Cp_2VCl_2-Catalyzed Meso-Selective Pinacol Coupling Reaction of Aldimines in the Presence of Chlorosilane and Zinc Metal

Bunpei Hatano, Akiya Ogawa, and Toshikazu Hirao*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan

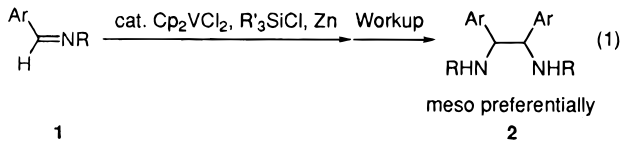
Received July 17, 1998

A catalytic reductive coupling of aldimines was achieved by using a catalyst Cp_2VCl_2/$PhMe_2SiCl$/Zn system. The influence of the catalyst, chlorosilane, co-reductant, solvent, and temperature on both the yield and diastereoselectivity of the coupling products was investigated in detail. As a result, the present Cp_2VCl_2-catalyzed reductive coupling of aldimines in the presence of $PhMe_2SiCl$ and zinc metal provided the corresponding 1,2-diamines in good yield with high meso selectivity (up to 92% meso), while the reductive coupling of aldehydes, ketones, and aldimines by the hitherto known catalytic methods leads to the preferential formation of *dl* isomers of the coupling products.

Introduction

The reductive dimerization of carbonyl compounds and their imine derivatives with low-valent metal complexes is an important method for vicinally bifunctionalized carbon−carbon bond formation.[1] Although the dimerization reactions usually require stoichiometric or more excess amounts of low-valent metal complexes, a catalytic reductive-coupling procedure has been disclosed recently by the combination of an early-transition-metal catalyst, a chlorosilane, and a zerovalent metal as a co-reductant. For example, Fürstner and co-workers reported the catalytic McMurry coupling of aldehydes promoted by the catalyst $TiCl_3$/R_3SiCl/Zn,[2] and, independently, we achieved the catalytic pinacol coupling of aldehydes induced by catalyst Cp_2VCl_2/Me_3SiCl/Zn, which provides 1,3-dioxolanes as a mixture of diastereoisomers (*dl*/meso = 63:37).[3] Furthermore, the catalytic pinacol coupling of aromatic aldehydes was reported to proceed with high diastereoselectivity using the catalytic systems of low-valent titanium complexes.[4] Very recently, we have revealed the highly *dl*-selective pinacol coupling reaction of secondary aliphatic aldehydes catalyzed by low-valent vanadium or titanium complexes.[5,6]

As for the catalytic dimerization of aldimines, there are only a few reports describing that the Cp_2TiCl_2-catalyzed reduction of aldimines with Sm metal exhibits high *dl* selectivity of the vicinal diamines (up to 80% *de*).[7,8] During the course of our studies on the catalytic pinacol coupling, we examined a catalytic dimerization of aldimines using the catalyst Cp_2VCl_2/$PhMe_2SiCl$/Zn, which successfully provides the corresponding 1,2-diamines in high yield, and more surprisingly, unprecedented high meso selectivity was observed (eq 1).



(1)

Results and Discussion

At first, we examined the reductive dimerization of *N*-benzylidenebenzylamine (**1a**) with Cp_2VCl_2 in the presence or absence of additives such as zinc metal and Me_3SiCl (eq 2, Table 1). When the reaction of **1a** with 2 equiv of Cp_2VCl_2 in refluxing THF was conducted for 24 h, the desired reductive-coupling product was not ob-

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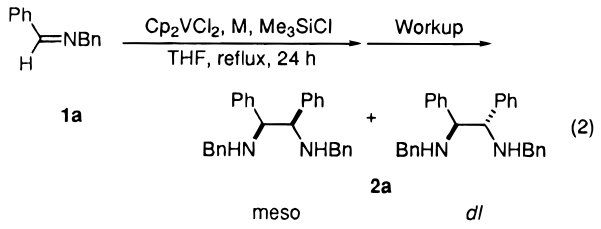
10.1021/jo981396o CCC: $15.00
Published on Web 11/19/1998

