMSBr promoted coupling of *N*-isobutylidenebenzylamine[a]

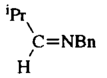
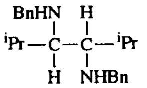
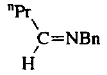
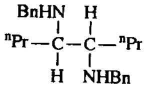
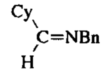
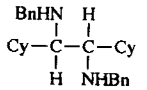
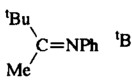
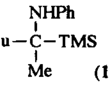
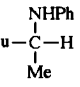
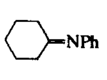
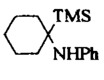
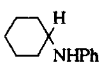
Entry	Imine (equiv.)	Yb (equiv.)	TMSBr (equiv.)	Solvent ($4\,cm^3$)	Yield (%)[b]
1	1	1/2	1	THF/HMPA[c]	64
2	1	1	1	THF/HMPA[c]	54
3	1	1	2	THF/HMPA[c]	86
4	1	1/2	2	THF/HMPA[c]	55
5	1	1	2	THF	23
6	1	1	2	Benzene	11
7	1	1	2	THF[d]	Trace

[a] Room temperature, 4.5 h.
[b] GLC yield based on imines (2 mmol).
[c] THF ($4\,cm^3$), hexamethylphosphoric triamide ($1\,cm^3$).
[d] Refluxed for 2 h.

2.4 Formation and characterization of ytterbium dibromide ($YbBr_2$)

In the reaction of ytterbium metal with trimethylsilyl bromide (TMSBr) in THF–HMPA, a green suspension was formed as the reaction proceeded.

Table 6 Yb/TMSBr promoted reaction of aliphatic imines[a]

Entry	Imine	Product and yield (%)[b]
1		 (**16**, 86)
2		 (**17**, 87)
3		 (**18**, 79)
4		 (**19**, 67)  (**20**, 28)
5		 (**21**, 64)  (**22**, 31)

Abbreviations: Bn, benzyl; Cy, cyclohexyl; TMS, trimethylsilyl.
[a] Imine (2 mmol), Yb (2 mmol), TMSBr (4 mmol), THF ($4\,cm^3$), HMPA ($1\,cm^3$), room temp. 4.5 h.
[b] GLC yield based on imines.

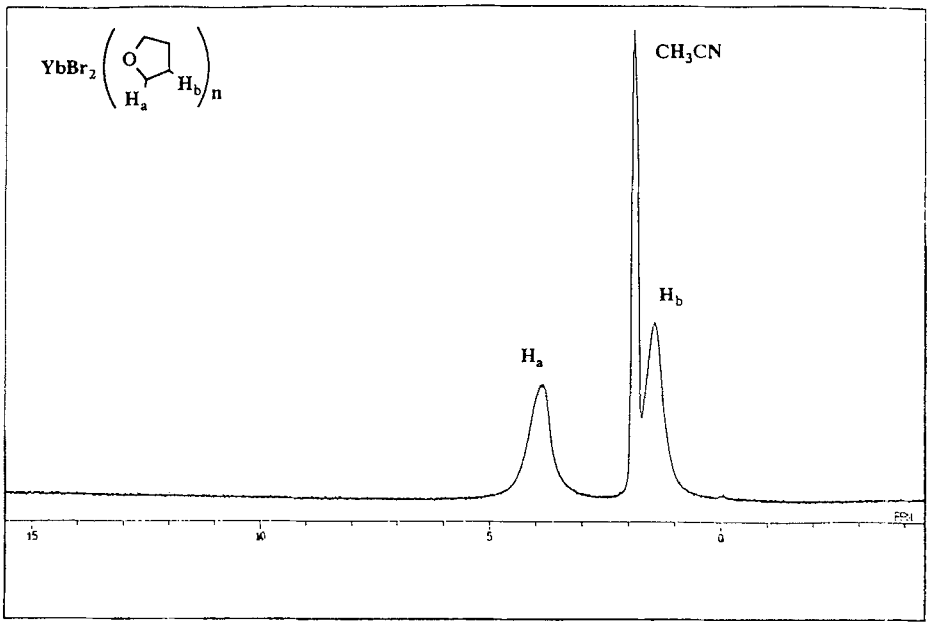


Figure 1 270 MHz proton NMR spectra of $YbBr_2(THF)_n$ in CD_3CN.

Decantation of the solution and washing with THF followed by removal of the solvent *in vacuo* gave a light-green solid. ^1H NMR analysis of this green solid in CD_3CN showed the two signals ($\delta = 1.40$ and 3.87 ppm) of THF and no signal of the trimethylsilyl group (Fig. 1). From the solution, volatile trimethylsilane [$(CH_3)_3SiH$] could not be detected by GLC analyses. We attempted to detect triethylsilane [$(C_2H_5)_3SiH$] by using triethylsilyl bromide instead of TMSBr. The reaction of triethylsilyl bromide with Yb metal in THF was carried out under the same conditions (Eqn [7]).

