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Selective Reduction of Carbonyl Compounds by Polymethylhydrosiloxane in the Presence of Metal Hydride Catalysts

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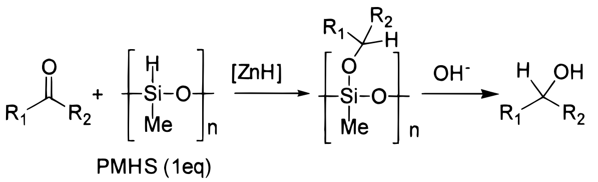
Introduction

Polymethylhydrosiloxane (PMHS) is a safe[1] and inexpensive polymer coproduct of the silicone industry representing ca. 5% of the world production.[2] Its use as a reducing silylating agent of carbonyl compounds (not esters) in the presence of organotin compounds has been first described by Nitzsche and Wick in 1957[3] and later developed by other authors with tin,[4] alkali or ammonium fluorides,[5] and titanocene catalysts activated by ^{n}BuLi[6] or RMgBr.[7] Recently, nonactivated Ti(OR)$_4$ complexes have also been shown to catalyze the reduction of esters by PMHS, albeit with lower turnover numbers (TON = 1−4).[8] Here we present an air stable, general, convenient, and inexpensive industrially important method for the highly selective hydrosilylation−reduction of aldehydes, ketones, esters, lactones, triglycerides, and epoxides to the corresponding alcohols in the presence of zinc hydride catalysts conveniently generated from the reaction of soluble zinc carboxylates with a hydride reducing agent (eqs 1 and 2).[9] The present catalytic systems generally do not disproportionate PMHS and therefore do not cause gummy deposits and adventitious solidification of the reaction medium, thus allowing multiton operations under safe conditions.

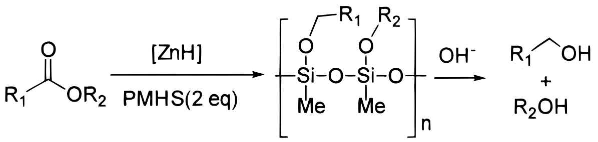
Results

Reduction of Aldehydes (R$_2$=H) and Ketones



(1)

Reduction of Esters and Lactones



(2)

Metal Hydride Catalysts for the Reduction of Methyl Benzoate by PMHS. Metal hydrides are generally considered to be key intermediates in hydrosilylation reactions,[10] and PMHS is known to reduce organotin oxides to tin hydrides.[11] We reasoned that a metal hydride hydrosilylation catalyst, particularly zinc hydride, should be preformed from the reaction of metal salts with an alkali metal hydride,[12] considering the fact that NaH−ZnCl$_2$−RONa mixtures have been used for the reduction and hydrosilylation of carbonyl compounds [13] and that zinc compounds catalyze the reductive silylation of ketones by a LiH−Me$_3$SiCl mixture.[14] Considering also the fact that zinc borohydride is an excellent reagent for the selective reduction of carbonyl compounds including esters,[15] we have undertaken the study of the catalytic properties of various zinc compounds as such, or preactivated by reaction with various reducing agents such as NaBH$_4$, BH$_3$, CH$_3$MgCl, AlEt$_3$, LiH, LiAlH$_4$, or sodium dihydrobis(2-methoxyethoxy)aluminate (SDMA)[16] in the reduction by PMHS, using methyl benzoate as a substrate model for esters. The reaction was carried out by reacting first 0.2 mmol of Zn compound with 0.2 mmol of additive unless otherwise stated (see Table 1) in isopropyl ether (IPE), then adding 10 mmol of methyl benzoate and 24 mmol of PMHS. The resulting mixture was heated at 70 °C for 4 h, hydrolyzed by an excess of aqueous NaOH 30%, and then analyzed by GC.

Zinc compounds such a ZnCl$_2$,[17] Zn(RCO$_2$)$_2$, ZnEt$_2$, Zn(BH$_4$)$_2$ or ZnH$_2$ (insoluble) are not active for the reduction

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(1) In contrast to other alkali metal hydride reductants, PMHS is stable to air and water, easy to pump, and soluble in most organic solvents.

