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New developments in zinc-catalyzed asymmetric hydrosilylation of ketones with PMHS

Virginie Bette,[a] André Mortreux,[a] Diego Savoia[b] and Jean-François Carpentier[c,*]

[a]*Chimie Organique Appliquée, UPRESA 8010 CNRS-Université de Lille 1, ENSCL, BP 108, 59652 Villeneuve d'Ascq Cedex, France*
[b]*Dipartimento di Chimica 'G. Ciamician', Università di Bologna, via Selmi 2, 40126 Bologna, Italy*
[c]*Organométalliques et Catalyse, UMR 6509 CNRS-Université de Rennes 1, Institut de Chimie, Campus de Beaulieu, 35042 Rennes Cedex, France*

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Abstract—The influence of structural modifications of the diamine ligand and the ZnR_2 precursor in the [ZnR_2–diamine]-catalyzed asymmetric hydrosilylation of prochiral ketones with PMHS in aprotic medium is reported. A new diamine ligand giving up to 91% ee in the reduction of acetophenone is described. The scope of this reduction system has been investigated using variously functionalized ketones and some deactivation pathways have been identified.

1. Introduction

Enantiomerically pure chiral alcohols are key intermediates in the synthesis of numerous biologically active molecules.[1] For this reason, much effort has been paid in the last 30 years to develop efficient techniques for asymmetric reduction of prochiral ketones. In particular, asymmetric catalysis provides organic chemists with a whole tool of efficient methods,[2] none of them being yet optimal.[3] Among others, asymmetric hydrosilylation leads to very high enantiomeric excesses on a large range of substrates, the best results being usually obtained with Rh- and Ti-based catalysts.[4] Nevertheless, the toxicity, price and low stability of the reagents (molecular hydrosilanes and hydrosiloxanes) and/or catalysts limit its industrial applications. The recent rediscovery of polymethylhydrosiloxane (PMHS), a stable inexpensive and non-toxic hydrosilane, has opened new perspectives to asymmetric hydrosilylation.[5] In this context, we got particularly interested in an original Zn–diamine catalytic system reported by Mimoun et al. for chemoselective hydrosilylation/reduction of aldehydes, ketones and esters.[6] An asymmetric version was also described, limited to the enantioselective reduction of acetophenone.[7]

We report here complementary studies on this zinc-based catalytic system. Our goals were (i) to further explore the influence of reaction parameters, for example, structural modifications of the diamine ligand and the ZnR_2 precursor, to improve eventually on the enantioselectivity in the hydrosilylation of simple alkyl aryl ketones; and (ii) to investigate the scope of this reduction system for variously functionalized ketones.

2. Results and discussion

2.1. Influence of ligand structure

In the results disclosed by Mimoun et al.,[7] the best ees for the reduction of acetophenone (**K1**) were reached with (*R*,*R*)-*N*,*N*′-ethylene-bis(1-phenylethylamine) (ebpe, **1a**, Scheme 1) (76% ee, Table 1, entry 1) and (*S*,*S*)-*N*,*N*′-dibenzyl-1,2-diphenyl-1,2-ethanediamine (*N*-Bn-dpen, **3a**) (88% ee, entry 6). Alternatively, we first modified the substituents on the skeleton of ebpe with the series of ligands **1b–d** (Scheme 1). It appears that replacing the phenyl ring by a bulkier aromatic substituent does not affect the catalyst activity (**1b**, entry 2). On the other hand, a significant decrease in activity is observed with a *p*-chlorophenyl substituted ligand (**1c**, entry 3); the latter decrease is tentatively ascribed to competitive reversible coordination of chlorine to the zinc center, leading to a catalytically less active or inactive species. Nevertheless, the level of enantioselectivity for the reduction of **K1** is equivalent irrespective of the aryl-derivative used within this series (**1a–c**). In sharp contrast, a dramatic loss of enantioselectivity is observed with the cyclohexyl-ebpe derivative (**1d**, entry 4), which likely accounts for the influence of electronic factors (vide infra). Moreover, the rigidity provided by a propylene bridge in ligand **2** seems

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* Corresponding author. Tel.: +33-223-235-950; fax: +33-223-236-939; e-mail address: jean-francois.carpentier@univ-rennes1.fr