$$2Et_3SiBr + Yb \xrightarrow{THF} YbBr_2 + 2Et_3SiH \qquad [7]$$

The reaction gave a green suspension which effected similar coupling reactions as to those of TMSBr. From the reaction mixture, $(C_2H_5)_3SiH$ was detected by GLC analysis in quantitative yield. $(C_2H_5)_3SiH$ is formed by the abstraction of a $H^{\bullet}$ radical from THF by a trialkylsilyl radical ($R_3Si^{\bullet}$) in the mother liquor of this suspension, and no hexaethyldisilane was detected as coupling product. X-ray analysis of the residual powder separated from this suspension was in fair agreement with authentic $YbBr_2$ prepared by the reaction of $HgBr_2$ with Yb (Fig. 2).[26] These results clearly indicate that the structure of the green solid is $YbBr_2(THF)_n$. The $YbBr_2(THF)_n$ obtained is very air-sensitive and hygroscopic. In addition, the reaction of the powder with 2-methyl-2-cyclohexenone gave the corresponding 1,6-diketone **8** in 92% yield. These results show that the Yb/TMSBr reagent generates $YbBr_2$ *in situ* and the $YbBr_2$ thus formed acts as a single-electron reductant for these coupling reactions. For the *in situ* preparation of $YbBr_2(THF)_n$, our method is a quite simple and easy route towards organic synthesis.

2.5 Reaction mechanism

Possible reaction mechanisms for the formation of $YbBr_2$ and its reaction with compounds having C=O and C=N double bonds are shown in Scheme 1. Yb metal reacts with two-fold quantities of TMSBr to give $YbBr_2$ and trimethylsilyl radicals. The $YbBr_2$ formed reacts with C=O and C=N double bonds to give the radical anion complex **A** along with Yb^{3+}. Radical coupling occurs exclusively to afford the corresponding adducts. The bulky radical anion **A** derived from ketimines gives silylated or hydrogenated monoamines.

3 EXPERIMENTAL

^1H and ^{13}C NMR spectra were obtained on a JEOL JNM-EX 270 spectrometer in $CDCl_3$ or C_6D_6 solution unless otherwise noted. Chemical shifts (δ) were expressed in parts per million (ppm) downfield from tetramethylsilane. IR spectra were recorded on a Perkin–Elmer 1600–FTIR. Mass spectra were obtained on a Shimadzu GCMS-QP1000 using a 1.1 m × 2.7 mm glass column packed with a 2% silicone OV17 on 60–80 mesh Chromosorb W. X-ray diffraction (XRD) analysis was performed on a Shimadzu X-ray diffractometer XD-D1. All melting points were measured on a Yanaco micro melting point apparatus. Elemental analyses were performed on a Yanagimoto MT-2 CHN corder.

Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl under argon prior to use. Hexamethylphosphoric triamide (HMPA) was distilled from CaH_2 and stored over activated molecular sieves 4A under argon.

Ytterbium metal (99.9%, 20–40 mesh; Shiga Rare Metal Co. Ltd, Japan) was commercially available.

2-Cyclohexenone, 2-cyclopentenone, 2-cycloheptanone, 3-methyl-2-cyclohexenone, 4-hexen-3-one, dibenzylideneacetone, chalcone and *N*,*N*-dimethylacrylamide were commercial grades. 2-Methyl-2-cyclohexen-1-one[42] and acetylmethylidenetriphenylphosphorane[43] were prepared by the literature procedures.

3.1 Preparation of (3*E*)-3-octen-2-one

A solution of acetylmethylidenetriphenylphosphorane (53 g, 0.17 mol) and n-valeraldehyde (0.16 mol) in dichloromethane (150 cm^3) was placed in a 500-cm^3 round-bottomed flask. The mixture was stirred at room temperature for two days. The reaction mixture was extracted with dichloromethane. The combined extracts were washed with brine, dried over $MgSO_4$, and evaporated. Crude product was obtained by SiO_2 column chromatography (hexane/ethyl acetate, 6:1) and was distilled under reduced pressure to give (3*E*)-3-octen-2-one in 71% yield. Colorless oil: b.p. 85 °C/ 21 mm Hg.

IR (neat): ν(C=C) 965, ν(C=C) 1620, ν(C=O) 1670 cm^{-1}. MS (70 eV): *m*/*z* 126 (M^+) 111 ($M^+ - CH_3$), 97 (M^+ − Et), 69 (M^+ − Bu). ^1H NMR ($CDCl_3$): δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.36 (tt, *J* = 7.3 and 6.9 Hz, 2H), 1.45 (tq, *J* = 7.3 and