(2) PMHS is industrially prepared by water hydrolysis of MeHSiCl$_2$, a coproduct of the Rochow "Direct Process" between Si and methyl chloride, giving Me$_2$SiCl$_2$ as the major building block for the silicone industry. The main industrial use of PMHS involves hydrofugation of clothes and building materials, and silicone curing reagents by hydrosilylation of polyvinylsilanes.

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(5) (a) Corriu, R. J. P.; Perz, R.; Réyé, C. *Tetrahedron* **1983**, *39*, 999. (b) Kobayashi, Y.; Takahisa, E.; Nakano, M.; Watatani, K. *Tetrahedron* **1997**, *53*, 1627. (c) Drew, M. D.; Lawrence, N. J.; Fontaine, D.; Sekhri, L.; Bowles, S. A.; Watson, W. *Synlett* **1997**, 989. (d) Drew, M. D.; Lawrence, N. J.; Watson, W.; Bowles, S. A. *Tetrahedron Lett.* **1997**, *38*, 5857.

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(8) (a) Breedon, S. W.; Lawrence, N. J. *Synlett* **1994**, 833. (b) Reding, M. T.; Buchwald, S. L. *J. Org. Chem.* **1995**, *60*, 7884.

(9) Mimoun, H. Patent WO 96/12694 (1995) to Firmenich S.A. The technology involved in this patent has been licensed exclusively to Morton International and is presently commercialized under the trade name of Venpure ERS Technology.

(10) (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 25, Part 2. (b) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8, Chapter 3.12.

(11) Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81.

(12) ZnCl$_2$ has been previously shown to catalyze the hydrosilylation of γ- and δ-lactones by triethylsilane at high temperatures (>120 °C). Frainnet, E.; Calas, R.; Berthault, A. *C. R. Acad. Sci.* **1964**, *258*, 613.

(13) (a) Caubere, P. *Top. Curr. Chem.* **1978**, *73*, 50 and references therein. (b) Brunet, J. J.; Besozzi, D.; Caubere, P. *Synthesis* **1982**, 721.

(14) Okhuma, T.; Hashiguchi, S.; Noyori, R. *J. Org. Chem.* **1994**, *59*, 217.

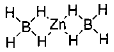
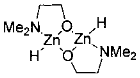
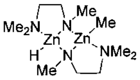
(15) Ranu, B. C. *Synlett*. **1993**, 885 and references therein.

(16) SDMA (NaAlH$_2$(OCH$_2$CH$_2$OMe)$_2$ is available as a 70% active solution from Morton International (Alkadride Solution) or Cambrex Chemical Corp (Vitride).

(17) Chandrasekhar, S.; Ravindra Reddy, Y.; Ramarao, C. *Synth. Commun.* **1997**, *27*, 2251.

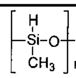
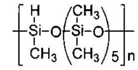
10.1021/jo982314z CCC: $18.00

Table 1. Reduction of Methyl Benzoate by PMHS Promoted by Zinc Catalysts[c]

Entry	Zinc compound	Reductant or Additive[a]	Conversion[b] (%)	Selectivity[b] (%)
1	$Zn(2\text{-}EH)_2$	-	0	
2	$ZnEt_2$	-	0	
3	ZnH_2	-	2	
4	$Zn(2\text{-}EH)_2$	$NaBH_4$ (1eq)	100	100
5	$Zn(benzoate)_2$	$NaBH_4$ (1eq)	96	96
6	$Zn(OAc)_2$	$NaBH_4$ (1eq)	2	-
7	$Zn(2\text{-}EH)_2$	CH_3MgCl (1eq)	100	100
8	$Zn(2\text{-}EH)_2$	$AlEt_3$ (2 eq)	8	-
9	$Zn(2\text{-}EH)_2$	BH_3 (1eq)	62	97
10	$Zn(2\text{-}EH)_2$	$AlH(^iBu)_2$ (1eq)	66	85
11	$ZnCl_2$	LiH (4eq)	78	95
12	$ZnCl_2$	$LiAlH_4$ (1eq)	13	-
13	$ZnEt_2$	$Me_2N(CH_2)_2OH$ (1eq)	13	-
14	$ZnEt_2$	$H_2N(CH_2)_2NH_2$ (1eq)	84	95
15	$ZnEt_2$	$Me_2N(CH_2)_2NMe_2$ (1eq)	84	75
16	 **1**	-	0	
17	 **2**	-	0	
18	 **3**	-	50	100
19	$(PhZnH)_2$.TMEDA	-	80	43
20	$[PhZnH.Py]_3$	-	2	-

[a] Equivalents of additive based on the zinc concentration. [b] GC yields after hydrolysis by 15% NaOH. [c] Reaction conditions: methyl benzoate = 10 mmol, zinc compound = 0.2 mmol, equiv of additive (see table), PMHS = 22 mmol, solvent = diisopropyl ether (2 mL); 70 °C (reflux), 4 h.

