[Zinc-Diamine]-Catalyzed Hydrosilylation of Ketones in Methanol. New Developments and Mechanistic Insights

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Abstract: The Zn-promoted direct reduction of various ketones, including alkyl aryl ketones, α- and β-keto esters, α- and β-keto amides, into the corresponding alcohols with polymethylhydrosiloxane (PMHS) in protic conditions is reported. The reaction proceeds chemoselectively under smooth conditions, with simple catalyst combinations based on a zinc precursor [$ZnEt_2$, $Zn(OMe)_2$, $Zn(OH)_2$] and a 1,2-diamine ligand, e.g., *N,N′*-dibenzylethylenediamine (dbea). The reaction rates are significantly faster than under aprotic conditions. For β-keto esters and amides, the use of an excess of PMHS is required. Moderate enantioselectivities (ee up to 55%) have been obtained using a variety of enantiopure diamine ligands. Two mechanisms are proposed for the new catalytic reaction, on the basis of the synthesis of [(diamine)$Zn(alkoxide)_2$] complexes which are models of the possible reaction intermediates and a study of their activity.

Keywords: alcohols; diamines; homogeneous catalysis; hydrosilylation; PMHS; zinc

Introduction

Secondary alcohols are rewarding intermediates in organic synthesis, especially when taking into account their importance as (chiral) building blocks for the preparation of numerous biologically active molecules.[1] As regards their preparation, in comparison with other major catalytic methods for the reduction of C=O bonds, i.e., hydrogenation and hydrogen transfer, hydrosilylation appears relatively less attractive, mainly due to the high toxicity and price of the generally employed monomeric silanes ($PhSiH_3$, ...).[2] In recent years, hydrosilylation has gained renewed interest following the rediscovery of the reductive abilities of polymethylhydrosiloxane (PMHS), a safe and inexpensive polymer co-product of the silicon industry, when associated to some transition metal-, Lewis acid- or fluoride-based catalysts.[3] Among the former ones, an original Zn catalyst system described by Mimoun et al. promoted the chemoselective reduction of non-functionalized and α,β-unsaturated ketones, aldehydes and even esters to the corresponding alcohols.[4] A chiral version using optically active secondary 1,2-diamines was also developed to reduce simple aryl alkyl ketones,[5] and received further developments from our and other groups by exploring the efficiency of new chiral diamines and aiming to expand the scope of the method.[6] Overall, the latter point constitutes the main limitation of this catalytic system. In fact, since the reaction is carried out in a non-polar solvent, typically toluene, the final product is a silyl ether that must be submitted to a subsequent hydrolysis step to recover the desired alcohol. Unfortunately, as exemplified later in this paper, this non-neutral work-up proved somewhat delicate for quite a few functionalized ketones. Therefore, it appeared necessary to set up an alternative system that would overcome this limitation. Hence, we focused our interest on a modified version of this [Zn-diamine]-PMHS catalytic system, able to give the free alcohol product in a one-step, mild and neutral procedure. One possibility to achieve this goal is to use a protic solvent. To our knowledge, only a few examples of hydrosilylation proceeding in protic solvents have been reported so far, which all employ tin-based catalysts in an alcohol.[7–9] In fact, although the dehydrogenation of PMHS by alcohols was shown to take place in the presence of zinc species,[4] we have observed that the Zn-catalyzed hydrosilylation of C=O and C=N bonds is effective in an alcohol solvent too.[10] In this contribution, we thoroughly describe the chemoselective reduction of functionalized ketones as well as a few imines in the presence of an alcohol. Several chiral diamine ligands were also evaluated in an asymmetric ver-

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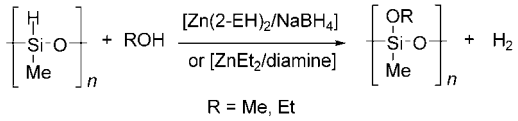
sion of this catalytic system. Finally, on the basis of the catalytic data and the preparation of several model zinc alkoxide-diamine complexes, possible mechanisms for this new catalytic system are proposed.

Results and Discussion

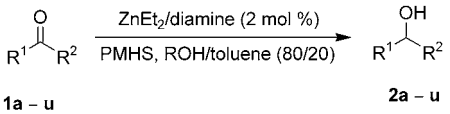
Scope of the Catalytic System

In the absence of a reducible C=O or C=N bond, the dehydrogenative coupling of PMHS with alcohols (MeOH, EtOH) takes place rapidly at room temperature using *ca.* 1 mol % of a zinc precursor activated by a diamine, e.g., $ZnEt_2$/dbea [dbea = *N,N′*-dibenzylethylenediamine], or a hydride, e.g., $Zn(EH)_2/NaBH_4$ [EH = 2-ethylhexanoate] or $Zn(EH)_2$/vitride® [vitride = sodium dihydrobis(2-methoxyethoxy)aluminate] (Scheme 1). Nonetheless, these systems proved surprisingly capable to convert efficiently, under the same conditions, a variety of ketones (**1a**–**u**, **3a**–**c**, **4**) and imines (**6a**–**d**) to the corresponding alcohols (Schemes 2 and 3, Tables 1–3) and amines (Scheme 4, Table 4). Most probably, a kinetic competition between the two reactions to the benefit of the second one accounts for this original and specific activity (*vide infra*).

The use of a protic medium proved quite valuable in terms of activity, work-up, and scope/selectivity. First, an important acceleration effect was observed in most cases when the reactions were carried out in methanol[11] as compared to toluene. For instance, the reduction of acetophenone (**1a**) was completed within 1 h in methanol, while only 10% conversion was observed in toluene over the same reaction time (Table 1, entries 2 and 3). Similarly, the conversion of α-chloroacetophenone (**1b**) in toluene reached a maximum of 43% after 24 h, but was quantitative within 1 h in methanol (Table 1, entries 4 and 5). Also, in the case of methyl phenylglyoxylate (**1g**), reaction rates up to 20 times higher in methanol than in toluene were observed (Table 2, entries 14–16).



Scheme 1.



	R^1	R^2		R^1	R^2
a	Ph	Me	**m**	Me	CO_2Me
b		CH_2Cl	**n**		CH_2CO_2Me
c		CF_3	**o**		CH_2CO_2Bu-*t*
d	2-pyridyl	Me	**p**		$CH_2CONHMe$
e	2-thienyl	Me	**q**		$CH_2CONHPh$
f		$(CH_2)_2NMe_2$	**r**	Bn	CO_2Me
g	Ph	CO_2Me	**s**		CONHBn
h		CO_2Et	**t**	$(CH_2)_2Ph$	CO_2Me
i		CH_2CO_2Me	**u**		CO_2Et
j		CH_2CO_2Et			
k		CONHBn			
l		$CH_2CONHBn$			

Scheme 2.

Table 1. Reduction of alkyl aryl ketones.[a]

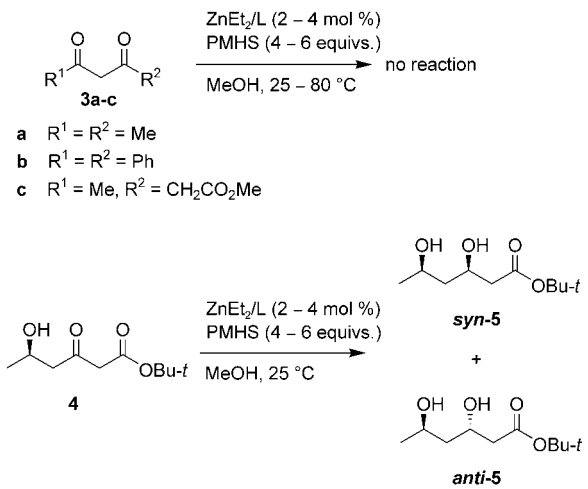
Entry	Substrate	Solvent	PMHS [equivs.]	Time[b] [h]	Yield **2** [mol %], (ee, configuration)[c]
1	**1a**	MeOH/toluene 80:20 (v/v)	2.0	1	>99 (48, S)
2	**1a**	MeOH/toluene 80:20 (v/v)	1.0	1	>99 (48, *S*)
3	**1a**	Toluene	1.2	1	10 (76, *S*)
4	**1b**	MeOH/toluene 80:20 (v/v)	1.0	1	>99 (42, *R*)
5	**1b**	Toluene	1.2	18	43 (62, *R*)
6	**1c**	MeOH/toluene 80:20 (v/v)	1.0	1	>99 (32, *R*)
7	**1c**	toluene	1.2	1	>99 (27, *R*)
8	**1d**	MeOH/toluene 80:20 (v/v)	2.0	18	68 (14, nd)
9	**1d**	toluene	1.2	4	69 (17, nd)
10	**1e**	MeOH/toluene 80:20 (v/v)	2.0	18	72 (55, *R*)
11	**1e**	toluene	1.2	48	>99 (78, *R*)
12	**1f**	MeOH/toluene 80:20 (v/v)	2.0	18	13 (nd)
13	**1f**	toluene	1.2	48	80 (35, nd)

[a] **1**/$ZnEt_2$/diamine = 50/1/1, [**1**] = 0.85 M.
[b] Reaction time not optimized.
[c] Data in parentheses refer to ees obtained using (*R*,*R*)-ebpe (**8a**) as the ligand.