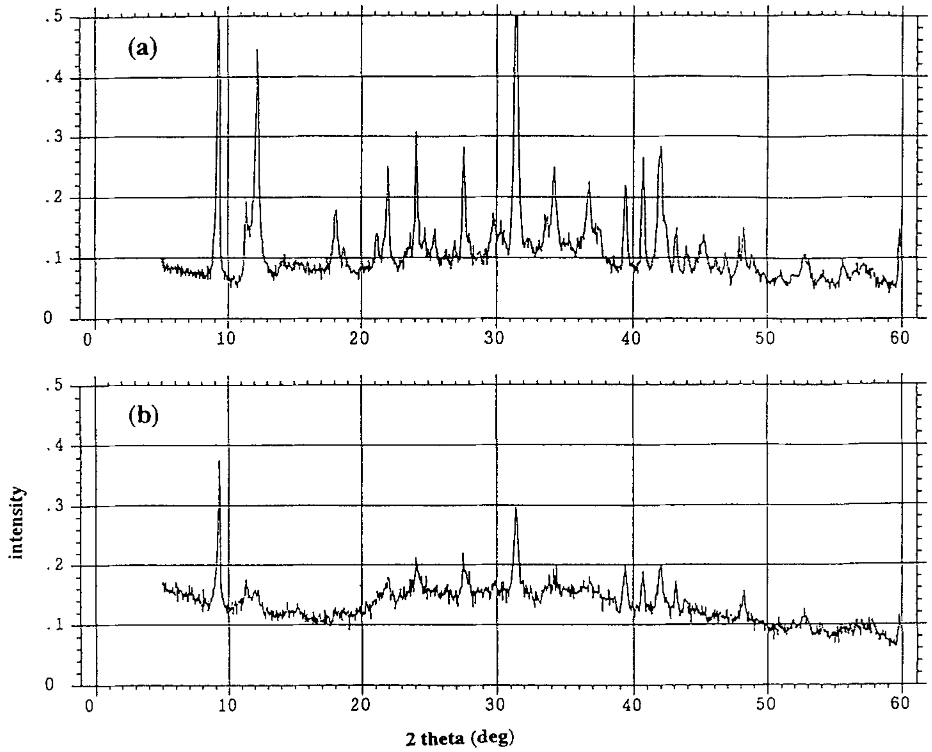
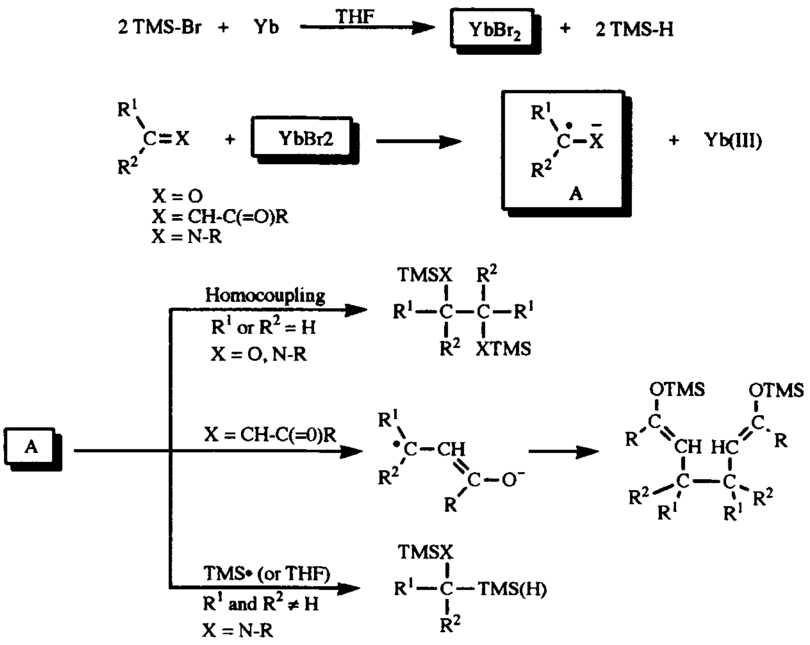


Figure 2 Powder X-ray diffraction patterns of $YbBr_2(THF)_n$, obtained from (a) Yb + $HgBr_2$ and (b) Yb + 2 TMSBr.



Scheme 1 Mechanism for the Yb/TMSBr promoted coupling reaction.

7.3 Hz, 2H), 2.23 (ddt, $J=6.9$, 1.3 and 6.9 Hz, 2H), 2.25 (s, 3H), 6.07 (dt, $J=15.8$ and 1.3 Hz, 1H), 6.81 (dt, $J=15.8$ and 6.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.8, 22.2, 26.8, 30.2, 32.1, 131.3, 148.6, 198.8.

Analysis: calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.86; H, 11.08%.

3.2 General procedure for the preparation of aliphatic aldimines

Benzylamine (0.2 mol) was placed in a 100-cm^3 round-bottomed flask equipped with a dropping funnel. Aldehyde (0.2 mol) was added at −10 °C for 2 h. After additional stirring at −10 °C for 30 min, KOH (0.2 mol) was added to the reaction mixture. The reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was extracted with dichloromethane (10 cm^3 × 3). The combined extracts were washed with brine (10 cm^3 × 3) and dried over $MgSO_4$. Filtration, removal of the solvents and distillation afforded the aldimine.

3.2.1 *N*-Isobutylidenebenzylamine

Quantitative yield. Colorless oil.

IR (neat): ν(C=N) 1670 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.07 (d, $J=6.9$ Hz, 6H), 2.38 (dtsep, $J=4.0$, 1.0 and 6.9 Hz, 1H), 4.52 (s, 2H), 7.18 (t, $J=7.3$ Hz, 1H), 7.29 (t, $J=7.3$ Hz, 2H), 7.39 (d, $J=7.3$ Hz, 2H), 7.46 (dt, $J=4.0$ and 1.3 Hz, 1H). ^{13}C NMR (C_6D_6): δ 19.6, 34.5, 65.4, 127.3, 128.4, 128.8, 140.9, 169.7.

3.2.2 *N*-Cyclohexylmethylidenebenzylamine

Quantitative yield. Colorless oil.

IR (neat): ν(C=N) 1667 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.85–1.25 (m, 6H), 1.30–1.45 (m, 1H), 1.45–1.55 (m, 2H), 1.65–1.75 (m, 2H), 1.90–2.05 (m, 1H), 4.35 (s, 2H), 7.00 (t, $J=7.0$ Hz, 1H), 7.11 (t, $J=7.0$ Hz, 2H), 7.21 (d, $J=7.0$ Hz, 2H), 7.29 (d, $J=3.6$ Hz, 1H). ^{13}C NMR (C_6D_6): δ 25.8, 26.4, 29.9, 43.4, 65.2, 126.9, 127.8, 128.5, 140.6, 168.6.