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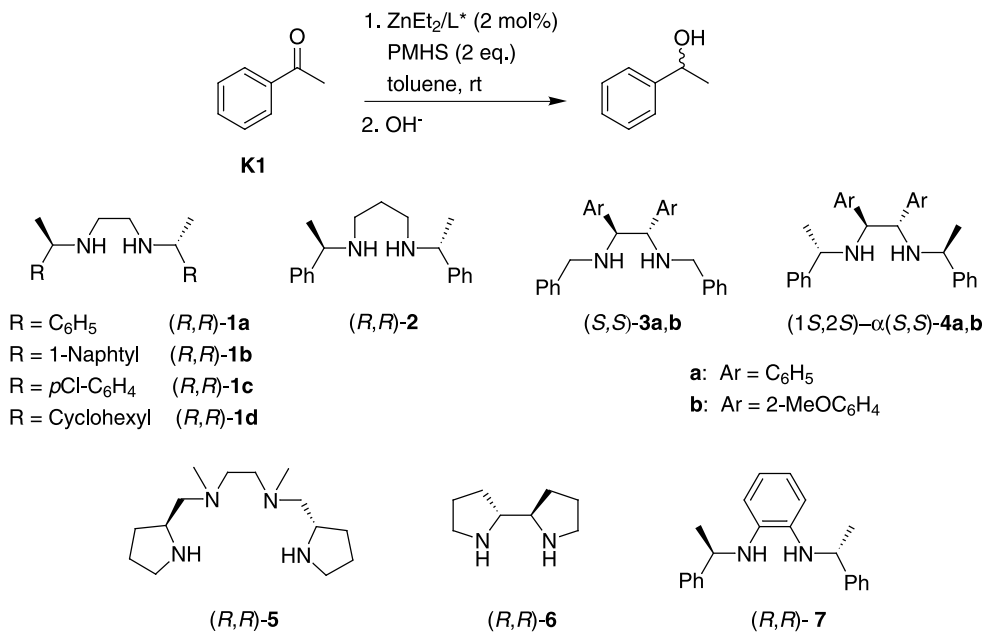


Scheme 1.

Table 1. Zinc-catalyzed reduction of acetophenone (**K1**) with PMHS using ligands **1**–**7**[a]

Entry	Ligand	Time[b] (h)	Yield (mol%)	ee (conf.) (%)
1[c]	(*R*,*R*)-**1a**	18	>99	76 (*S*)
2	(*R*,*R*)-**1b**	6	94	78 (*S*)
3	(*R*,*R*)-**1c**	6	14	76 (*S*)
4	(*R*,*R*)-**1d**	6	68	22 (*S*)
5	(*R*,*R*)-**2**	4	15	0
6[c]	(*S*,*S*)-**3a**	18	>99	88 (*R*)
7	(*S*,*S*)-**3b**	72	>99	83 (*R*)
8	(1*S*,2*S*)-α(*S*,*S*)-**4a**	170	56	84 (*R*)
9	(1*S*,2*S*)-α(*S*,*S*)-**4b**	288	66	91 (*R*)
10	(*R*,*R*)-**5**	16	91	0
11	(*R*,*R*)-**6**	18	>99	22 (*R*)
12	(*R*,*R*)-**7**	2	2	<5

[a] PMHS/**K1**/$ZnEt_2$/diamine=60:50:1:1 [**K1**]=0.89 M in toluene.
[b] Reaction time not optimized.
[c] Results from Ref. 7.

insufficient to enable effective activation and enantiodifferentiation for the reduction, as reflected by the limited racemic conversion (entry 5). C_2-symmetric secondary diamine ligands **5** and **6** that bear no aromatic substituents proved also inefficient in terms of enantioselectivity, and bis-aniline-type diamine **7** showed only poor activity (entries 10–12). In light of these results, it appears thus important to keep both a C_2-symmetric 1,2-ethylenediamine ligand backbone as well as a *N*-benzyl group, either α to the nitrogen or on the 1,2 positions of the ethylene bridge.