Table 1. Reduction of 1a with Cp_2VCl_2 in the Presence of Additive[a]

				2a	
entry	Cp_2VCl_2	M	Me_3SiCl	isolated yield, %	meso:*dl*[b]
1	+		−	0	
2	+		+	0	
3	+	Zn	−	40	58:42
4	−	Zn	−	0	
5	+	Zn	+	73	66:34
6	−	Zn	+	trace	46:54
7	+[c]	Zn	+	37	66:34
8	+[c]	Mg	+	20	80:20
9	+[c]	Sm	+	complex mixture	

[a] Reaction conditions: 2.0 mmol of **1a**, 1 equiv of Cp_2VCl_2, 2 equiv of M, 2.5 equiv of Me_3SiCl, 5 mL of THF, reflux, 24 h, Ar. [b] Determined by ^1H NMR. [c] 10 mol % of Cp_2VCl_2 was used.



tained at all (entry 1). While the absence of zinc metal in the Cp_2VCl_2-reduction system did not cause the reduction of **1a**, even in the presence of Me_3SiCl (entry 2), the combination of Cp_2VCl_2 and zinc metal led to the coupling product **2a** in 40% yield (entry 3). Since no reduction took place with zinc metal alone (entry 4), the active reducing species is likely to be a low-valent vanadium complex formed in situ by the reduction of Cp_2VCl_2 with zinc metal. Furthermore, the addition of Me_3SiCl to this system successfully improved the yield of **2a** (entry 5). The fact that the attempted reduction of **1a** using a Me_3SiCl/Zn system[9] gave only trace amounts of **2a** (entry 6) clearly indicates that the efficient pinacol-type coupling of aldimines requires a reduction system composed of Cp_2VCl_2, Me_3SiCl, and Zn. We next examined the reductive coupling in the presence of a catalytic amount of Cp_2VCl_2 (i.e., catalyst Cp_2VCl_2/Me_3SiCl/Zn), which successfully provided the reductive coupling product **2a** in moderate yield (entry 7). The use of Mg as a co-reductant led to **2a** in poor yield with moderate selectivity (entry 8). Moreover, the attempted reduction of **1a** using catalyst Cp_2VCl_2/Me_3SiCl/Sm gave rise only to a complex mixture (entry 9).

Since the best combination has been revealed to be catalyst Cp_2VCl_2/Me_3SiCl/Zn, the influence of solvent, temperature, and silyl compounds on the reductive coupling of **1a** was studied by using catalyst Cp_2VCl_2/$PhMe_2SiCl$/Zn (Table 2). In place of THF, the reductive coupling of **1a** in CH_2Cl_2 yielded 48% of **2a** without any diastereoselection (entry 2). When polar solvents such as HMPA and DMF were used, the yield increased dramatically as shown in entries 3 and 4. In particular, the use of DMF improved not only the yield but also the diastereoselectivity, giving the *meso*-1,2-diamine **2a** preferentially. Moreover, when the reductive coupling was performed at −25 °C, the diastereoselectivity was improved up to 83:17 (entry 5). On the other hand, heating at 75 °C led to a decrease in both the yield and selectivity (entry 6). The use of Me_3SiCl resulted in the low yield

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Table 2. Influence of Solvent, Temperature, and Silyl Compound on the Reductive Coupling of 1a[a]

				2a	
entry	$R'_2R''SiX$	solvent	temp, °C	isolated yield, %	meso:*dl*[b]
1	$PhMe_2SiCl$	THF	rt	45	52:48
2	$PhMe_2SiCl$	CH_2Cl_2	rt	48	50:50
3	$PhMe_2SiCl$	HMPA	rt	quant	61:39
4	$PhMe_2SiCl$	DMF	rt	88	73:27
5	$PhMe_2SiCl$	DMF	−25	79	83:17
6	$PhMe_2SiCl$	DMF	75	69	64:36
7	Me_3SiCl	DMF	rt	52	75:25
8	$^tBuMe_2SiCl$	DMF	rt	48	65:35
9	Me_3Si-Im[c]	DMF	rt	trace	
10	BSA[d]	DMF	rt	no reaction	
11	benzyl bromide	DMF	rt	61[e]	60:40