3.2.3 *N*-Butylidenebenzylamine:

23% yield. Colorless oil: b.p. = 54 °C/0.1 mm Hg.

IR (neat): ν(C=N) 1668 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.95 (t, $J=7.6$ Hz, 3H), 1.58 (sextet, $J=7.3$ Hz, 2H), 2.27 (dt, $J=4.7$ and 7.3 Hz, 2H), 4.54 (s, 2H), 7.18–7.38 (m, 5H), 7.74 (t, $J=4.7$ Hz, 1H).

3.3 General procedure for the preparation of aliphatic ketimines

A solution of aniline (0.2 mol), ketone (0.2 mol) and *p*-toluenesulfonic acid monohydrate (2.0 mmol) in benzene (200 cm^3) was placed in a

200-cm^3 round-bottomed flask equipped with a Dean–Stark trap. The mixture was refluxed for 6 h and was dehydrated. Removal of the solvent followed by distillation or purification by column chromatography (Al_2O_3) afforded the ketimine.

3.3.1 *N*-Cyclohexylideneaniline

4% yield. Colorless oil: b.p. = 130 °C/0.5 mm Hg.

IR (neat): ν(C═N) 1645 cm^{-1}. MS (70 eV): *m/z* 175 (M^+). ^{1}H NMR ($CDCl_3$): δ 0.86–1.64 (m, 8H), 2.45 (dt, J = 7.4 and 4.9 Hz, 2H), 6.64–7.71 (m, 4H), 7.82 (t, J = 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.8, 22.4, 25.5, 29.8, 31.4, 120.4, 125.2, 128.8, 152.3, 166.4.

3.3.2 *N*-(1-t-Butyl)ethylideneaniline

27% yield. Colorless oil.

IR (neat): ν(C═N) 1653 cm^{-1}. MS (70 eV): *m/z* 175 (M^+). ^{1}H NMR (C_6D_6): δ 1.17 (s, 9H), 1.51 (s, 3H), 6.67 (d, J = 7.3 Hz, 2H), 6.95 (t, J = 7.3 Hz, 1H), 7.20 (t, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.8, 27.9, 40.4, 119.3, 122.7, 129.2, 152.9, 176.3.

3.4 General procedure for ytterbium metal promoted homocoupling reaction of aliphatic ketones

Ytterbium metal (0.345 g, 2 mmol) and a magnetic stirring bar were placed in a 20-cm^3 two-necked flask equipped with a three-way stopcock and a rubber septa. The flask was flame-dried under reduced pressure. After being cooled to room temperature, the atmosphere in the flask was replaced with argon. To this flask, THF (4 cm^3), HMPA (1 cm^3) and then trimethylsilyl bromide (0.40 cm^3, 3 mmol) were added by a syringe, successively. The mixture was degassed through repetition of three freeze–pump–thaw cycles, then stirred at room temperature for 30 min. The reaction mixture became a suspension, and its color turned light green. Then ketone (2 mmol) was added to the flask. The reaction mixture was stirred under the conditions described in Tables 1 and 2. Usual work-up followed by silica gel column chromatography (n-hexane/ethyl acetate) gave bis-silylated diols. Representative results are listed in Tables 1 and 2.

3.4.1 1-(1′-Trimethylsilyloxycyclohexyl)cyclohexyl trimethylsilyl ether (1)

Colorless crystals: m.p. 120 °C.

IR (Nujol): δ_S(Si—CH$_3$) 837, ν(Si—O) 1089, ν(C—O—Si) 1141, δ_S(Si—CH$_3$) 1249 cm^{-1}. MS (70 eV): *m/z* 171 (M^+/2). ^{1}H NMR (C_6D_6): δ 0.28 (s, 18H, TMS), 1.10–1.30 (m, 2H), 1.50–1.85 (m, 18H). ^{13}C NMR (C_6D_6): δ 3.1 (TMS), 22.7, 26.3, 30.7, 81.6.

Analysis: calcd for $C_{18}H_{38}O_2Si_2$: C, 63.09; H, 11.18. Found: C, 62.70; H, 11.47%.

3.4.2 1-(1′-Trimethylsilyloxycyclopentyl)cyclopentyl trimethylsilyl ether (2)

Colorless crystals: m.p. 39–43 °C.

IR (Nujol): δ_S(Si—CH$_3$) 839, ν(Si—O) 1086, δ_S(Si—CH$_3$) 1250 cm^{-1}. MS (70 eV): *m/z* 157 (M^+/2). ^{1}H NMR (C_6D_6): δ 0.20 (s, 18H, TMS), 1.23–2.23 (m, 16H). ^{13}C NMR (C_6D_6): δ 3.1 (TMS), 26.8, 37.5, 91.3.

Analysis: calcd for $C_{16}H_{34}O_2Si_2$: C, 61.08; H, 10.89. Found: C, 60.90; H, 10.63%.