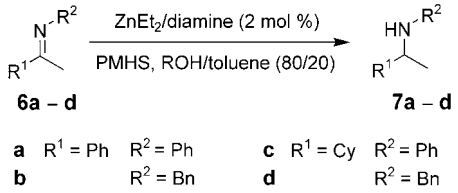
Table 2. Reduction of α- and β-keto esters, and α- and β-keto amides.[a]

Entry	Ketone	Solvent[b]	PMHS [equiv.]	Time[c] [h]	Yield **2** [mol %], (ee, configuration)[d]
14	**1g**	protic	2.0	0.3	>99 (34, *R*)
15	**1g**	protic	1.0	0.5	>99 (34, *R*)[e]
16	**1g**	toluene	1.2	6	>99 (28, *R*)
17	**1h**	protic[f]	2.0	1	>99 (34, *R*)
18	**1h**	toluene	1.2	4	69 (28, *R*)
19	**1m**	protic	2.0	6	>99 (13, *R*)
20	**1r**	protic	2.0	24	68 (21, *S*)
21	**1t**	protic	2.0	24	>99 (25, nd)
22	**1u**	protic[f]	2.0	24	85 (12, nd)
23	**1i**	protic	2.0	18	52 (43, *R*)
24	**1i**	protic	5.0	24	75 (47, *R*)
25	**1i**	protic[g]	2.0	18	62 (−)
26	**1i**	toluene	5.0	18	0 (−)
27	**1j**	protic[f]	2.0	72	24 (38, *R*)
28	**1n**	protic	2.0	6	68 (22, *S*)
29	**1n**	protic	5.0	1	>99 (17, *S*)
30	**1o**	protic	2.0	8	93 (nd)
31	**1o**	protic[h]	2.0	48	42 (nd)
32	**1k**	protic	2.0	1	>99 (15, *R*)[i]
33	**1s**	protic	2.0	18	>99 (15, *R*)
34	**1l**	protic	2.0	18	70 (26, *R*)
35	**1l**	protic	5.0	1	>99 (26, *R*)
36	**1p**	protic	2.0	18	75 (20, nd)
37	**1q**	protic	1.0	18	75 (28, *R*)
38	**1q**	protic	2.0	3	>99 (28, *R*)[j]

[a] **1**/$ZnEt_2$/diamine = 50/1/1, [**1**] = 0.85 M.
[b] Unless otherwise stated, protic solvent: MeOH/toluene = 80/20 (v/v).
[c] Reaction time not optimized.
[d] Data in parentheses refer to ees obtained using (*R*,*R*)-ebpe (**8a**) as ligand.
[e] Isolated yield of spectroscopically pure product = 67%.
[f] Protic solvent: EtOH/toluene = 80/20 (v/v).
[g] protic solvent: MeOH/toluene = 66/33 (v/v).
[h] Protic solvent: *t*-BuOH/toluene = 80/20 (v/v).
[i] Isolated yield of spectroscopically pure product = 98%.
[j] Isolated yield of spectroscopically pure product = 96%.



Scheme 3.



Scheme 4.

Interesting features of the process are its tolerance of several functional groups and the direct formation of the alcohol, so avoiding the additional hydrolytic work-up which is required in toluene and is somehow troublesome for certain substrates. In particular, the catalyst system in methanol is totally chemoselective for the reduction of C=O *vs.* CO_2R functions. This enabled the valuable conversion of aromatic and aliphatic α- and

Table 3. Reduction of δ-hydroxy-β-keto ester **4**.[a]

Entry	Ligand	**4** Configuration	PMHS [equivs.]	Time[b] [h]	Yield **5** [mol %]	de **5** [%], (configuration)
39	dbea	*S*	6.0	24	>99	50 (*syn*)
40	(*R*,*R*)-**8a**	*S*	4.0	4	>99	42 (*syn*)
41	(*R*,*R*)-**8a**	*R*	4.0	4	>99	58 (*syn*)
42	(*R*,*R*)-**8b**	*R*	4.0	3	>99	37 (*syn*)
43	(*R*,*R*)-**8d**	*R*	4.0	4	>99	56 (*syn*)
44	(*R*,*R*)-**10**	*R*	2.0	18	>99	39 (*syn*)
45	(*R*,*R*)-**12**	*R*	2.0	3	>99	50 (*syn*)
46	(*S*,*S*)-**12**	*R*	2.0	18	>99	50 (*syn*)

[a] **4**/$ZnEt_2$/diamine = 25 : 1 : 1, MeOH/toluene = 80/20.
[b] Reaction time not optimized.

Table 4. Reduction of imines.[a]

Entry	Imine	Solvent[c]	PMHS [equivs.]	Time[b] [h]	Yield **7** [mol %], (ee, configuration)[d]
47	**6a**	protic	2.0	48	30 (nd)
48	**6a**	toluene	1.2	18	0 (–)
49	**6b**	protic	2.0	3	55 (4, *R*)
50	**6b**	protic	+2.0	+2	67 (4, *R*)
51	**6c**	protic	2.0	18	65 (0)
52	**6c**	protic	+2.0	+18	>99 (0)
53	**6d**	protic	2.0	1	>99 (<2)

[a] **6**/$ZnEt_2$/diamine = 50/1/1, [**6**] = 0.85 *M*.
[b] Reaction time not optimized.
[c] Protic solvent: MeOH/toluene = 80/20 (v/v).
[d] Data in parentheses refer to ees obtained using (*R*,*R*)-ebpe (**8a**) as ligand.

β-keto esters into the corresponding α- and β-hydroxy esters (Table 2, entries 14–31), while most of these substrates were not reduced and/or the products could not be recovered in significant yields (<10%) using the two-step procedure in toluene. Similarly, α- and β-keto amides were chemoselectively reduced to α- and β-hydroxy amides (Table 2, entries 32–38), which were isolated in a pure state and with high yields by simple treatment of the reaction mixtures with pentane, causing their precipitation, whereas the silicon residues were completely dissolved.

The reduction of 1,3-diketones **3a, b** and β,δ-diketo ester **3c** did not take place even under forced reaction conditions and the starting materials were recovered (Scheme 3). Fast, irreversible deactivation of zinc catalyst species *via* formation of acac-type complexes is suspected in this case.[6b,12] The reduction of functionalized diketones of the type of **3c** is of high interest, since it can provide access to *syn*-β,δ-dihydroxy esters, which are key intermediates in the synthesis of HMG-CoA reductase inhibitors.[13,14] Thus, another route toward these products was attempted, employing the chemo- and diastereoselective reduction of an optically pure δ-hydroxy-β-keto ester, e.g. **4** (Scheme 3).[15] Consistent with the activity of the [$ZnEt_2$/dbea] system towards β-keto esters in methanol, this route proved operative, readily giving the dihydroxy ester **5** with high yield and 50% *syn*-diastereoselectivity (Table 3). However, the use of a chiral diamine instead of the achiral ligand dbea showed only a moderate "matched-mismatched" effect that did not significantly improve the de (*vide infra*).

Finally, various imines (**6a**–**d**), which could not be reduced by the [$ZnEt_2$/dbea] system in toluene, were chemoselectively reduced by the same catalytic system in methanol (Scheme 4, Table 4).

Optimization of the Catalytic System

Nature and Amount of the Hydrosilane, Affecting the Importance of Competitive Processes

The ratio PMHS/substrate proved to be an important parameter for the process optimization. In a few cases, the stoichiometric amount of reducing agent, i.e., 1.0 equiv. of PMHS *vs.* C=O (C=N), was sufficient for a complete reduction (Table 1, entries 2, 4, 6; Table 2, entry 15). However, in most cases, excess PMHS (2–5 equivs.) was necessary, in particular for the enolizable

ketones **1i** and **1 l** (Table 2, entries 24, 35). In the same line, the reduction of some imines, e.g., **6d**, occurred readily using only a slight excess of PMHS, whereas for other imines, e.g., **6c**, the complete reduction required a larger amount (up to 4 equivs.) of PMHS (Table 4, entries 51 and 52).

In the case of β-keto esters and β-keto amides, three explanations can be proposed for the need of extra equivalents of PMHS and limited conversion. (i) The formation of an [acac-Zn] complex may consume part of the catalyst, as suggested in the case of β-diketones (*vide supra*). However, we have observed that, after a first stop of the conversion, the addition of two extra equivalents of PMHS always enabled the reduction to go to completion; this indicates that the precursor of the active catalytic species was still active and the reaction did not proceed because PMHS was lacking. Discarding the hypothesis of catalyst deactivation by β-keto acid derivatives is also suggested by the observation that the reduction of the α-keto ester **1g** proceeded readily in the presence of an equimolar amount of **1i**. (ii) The catalyst system may also be operative in the dehydrogenative silylation of the ketone (*via* the enol) to give a silyl enol ether (not observed by NMR) that would hydrolyze back in methanol to the enol/ketone (and polymeric methoxysilyl species), hence consuming PMHS "inefficiently"; however, in some additional experiments, preliminarily prepared silyl enol ethers, e.g., $PhCH(OSiMe_3)CH_3$, did not hydrolyze readily under the catalytic conditions in methanol, so casting doubt on this hypothesis. (iii) More likely, since the [Zn-diamine] system is also active in the dehydrogenative coupling of PMHS and MeOH (Scheme 1), the efficiency of the reduction process depends on the relative kinetics of the C=O (C=N) reduction *vs.* MeOH silylation. In fact, we have observed that lowering the MeOH/toluene ratio enabled to improve the conversion of **1i** with two equivalents of PMHS (Table 2, entry 25).