[a] Reaction conditions: 2.0 mmol of **1a**, 0.1 equiv of Cp_2VCl_2, 2 equiv of Zn, 2 equiv of $R'_2R''SiX$, 5 mL of solvent, 24 h, Ar. [b] Determined by ^1H NMR. [c] Me_3Si-Im = trimethylsilylimidazole. [d] BSA = *N*,*O*-bis(trimethylsilyl)acetamide. [e] A trace of the *N*-benzylation product was obtained.

Table 3. Optimization of Catalyst for Reductive Coupling of 1a[a]

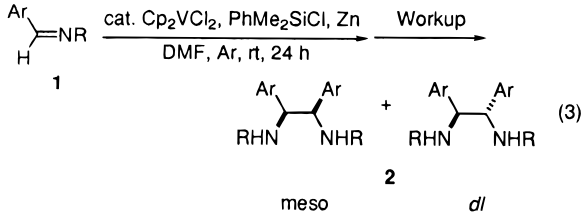
		2a	
entry	catalyst	isolated yield, %	meso:*dl*[b]
1	Cp_2VCl_2	88	73:27
2	VCl_3	45	82:18
3	$CpV(CO)_4$	52	75:25
4	Cp_2TiCl_2	35	74:26

[a] Reaction conditions: 2.0 mmol of **1a**, 0.1 equiv of catalyst, 2 equiv of Zn, 2.5 equiv of $PhMe_2SiCl$, 5 mL of DMF, rt, 24 h, Ar. [b] Determined by ^1H NMR.

of **2a** (entry 7). The sterically hindered TBDMSCl may be expected to induce higher diastereoselectivity, but **2a** was obtained in moderate yield with low selectivity (entry 8). In the case using 1-(trimethylsilyl)imidazole or *N*,*O*-bis(trimethylsilyl)acetamide, no reduction took place at all (entries 9 and 10). These results suggest that the electronic and steric effects of the silyl substituents play an important role in this reductive coupling of the aldimine **1a**. Interestingly, the desired reaction could proceed using benzyl bromide (entry 11).

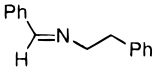
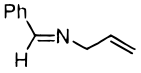
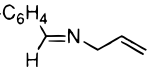
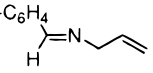
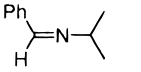
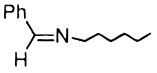
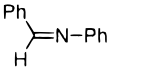
Table 3 represents the reduction of **1a** catalyzed by several vanadium compounds. The reductive coupling by use of VCl_3 or $CpV(CO)_4$ gave *meso*-1,2-diamine in moderate yield (entries 2 and 3). With Cp_2TiCl_2, the reduction gave **2a** with moderate selectivity (entry 4), but the complex formed in situ from Cp_2VCl_2 and Zn was found to be the more efficient catalyst.

Optimized conditions were employed for the reductive coupling of several aldimine derivatives (eq 3, Table 4).



Treatment of a variety of aldimines with the catalyst Cp_2VCl_2/$PhMe_2SiCl$/Zn afforded the coupling products successfully. Starting from *N*-phenethylaldimine **1b**, the 1,2-diamine **2b** was obtained in good yield with moderate diastereoselectivity (entry 1). In particular, the excellent meso diastereoselectivity was realized with *N*-allyl-