3.4.3 1-(1′-Trimethylsilyloxy-3′-methylcyclohexyl)-3-methylcyclohexyl trimethylsilyl ether (3)

For the major diastereomer: Colorless crystals: m.p. 36–44 °C. IR (Nujol): δ_S(Si—CH$_3$) 836, ν(Si—O) 1094, ν(C—O—Si) 1148, δ_S(Si—CH$_3$) 1249 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.28 (s, 18H, TMS), 0.63–1.13 (m, 24H). ^{13}C NMR (C_6D_6): δ 3.6 (TMS), 23.1, 23.6, 29.1, 30.9, 35.5, 40.2, 82.8.

^{13}C NMR signals of the minor diastereomers cannot be assignable exactly, except for those of the quarternary carbons (δ = 81.7, 82.8 and 84.0). The ratio of the three signals is 15 : 79 : 6.

Analysis: calcd for $C_{20}H_{42}O_2Si_2$: C, 64.80; H, 11.42. Found: C, 64.61; H, 11.64%.

3.4.4 1-(1′-Trimethylsilyloxycycloheptyl)cycloheptyl trimethylsilyl ether (4)

Colorless crystals: m.p. 90–93 °C.

IR (Nujol): δ_S(Si—CH$_3$) 837, ν(Si—O) 1091, δ_S(Si—CH$_3$) 1248 cm^{-1}. MS (70 EV): *m/z* 370 (M^+), 185 (M^+/2). ^{1}H NMR ($CDCl_3$): δ 0.12 (s, 18H, TMS), 0.90–1.94 (m, 24H). ^{13}C NMR ($CDCl_3$): δ 3.1 (TMS), 24.3, 31.5, 37.2, 86.0.

Analysis: calcd for $C_{20}H_{42}O_2Si_2$: C, 64.80; H, 11.42. Found: C, 64.80; H, 11.37%.

3.4.5 1-(1′-Trimethylsilyloxycyclo-octyl)cyclooctyl trimethylsilyl ether (5)

Colorless crystals: m.p. 104–107 °C.

IR (Nujol): δ_S(Si—CH_3) 837, ν(Si—O) 1075 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.13 (s, TMS, 18H), 1.15–1.45 (m, 8H), 1.50–1.95 (m, 20H). ^{13}C NMR ($CDCl_3$): δ 3.3 (TMS), 24.1, 26.2, 29.0, 32.9, 85.0.

Analysis: calcd for $C_{22}H_{46}O_2Si_2$: C, 66.26; H, 11.63. Found: C, 66.13; H, 11.84%.

3.5 General procedure for ytterbium metal promoted homocoupling reaction of aliphatic α,β-unsaturated ketones

The light green Yb/TMSBr reagent was prepared as described above using Yb metal (0.173 g, 1 mmol), trimethylsilyl bromide (0.26 cm^3, 2 mmol), THF (2.4 cm^3) and HMPA (0.6 cm^3) in a 20-cm^3 two-necked flask equipped with a three-way stopcock and a rubber septa. Then, α,β-unsaturated ketone (1 mmol) was added to the flask. The reaction mixture was stirred under the conditions described in Tables 3 and 4. The usual work-up was followed by silica gel column chromatography (*n*-hexane/ethyl acetate) to give 1,6-diketones. Representative results are listed in Tables 3 and 4.

3.5.1 3-(3′oxycyclohexyl)cyclohexanone (6)[44]

A mixture of two diastereomers (DL: *meso*) was formed in a ratio of 50:50 according to ^{13}C NMR analysis. Colorless oil:

IR (neat): ν(C=O) 1712 cm^{-1}. MS (70 eV): *m/z* 194 (M^+), 97 ($M^+/2$). ^{1}H NMR ($CDCl_3$): δ 1.26–2.49 (m, 18 H). ^{13}C NMR ($CDCl_3$): δ 25.1 and 25.2 (ratio = 1 : 1), 28.2 and 28.3 (ratio = 1 : 1), 41.3, 43.6 and 43.7 (ratio = 1 : 1), 44.8 and 45.2 (ratio = 1 : 1), 211.2.

Analysis: calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.14; H, 9.30%.

3.5.2 3-(3′-Oxocyclopentyl)cyclopentanone (7)

A mixture of two diastereomers (DL: *meso*) was formed in a ratio of 50:50 according to ^{13}C NMR analysis. Colorless crystals: m.p. 33–35 °C.

IR (Nujol): ν(C=O) 1738 cm^{-1}. MS (70 eV): *m/z* 166 (M^+), 83 ($M^+/2$). ^{1}H NMR ($CDCl_3$): δ 1.49–2.49 (m, 14H). ^{13}C NMR ($CDCl_3$): δ 27.7 and 28.5 (ratio = 1 : 1), 38.45 and 38.49 (ratio = 1 : 1), 42.6 and 42.7 (ratio = 1 : 1), 43.4 and 43.9 (ratio = 1 : 1), 218.29 and 218.34 (ratio = 1 : 1).

Analysis: calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.12; H, 8.45%.

3.5.3 2-Methyl-3-(2′-methyl-3′-oxocyclohexyl)cyclohexanone (8)

The reaction gave a single diastereomer. Colorless crystals: m.p. 157.5–158 °C.

IR (Nujol): ν(C=O) 1705 cm^{-1}. MS (70 eV): *m/z* 222 (M^+), 111 ($M^+/2$). ^{1}H NMR ($CDCl_3$): δ 0.96 (d, J = 6.6 Hz, 6H), 1.0–2.5 (m, 16H). ^{13}C NMR ($CDCl_3$): δ 10.9, 24.1, 26.1, 41.7, 45.8, 47.7, 212.9.