Table 2. Hydrosilylation of Methyl Benzoate by Various Silanes in the Presence of $Zn(2\text{-}EH)_2 + NaBH_4$ Catalyst[c]

Entry	Silane	Conversion[b] (%)	Selectivity[b] (%)
1	 PMHS	100	100
2[a]		98	100
3	$(EtO)_3SiH$	97	92
4	$(MeO)_3SiH$	98	93
5	Ph_2SiH_2	100	92
6	Et_3SiH	4	-
7	Ph_3SiH	0	-

[a] Rhodorsil 628 from Rhone Poulenc. [b] GC yields after hydrolysis by NaOH 15%. [c] Reaction conditions: methyl benzoate = 10 mmol, $Zn(2\text{-}EH)_2$ = 0.2 mmol, $NaBH_4$ = 0.2 mmol, silane = 22 mmol (equiv of SiH), solvent = isopropyl ether (2 mL); 70 °C (reflux), 4 h.

of methyl benzoate by PMHS (entries 1−3). Addition of an equimolecular amount of $NaBH_4$ to Zn(2-ethylhexanoate)$_2$[18] (hereinafter $Zn(2\text{-}EH)_2$) results in the evolution of 0.5 mol of H_2/mol of Zn which stops after 0.5 molar equiv of $NaBH_4$ has been added and the formation of a very active soluble catalyst which allows almost quantitative transformation of methyl benzoate first to benzyloxypolysiloxane and then to benzyl alcohol after hydrolysis (entry 4). The reaction can be operated in aprotic solvents such as hydrocarbons and ethers, or without solvent, in the presence of a catalytic quantity of zinc + reductant as low as 1 mol % based on the substrate. Protic solvents such as alcohols and carboxylic acids are not suitable, since they are silylated by PMHS in the presence of zinc hydride catalysts (vide infra). Other soluble zinc carboxylates such as benzoate, isobutyrate, 2-methylbutyrate, and undecylenate, are active as well, while insoluble zinc acetate is almost inactive. Activation of $Zn(2\text{-}EH)_2$ by CH_3MgCl also results in the formation of a very active catalyst (entry 7), but $AlEt_3$, BH_3, and DIBAL-H (entries 8−10) are less efficient activators. $ZnCl_2$ can be activated by 4 equiv of LiH (entry 11), but in the presence of $LiAlH_4$ it gave inferior results (entry 12).

While $ZnEt_2$ alone does not catalyze the present reaction (entry 2), it can be activated by ethylenediamine (entry 14) or TMEDA (entry 15).[19] Diamines are known to transform the linear C−Zn−C backbone of dialkylzinc into monomeric tetrahedral zinc complexes ZnR_2(diamine) in which the diamine acts as a bidendate ligand.[20] These complexes thus appear to catalyze efficiently the reduction of methyl benzoate without the need for hydride activation.

We also tested isolated zinc hydride complexes as catalysts for the PMHS reduction of methyl benzoate. Zinc borohydride $Zn(BH_4)_2$ **1** was found inactive despite its reducing properties toward esters (entry 16), as well as $[HZnOC_2H_4NMe_2]_2$[21] **2** (entry 17) and $[PhZnH.Py]_3$[22] (run 20). Other zinc hydride complexes such as $[HZnN(Me)C_2H_4NMe_2]_2$ **3** (entry 18),[23] and $(PhZnH)_2$·TMEDA[22] (entry 19) were found active for the hydrosilylation but less effective than the hydride species generated from the reaction of $Zn(2\text{-}EH)_2 + NaBH_4$.