The 2-methoxyphenyl-substituted diamine **3b** was synthesized in order to assess the effect of a restricted rotation of the aryl ring on the catalyst performance. As somewhat lower activity is obtained, the enantioselectivity remains slightly below that promoted by *N*-Bn-dpen (**3a**, entries 6 and 7). The association of the aforementioned two types of chiral centers (α and 1,2) was realized through the new diamines **4a**,**b**. $ZnEt_2$-catalyst systems based on these bulky ligands promote hydrosilylation/reduction of **K1**, but only with modest rates (entries 8 and 9). On an enantioselective point of view, the results show that no cooperative effect of the α and (1,2) chiral centers takes place within ligand **4a**. Indeed, although both (*S*,*S*)-dpen (**3a**) and (*S*,*S*)-ebpe (**1a**) lead to the same major product of absolute configuration (*R*), the performance of the 'matched' ligand **4a** (84% ee, entry 8) is only in between that of each individual ebpe **1a** and dpen **3a**. Thus, with respect to **3a**, the introduction of a α-methyl substituent on the *N*-benzyl arm only lowers the catalyst performances. Nevertheless, further improvement of enantioselectivity in the hydrosilylation/reduction of **K1** was obtained with the 2-methoxyphenyl-substituted diamine **4b**, which delivers the best ee with the so-called matched-pair of this ligand (91% ee, entry 9). This improvement is possibly due to the hindered rotation of the phenyl moiety, assisted in this case by the α-methyl arms.

2.2. Other reaction parameters: zinc precursor, hydrosilane

The influence of the catalyst precursor ZnR_2 was investigated by varying the bulkiness and electronic properties of the R residues (R=Et, *i*Pr, Ph). While the use of $Zn(iPr)_2$ in place of $ZnEt_2$ was not so sensitive in the case of **K1**, the use of $ZnPh_2$ greatly affected the reaction rate (Table 2, entries 13 and 14; compare with Table 1, entry 1). A similar trend was observed in the reduction of methyl phenylglyoxylate (**K2**, entries 15–17). For both **K1** and **K2**, the impact of the R residue on the enantioselectivity is noticeable although rather limited. Mechanistically, this evidences that at least one R residue remains coordinated onto the Zn center throughout catalysis (vide infra).[†] Though the $ZnPh_2$/(*R*,*R*)-ebpe system leads to 82% ee in the case of **K1**, i.e., an increase in $\Delta\Delta G^{\#}$ of ca. 0.2 kcal mol^{-1} as compared to $ZnEt_2$, this parameter can not be, however, advantageously exploited from a synthetic point of view, due to the poor

[†] The enantioselectivity of all the systems reported in this paper is constant over the whole reaction time, as probed by GLC monitoring.

Table 2. Zinc–(*R*,*R*)-ebpe (**1a**)-catalyzed reduction of acetophenone (**K1**) and methyl phenylglyoxylate (**K2**): influence of the zinc precursor and silane[a]

Entry	Ketone	ZnR_2 (R)	Silane	Time[b] (h)	Yield (mol%)	ee (conf.) (%)
13	**K1**	*i*Pr	PMHS	48	>99	76 (*S*)
14	**K1**	Ph	PMHS	18	31	82 (*S*)
15	**K2**	Et	PMHS	6	>99	28 (*R*)
16	**K2**	*i*Pr	PMHS	6	>99	33 (*R*)
17	**K2**	Ph	PMHS	4	31	48 (*R*)
18	**K1**	Et[c]	PMHS	44	19	82 (*S*)
19	**K1**	Et	Et_3SiH	48	0	—
20	**K1**	Et	Ph_2SiH_2	5	>99	79 (*S*)
21	**K1**	Et	$PhSiH_3$	18	>99	76 (*S*)

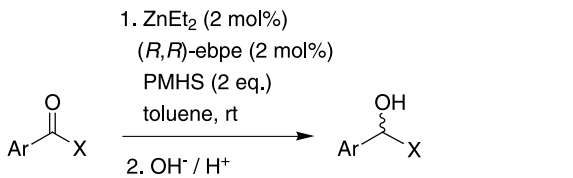
[a] SiH/**K**/ZnR_2/(*R*,*R*)-**1a**=60:50:1:1 [**K**]=0.89 M in toluene.
[b] Reaction time not optimized.
[c] *T*=−20 °C.

reduction rate associated. Therefore, no further preparation of $Zn(Ar)_2$ precursor was attempted. Similarly, only a slight improvement of the enantioselectivity was noticed when the reduction was carried out at −20 °C, along a neat decrease of the reaction rate (entry 18). Pre-activation of the catalyst, through brief heating (50 °C) of $ZnEt_2$, diamine and 1 equiv. of substrate together, proved useless.