Other silanes could be equally used in place of PMHS. The reduction of acetophenone (**1a**) and methyl phenylglyoxylate (**1g**) proceeded rapidly when monomeric hydrosilanes such as $PhSiH_3$, Ph_2SiH_2, Et_2SiH_2 were employed.[16] Thus, no acceleration effect linked to the use of polymeric PMHS was observed.[3d] However, the availability, low price and low toxicity of PMHS, as compared to the monomeric silanes, largely justify its use as the reductive agent in this alternative procedure.

Nature and Amount of Metal Catalyst Precursor

A screening of various catalyst precursors for the reduction of acetophenone (**1a**) in a protic solvent disclosed $Zn^{(II)}$ as the preferred metal, but also $Co^{(II)}$ showed a comparable activity. Conversely, $Mn^{(II)}$, $Fe^{(II)}$ and $Cu^{(II)}$ seemed inappropriate, as no or poor conversions were observed in the same conditions (Table 5, entries 54–59). Zn alkoxides such as EtZnOMe and $Zn(OMe)_2$[17] proved as valuable as $ZnEt_2$ and other dialkylzincs for the reduction of **1a**, providing the same activity and

Table 5. Screening of metal catalyst precursors for hydrosilylation with PMHS in methanol.[a]

Entry	Catalytic precursor	Ketone	Time[b] [h]	Yield **2** [mol %] (ee, configuration)[c]
54	$Co(2\text{-}EH)_2$/vitride	**1g**	2	>99 (38, *R*)
55	$Cu(OTf)_2$	**1g**	2	0 (–)
56	$Mn(2\text{-}EH)_2$/vitride	**1g**	2	14 (nd)
57	$Fe(2\text{-}EH)_2$	**1g**	2	22 (nd)
58	$Zn(2\text{-}EH)_2$/vitride	**1g**	1	>99 (28, *R*)
59	$ZnEt_2$	**1g**	1	>99 (30, *R*)
60	$Zn(i\text{-}Pr)_2$	**1g**	1	>99 (33, *R*)
61	$ZnPh_2$	**1g**	1	>99 (31, *R*)
62	$Zn(2\text{-}EH)_2$/vitride	**1a**	2	50 (40, *S*)
63	$ZnEt_2$	**1a**	2	>99 (48, *S*)
64	$Zn(i\text{-}Pr)_2$	**1a**	2	>99 (48, *S*)
65	$ZnPh_2$	**1a**	1	>99 (48, *S*)
66	EtZnOMe	**1a**	1	>99 (48, *S*)
67	$Zn(OMe)_2$	**1a**	1	>99 (48, *S*)
68	$Zn(OMe)_2$[d]	**1a**	1	37 (47, *S*)
		1a	72	82 (49, *S*)
69	$Zn(OH)_2$	**1a**	1	15 (45, *S*)
		1a	72	>99 (48, *S*)

[a] Unless otherwise stated, **1**/[M]/dbea = 50 : 1 : 1, [**1**] = 0.85 *M*, PMHS = 2.0 equivs., MeOH/toluene = 80/20.
[b] Reaction time not optimized.
[c] Data into parentheses refer to ees obtained using (*R*,*R*)-ebpe (**8a**) as the ligand.
[d] **1a**/$Zn(OMe)_2$/(*R*,*R*)-ebpe (**8a**) = 500/1/1.

enantioselectivity (*vide infra*, Table 5, entries 66 and 67). It should be underlined that the strict exclusion of water in the [$ZnEt_2$/diamine]/MeOH system, although enhancing the reaction rate, was not a requisite: as a matter of fact, the reduction of **1a** still proceeded readily when 5 vol % H_2O was added to the solution (85% conversion after 1 h). A most interesting consequence of this observation is the possibility to use the cheap zinc hydroxide[17] to promote the reduction, although at the expense of the rate (entry 69). With this regard, it is known that in alcohol solution the hydroxy-Zn species (less active or inactive) are in equilibrium with alkoxy-Zn species.[18]

Although experiments were routinely carried out using 2.0 mol % of $ZnEt_2$ as the catalyst precursor, the reduction of methyl phenylglyoxylate (**1g**) using as low as 0.5 mol % of [Zn/dbea] was complete within 75 min. $ZnEt_2$, which has no catalytic activity alone, may also act as a scavenger of catalyst poisons;[4] in fact, a sub-stoichiometric amount of dbea, as low as 0.2 mol %, sufficed to activate 1 mol % of $ZnEt_2$ and a total conversion of **1g** was obtained within 2 h. In these conditions, the TOF was relatively high: 340 h^{-1} at 85% conversion (Figure 1).

Nature of the Diamine Ligand – Asymmetric Reduction

In order to evaluate the enantiodiscriminating properties potential of the catalytic system, several chiral diamines were tested in association with $ZnEt_2$ (Figure 2). Unfortunately, the reductions in the protic solvent often led to alcohols with lower enantiomeric excesses (ees) than those obtained by the aforementioned two-step procedure in toluene (Tables 1 and 2).[5,6] For instance, using *N*,*N*′-ethylenebis(1-phenylethylamine) (ebpe, **8a**), acetophenone (**1a**) was reduced to 1-phenylethanol (**2a**) with 48% ee, while 76% ee was obtained in toluene (Table 1, entries 1 and 3). Other ketones, e.g., trifluoroacetophenone (**1c**) and methyl phenylglyoxylate (**1g**), were reduced with similar enantioselectivities in toluene and in the presence of methanol (Table 1, entries 6 and 7; Table 2, entries 14 and 16). Particularly, the reduction of **1g** proceeded very rapidly even with the sterically bulky ligands **11a**–**c**, and did not seem affected by the chloride function present in the ligand framework of **8c** (Table 6, entry 72). As for the reductions in toluene, the ligands bearing an ethylene bridge in their framework usually led to better results than the propylene-bridged ligand **9** (entry 74). Nevertheless, variation of either the ligand/Zn ratio or the ligand structure did not improve significantly the ees in the reduction of **1g**. This very moderate impact of a chiral diamine ligand on the stereoselectivity is also consistent with the scarce influence on the diastereoselectivity of the reduction of the chiral δ-hydroxy-β-keto ester **4** (*vide supra*, Scheme 3, Table 3).

Nature and Amount of the Alcohol

The alcohol used as co-solvent plays a major role in the reaction. Even a small amount of methanol was sufficient to induce simultaneously a better activity and a significant change in the enantioselectivity. Thus, using only 2.8 equivalents of MeOH *vs.* acetophenone (**1a**), this was reduced with 40% conversion and 56% ee after 1 h; this result should be compared with the 10% conversion and 76% ee obtained in toluene (Table 7, entries 79–81). Using more than 10 equivalents of MeOH, no change in the catalyst performance occurred, and similar reactivity and selectivities were observed when the reactions were conducted in pure MeOH. Methanol proved to be the best alcohol, leading in most cases to better chemoselectivity and higher reaction rate with re-

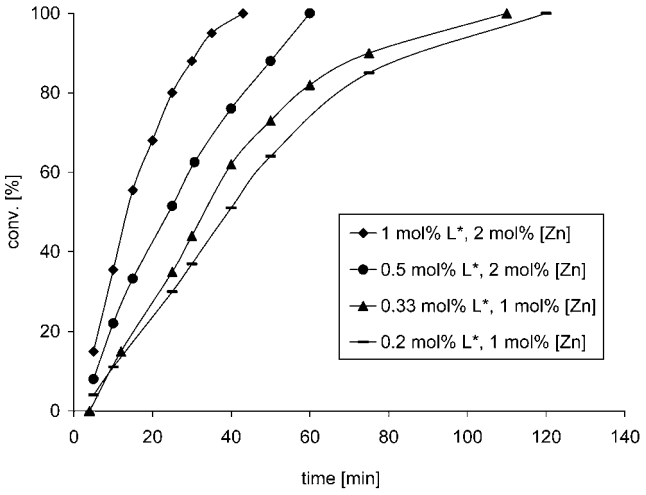


Figure 1. Reduction of **1g** in MeOH/toluene 80:20: L* = dbea, [**1g**] = 0.85 *M*, PMHS = 2.0 equivalents.

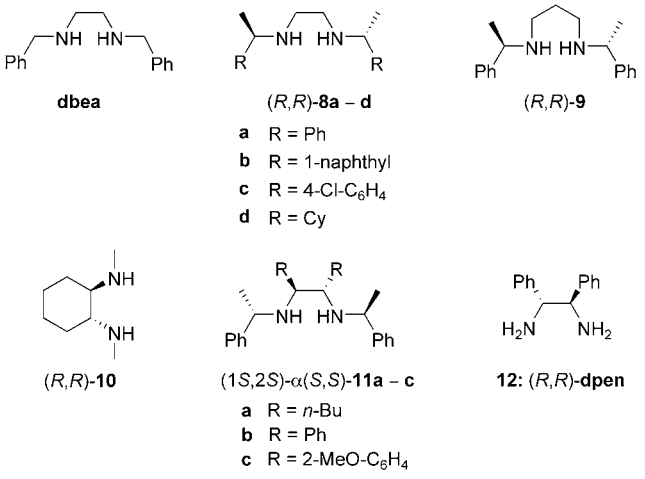


Figure 2. Diamine ligands used in this study.