Thus, soluble zinc hydride species, best generated from the reduction of soluble zinc carboxylates by $NaBH_4$, as well as dialkylzinc coordinated by 1,2-diamines are very effective catalysts for the reduction by PMHS of esters to the corresponding alcohols.

Although PMHS is the most economical, safest, and most effective silylating agent, other silanes such as $(EtO)_3SiH$ and $(MeO)_3SiH$ hydrosilylate methyl benzoate in the presence of $Zn(2\text{-}EH)_2 + NaBH_4$ catalyst as well (Table 2, entries 3−4), while Et_3SiH and Ph_3SiH were found completely ineffective (entries 6−7), in contrast to Ph_2SiH_2 (entry 5). A silane copolymer where Si−H and Si−Me groups alternate randomly (Rhodorsil 628, HSiMe:$SiMe_2$ = 5, entry 2) was also operative in the hydrosilylation of methyl benzoate, provided the fact that SiH/ester ratio is > 2. Thus, in contrast to the recently reported NBu_4F- or Triton B-catalyzed hydrosilylation of carbonyl compounds,[5c] there is no clear evidence here of a considerable rate acceleration with PMHS in comparison with other silylating agents, favoring a "zipper" mechanism where the catalyst jumps from one Si−H to the next adjacent one along the polymeric silicon backbone.

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[18] Metal soaps M(2-EH)$_n$ used in this paper are commercially available 2-ethylhexanoates used as drying agents in the paint industry or easily prepared from the metal oxide or carbonate and 2-ethylhexanoic acid (see Experimental Section).

[19] TMEDA = tetramethylethylenediamine.

(20) (a) O'Brien, P.; Hursthouse, M. B.; Motevalli, M.; Walsh, J. R.; Jones, A. C. *J. Organomet. Chem.* **1993**, *449*, 1. (b) Motevalli, M.; O'Brien, P.; Robinson, A. J.; Walsh, J. R.; Wyatt, P. B.; Jones, A. C. *J. Organomet. Chem.* **1993**, *461*, 5.

(21) (a) Bell, N. A.; Coates, G. E. *J. Chem. Soc. A* **1968**, 823. (b) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354.

(22) De Koning, A. J.; Boersna, J.; Van Der Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *195*, 1.

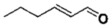
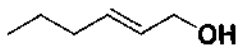
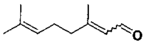
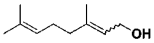
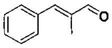
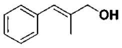
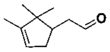
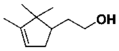
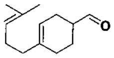
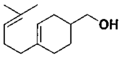
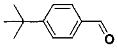
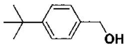
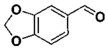
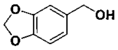
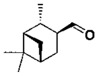
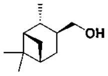
(23) Bell, N. A.; Moseley, P. T.; Shearer, H. M. M.; Spencer, C. B. *J. Chem. Soc., Chem. Commun.* **1980**, 359.

Table 3. Reduction of Methyl Benzoate by PMHS. Catalytic Activity of Various Soluble Metal Species Activated by $NaBH_4$[a]

entry	metal compound	convn (%)	selectivity (%)
1	$Zn(2\text{-}EH)_2$	100	100
2	$Mn(stearate)_2$	100	100
3[b]	$Fe(2\text{-}EH)_2$	73	100
4	$Cd(propionate)_2$	8	100
5	$Ti(O^iPr)_4$	6	83
6	$Sn(2\text{-}EH)_2$	0	
7	$Zr(O^iPr)_4$	0	

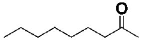
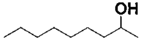
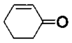
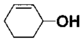
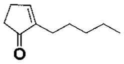
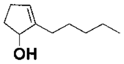
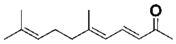
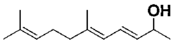
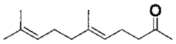
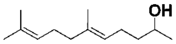
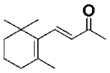
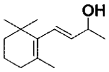
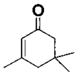
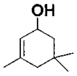
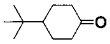
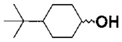
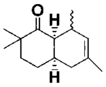
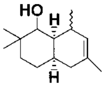
[a] Reaction conditions: methyl benzoate = 10 mmol, metal compound = 0.2 mmol, $NaBH_4$ = 0.2 mmol, PMHS= 22 mmol, solvent = diisopropyl ether (2 mL); 70 °C (reflux), 4 h. [b] Solidification occurred during the reaction.