Analysis: calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.46; H, 9.70%.

3.5.4 3-Methyl-3-(1′-methyl-3′-oxocyclohexyl)cyclohexanone (9)

The reaction gave a single diastereomer. Colorless crystals: m.p. 144 °C.

IR (neat): ν(C=O) 1702 cm^{-1}. MS (70 eV): *m/z* 207 ($M^+ - CH_3$), 192 ($M^+ - 2CH_3$), 111 ($M^+/2$). ^{1}H NMR ($CDCl_3$): δ 0.9 (s, 6H), 1.5–2.5 (m, 16H). ^{13}C NMR ($CDCl_3$): δ 18.5, 21.8, 29.7, 40.8, 43.9, 47.9, 212.5.

Analysis: calcd for $C_{14}H_{22}O_2$; C, 75.63; H, 9.97. Found: C, 75.45; H, 9.80%.

3.5.5 3-Methyl-3-(5′-methylcyclohexa-1′,5′-dienyl)cyclohexanone (10)

Colorless oil.

IR (neat): ν(C=O) 1712 cm^{-1}. MS (70 eV): *m/z* 204 (M^+), 93 ($C_7H_9^+$). ^{1}H NMR (C_6D_6): δ 0.95 (s, 3H), 1.5–2.5 (m, 12H), 1.68 (s, 3H), 5.56, (t, J = 3.0 Hz, 1H), 5.69 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 22.2, 23.8, 24.0, 27.7, 28.4, 35.4, 41.1, 42.2, 52.5, 118.2, 119.4, 137.3, 141.5, 209.0.

3.5.6 3-(3′-Oxocycloheptyl)cycloheptanone (11)

A mixture of two diastereomers (DL: *meso*) was formed in a ratio of 50:50 according to ^{13}C NMR analysis. Colorless oil.

IR (Nujol): ν(C=O) 1688 cm^{-1}. MS (70 eV): *m/z*

222 (M^+), 111 ($M^+/2$). ^{1}H NMR ($CDCl_3$): δ 1.29–2.04 (m, 14H), 2.29–2.57 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 24.4, 29.0 and 29.1 (ratio = 1 : 1), 33.4 and 33.8 (ratio = 1 : 1), 42.3, 43.6, 46.7 and 47.1 (ratio = 1 : 1), 213.9 and 214.0 (ratio = 1 : 1).

3.5.7 5,6-Dimethyldecane-3,8-dione (12)

A mixture of two diastereomers (DL: *meso*) was formed in a ratio of 50 : 50 according to ^{13}C NMR analysis. Colorless oil.

IR (neat): ν(C=O) 1710 cm^{-1}. MS (70 eV): *m/z* 99 ($M^+/2$). ^{1}H NMR ($CDCl_3$): δ 0.69 (d, J = 6.6 Hz, 3H), 0.73 (d, J = 6.3 Hz, 3H), 0.92 (t, J = 7.3 Hz, 6H), 1.91 (m, 2H), 2.29 (m, 4H), 3.35 (dd, J = 14.0 and 6.9 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 7.51, 14.8 and 14.9 (ratio = 1 : 1), 32.7 and 33.2 (ratio = 1 : 1), 36.1 and 36.2 (ratio = 1 : 1), 46.0 and 47.2 (ratio = 1 : 1), 210.7 and 210.8 (ratio = 1 : 1).

3.5.8 2,7-Bistrimethylsilyloxy-4,5-dibutyl-2,6-octadiene (13)

The concentrated reaction mixture was column chromatographed on silica gel (hexane) without aqueous work-up to give a mixture of stereoisomers. Colorless oil.

IR (neat): ν(C=C—O) 1663 cm^{-1}. MS (70 eV): *m/z* 383 (M^+ − Me), 199 ($M^+/2$).

Analysis: calcd for $C_{22}H_{46}O_2Si_2$: C, 66.26; H, 11.63. Found: C, 66.40; H, 11.63%.

Then, the mixture was further separated by MPLC (SiO_2) into two geometric isomers [(2*Z*,6*Z*)- and (2*E*,6*Z*)-isomers (3 : 1)], which were determined by a nuclear Overhauser enhancement (NOE) experiment. Each geometric isomer was composed of two diastereomers (DL and *meso*) in a ratio of 60 : 40 according to ^{13}C NMR analysis.

For the major (2Z,6Z)-isomer (13a)
^{1}H NMR ($CDCl_3$): δ 0.07 (s, 18H), 0.90 (t, J = 6.9 Hz, 6H), 1.21 (d, J = 3.0 Hz, 6H), 1.27–1.35 (m, 12H), 1.95–2.07 (m, 2H), 5.40–5.60 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 2.5, 14.1, 22.2, 22.3, 31.7, 32.1, 80.0, 129.0, 134.9.

For the minor (2Z,6Z)-isomer
^{1}H NMR ($CDCl_3$): δ 0.08 (s, 18H), 0.90 (t, J = 6.9 Hz, 6H), 1.21 (d, J = 3.0 Hz, 6H), 1.27–1.35 (m, 12H), 1.95–2.07 (m, 2H), 5.40–5.50 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 2.6, 13.9, 22.2, 22.3, 31.6, 32.1, 80.3, 129.2, 135.0.