Table 6. Reduction of **1g** using various diamine ligands.[a]

Entry	Ligand	Time[b] [h]	Yield **2g** [mol %]	ee **2g** of [%], (configuration)
70	(*R*,*R*)-**8a**	0.3	>99	34 (*R*)
71	(*R*,*R*)-**8b**	1	>99	22 (*R*)
72	(*R*,*R*)-**8c**	1	>99	28 (*R*)
73	(*R*,*R*)-**8d**	1	>99	2 (*S*)
74	(*R*,*R*)-**9**	1	>99	9 (*R*)
75	(*R*,*R*)-**10**	4	>99	30 (*R*)
76	(1*S*,2*S*)α(*S*,*S*)-**11a**	1	>99	28 (*S*)
77	(1*S*,2*S*)α(*S*,*S*)-**11b**	2	>99	13 (*S*)
78	(1*S*,2*S*)α(*S*,*S*)-**11c**	18	>99	21 (*S*)

[a] **1 g**/$ZnEt_2$/L* = 50/1/1, [**1 g**] = 0.85 *M*, PMHS = 2.0 equivs., MeOH/toluene = 80/20.
[b] Reaction time not optimized.

Table 7. Influence of the MeOH/toluene ratio in the enantioselective reduction of ketones using (*R*,*R*)-ebpe (**8a**).[a]

Entry	Ketone	MeOH [%] (equivs. *vs.* C=O)	Time[b] [h]	Yield **2** [mol %]	ee of **2** [%], (configuration)
79	**1a**	0 (0)	1	10	76 (*S*)
80	**1a**	10 (2.8)	1	42	56 (*S*)
81	**1a**	80 (18)	1	>99	48 (*S*)
82	**1a**	100 (22)	1	>99	48 (*S*)
83	**1g**	0 (0)	4	69	28 (*R*)
84	**1g**	10 (2.8)	1	40	35 (*R*)
85	**1g**	80 (18)	1	>99	34 (*R*)

[a] **1**/$ZnEt_2$/**8a** = 50/1/1, PMHS = 2.0 equivs.
[b] Reaction time not optimized.

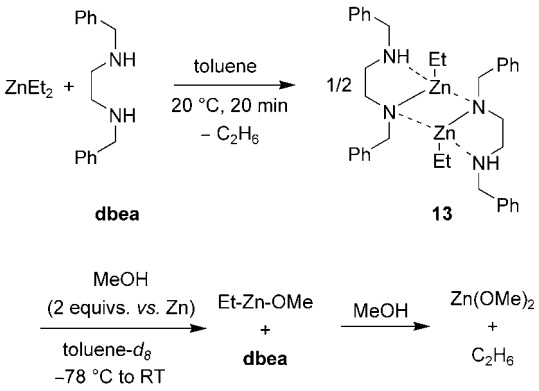
spect to ethanol or even more encumbered alcohols such as *tert*-butyl alcohol (Table 2, entries 27, 30, 31).[10] The reductions of ketones containing ethoxycarbonyl moieties in MeOH were plagued by partial transesterification of that function, but this side reaction was not observed for *tert*-butoxycarbonyl groups.[19] Consequently, ethyl ester-containing substrates are preferably reduced in EtOH, although with slightly lower activity and chemoselectivity. Alternatively, one can work in MeOH over a longer reaction time, so recovering the methyl esters by a complete transesterification.

Mechanistic Investigations

Some experimental observations should be taken into account in order to understand the mechanism of the catalytic reduction. First of all, the great influence of the solvent on the performances of [Zn-diamine] catalyst combinations suggests a role of methanol either in the catalytic cycle and/or in modifying the nature of the catalytic species, probably through the formation of methoxy-Zn species. This hypothesis is supported by the ready alcoholysis of dialkylzinc, ZnR_2, species in methanol and lack of influence of such ZnR_2 precursors in catalysis. In fact, reductions of various substrates proceeded quantitatively within 1 h whatever the R substituent; also, the absolute configurations of the products, as well as the enantioselectivity of the reductions, were not modified (Table 5, entries 59–61, 63–65). Moreover, pre-formation of a [Zn-diamine] species is not a prerequisite to obtain an active catalyst; as a matter of fact, the conversion, reduction rate and enantioselectivity were equal whatever the order of introduction of diamine, PMHS and substrate. All these elements demonstrate that the [Zn-diamine]-MeOH system is not the same as the corresponding toluene system, and that different mechanisms and/or active species are operative in these processes.

Synthesis of Model Zinc Complexes

Because of the high activity of catalyst systems based on [$Zn(OMe)_2$/diamine] combinations (Table 5, entries 67 and 68), we considered the [(diamine)$Zn(OMe)_2$] complexes as probable intermediates/precursors of the active catalytic species. Monomeric [(diamine)$Zn(OR)_2$] compounds have been scarcely reported in the literature, we are only aware of a bipyridine-phenolate-zinc complex.[20,21] In spite of many efforts, we could not isolate species of this type, nor observe them by variable



Scheme 5.

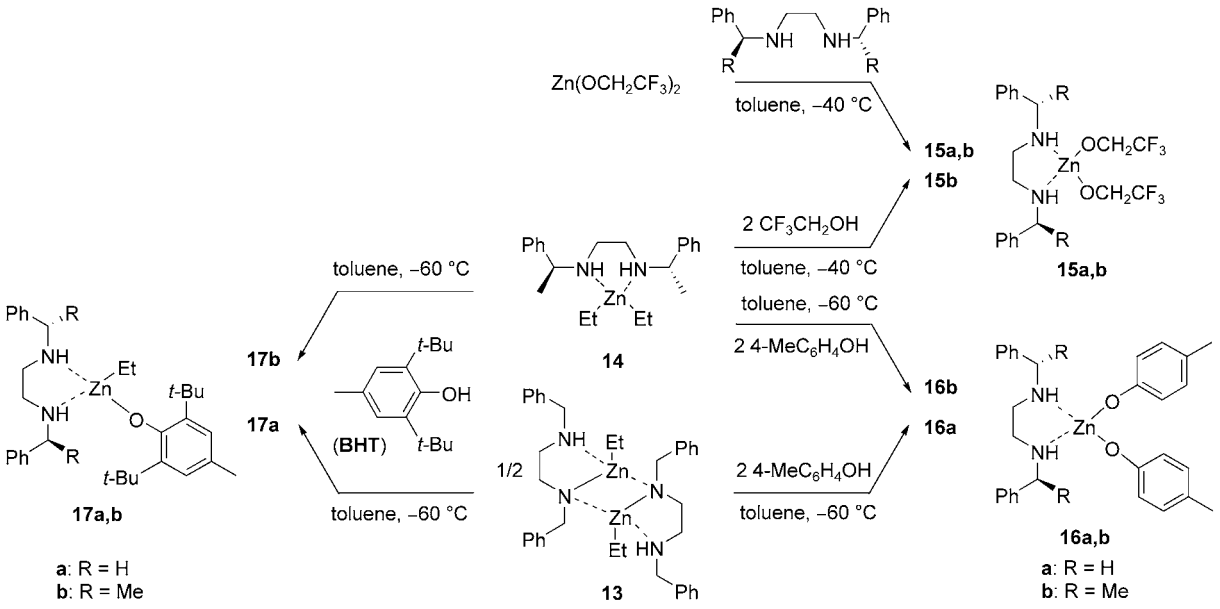
temperature NMR spectroscopy in the usually performed catalytic reactions. Careful addition of MeOH (2–10 equivs.; −60 to 5 °C) to the dimeric alkyl(amino-μ-amido) complex $[EtZnNBn(C_2H_4)NHBn]_2$ [**13**], which we previously isolated from the $[ZnEt_2$-dbea] combination in toluene,[10] resulted in the rapid decoordination of the diamine and concomitant precipitation of $Zn(OMe)_2$. An NMR monitoring showed that in this case the reaction was proceeding through the intermediacy of EtZn(OMe) species and was complete within 20 min at 5 °C (Scheme 5). It was not possible either to coordinate a 1,2-diamine [dbea, ebpe (**8a**)] onto Zn starting from $Zn(OMe)_2$ or even EtZn(OMe). The difficulty in isolating coordination complexes from $Zn(OMe)_2$ is possibly due to the strong tendency of the latter material to form insoluble aggregates,[17] as evidenced by its poor solubility in methanol and methanol/toluene mixtures.[22]

To obtain models of these potential intermediates, we envisioned that a more electron-withdrawing alkoxy group such as CF_3CH_2O or an aryloxy group should disfavor the aggregation of the corresponding ZnOR/ZnOAr species, eventually resulting in a higher tendency to form stable $[(diamine)Zn(OR)_2]$ complexes. In fact, this strategy led us to the effective synthesis of the new species **15a**,**b** and **16a**,**b** from both the achiral diamine dbea and the chiral one ebpe (**8a**), by addition of the diamine to the zinc dialkoxide and/or careful alcoholysis of the appropriate EtZn complexes **13**/**14** (Scheme 6). By using the bulky 2,6-di-*tert*-butyl-*p*-cresol (BHT) for the alcoholysis of the EtZn precursors, the reaction selectively produced the heteroleptic mono-aryloxide complexes **17a**,**b** (Scheme 6). It is noteworthy that **17b** did not react further with an excess of BHT, even during several hours at 50 °C. The complexes **15**–**17** were characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy.[23]

Catalytic and Stoichiometric Reactivity of the Model Zinc Complexes

All the isolated (chiral) complexes, when tested in the hydrosilylation of acetophenone (**1a**) with PMHS in methanol, proved to be as effective and enantioselective catalyst precursors as the combinations produced *in situ* from methanol, $ZnEt_2$ and the corresponding diamine ligand. This indicated that the same catalytic species were operative in the two systems.