Table 4. Reduction of Aldehydes[c]

Entry	Aldehydes	Alcohol	Yield (%)[b]
1	 **4a**	 **4b**	94
2[a]	 **5a**	 **5b**	93
3	 **6a**	 **6b**	95
4	 **7a**	 **7b**	90
5	 **8a**	 **8b**	94
6	 **9a**	 **9b**	95
7	 **10a**	 **10b**	96
9	 **11a**	 **11b**	with PMHS = 20% $(MeO)_3SiH$ = 95%

[a] *E*:*Z* = 50:50 (synthetic citral). [b] Isolated yields. [c] Reaction conditions: aldehyde = 100 mmol, $Zn(2\text{-}EH)_2$ = 2 mmol, $NaBH_4$ = 2 mmol, PMHS = 110 mmol, solvent = diisopropyl ether (20 mL), 70 °C (reflux), 4−6 h.

Table 5. Reduction of Ketones[a]

Entry	Ketones	Alcohol	Yield (%)
1	 **12a**	 **12b**	96
2	 **13a**	 **13b**	95
3	 **14a**	 **14b**	94
4	 **15a**	 **15b**	90
5	 **16a**	 **16b**	92
6	 **17a**	 **17b**	90
7	 **18a**	 **18b**	95
8	 **19a**	 **19b**	92 trans:cis = 87:13
10	 **20a**	 **20b**	With PMHS = 5% $(MeO)_3SiH$ = 72%

[a] Reaction conditions: same as in Table 4.

Various combinations of other soluble metal carboxylates with $NaBH_4$ (2 mol % each) were tested for the reduction of methyl benzoate by PMHS, as shown in Table 3. Although zinc catalysts were found to be the most effective, manganese(II) stearate and iron(II) 2-ethylhexanoate reduced by $NaBH_4$ also catalyzed the hydrosilylation reaction (Table 3, entries 2−3). Manganese carbonyl complexes, e.g., $(PPh_3)(CO)_4MnC(O)CH_3$, have recently been shown to catalyze the hydrosilylation of aldehydes and ketones by monomeric silanes.[24] Other metal precursors such as Cd, Ti, Sn, Co, and Zr carboxylates or alkoxides activated by $NaBH_4$ were not nearly as effective for this transformation (entries 4−7). This contrasts with the known catalytic activity (not for esters) of $[Bu_2Sn(OAc)]_2O$ operating in alcoholic solvents[4] and that of titanocenes activated by BuLi or RMgX reagents.[6]

Reduction of Aldehydes. Table 4 shows that a large variety of aldehydes are almost quantitatively reduced by PMHS (1 molar equiv) in the presence of $Zn(2\text{-}EH)_2$ + $NaBH_4$ catalyst. Conjugated or nonconjugated double bonds present in the substrate are not affected by the reduction. Thus, (*E*)-2-hexenal **4a** is transformed to (*E*)-2-hexenol **4b** (Table 4, entry 1), citral **5a** to a 50:50 geraniol−nerol mixture (entry 2), methylcinnamic aldehyde **6a** to the corresponding alcohol **6b**, and campholenic aldehyde **7a** to campholenic alcohol **7b**. Sterically hindered aldehydes such as (+)-formylpinane **11a** are much more readily reduced to the corresponding alcohol **11b** with trimethoxysilane (95% yield) than with PMHS (20% yield). This suggests that the silane and the active zinc species are associated in the catalytic intermediate.