Except trialkylsilanes (entry 19), various molecular monoalkyl- and dialkylsilanes lead to as effective systems as PMHS for the reduction of **K1**, with ees in the same range (entries 20 and 21). No specific rate acceleration was detected with PMHS as compared to other silanes.[8] Nevertheless, the intrinsic characteristics of this polymeric siloxane (low price, low toxicity, stability to air and moisture) largely justify its use as reducing agent in current efforts to access inexpensive and efficient reducing systems.

2.3. Scope of the catalytic reaction—deactivation pathways

Another point of interest was to assess the reductive abilities of this Zn/diamine catalyst system in toluene towards functionalized ketones, since only the reduction of simple alkyl aryl ketones has been reported so far. Using $ZnEt_2$–(*R*,*R*)-**1a** as the model catalyst, a variety of ketones were reduced with moderate to good activities, total chemoselectivity for the corresponding alcohol, and interesting levels of enantioselectivities for some of them (Scheme 2, Table 3). For instance, reduction of 2-acetylthiophene (**K6**) provides



Ar = Ph, X = Me **K1**
$COCH_3$ **K2**
CF_3 **K3**
CH_2Cl **K4**
$CH_2CO_2CH_3$ **K5**
Ar = 2-Thienyl, X = Me **K6**
$CH_2CH_2NMe_2$ **K7**
Ar = 2-Pyridyl, X = Me **K8**

Scheme 2.

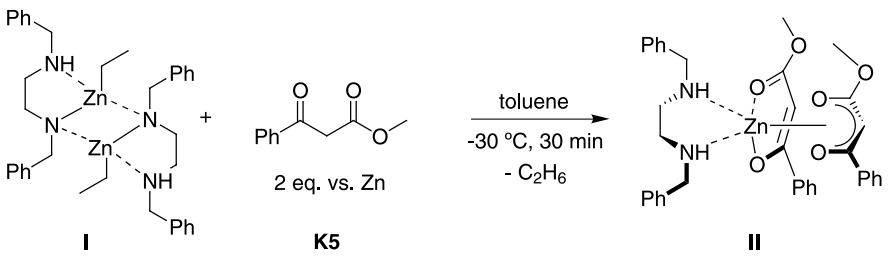
Table 3. Zinc–(*R*,*R*)-ebpe (**1a**)-catalyzed reduction of carbonyl compounds **K3**–**K8**[a]

Entry	Ketone	Time[b] (h)	Yield (mol%)	ee (conf.) (%)
22	**K3**	1	>99	27 (*R*)
23	**K4**	18	43	62 (*R*)
24	**K5**	18	0	—
25	**K6**	48	>99	78 (*R*)
26	**K7**	48	80	35 (*R*)
27	**K8**	4	69	17 (*R*)

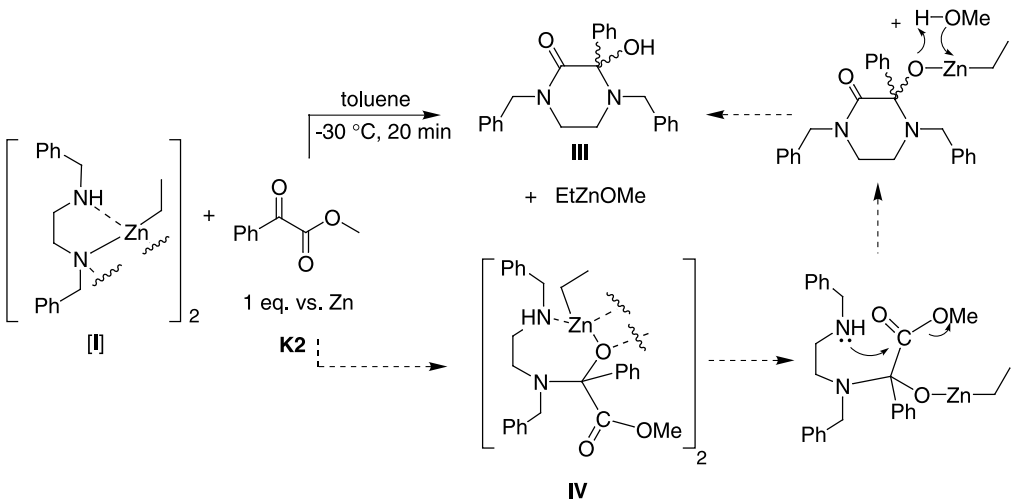
[a] PMHS/**K**/$ZnEt_2$/(*R*,*R*)-**1a**=60:50:1:1, [**K**]=0.89 M in toluene.
[b] Reaction time not optimized.