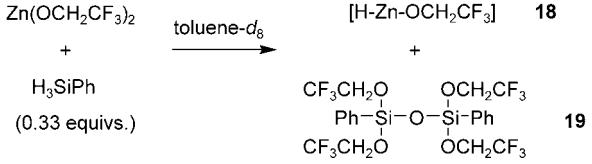
Since the complexes **15**–**17** appeared to be valuable models for mechanistic studies, we became interested in evaluating their reactivity towards methanol and, in



Scheme 6. Model complexes prepared for catalytic studies.

particular, verifying if the alkoxide/aryloxide ligands can be displaced by a methoxy group. As a matter of fact, the mixed alkyl-aryloxide complex **17a** reacted rapidly with one equivalent of methanol to give a mixture of complexes,[24] whereas the bis(alkoxy) complexes **15a** and **16a** proved totally unreactive, even upon prolonged heating at 50 °C with an excess of methanol.

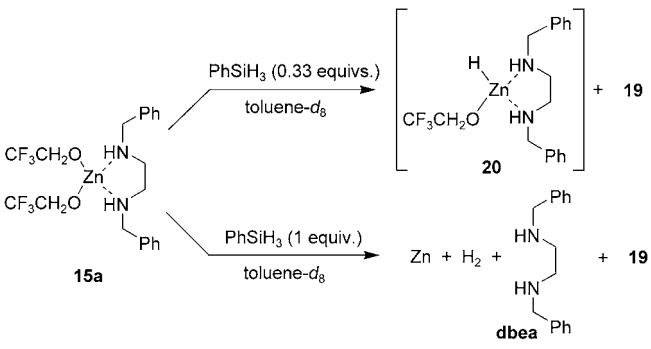
The reactivity of zinc dialkoxides $Zn(OMe)_2$ and $Zn(OCH_2CF_3)_2$ and the corresponding dbea complexes **15a**,**b** towards hydrosilanes was next investigated. The monomeric silanes $PhSiH_3$, Ph_3SiH and $HSi(OEt)_3$, rather than PMHS, were chosen for these studies in order to facilitate the spectroscopic studies (NMR, IR) and the formation of isolable complexes. All the bis(alkoxide) complexes appeared very reactive towards hydride donors under gentle conditions (-40 to $+25$ °C; toluene, pentane or methanol as solvent), but the resulting zinc complexes were found to be quite sensitive and it was difficult to isolate them in a pure form, hampering in most cases their unambiguous authentication. Two relevant examples are as follows: The reaction of $Zn(OCH_2CF_3)_2$ with 0.33 equivs. of $PhSiH_3$, i.e., 1 equiv. of Si–H *vs.* Zn, in toluene or pentane led to two products, a zinc complex **18** and a siloxane **19**, isolated in 47% and 38% yields, respectively (Scheme 7). Complex **18** is insoluble in common aprotic NMR solvents (THF-d_8, toluene-d_8, dichloromethane-d_2) and was tentatively assigned to the mixed hydrido-alkoxy complex of empirical formula "H–Zn–OCH_2CF_3"[25] on the basis of elemental analysis, an hydrolysis experiment and FTIR; the latter featured a broad band at 1600–1500 cm^{-1} that can be attributed to ν(Zn–H).[25] The siloxane **19** was recovered from the supernatant solution and characterized by ^1H, ^{13}C, ^{19}F NMR and ES-MS. The reaction of $PhSiH_3$ with [(dbea)$Zn(OCH_2CF_3)_2$] (**15a**) under the same conditions only gave toluene-soluble products. ^1H, ^{13}C and ^{19}F NMR spectroscopy indicated the formation of the same siloxane **19** (ES-MS) and the conversion of **15a** to another complex **20** having a coordinated dbea ligand (Scheme 8). The ^1H and ^{13}C resonances of **20** are very close to those of **15a**: particularly, a low intensity signal at $\delta = 4.50$, emerging from a broad signal which does not sharpen upon cooling or heating, may indicate the formation of a hydride species [(dbea)Zn(H)(OCH_2CF_3)] (Scheme 8). It is known that ^1H NMR resonances for Zn–H in benzene-d_6 appear at *ca.* $\delta =$ 4.4–4.6 ppm, but in some instances could not be observed.[25] However, **20** could not be isolated in a pure form. Also, when the reaction of **15a** was investigated by using a slight excess of $PhSiH_3$ (1 equiv. *vs.* Zn, i.e., 3 equivs. of Si–H), the formation of a black deposit, presumably zinc dust, and evolution of gas (H_2) were immediately observed, and the diamine dbea and siloxane **19** were isolated.



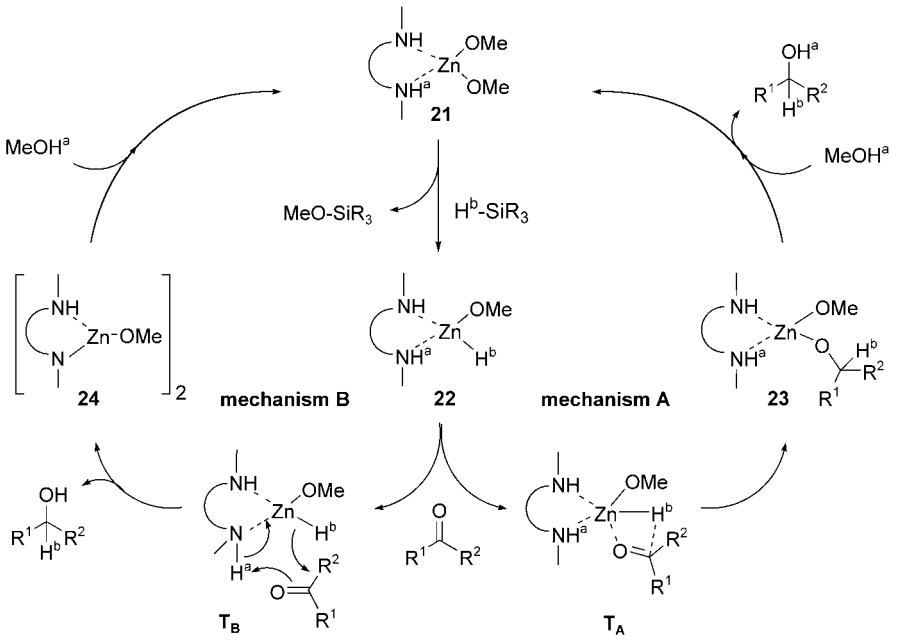
Scheme 7.

Possible Mechanisms for the [Zn-Diamine]-Catalyzed Hydrosilylation in Methanol

Since the methanolysis rates of some isolated silyl ethers were very slow under our reaction conditions and do not account for the high activity observed in catalytic reductions (*vide supra*), pathways similar to those proposed for the reduction of ketones by PMHS in toluene[4b] can be, in principle, discarded. We thus propose two different mechanisms, in both of which the role of PMHS is to generate a [(diamine)Zn(H)(OR)] species **22** (Scheme 9). This putative hydride, whose formation in stoichiometric reactions of [(diamine)$Zn(OR)_2$] precursors with monomeric hydrosilanes could not be demonstrated (*vide supra*), might act as the reducing agent of the carbonyl group to give **23** through the four-membered transition state $\mathbf{T_A}$; subsequent methanolysis by MeOH would liberate the corresponding alcohol and regenerate the initial [(diamine)$Zn(OR)_2$] precursor **21** (mechanism A). Such a mechanism is similar to that assumed by Buchwald et al. for the reduction of ketones using a Ti catalyst in the presence of MeOH.[3i] Alternatively, from the same [(diamine)Zn(H)(OR)] species **22**, a concerted hydride transfer to the carbonyl group can be considered, through a six-membered intermediate/transition state $\mathbf{T_B}$ which features an NH···O=C hydrogen bond,[26] and leads directly to the alcohol (mechanism B); then methanolysis of the [(amide-amine)-Zn(OMe)] species **23** would regenerate the [(diamine)$Zn(OR)_2$] precursor **21**. The neat drop in activity of catalyst systems based on tertiary diamines (< 20% conversion of **1a** with 2 equivs. of PMHS) can be explained by the at least partial occurrence of such a mechanism.



Scheme 8.



Scheme 9. Possible mechanisms for the reduction of ketones in methanol.

Conclusion

We have described a new effective catalyst system, which is generated from simple zinc precursors, commercially available secondary diamines and PMHS, and allows the direct reduction of a large variety of ketones and imines in methanol-toluene mixtures. In contrast with previous zinc-based hydrosilylation systems, this procedure is operative in a protic, neutral medium and the active species appears robust, even in the presence of significant amounts of water. Moreover, various functional groups are tolerated and the reactions proceed fast under mild conditions. These features make this reduction procedure a valuable tool for organic chemists. Preliminary mechanistic investigations demonstrate that this catalyst system differs from the corresponding zinc-diamine systems in toluene, and indicate a role of the alcohol co-solvent in the *in situ* production of the active catalyst. Low to moderate enantioselectivities are obtained in typical substrate reductions using optically pure 1,2-diamines. A better definition of the active catalytic species, which is presumably a hydrido-alkoxy-zinc complex, shall hopefully contribute in the near future to the choice of better chiral ligands for the asymmetric version of this reaction.