Reduction of Ketones. The use of $Zn(2\text{-}EH)_2$ + $NaBH_4$ catalyst also applies for the selective reduction of ketones by PMHS, as shown in Table 5. Both saturated and α,β-unsaturated ketones are very efficiently reduced to the corresponding alcohols. 2-Cyclohexen-1-one **13a**, 2-pentylcyclopent-2-ene-1-one **14a**, pseudoionone **15a**, geranylacetone **16a**, β-ionone **17a**, and isophorone **18a** are almost quantitatively reduced to the corresponding secondary alcohol. The reduction is very sensitive to steric effects, as shown by the absence of reactivity of the encumbered ketone **20a** with PMHS (Table 5, entry 10), whereas trimethoxysilane gave 72% yield of the corresponding alcohol **20b**. 4-*tert*-Butylcyclohexanone **20a** is reduced to an 87:13 trans:cis mixture of 4-*tert*-butylcyclohexanol isomers, in a manner similar to that of NBu_4F and Triton B catalysis but in contrast to the L-Selectride reagent.[25]

While zinc, manganese, and iron carboxylates activated by $NaBH_4$ are best able to catalyze the reduction of methyl benzoate to benzyl alcohol (Table 3), various metal hydrides allowed the reduction of ketones by PMHS, but with different selectivities, as shown in Table 6. Taking 2-cyclohexen-1-one as a model, we could distinguish between metals capable of 1,2-reduction which gave 2-cyclohexen-1-ol as product and metals capable of 1,4-reduction which gave cyclohexanone first and then cyclohexanol in some cases.

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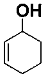
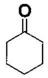
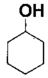
[24] Dibiase Cavanaugh, M.; Gregg, B. T.; Cutler, A. R. *Organometallics* **1996**, *15*, 2764.

[25] Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7151.

Table 6. Reduction of Cyclohexen-1-one-2 by PMHS. Influence of Various Metal Hydride Catalysts: 1,2 vs 3,4 Reduction[a]

Entry	Metal	Conversion	Selectivity (%)		
		%			
1	$Zn(2\text{-}EH)_2$	100	100	0	0
2	$Co(2\text{-}EH)_2$	88	100	0	0
3	$Mn(stearate)_2$	83	100	0	0
4	$Sn(2\text{-}EH)_2$	82	100	0	0
5	$Fe(2\text{-}EH)_2$	80	100	0	0
6	$Cd(propionate)_2$	78	100	0	0
7	$Zr(OiPr)_4$	14	100	0	0
8	$RuCl_2(PPh_3)_3$	92	46	40	13
9	$Ni(2\text{-}EH)_2$	46	20	68	11
10	$Pd(OAc)_2(PPh_3)_2$	100	2	92	6
11	$Cu(2\text{-}EH)_2$	55	0	98	1

[a] Reaction conditions: 20 mmol of 2-cyclohexen-1-one, 22 mmol of PMHS, 0.4 mmol of metal compound (except for Ru and Pd where 0.04 mmol were used), 0.4 mmol of $NaBH_4$, solvent = diisopropyl ether (2 mL), 70 °C, 4 h.

(i) Activated metals which give 2-cyclohexen-1-ol by 1,2-reduction are Zn(II), Co(II), Mn(II), Sn(II), Fe(II), and Cd(II) carboxylates (entries 1−6). $Zr(OiPr)_4$ was found to be only slightly active and Cp_2TiCl_2 was inactive.

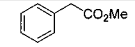
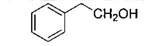
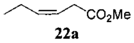
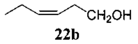
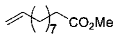
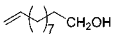
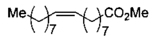
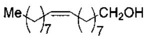
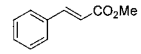
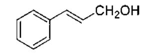
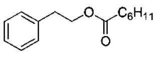
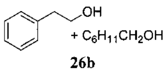
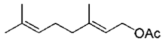
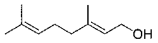
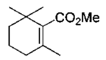
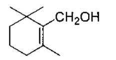
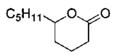
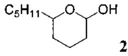
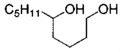
(ii) Activated metals which give conjugate reduction to cyclohexanone with almost no consecutive reduction to cyclohexanol are $Cu(2\text{-}EH)_2$ and $Pd(OAc)_2(PPh_3)_2$ (entries 10−11). The peculiar behavior of copper hydride catalysts in the hydrosilylation of enones by PMHS is reminiscent of the catalytic property of copper(I) hydride such as $[CuH(PPh_3)]_6$ in the selective 1,4-reduction of enones to their corresponding saturated ketones by molecular hydrogen.[26] This conjugate reduction has been shown to occur via a Cu(I) enolate resulting from the conjugate addition of Cu(I) hydride to the enone. Here, enol polysilyl ethers are presumably formed from the reduction of enones by PMHS in the presence of $Cu(2\text{-}EH)_2 + NaBH_4$ catalysts.