Table 4. Cp_2VCl_2/$PhMe_2SiCl$/Zn-Catalyzed Reductive Coupling of 1[a]

entry	1	2	isolated yield, %	meso : *dl* [b]
1		**1b**	**2b**	64	83 : 17
2		**1c**	**2c**	56	92 : 8
3		**1d**	**2d**	51	90 : 10
4		**1e**	**2e**	46	84 : 16
5		**1f**	**2f**	88	50 : 50
6		**1g**	**2g**	quant	67 : 33
7		**1h**	**2h**	90	75 : 25

[a] Reaction conditions: 2.0 mmol of **1**, 0.1 equiv of Cp_2VCl_2, 2 equiv of Zn, 2.5 equiv of $PhMe_2SiCl$, 5 mL of DMF, rt, 24 h, Ar. [b] Determined by ^1H NMR.

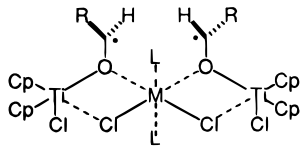


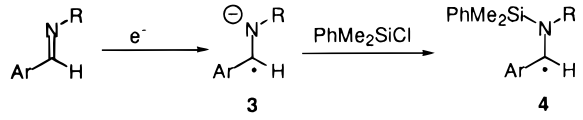
Figure 1.

substituted imines. Both *p*-methyl- and *p*-chloro-substituted phenylaldimines (**1d** and **1e**) underwent reductive coupling similarly, as in the case of the phenylaldimine **1c** itself (entries 2−4). In the case of **1f** bearing an *N*-isopropyl group, the diastereoselectivity was not observed (entry 5). The use of *n*-hexyl or phenyl substituent on the nitrogen afforded the corresponding 1,2-diamine **2g** or **2h**, respectively, in good yield with moderate meso selectivity (entries 6 and 7). These results suggest that the diastereoselectivity strongly depends on the substituent on the nitrogen of **1**.

In the catalytic dimerization of aldehydes, the cyclic intermediate has been proposed, in which two pair of lone pair on oxygen participate in the coordination to both the low-valent metal complex (Ti) and reductant (Mg, Zn, Mn), and R groups are consequentially arranged anti to each other to optimize the steric influence (Figure 1), providing the 1,2-diol with excellent *dl* selectivity.[4b−d,6a]

However, a similar model cannot explain the stereochemistry of the present reductive coupling of aldimines, and another intermediate model[10] may be operative. Although the real mechanism for this reductive coupling requires further detailed mechanistic experimentation, a possible pathway for the preferential formation of *meso*-1,2-diamines may be accounted for by the dimerization of an α-amino radical intermediate **4** formed in situ by the reduction of aldimine with a low-valent vanadium complex and subsequent rapid silylation of the reactive nitrogen anion radical **3** (Scheme 1). In the dimerization

Scheme 1



of **4**, the repulsion of the lone pair on nitrogen and steric hindrance between the aryl groups seem to contribute to the meso selection. A related stereochemistry has been reported in the photoinduced dimerization of aldimines in the presence of alcohols, giving *meso*-diamines selectively.

Conclusion

It has been demonstrated that the reductive coupling of aldimines can be catalyzed effectively by Cp_2VCl_2 in the presence of chlorodimethylphenylsilane and zinc metal. High meso selectivity has been attained for the first time in the pinacol-type coupling reaction.

Experimental Section

General. Melting points were determined on a Yanagimoto micromelting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 1600. ^1H NMR or ^{13}C NMR spectra were recorded on a Varian MERCURY300 spectrometer in chloroform-*d* with tetramethylsilane or residual chloroform as an internal standard. Mass spectra were recorded on a Varian Saturn 3 or JEOL JMS-DX-303. Elemental analyses were performed in the analytical section of our department. TLC was carried out on aluminum sheets precoated with silica gel 60 F_{254} (E. Merck). Column chromatography was performed on silica gel 60 (E. Merck). All reagents are of commercial quality. All dry solvents were freshly distilled under argon over an appropriate drying agent before use.