Experimental Section

General

Catalytic reactions and complexes syntheses were performed under nitrogen using standard Schlenk techniques or in a glove-box. Methanol was dried over Mg, other alcohols were dried over CaH_2, freshly distilled and degassed by freeze-thaw-vacuum cycles before use. Toluene and pentane were freshly distilled from Na/K amalgam and degassed before use. Ketones were distilled over CaH_2 and degassed before use. PMHS (Aldrich) was degassed before use. $ZnEt_2$ (1.1 M solution in toluene) was purchased from Aldrich and used as received. 2-Ethyl hexanoate complexes were kindly provided by Sicanor SA. $Zn(OMe)_2$, $Zn(OCH_2CF_3)_2$, $Zn(OH)_2$ were prepared according to known procedures.[27] *N,N′*-Dibenzylethylenediamine (dbea) was purchased from Aldrich and distilled from KOH before use. Diamines **8a–d**,[5] **9**,[5] and **11a–c**[6b, c] were prepared following reported procedures and strictly purified by distillation or column chromatography and subsequent recrystallization. Diamine **10** was kindly provided by Prof. A. Alexakis (University of Geneva). Diamine **12** was purchased from Aldrich and used as received. Complex **14** was prepared as described in the literature.[5]

^1H, ^{13}C and ^{19}F NMR spectra were recorded on AC-200 and AC-300 Bruker spectrometers at 293 K unless otherwise stated; ^1H and ^{13}C chemical shifts are reported in ppm downfield from $SiMe_4$ and were determined by reference to the residual solvent peaks; ^{19}F NMR spectra were referenced externally to neat $BF_3 \cdot Et_2O$; all coupling constants are reported in Hz. The ees of the alcohol products were determined by GLC or polarimetry analysis and their absolute configuration determined by comparison with authentic samples. GLC analyses were performed on Chrompack CP 9001 apparatus equipped with a flame ionization detector and a BPX5 (25 m × 0.32 mm, SGE) or a chiral Chirasil-DEX CB (25 m × 0.25 mm, Chrompack) column. 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 FTIR spectrophotometer in a KBr cell and are expressed by wave number (cm^{-1}). Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory at the Institute of Chemistry of

Rennes and are the average of two independent determinations.

Zn-Diamine-Catalyzed Asymmetric Hydrosilylation of Acetophenone by PMHS; General Procedure (Table 1, entry 1)

To a solution of (*S*,*S*)-**8a** (14.7 mg, 0.055 mmol) in freshly distilled toluene (0.5 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), PMHS (0.36 mL, 5.50 mmol, 2 equivs.) and finally methanol (2.5 mL). The solution was stirred at room temperature and the reaction was monitored 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 concentrated under vacuum and subjected either to column chromatography, yielding spectroscopically pure 1-phenylethanol in more than 95% isolated yield.

Reduction of β-Keto Amide 1q and Isolation of the Pure Corresponding β-Hydroxy Amide

To a solution of dbea (54.2 mg, 0.22 mmol) in freshly distilled toluene (2.0 mL), were successively added $ZnEt_2$ (0.20 mL of a 1.1 M solution in toluene, 0.22 mmol), a solution of **1q** (2.00 g, 11.3 mmol) in MeOH (12.0 mL), and finally PMHS (1.46 mL, 22.6 mmol). The resulting solution was stirred with a magnetic stir bar and the reaction was monitored by GLC. After completion of the reaction, volatiles were removed under vacuum to give a colorless oil which was triturated with pentane (10 mL). The β-hydroxy amide **2q** precipitated and was separated off from the liquid phase containing the silicon residues, washed with a minimal amount of pentane, and dried under vacuum to leave a spectroscopically pure white powder; yield: 1.94 g (96%).

Reduction of Functionalized Ketones and Recovery of Soluble Alcohols

Other functionalized ketones were reduced as described above. To isolate the final alcohol product, the solution was concentrated under vacuum leaving a colorless pasty residue. The latter was either subjected to distillation (for light alcohols such **2a**–**c**, **2m**, **2n**) or (for higher alcohols) washed with a minimal amount (*ca.* 1 mL) of cold pentane to remove most of silicon products and then subjected to a column chromatography to recover the alcohol product.

$[ZnEt(dbea)]_2$ (13)

Diethylzinc (19.3 mL of a 1.1 M solution in toluene, 21.2 mmol) was added dropwise to a solution of dbea (5.00 mL, 21.2 mmol) in toluene (5 mL) cooled at −20 °C. The resulting suspension was stirred with a magnetic stir bar for 20 min at −20 °C, and then for 1 h at 25 °C. Volatiles were removed under vacuum to give a yellow oil which was triturated with pentane (10 mL). The resulting precipitate was separated off from the liquid phase, washed with pentane (2 × 10 mL) and dried under vacuum to give **13** as a white powder; yield: 5.05 g (71%). Colorless crystals of **13** suitable for X-ray diffraction were grown from a toluene/pentane (1:1) solution at −30 °C.[10] ^{1}H NMR (toluene-d_8, 323 K): δ = 7.20 (d, *J* = 7.9 Hz, 4H, arom.), 7.30–6.90 (m, 16H, arom.), 6.76–6.72 (m, 4H, arom.), 3.56 (d, *J* = 6.5 Hz, 2H, NCH*H*-Ph), 3.44 (d, *J* = 7.0 Hz, 4H, NHCH_2Ph), 2.75 (m, 4H, NC*H*HPh + C*H*HNBn), 2.55 (m, 6H, CH_2NHBn + CH*H*NBn), 1.64 (t, *J* = 7.9 Hz, 6H, CH_2CH_3), 1.42 (m, 2H, N*H*), 0.48 (q, *J* = 7.9 Hz, 4H, CH_2CH$_3$); ^{1}H NMR (toluene-d_8, 298 K): δ = 7.44 (d, *J* = 7.5 Hz, 4H, arom.), 7.23 (t, *J* = 7.5 Hz, 4H, arom.), 7.10–6.90 (m, 8H, arom.), 6.70 (m, 4H, arom.), 4.20–4.0 (br s, 4H), 3.60–3.20 (bs, 4H), 3.0–2.30 (br s, 8H), 1.69 (t, *J* = 8.1 Hz, 6H, CH_2CH_3), 1.40 (br s, 2H, N*H*), 0.52 (q, *J* = 8.1 Hz, 4H, CH_2CH$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 298 K): δ = 144.4 (*C* arom.), 128.8 (*C* arom.), 128.2 (*C* arom.), 126.6 (*C* arom.), 60.9 (N*C*H$_2$-Ph), 53.2, 49.2 (*C*H$_2$-NH-Bn), 15.1 (CH_2CH_3), −1.1 (*C*H$_2$CH$_3$); ^{1}H NMR (toluene-d_8, 253 K, major series of signals): δ = 7.52 (d, *J* = 7.3 Hz, 4H, arom.), 7.29 (t, *J* = 7.6 Hz, 4H, arom.), 7.20–7.0 (m, 8H, arom.), 6.60 (m, 4H, arom.), 4.20 (d, *J* = 14.9 Hz, 2H, NCH*H*Ph), 3.98 (d, *J* = 14.9 Hz, 2H, NC*H*HPh), 3.65 (dd, *J* = 4.4 and 13.65 Hz, 2H, NHCH*H*Ph), 3.05 (dd, *J* = 3.7 and 13.65 Hz, 2H, NHC*H*HPh), 2.91 (d, *J* = 7.3 Hz, 2H, C*H*HNBn), 2.48 (m, 4H, BnNHCH*H*, 2.20 (m, 2H, BnNHC*H*H), 1.87 (t, *J* = 8.1 Hz, 6H, CH_2CH_3), 0.63 (q, *J* = 8.1 Hz, 4H, CH_2CH$_3$); (minor series of signals): δ = 7.50 (d, *J* = 7.6 Hz, 4H arom.), 7.43 (d, *J* = 7.6 Hz, 4H, arom.), 7.35 (q, *J* = 7.3 Hz), 6.50 (d, *J* = 6.8 Hz, 4H, arom.), 4.68 (d, *J* = 16.1 Hz, 2H, NCH*H*Ph), 4.33 (d, *J* = 16.3 Hz, 2H, NC*H*HPh), 4.08 (s, 1H), 3.86 (d, *J* = 15.4 Hz, 2H), 3.73 (s, 1H), 3.52 (d, *J* = 6.3 Hz), 0.80–0.70 (m, 6H, CH_2CH$_3$); ^{13}C{^{1}H} 0NMR (toluene-d_8, 253 K; major series of signals): δ = 144.0 (*C* arom.), 128.8 (*C* arom.), 128.1 (*C* arom.), 126.5 (*C* arom.), 60.6 (N*C*H$_2$Ph), 51.9 (*C*H$_2$NBn), 51.2 (NH*C*H$_2$Ph), 48.3 (*C*H$_2$NHBn), 15.4 (CH_2CH_3), −1.1 (*C*H$_2$CH$_3$); (minor series of signals): δ = 143.8 (*C* arom.), 143.6 (*C* arom.), 60.2 (N*C*H$_2$Ph), 54.4, 54.0, 53.7, 50.9, 50.5, 48.9 (*C*H$_2$NHBn), 15.6 (CH_2CH_3), 15.3 (CH_2CH_3); anal. calcd. for $C_{36}H_{48}N_4Zn_2$ (667.52): C 64.77, H 7.25, N 8.39; found: C 64.28, H 7.41, N 8.67.