(iii) $NaBH_4$-activated $RuCl_2(PPh_3)_3$ and $Ni(2\text{-}EH)_2$ which give a mixture of 1,2- and 1,4-reduction products: 2-cyclohexen-1-ol, cyclohexanone, and cyclohexanol.

(iv) $NaBH_4$-activated molybdenum(VI) naphthenate, chromium(III) 2-ethylhexanoate, and $Ce(2\text{-}EH)_3$ were found to be completely inactive for the reduction of 2-cyclohexen-1-one.

Thus, the use of soluble metal hydrides as catalysts for the hydrosilylation by PMHS reveals, by the variety of their behavior, unexplored ways for fine-tuning the reduction of carbonyl compounds and requires further studies for other specific substrates.

Table 7. Reduction of Esters and Lactones[a]

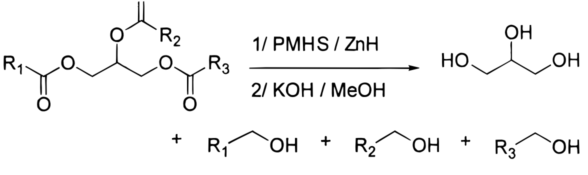
Entry	Esters	Alcohol(s)	Yield (%)
1	 **21a**	 **21b**	91
2	 **22a**	 **22b**	95
3	 **23a**	 **23b**	94
4	 **24a**	 **24b**	94
5	 **25a**	 **25b**	90
6	 **26a**	 **26b**	95
7	 **27a**	 **27b**	95
8	 **28a**	 **28b**	0
9	 **29a**	 **29b.** 1 eq PMHS  **29c.** 2 eq PMHS	70 solidification

[a] Reaction conditions: substrate = 20 mmol, PMHS = 44 mmol, $Zn(2\text{-}EH)_2$ = 0.4 mmol, $NaBH_4$ = 0.4 mmol, solvent = diisopropyl ether (2 mL), 70 °C, 4 h.

Reduction of Esters and Lactones. Esters and lactones are very efficiently reduced by PMHS to the corresponding alcohols in the presence of $Zn(2\text{-}EH)_2 + NaBH_4$ catalyst, as shown in Table 7. This reduction, which requires 2 molar equiv of PMHS per mol ester, occurs without affecting C=C double bonds in their position and stereochemistry. Thus, methyl (*Z*)-3-hexenoate **22a** is selectively transformed into (*Z*) -3-hexen-1-ol **22b**, methyl undecylenate **23a** into undecenyl alcohol **23b**, methyl oleate **24a** into oleyl alcohol **24b**, methyl cinnamate **25a** into cinnamyl alcohol **25b**, phenethyl caproate **26a** into phenethyl alcohol and *n*-hexanol, and geranyl acetate **27a** into geraniol. As previously shown for the encumbered ketone **20a** (Table 5, entry 10), the reduction of esters is very sensitive to steric effects. For example, methyl *β*-cyclogeraniate **30a** is not hydrosilylated under these conditions (Table 7, entry 8).

While no aldehyde was detected in the partial reduction of esters by 1 molar equiv of PMHS, lactols can be clearly identified from the half-reduction of lactones and isolated in yields of ca. 70% (entry 10). Addition of another equivalent of PMHS led to complete reduction to the corresponding diol and solidification of the reaction medium, owing to the cross-coupling of two polysiloxane chains by the resulting diol. This contrasts with Buchwald's $Cp_2Ti(p\text{-}ClC_6H_4O)_2$/TBAF system which requires a large excess of PMHS and stops at the lactol stage.[6e,f]

One of the most peculiar properties of the present $Zn(2\text{-}EH)_2 + NaBH_4$ catalyst is its ability to catalyze the hydrosilylation−reduction of fatty oils to the corresponding natural fatty alcohols in high yields (eq 3).