Preparation of Aldimine Derivative 1.[11] The carbonyl compound (50 mmol) was stirred with chromatographic alumina (Nakalai Tesque, Alumina Activated 200, 25.0 g; about 200 mesh) under argon. The amine (50 mmol) was slowly added to the carbonyl compound dispersed on alumina. Then, the mixture was stirred at room temperature for 2 h. The aldimine derivative **1** was extracted with $CHCl_3$ (30 mL × 2), and the extract was evaporated under reduced pressure. The residue was purified with a bulb-to-bulb apparatus to give **1**.

Representative Procedure for the Reductive-Coupling Reaction of an Aldimine Derivative. To a mixture of Cp_2VCl_2 (25 mg, 0.10 mmol) and zinc (262 mg, 4.0 mmol) in DMF (5 mL) was added $PhMe_2SiCl$ (683 mg, 4.0 mmol) at room temperature under argon. After being stirred for 1 h, **1** (2.0 mmol) was added to the mixture. The mixture was kept at room temperature with magnetic stirring for 24 h. $CHCl_3$ (10 mL) and aqueous HCl (1.5 M, 10 mL) were added to the resulting mixture, and the two liquid layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL × 2), and brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (25 g; eluent, hexane/ethyl acetate = 50:0, 48:2, 46:4, 44:6, 42:8, 40:10, 35:15, 30:20, 25:25, 50 mL × each), giving **2**.

Structure Determination of 2. The structures of 1,2-diamines were determined by comparison of spectral data with those of the authentic samples reported[8] or prepared shown below (**2a**, **2c**, and **2e**). The structures of **2d** and **2e** were determined on the analogy of other compounds.

Synthesis of 2c. To a solution of tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol) in THF (5 mL) was added allyl acetate (110 mg, 1.1 mmol) at reflux under argon. After the reaction mixture was stirred for 0.5 h, *dl*-1,2-diphenyl-1,2-ethylenediamine (106 mg, 0.50 mmol) was added

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(11) Texier-Boullet, F. *Synthesis* **1985**, 679.

to the mixture. The solution was kept at reflux with magnetic stirring for 24 h. $CHCl_3$ (10 mL) and aqueous HCl (1.5 M, 10 mL) were added to the resulting mixture, and the two liquid layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL × 2), and brine (10 mL), dried over Na_2SO_4, and concentrated to give **2c** (*dl*-isomer).

Synthesis of 2a or 2h.[7b] To a mixture of Cp_2TiCl_2 (25 mg, 0.10 mmol) and samarium (150 mg, 1.0 mmol) in THF (5 mL) was added **1** (2.0 mmol) at reflux under argon. The reaction mixture was stirred for 24 h. $CHCl_3$ (10 mL) and aqueous HCl (1.5 M, 10 mL) were added, and the two liquid layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL × 2), and brine (10 mL), dried over Na_2SO_4, and concentrated to give **2** (*dl* isomer as a major product). The residue was purified by column chromatography on silica gel (25 g; eluent, hexane/ethyl acetate = 50:0, 48:2, 46:4, 44:6, 42:8, 40:10, 35:15, 30:20, 25:25, 50 mL × each).

(*R*,*S*)-*N*,*N*′-Dibenzyl-1,2-diphenyl-1,2-ethylenediamine (2a). The registry no. is as follows: 27549-76-4.

(*R*,*S*)-*N*,*N*′-Diphenethyl-1,2-diphenyl-1,2-ethylenediamine (2b). The registry no. is as follows: 103276-50-2.

(*R*,*S*)-*N*,*N*′-Diallyl-1,2-diphenyl-1,2-ethylenediamine (2c): a pale yellow solid (obtained as a stereoisomeric mixture (meso/*dl* = 92:8)); mp 55−56 °C (uncorrected); IR (neat) ν 3053, 1453, 740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28−7.15 (m, 10 H), 5.64−5.51 (m, 2 H), 4.89−4.80 (m, 4 H), 3.75 (s, 2 H), 2.94−2.92 (m, 2 H), 2.78−2.70 (m, 2 H), 1.51 (br, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6 (C), 136.4 (C), 128.2 (CH), 128.2 (CH), 127.4 (CH), 115.5 (CH_2), 67.3 (CH_2), 49.4 (CH_2); MS (EI) *m*/*z* 293 ($[M + H]^+$, 91), 236 (11), 146 (100), 104 (16), 91 (18), 77 (5). Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 81.82; H, 8.35; N, 9.48.