$[Zn(dbea)(OCH_2CF_3)_2]$ (15a)

A solution of dbea (0.45 mL, 1.89 mmol) in toluene (15 mL) was added dropwise to a suspension of $Zn(OCH_2CF_3)_2$ (500 mg, 1.89 mmol) in toluene (15 mL) cooled at −60 °C. The resulting suspension was stirred with a magnetic stir bar for 30 min at −40 °C, and then for 20 min at 25 °C. Volatiles were removed under vacuum to give a white solid which was triturated with pentane (10 mL). The resulting precipitate was separated off from the liquid phase, washed with pentane (2 × 5 mL) and dried under vacuum to give **15a** as a white powder; yield: 474 mg (49%); ^{1}H NMR (toluene-d_8): δ = 7.30–7.0 (m, 10H, arom.), 4.10 (br s, 4H, OCH_2CF$_3$), 3.60 (s, 4H, NHCH_2Ph), 2.33 (s, 4H, CH_2NHBn); ^{1}H NMR (toluene-d_8, 343 K): δ = 7.40–7.0 (m, 10H, arom.), 4.09 (q, *J* = 9.2 Hz, 4H, OCH_2CF$_3$), 3.62 (s, 4H, NHCH_2Ph), 2.39 (s, 4H, CH_2NHBn); ^{13}C{^{1}H} NMR (toluene-d_8): δ = 137.4 (*C* arom.), 128.8 (*C* arom.), 128.2 (*C* arom.), 126.6 (*C* arom.), 129.8 (q, $^1J_{C,F}$ = 281.5 Hz, *C*F$_3$), 65.3 (q, $^2J_{C,F}$ = 32.9 Hz, *C*H$_2$CF$_3$), 53.7

(NHCH_2Ph), 47.4 (CH_2NHBn); ^{19}F{^{1}H} NMR (toluene-d_8): δ = −72.40; anal. calcd. for $C_{20}H_{24}N_2O_2F_6Zn$ (503.79): C 47.68, H 4.80, N 5.56; found: C 47.60, H 4.60, N 5.19.

[Zn((*S*,*S*)-ebpe)(OCH$_2$CF$_3$)$_2$] (15b)

The same procedure as for complex **15a** was used, starting from diamine (*S*,*S*)-ebpe (**8a**) (153 mg, 0.57 mmol). Removing of the volatiles and triturating with pentane gives **15b** as a colorless oil; yield: 120 mg (39%); ^{1}H NMR (toluene-d_8): δ = 7.30–7.0 (m, 10H, arom.), 4.30 (br s, 4H, OCH_2CF$_3$), 3.65 [br s, 1H, NHC*H*(Me)Ph], 3.48 [br s, 1H, NHC*H*(Me)Ph], 2.36 (s, 2H, CH_2NH), 2.10 (br s, 2H, CH_2NH), 1.48 (s, 3H, CH_3), 1.18 (m, 3H, CH_3); ^{1}H NMR (toluene-d_8, 353 K): δ = 7.30–7.0 (m, 10H, arom.), 4.25 (q, *J* = 9.2 Hz, 4H, OCH_2CF$_3$), 3.61 [br s, 2H, NHC*H*(Me)Ph], 2.30 (br s, 4H, CH_2NH), 1.33 (br s, 6H, CH_3); ^{13}C{^{1}H} NMR (toluene-d_8): δ = 146.9 (*C* arom.), 141.5 (*C* arom.), 129.3 (*C* arom.), 128.4 (*C* arom.), 127.5 (*C* arom.), 126.9 (*C* arom.), 65.4 (q, $^2J_{C,F}$ = 76.3 Hz, *C*H$_2$CF$_3$), 58.8 [NH*C*H(Me)Ph], 51.4 [NH*C*H(Me)Ph], 47.9 (*C*H$_2$NH), 46.2 (*C*H$_2$NH), 24.9 (*C*H$_3$), 22.6 (*C*H$_3$); CF$_3$ signals overlapped with signals of aromatic carbons and were not unambiguously determined; ^{19}F{^{1}H} NMR (toluene-d_8): δ = −72.0, −72.3.

[Zn(dbea)(4-MeC$_6$H$_4$O)$_2$] (16a)

A solution of *p*-cresol (195 mg, 1.80 mmol) in toluene (10 mL) was added dropwise under nitrogen to a solution of complex **13** (301 mg, 0.45 mmol, 0.90 mmol Zn) in toluene (10 mL) cooled at −60 °C. The resulting solution was stirred with a magnetic stir bar for 30 min at −40 °C, and then for 30 min at 25 °C. Volatiles were removed under vacuum to give a white solid which was triturated with pentane (10 mL). The resulting precipitate was separated off from the liquid phase, washed with pentane (2 × 5 mL) and dried under vacuum to give **16a** as a white powder; yield: 289 mg (61%); ^{1}H NMR (toluene-d_8): δ = 7.25 (d, *J* = 7.0 Hz, 4H, 4-MeC$_6$H$_4$O, arom.), 7.20–7.0 (m, 10H, dbea, arom.), 6.75 (s, 4H, 4-MeC$_6$H$_4$O, arom.), 3.72 (m, 4H, NHCH_2Ph), 2.60 (br s, 2H, N*H*), 2.23 (s, 6H, CH_3, 4-MeC$_6$H$_4$O), 2.10 (s, 4H, CH_2NHBn); ^{13}C{^{1}H} NMR (toluene-d_8): δ = 164.0 (*C*-O-Zn), 138.4 (*C* arom.), 130.7 (*C* arom.), 129.3 (*C* arom.), 129.0 (*C* arom.), 128.6 (*C* arom.), 128.4 (*C* arom.), 127.6 (*C* arom.), 125.4 (*C* arom.), 120.5 (*C*, 4-MeC$_6$H$_4$O), 52.6 (NH*C*H$_2$Ph), 44.5 (*C*H$_2$NHBn), 20.7 (*C*H$_3$, 4-MeC$_6$H$_4$O); anal. calcd. for $C_{30}H_{34}N_2O_2Zn$ (520.00): C 69.29, H 6.59, N 5.39; found: C 69.06, H 6.74, N 5.23.

[Zn((*S*,*S*)-ebpe)(4-MeC$_6$H$_4$O)$_2$] (16b)

The same procedure as for **16a** was used starting from complex **14** (231 mg, 0.59 mmol). Removal of the volatiles and trituration with pentane gave **16b** as a colorless oil; 120 mg (37%); ^{1}H NMR (toluene-d_8): δ = 7.30–6.80 (m, 18H, arom.), 3.65 [m, 2H, NHC*H*(CH$_3$)Ph], 2.18 (m, 6H, CH_3, 4-MeC$_6$H$_4$O + 4H CH_2NH), 1.39 [m, 6H, NHCH(CH_3)Ph]; ^{13}C{^{1}H} NMR (toluene-d_8): δ = 162.2 (*C*-O-Zn), 161.5 (*C*-O-Zn), 141.6 (*C* arom.), 130.3 (*C* arom.), 129.2 (*C* arom.), 128.3 (*C* arom.), 127.4 (*C* arom.), 120.9 (*C* arom., 4-MeC$_6$H$_4$O), 120.1 (*C* arom., 4-MeC$_6$H$_4$O), 59.1 [NH*C*H(CH$_3$)Ph], 45.9 (*C*H$_2$NH), 23.1 and 20.6 (*C*H$_3$ diamine and 4-MeC$_6$H$_4$O); anal. calcd. for $C_{32}H_{38}N_2O_2Zn$ (548.06): C 70.13, H 6.99, N 5.11; found: C 69.86, H 7.24, N 4.98.

[ZnEt(dbea)(O-2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$)] (17a)

One-pot procedure: Diethylzinc (11.6 mL of a 1.1 M solution in toluene, 12.8 mmol) was added dropwise to a solution of dbea (3.00 mL. 12.7 mmol) in toluene (30 mL) cooled at −20 °C. The resulting solution was stirred with a magnetic stir bar for 30 min at −20 °C, for 20 min at 25 °C and then concentrated under vacuum to *ca.* 20 mL and cooled at −60 °C. A solution of BHT (2.80 g. 12.7 mmol) in toluene (30 mL) cooled at −60 °C was then added dropwise to the zinc solution. The resulting mixture was stirred for 15 min at 60 °C and allowed to warm up slowly to 25 °C. Volatiles were removed under vacuum to give a white powder that was triturated with pentane (15 mL). The resulting precipitate was separated off from the liquid phase, washed with pentane (2 × 15 mL) and dried under vacuum to give **17a** as a white powder; yield: 6.71 g (99%). Crystals for X-ray diffraction of **17a** were grown from toluene/pentane (1/1) at −30 °C. ^{1}H NMR (toluene-d_8): δ = 7.21 (s, 2H, arom., O-2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$), 7.10–6.90 (m, 10H, arom. dbea), 3.65 (br s, 4H, NHCH_2Ph), 2.68 (br s, 2H, CH_2NHBn), 2.45 (s, 3H, CH_3, O-2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$), 2.10 (s, 2H, CH_2NHBn, overlapped with toluene resonances), 1.69 (s, 18H, *t*-Bu), 1.48 (t, *J* = 8.0 Hz, 3H, CH_3, Et), 0.48 (q, *J* = 8.0 Hz, 2H, CH_2, Et); ^{13}C{^{1}H} NMR (toluene-d_8): δ = 164.3 (*C*arom., *C*-O-Zn), 137.1 (*C* arom.), 128.7 (*C* arom.), 128.2 (*C* arom.), 125.8 (*C* arom.), 121.0 (*C* arom., O-2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$), 52.2 (NH*C*H$_2$Ph), 44.3 (*C*H$_2$NHBn), 35.4 (*C*H$_3$, BHT), 31.2 (*C*H$_3$, *t*-Bu), 21.8 (*C*, *t*-Bu), 13.9 (*C*H$_3$, Et), −1.4 (*C*H$_2$, Et); anal. calcd. for $C_{33}H_{48}N_2OZn$ (554.15): C 71.52, H 8.73, N 5.06; found: C 71.13, H 8.94, N 5.14.