2-(1-thienyl)ethanol with excellent chemoselectivity and 78% ee (entry 25). The presence of a strongly electron-withdrawing group α to the carbonyl function, such as in α,α,α-trifluoroacetophenone (**K3**), activates greatly the reaction, however ending with quite a low enantioselectivity in this case (entry 22). Also, as already mentioned, higher α-ketoesters such as methyl phenylglyoxylate (**K2**) are quantitatively reduced to the corresponding α-hydroxy-esters, which can be readily recovered in high yields after careful hydrolysis (Table 2, entry 15). This result is noteworthy if one takes into account the excellent activity of this Zn–diamine system in the chemoselective reduction of esters and lactones under harsher conditions.[6] In spite of these encouraging results, limitations of this system appeared. For instance, the final hydrolysis step proved somehow troublesome, particularly in the case of lower α-ketoesters such as ethyl and methyl pyruvate, though initial reduction appeared quantitative and chemoselective (^{1}H NMR). More problematic is the presence of potentially coordinating functionalities, such as chlorine (**K4**) and amino groups (**K7**, **K8**), either on the alkyl or aryl moieties of the ketones, which lower the activity of the system (entries 23, 26 and 27). This observation is consistent with the detrimental effect of a chloro group on the ligand backbone (vide supra, entry 3) and suggests also poisoning of the catalytically active zinc species by competitive coordination of the chloro/amino group onto the metal center. Moreover, substrates prone to the formation of enols, for example, β-ketoesters such as **K5**, cannot be reduced with this catalyst system in toluene (entry 24). ^{1}H NMR analysis of the reaction mixture (before hydrolysis) indicated that the substrate (**K5**) remains intact under those conditions; no silyl ether nor silylated enol was detected. Also, cross-experiments showed that β-ketoester **K5** inhibits the catalytic reduction of **K1** and **K2**. The formation of a [Zn–acetylacetonate] species was suspected to account for this inhibition. Indeed, in a separate reaction, the addition of 2 equiv. (vs Zn) of benzoylacetoacetate **K5** on the dimeric amine–amido Zn precursor **I**[9] was found to give the zinc–bis(acac) complex **II**, which was isolated in high yield and identified by elemental analysis and ^{1}H, ^{13}C and 2D NMR (Scheme 3).[10] Complex **II** proved totally inefficient in promoting the reduction of **K1** under standard conditions in toluene, in contrast to **I** which is a highly effective catalyst.

In a parallel experiment, the addition of 1 equiv. (vs Zn) of methyl phenylglyoxylate (**K2**) on amine–amido Zn complex **I** enabled us to isolate, as the major product (50% yield), the 3-hydroxypiperazin-2-one **III**, identified by ^{1}H,



Scheme 3.



Scheme 4.

^{13}C and 2D NMR, and X-ray diffraction.‡ The formation of **III**[11] can be explained on the basis of Mimoun's mechanism,[7] by degradation of a transient (not observed) intermediate complex of type **IV**, that would initially arise from insertion of the carbonyl function of the substrate into the Zn–*N*(amido) bond of complex **I** (Scheme 4). Interestingly, this stoichiometric reaction does not seem to take place under catalytic conditions with ZnR_2–(*R*,*R*)-ebpe systems, since **K2** is quantitatively reduced to methyl mandelate with constant enantioselectivity (Table 2, entries 15 and 16). We assume that the higher bulkiness of ebpe (**1a**) (as compared to that of *N*,*N*-dibenzylethylenediamine) may prevent this side reaction.§ Also, the hydrosilane present under catalytic conditions may likely convert the [$ZnEt_2$–diamine] precursor into another (hydrido) species, which has its own reactivity towards **K2**.