(*R,*R**)-*N*,*N*′-Diallyl-1,2-diphenyl-1,2-ethylenediamine (2c):** *dl* product; IR (neat) ν 3431, 1454, 760, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.17−7.00 (m, 10 H), 5.92−5.79 (m, 2 H), 5.11−5.02 (m, 4 H), 3.70 (s, 2 H), 3.16−2.98 (m, 2 H), 2.96−2.93 (m, 2 H), 2.06 (br, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0 (C), 136.9 (C), 127.8 (CH), 127.7 (CH), 126.7 (CH), 115.5 (CH_2), 68.2 (CH_2), 50.0 (CH_2). Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 82.42; H, 8.26; N, 9.31.

(*R*,*S*)-*N*,*N*′-Diallyl-1,2-di(4-methylphenyl)-1,2-ethylenediamine (2d): a pale yellow oil (obtained as a stereoisomeric mixture (meso/*dl* = 90:10)); IR (neat) ν 2921, 1454, 824, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.08−7.07 (m, 4 H), 7.00−6.98 (m, 4 H), 5.59−5.43 (m, 2 H), 4.83−4.76 (m, 4 H), 3.65 (s, 2 H), 2.89−2.82 (m, 2 H), 2.74−2.67 (m, 2 H), 2.22 (s, 6 H), 1.72 (br, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8 (C), 136.9 (C), 128.9 (CH), 128.5 (CH), 127.7 (CH), 115.4 (CH_2), 67.4 (CH_2), 49.7 (CH_2), 21.1 (CH_3); MS (EI) *m*/*z* 321 ($[M - H]^+$, 7), 264 (8), 160 (100), 105 (12), 91 (9), 77 (2). Anal. Calcd for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.37; H, 8.79; N, 8.59.

(*R*,*S*)-*N*,*N*′-Diallyl-1,2-di(4-chlorophenyl)-1,2-ethylenediamine (2e): a pale yellow solid (obtained as a stereoisomeric mixture (meso/*dl* = 84:16)); mp 57−58 °C; IR (neat) ν 3434, 1456, 1091, 739 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.16−6.95 (m, 8 H), 5.53−5.40 (m, 2 H), 4.76 (m, 4 H), 3.61 (s, 2 H), 2.78 (dd, J = 7.1, 2.6 Hz, 2 H), 2.61 (dd, J = 14.4, 6.6 Hz, 2 H), 2.11 (br, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2 (C), 132.9 (C), 129.6 (CH), 128.4 (CH), 127.7 (CH), 116.0 (CH_2), 66.5 (CH_2), 49.6 (CH_2); MS (EI) *m*/*z* 180 ($[M/2]^+$, 100), 178 (58), 144 (5), 115 (4), 89 (7). Anal. Calcd for $C_{20}H_{22}N_2Cl_2$: C, 66.49; H, 6.14; N, 7.75. Found: C, 66.27; H, 6.11; N; 7.72.

(*R*,*S*)-*N*,*N*′-Di(1-methylethyl)-1,2-diphenyl-1,2-ethylenediamine (2f). The registry no. is as follows: 55079-98-6.

(*R*,*S*)-*N*,*N*′-Dihexyl-1,2-diphenyl-1,2-ethylenediamine (2g). The registry no. is as follows: 60509-69-5.

(*R*,*S*)-*N*,*N*′-Diphenyl-1,2-diphenyl-1,2-ethylenediamine (2h). The registry no. is as follows: 35583-26-7.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, and Culture, Japan.

JO981396O