For the major (2E,6Z)-isomer (13c)
^{1}H NMR ($CDCl_3$): δ 0.08 and 0.18 (s, 18H), 0.84–0.93 (m, 6H), 1.18–1.43 (m, 12H), 1.20 (s, 3H), 1.70 (s, 3H), 1.90–2.10 (m, 2H), 5.40–5.60 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 1.3, 2.4, 13.9, 14.0, 22.3, 23.0, 25.1, 30.1, 30.6, 30.7, 31.5, 32.1, 45.3, 46.4, 129.8, 134.4.

For the minor (2E,6Z)-isomer (13d)
^{1}H NMR ($CDCl_3$): δ 0.06 and 0.16 (s, 18H), 0.84–0.93 (m, 6H), 1.18–1.43 (m, 12H), 1.20 (s, 3H), 1.70 (s, 3H), 1.95–2.10 (m, 2H), 5.40–5.60 (m, 2H).

3.5.9 (2*E*,4*E*)-1,5-diphenyl-1-trimethylsilyl-3-trimethylsilyloxy-2,4-pentadiene (14)

Colorless needles: m.p. 75.5–76.0 °C.

IR (Nujol): ν(C=C—O) 1650 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.05 (s, 9H), 0.15 (s, 9H), 3.59 (d, J = 11.6 Hz, 1H), 5.43 (d, J = 11.6 Hz, 1H), 6.68 (d, J = 15.5 Hz, 1H), 6.82 (d, J = 15.8 Hz, 1H), 7.03–7.33 (m, 10H). ^{13}C NMR (C_6D_6): δ −3.50, −0.02, 36.5, 115.5, 124.1, 125.9, 126.2, 126.5, 126.6, 126.8, 127.1, 127.2, 127.5, 127.9, 128.1, 136.9, 141.8, 147.0.

3.5.10 *N*,*N*-Dimethyl 3-trimethylsilylpropanamide (15)

Colorless oil.

^{1}H NMR (C_6D_6): δ 0.10 (s, 9H), 1.01 (t, J = 8.2 Hz, 2H), 2.13 (t, J = 8.2 Hz, 2H), 2.32 (s, 3H), 2.78 (s, 3H). ^{13}C NMR (C_6D_6): δ −1.6, 11.7, 27.9, 35.1, 36.2, 172.8.

3.6 General procedure for ytterbium metal promoted homocoupling reaction of aliphatic imines

The light green Yb/TMSBr reagent was prepared as described above using Yb metal (0.346 g, 2.0 mmol), trimethylsilyl bromide (0.52 cm^3, 4.0 mmol), THF (4 cm^3) and HMPA (1 cm^3) in a 20-cm^3 test-tube equipped with a three-way stopcock. Then imine (2.0 mmol) was added to the test-tube. The reaction mixture was stirred under the conditions described in Tables 5 and 6. The usual work-up of the reaction mixture followed by Al_2O_3 column chromatography (n-hexane/ethyl acetate) gave the corresponding adducts. Representative results are listed in Tables 5 and 6.

3.6.1 *N,N'*-Dibenzyl-1,2-di-isopropyl-1,2-ethylenediamine (16)

Yellow oil.

IR (neat): ν(N—H) 3339 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 0.95 (d, J=6.6 Hz, 6H), 1.02 (d, J=6.6 Hz, 6H), 1.20 (brs, 2H), 1.75–1.90 (m, 2H), 2.38 (d, J=3.6 Hz, 2H), 3.71 (s, 4H), 7.14 (t, J=7.2 Hz, 2H), 7.23 (dd, J=7.2 and 7.2 Hz, 4H), 7.38 (d, J=7.2 Hz, 4H). ^{13}C NMR (C$_6$D$_6$): δ 18.9, 22.0, 30.1, 55.0, 64.2, 127.0, 128.4, 128.5, 142.0.

3.6.2 *N,N'*-Dibenzyl-1,2-dipropyl-1,2-ethylenediamine (17)

Colorless oil.

IR (neat): ν(N—H) 3297 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 0.92 (t, J=6.6 Hz, 6H), 1.31–1.39, (m, 10H), 2.55–2.63 (m, 2H), 3.63 (d, J=13.2 Hz, 2H), 3.69 (d, J=13.2 Hz, 2H), 7.15 (t, J=7.3 Hz, 2H), 7.24 (dd, J=7.3 and 7.3 Hz, 4H), 7.37 (d, J=7.3 Hz, 4H). ^{13}C NMR (C$_6$D$_6$): δ 14.6, 20.3, 32.7, 52.4, 57.9, 123.0, 128.5, 128.6, 142.0.

3.6.3 *N,N'*-Dibenzyl-1,2-dicyclohexyl-1,2-ethylenediamine (18)

Two diastereomers (DL: *meso*) were formed in the ratio of 63:37 accordiong to ^{13}C NMR analysis of the reaction mixture before separation. Each diastereomer was separated by Al$_2$O$_3$ column chromatography. The minor diastereomer was obtained as colorless needles from the first fraction (n-hexane/ethyl acetate = 40:1). The major diastereomer was obtained as a colorless oil from the second fraction (n-hexane/ethyl acetate = 10:1).

For the major isomer **(18a)**

Colorless oil.