3. Conclusion

Although the ZnR_2–diamine–PMHS hydrosilylation system in aprotic solvents proved relatively limited in scope, its activity and enantioselectivity in the reduction of simple alkyl aryl ketones are noteworthy for such an unusual catalyst system. The enantioselectivity (91% ee) reached with the new 2-methoxyphenyl derivative **4b** compares favorably with recent [Rh]–diphosphine catalysts, such as those based on EtTRAP-H,[12] MiniPHOS[13] or BMPF[14] leading to 85–94% ee on alkyl aryl ketones. Its reactivity and chemoselectivity towards α-ketoesters is also remarkable, though modest enantioselectivity could be achieved so far. As previously reported,[9] the use of similar Zn–diamine systems in protic solvents (alcohol) is an interesting alternative to avoid the final hydrolysis step, which turns out sometimes problematic, and to broaden the scope of this hydrosilylation reaction. Further results obtained under these conditions will be reported soon.

4. Experimental

4.1. General

GLC analyses were performed on Chrompack CP 9001 apparatuses equipped with a flame ionization detector and, respectively, a BPX5 (25 m×0.32 mm, SGE) and a chiral Chirasil-DEX CB (25 m×0.25 mm, Chrompack) column. ^{1}H NMR spectra were recorded on AC-200 and AC-300 Bruker spectrometers at 23 °C in $CDCl_3$; chemical shifts are reported in ppm downfield from TMS and were determined by reference to the residual ^{1}H (δ 7.25) solvent peak; all coupling constants are reported in Hz. Optical rotations were measured on a Perkin–Elmer 343 polarimeter at 25 °C in a 1 dm cell. IR spectra were recorded on a Nicolet 510

‡ Poor final *R* values (*R*=0.1066; wR_2=0.2704) were obtained in this X-ray diffraction analysis due to poor quality crystals and disorder problems associated to solvent molecules. However, the data confirmed unambiguously the atom connectivity of **III**.

§ Note that ebpe (**1a**) reacts with $ZnEt_2$ at room temperature to form the diamine complex $ZnEt_2$(ebpe),[7] while *N*,*N*-dibenzylethylenediamine reacts rapidly with $ZnEt_2$ to form the amine–amido complex **I**.[9]

FTIR spectrophotometer in a KBr cell and are expressed by wave number (cm^{-1}). Melting points are uncorrected.

Diamines **1a–d** and **2**,[7] *N*-Bn-Dpen (**3a**),[15] **5**,[16] and **7**[17] were prepared following slightly modified reported procedures and strictly purified by distillation or column chromatography and subsequent recrystallization. The new diamines **3b** and **4a**,**b** were prepared according to known procedures and their synthesis will be described elsewhere. Diamine **6**[18] was kindly provided by Pr. A. Alexakis (University Geneva). $ZnEt_2$ (1.1 M solution in toluene) was purchased from Aldrich and used as received. Complex **I** was prepared as described previously.[9] Ketones were distilled over CaH_2 and degassed before use. PMHS (Aldrich) was degassed before use. Toluene was freshly distilled from Na/K amalgam and degassed before use.

4.1.1. Complex II. Methyl benzoylacetoacetate (**K5**, 0.19 mL, 1.20 mmol, 2.0 equiv. vs Zn) was added dropwise under nitrogen to a solution of complex **I** (0.200 g, 0.30 mmol of dimer, 0.60 mmol of Zn) in toluene (5 mL) cooled at −20 °C. The resulting solution was stirred with a magnetic stir bar for 20 min at −20 °C, and then for 30 min at 25 °C. Volatiles were removed under vacuum to give a yellow oil which was triturated with pentane (5 mL). The resulting precipitate was separated off from the liquid phase, washed with pentane (2×5 mL), and dried under vacuum to give **II** as a white powder (0.260 g, 70%). ^{1}H NMR ($C_6D_5CD_3$): δ 8.13 (d, J=6.4 Hz, 4H, *o*-Ph), 7.70–6.85 (m, 16H, arom.), 6.00 (s, 2H, C*H* acac), 4.09 (s, 4H, NHCH_2Ph), 3.50 (s, 6H, OCH_3), 2.25 (s, 4H, CH_2NHBn). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$): δ 183.4 (ZnO*C*(Ph)=), 175.4 (*C*OOMe), 143.1, 139.1, 133.6, 130.0, 129.3, 129.2, 129.0, 128.6, 127.5 (all *C* arom.), 82.2 (*C*H), 53.2 (NH*C*H_2Ph), 50.6 (O*C*H_3), 45.7 (*C*H_2NHBn). Anal. calcd for $C_{36}H_{38}N_2O_6Zn$ (660.09): C 65.44, H 5.75, N 4.24; found C 65.79, H 5.88, N 3.89.