[ZnEt((*S*.*S*)-ebpe)(O-2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$)] (17b)

The same procedure as for **17a** was used, starting from isolated complex **14** (104 mg, 0.26 mmol). Removal of volatiles and trituration with pentane gave **17b** as a white powder; yield: 42 mg (28%); ^{1}H NMR (toluene-d_8): δ = 7.23 (s, 2H arom, BHT), 7.10–6.90 (m, 10H arom, ebpe), 3.72 [m, 2H, NHC*H*(CH$_3$)Ph], 2.86 (br s, 2H, CH_2NH), 2.45 (s, 3H, CH_3 BHT), 1.93 (br s, 2H, CH_2NH), 1.74 (s, 18H, CH_3, *t*-Bu), 1.49 (m, 6H, CH_3, diamine + 3H, CH_3, Et), 1.20 (br s, 2H, N*H*), 0.58 (q, *J* = 8.0 Hz, 2H, CH_2, Et); ^{13}C{^{1}H} NMR (toluene-d_8): δ = 164.2 (*C*-O-Zn), 141.9 (*C* arom.), 137.0 (*C* arom.), 129.3 (*C* arom.), 128.3 (*C* arom.), 127.4 (*C* arom.), 126.9 (*C* arom.), 125.8 (*C* arom.), 120.8 (*C* BHT), 56.8 [NH*C*H(CH$_3$)Ph], 42.2 (*C*H$_2$NH), 35.5 (*C*H$_3$, BHT), 31.5 (*C*H$_3$, *t*-Bu), 21.7 (*C*H$_3$, diamine), 13.7 (*C*H$_3$, Et), 3.6 (*C*H$_2$, Et).

Reaction of Zn(OCH$_2$CF$_3$)$_2$ with PhSiH$_3$

PhSiH$_3$ (62 μL, 0.50 mmol) was added dropwise to a suspension of Zn(OCH$_2$CF$_3$)$_2$ (400 mg, 1.52 mmol) in pentane (5 mL). The resulting suspension was stirred for 48 h at 25 °C. A white precipitate formed, which was filtered off, washed with pentane (2 × 5 mL) and dried under vacuum to afford a white powder (**18**, "HZnOCH$_2$CF$_3$"); yield: 122 mg (47%); IR (Nujol): ν = 1600–1500 (br, Zn–H), 1422 (s, OMe), 1422

(C–F), 1363 (s, O–CH_2), 1116 (vs, C–O); anal. calcd. for $ZnC_2H_3OF_3$ (165.5): C 14.51, H 1.81; found: C 16.68, H 1.79.

A 85 mg (0.514 mmol) sample of **18** produced 10.5 mL (0.429 mmol) of gas (H_2) at 25 °C, 1 atm when hydrolyzed with acidified water. Removing of volatiles from the filtrate gave a colorless oil, identified according to ES-MS as the siloxane **19**; yield: 60 mg (38%); ^{1}H NMR (toluene-d_8): δ = 7.50 (d, J = 7.3 Hz, 2H, arom.), 7.10 (d, J = 7.3 Hz, 3H, arom.), 3.67 (q, J = 8.3 Hz, 6H, CH_2CF$_3$); ^{13}C{^{1}H} NMR (toluene-d_8): δ = 135.0 (*C* arom.), 132.32 (*C* arom.), 129.3 (*C* arom.), 128.7 (*C* arom.), 128.4 (*C* arom.), 127.5 (*C* arom.), 124.1 (q, $^1J_{C,F}$ = 278.6 Hz, *C*F$_3$), 61.4 (q, $^2J_{C,F}$ = 36.8 Hz, *C*H$_2$CF$_3$); ^{19}F{^{1}H} NMR (toluene-d_8): δ = −71.86; MS (electrospray, direct introduction): m/z = 622 (M).

Reaction of [Zn(dbea)(OCH$_2$CF$_3$)$_2$] (15a) with PhSiH$_3$

1) Reaction with 1 equiv. of PhSiH$_3$: In the glove-box, PhSiH$_3$ (12.5 μL, 0.10 mmol, 1.0 equiv. *vs.* Zn) was added to a solution of [Zn(dbea)(OCH$_2$CF$_3$)$_2$] (**15a**) (51 mg, 0.10 mmol) in toluene-d_8 (ca. 1.0 mL) placed in an NMR tube. Upon addition of the silane, a fine white precipitate formed immediately and gas evolution was observed. A grey deposit formed after a few hours which was filtered off on a short celite bed. Removal of volatiles from the clear filtrate gave a yellow oil that was analyzed by NMR as a mixture of free dbea and an unidentified silylated species. ^{1}H NMR (toluene-d_8): δ = 7.50 (d, J = 6.4 Hz, 2H, arom., SiPh), 7.30–6.90 (m, 10H arom., dbea + 3H arom., SiPh), 4.49 (s, weak), 4.18 (s, weak), 3.68 (q, J = 8.3 Hz, 4H, OCH_2CF$_3$), 3.56 (d, J = 6.3 Hz, 4H, NHCH_2Ph, dbea), 2.49 (br s, 4H, CH_2NHBn, dbea), 1.09 (br s, 2H, N*H*, dbea); ^{13}C{^{1}H} NMR (toluene-d_8): δ = 141.5 (*C* arom.), 135.0 (*C* arom.), 132.2 (*C* arom.), 129.3 (*C* arom.), 128.8 (*C* arom.), 128.7 (*C* arom.), 128.4 (*C* arom.), 128.3 (*C* arom.), 127.48 (*C* arom.), 126.9 (*C* arom.), 128.1 (q, $^1J_{C,F}$ = 246.6 Hz, *C*F$_3$), 61.4 (q, $^2J_{C,F}$ = 36.9 Hz, OCH_2CF$_3$), 54.2 (NH*C*H$_2$Ph dbea), 49.3 (*C*H$_2$NHBn dbea); ^{19}F{^{1}H} NMR (toluene-d_8): δ = −71.80.

2) Reaction with 0.33 equivs. of PhSiH$_3$: In the glove-box, PhSiH$_3$ (4.5 μL, 0.037 mmol, 0.33 equivs. *vs.* Zn) was added to a solution of [Zn(dbea)(OCH$_2$CF$_3$)$_2$] (**15a**) (56 mg, 0.109 mmol) in toluene-d_8 (*ca.* 1 mL) placed in an NMR tube. A white cloudiness formed transiently with the addition of the silane, but no precipitate was observed. ^{1}H NMR (toluene-d_8): δ = 7.50 (d, J = 6.0 Hz, 2H, arom., SiPh), 7.30–6.90 (m, 10H, arom., dbea + 3H, arom., SiPh), 4.50 (s, 1H, Zn-H [20]?), 4.0 (br s, 4H, OCH$_2$CF$_3$ [20]), 3.65 (q, J = 8.3 Hz, 4H, OCH_2CF$_3$ [19]), 3.55 (d, J = 6.3 Hz, 4H, NHCH_2Ph [20]), 2.3 (br s, 4H, CH_2NHBn [20]); ^{13}C{^{1}H} NMR (toluene-d_8): δ = 135.0 (*C* arom.), 128.7 (*C* arom.), 128.2 (*C* arom.), 125.4 (*C* arom.), 125. 4 (q, $^1J_{C,F}$ = 268.7 Hz, *C*F$_3$), 65.4 (q, $^2J_{C,F}$ = 33.4 Hz, OCH$_2$CF$_3$ [20]), 61.4 (q, $^2J_{C,F}$ = 36.9 Hz, OCH$_2$CF$_3$ [19]), 53.8 (NHCH$_2$Ph [20]), 46.6 (*C*H$_2$NHBn [20]); ^{19}F{^{1}H} NMR (toluene-d_8): δ = −71.84.

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[23] The atom connectivity of complex **17a** was also confirmed by an X-ray diffraction study but the crystals were of poor quality ($R_{int} = 0.0901$), hampering a detailed discussion of structural features.
[24] Complex **17a** reacted at room temperature in toluene with 1 equiv. of MeOH to give dbea (50% yield), free BHT and a white powder identified as $Zn(OMe)_2$; 50% of the starting complex was left unreacted. Reactions carried out under the same conditions with more acidic alcohols (CF_3CH_2OH, Ph_3SiOH) mainly led to the corresponding [(dbea)$Zn(OR)_2$] species (35–60%), unreacted **17a** (30–45%), and minor amounts of the mixed species [(dbea)Zn(OR)(OAr)] (5–15%).
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