IR (neat) ν(N—H) 3342 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 0.91–1.85 (m, 24H), 2.38 (d, J=4.6 Hz, 2H), 3.74 (d, J=12.9 Hz, 2H), 3.85 (d, J=12.9 Hz, 2H), 7.14 (t, J=7.8 Hz, 2H), 7.23 (dd, J=6.9 and 7.8 Hz, 4H), 7.39 (d, J=6.9 Hz, 4H). ^{13}C NMR (C$_6$D$_6$): δ 27.3, 30.2, 30.3, 42.5, 54.6, 62.9, 127.0, 128.5, 128.6, 142.1.

For the minor isomer **(18b)**

Colorless needles: m.p. 101.0–101.5 °C.

IR (Nujol): ν(N—H) 3340 cm^{-1}. ^{1}H-NMR (C$_6$D$_6$): δ 0.89–1.98 (m, 24H), 2.45 (d, J=2.6 Hz, 2H), 3.71 (d, J=14.0 Hz, 2H), 3.76 (d, J=14.0 Hz, 2H), 7.14 (t, J=6.9 Hz, 2H), 7.20–7.27 (m, 4H), 7.41 (d, J=7.9 Hz, 4H). ^{13}C NMR (C$_6$D$_6$): δ 26.98, 27.05, 27.3, 29.5, 32.3, 40.8, 55.1, 63.8, 127.0, 128.5, 142.1.

Analysis: calcd for $C_{28}H_{40}N_2$: C, 83.11; H, 9.96; N, 6.92. Found: C, 83.08; H, 9.95; N, 6.81%.

3.6.4. *N*-(2-Trimethylsilyl-3,3-dimethyl-2-butyl)aniline (19)

Colorless oil.

IR (neat): ν(N—H) 3407 cm^{-1}. MS (70 eV): m/z 192 (M^+ – t-Bu). ^{1}H NMR (C$_6$D$_6$): δ 0.09 (s, 9H), 0.89 (s, 9H), 1.23 (s, 3H) 3.61 (brs, 1H), 6.74 (m, 2H), 7.18 (m, 3H). ^{13}C NMR (C$_6$D$_6$): δ 0.00, 17.8, 27.5, 40.4, 54.5, 118.1, 118.3, 128.9, 148.4.

Analysis: calcd for $C_{15}H_{27}NSi$: C, 72.21; H, 10.90; N, 5.61. Found: C, 72.00; H, 10.90; N, 5.40%.

3.6.5 *N*-(2,2-Dimethyl-3-butyl)aniline (20)

Yellow oil.

IR (neat): ν(N—H) 3406 cm^{-1}. MS (70 eV): m/z 177 (M^+). ^{1}H NMR (C$_6$D$_6$): δ 0.84 (s, 9H), 0.89 (d, J=5.9 Hz, 3H), 3.09 (brs, 2H), 6.50 (d, J=7.6 Hz, 2H), 6.77 (t, J=7.6 Hz, 1H), 7.20 (t, J=7.6 Hz, 2H). ^{13}C NMR (C$_6$D$_6$): δ 15.8, 26.5, 34.8, 57.2, 113.6, 117.2, 129.6, 148.9.

3.6.6 *N*-(1-Trimethylsilyl-1-cyclohexyl)aniline (21)

Colorless oil.

IR (neat): ν(N—H) 3412 cm^{-1}. MS (70 eV): m/z 247 (M^+), 174 (M^+ – TMS). ^{1}H NMR (C$_6$D$_6$): δ 0.05 (s, 9H), 1.14–1.25 (m, 1H), 1.30–1.45 (m, 4H), 1.63–1.80 (m, 3H), 1.80–1.95 (m, 2H), 2.90 (s, 1H), 6.65 (d, J=8.0 Hz, 2H), 6.76 (t, J=7.3 Hz, 1H), 7.15 (dd, J=7.3 and 8.0 Hz, 2H). ^{13}C NMR (C$_6$D$_6$): δ –2.38, 20.4, 26.7, 32.7, 47.7, 116.4, 117.6, 129.2, 149.0.

Analysis: calcd for $C_{15}H_{25}NSi$: C, 72.81; H, 10.18; N, 5.66. Found: C, 72.78; H, 10.14; N, 5.65%.

3.6.7 *N*-(Cyclohexyl)aniline (22)

Yellow oil.

IR (neat): ν(N—H) 3398 cm^{-1}. MS (70 eV): m/z 175 (M^+). ^{1}H NMR (C$_6$D$_6$): δ 0.81–1.00 (m, 2H), 1.00–1.25 (m, 3H), 1.46–1.60 (m, 3H), 1.88 (d, J=12.2 Hz, 2H), 3.07 (tt, J=3.8 and 10.2 Hz, 1H), 3.12 (brs, 1H), 6.49 (d, J=8.5 Hz, 2H), 6.75 (t, J=7.3 Hz, 1H), 7.18 (dd, J=7.3 and 8.5 Hz, 2H). ^{13}C NMR (C_6D_6): δ 2.54, 26.2, 33.5, 51.5, 113.5, 117.1, 129.5, 147.8.

Analysis: calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.77; N, 7.99. Found: C, 82.11; H, 9.77; N, 7.88%.

Acknowledgements The authors gratefully acknowledge Shin-Etsu Chemical Co. Ltd for the generous gift of some silicon compounds. We also would like to thank Idemitsu Petrochemical Co. Ltd for the X-ray analyses of $YbBr_2$. This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas of Reactive Organometallics No. 05236106 from the Ministry of Education, Science and Culture, Japan.

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