4.1.2. 3-Hydroxy-1,4-dibenzyl-piperazin-2-one (III). Methyl phenylglyoxylate (**K2**, 0.13 mL, 0.92 mmol, 1.03 equiv. vs Zn) was added dropwise under nitrogen to a solution of complex **I** (0.296 g, 0.445 mmol of dimer, 0.890 mmol of Zn) in toluene (10 mL) cooled at −30 °C. The solution was stirred for 30 min at −30 °C, then for 1 h at 25 °C. Volatiles were removed under vacuum to give a white solid which was triturated with pentane (5 mL). The resulting precipitate was separated off from the liquid phase, washed with pentane (2×5 mL), and dried under vacuum to give a small amount of **III** (0.020 g). The residue was dried under vacuum (0.206 g) and extracted with pentane (5×5 mL). The solution was filtered and volatiles were removed under vacuum to afford **III** as a white powder (total: 0.164 g, 50%). Crystals for X-ray diffraction were grown from toluene/pentane (2:1) at −30 °C. ^{1}H NMR ($CDCl_3$): δ 7.74 (d, J=7.0 Hz, 2H, arom.), 7.40–7.10 (m, 13H, arom.), 4.69 (d, J=14.3 Hz, 1H, CONC*H*HPh), 4.56 (d, J=14.3 Hz, 1H, CONCH*H*Ph), 3.74 (d, J=14.6 Hz, 1H, C(OH)NC*H*HPh), 3.54 (d, J=14.3 Hz, 1H, C(OH)NCH*H*Ph), 3.55 (m, 1H, C*H*HN(Bn)CO), 3.15 (m, 2H, CH*H*N(Bn)CO+C*H*HN(Bn)C(OH)), 2.83 (s, 1H, O*H*), 2.70 (m, 1H, CH*H*N(Bn)C(OH)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 170.4 (*C*O), 142.5, 138.9, 136.3, 129.9, 128.8, 128.3, 128.2, 128.10, 128.0, 127.7, 126.9, 126.6 (all *C* arom.), 89.7 (*C*OH), 52.2 (C(OH)N*C*H_2Ph), 50.7 (CON*C*H_2Ph), 47.0 (*C*H_2N(Bn)CO), 41.1 (*C*H_2N(Bn)C(OH)).

4.1.3. Zn–diamine-catalyzed asymmetric hydrosilylation of acetophenone by PMHS. *General procedure*. Catalytic reactions were performed under nitrogen using standard Schlenk techniques. In a typical experiment (Table 1, entry 1), to a solution of (*S*,*S*)-**1a** (14.7 mg, 0.055 mmol) in freshly distilled toluene (2.5 mL), were added $ZnEt_2$ (50 μL of a 1.1 M solution in toluene, 0.055 mmol), then acetophenone (0.32 mL, 2.75 mmol) and finally PMHS (0.21 mL, 3.30 mmol). The solution was stirred at room temperature and the reaction was monitored by GLC as follows: aliquot samples (ca. 0.1 mL) from the reaction mixture were hydrolyzed by aqueous KOH (45 wt%), the organic products (**K1** and 1-phenylethanol) were extracted in diethyl ether, and this organic phase was analyzed by quantitative GLC. The enantiomeric purity of 1-phenylethanol was assessed by GLC on a Chirasil-DEX CB column (110 °C, 0.7 bar). When the same reaction was carried out on a preparative scale, no aliquots were sampled and the final mixture was hydrolyzed after 3 days and extracted as described above, yielding spectroscopically pure 1-phenylethanol in more than 95% isolated yield.

Acknowledgements

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