(3)

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[26] (a) Strycker, J. M.; Mahoney, W. S.; Daeuble, J. F.; Brestensky, D. M. In *Catalysis of Organic Reactions*; Pascoe, W. E., Ed.; Marcel Dekker: New York, 1992; pp 29−44. (b) Mahoney, W. S.; Strycker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8818. (c) For heterogeneous version of the 1,4-reduction of *α*,*β*-unsaturated ketones in the presence of Cu/SiO_2 catalyst, see: Ravasio, N.; Antenori, M.; Gargano, M.; Mastrorilli, P. *Tetrahedron Lett.* **1996**, *37*, 3529.

Table 8. Reduction of Triglycerides[a]

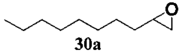
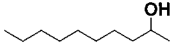
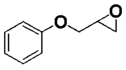
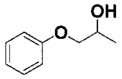
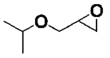
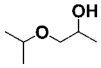
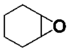
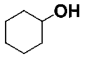
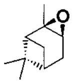
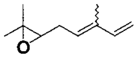
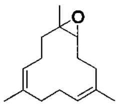
entry	oils	yield, mol %	∠C_{10}	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{18}:1	C_{18}:2	C_{18}:3	C_{20}:1	C_{22}:1	C_{24}:1
1	triolein	95							94.0	3.0				
2	coconut	94	12.2	48.8		19.3	8.5	-	13.3					
3	cocoa butter	92					31.6	33.1	30.9					
4	palm kernel	78		6.8	53.3	17.1	7.9	1.3	12.1	1.4				
5	peanut	94.					13.0	6.2	49.1	26.3				
6	sunflower	81					8,1	4.6	24.6	62.8				
7	linseed	75					5.7	3.1	16.9	14.0	55.0			
8	Jojoba	95							6.5			59.4	26.8	3.9

[a] Reaction conditions: oil = 1 molar equiv, PMHS = 7 molar equiv (based on the saponification value), $Zn(2\text{-}EH)_2$ = 4 mol % based on the ester content, $NaBH_4$ = 4 mol %, solvent = diisopropyl ether, 70 °C, 4 h.

The reduction of triglycerides is carried out in diisopropyl ether or toluene solvent and requires at least 2 molar equiv of PMHS per mole of ester (based on the saponification value) and ca. 4 mol % of activated Zn catalyst. The reaction can be operated safely, inexpensively, and conveniently in a multipurpose reactor, without the need for dangerous molten sodium in the Bouveault and Blanc synthesis, and without the need for transesterification to methyl fatty esters before high pressure and temperature hydrogenation in the presence of copper chromite catalysts which affects the *Z* double bonds.[27] As shown in Table 8, the natural alcohols obtained by this reduction by PMHS accurately correspond, in their constitution and stereochemistry, to the fatty esters precursors. Thus, triolein is reduced in almost quantitative yield to oleyl alcohol. Coconut, cocoa butter, and palm kernel oils are transformed to a mixture of C_{10}–C_{18} alcohols (Table 8, entries 2–4). Peanut oil gave a mixture of alcohols composed of 13% hexadecanol-1 (C_{16}), 6% octadecanol-1 (C_{18}), 49% of 9(*Z*)-octadecen-1-ol (oleyl alcohol, C_{18}:1), and 26% of 9(*Z*),12(*Z*)-octadecadien-1-ol (linoleyl alcohol, C_{18}:2). Linseed oil was reduced to a mixture of alcohols containing 55% of 9(*Z*),12(*Z*),15(*Z*)-octadecatrien-1-ol (linolenyl alcohol, C_{18}:3), a high value precursor for many important natural products. Jojoba oil, an ester mixture of straight chain C_{18}–C_{24} (Z)-9 monounsaturated acids and alcohols, was cleanly and almost quantitatively converted into a mixture of oleyl alcohol (C_{18}:1, 6.5%), (*Z*)-9-icosen-1-ol (C_{20}:1, 59.4%), (*Z*)-9-docosen-1-ol (C_{22}:1, 26.8%), and (*Z*)-9-tetracosen-1-ol (C_{24}:1, 3.9%).

Reduction of Epoxides. Table 9 shows that only terminal primary epoxides such as 1,2-epoxydecane **30a**, phenylglycidyl ether **31a**, and isopropylglycidyl ether **32a** are efficiently reduced by PMHS only to the corresponding secondary alcohol, with no evidence of primary alcohol formation. Other substituted epoxides such as α-pinene epoxide, *β*-pinene epoxide, and trimethylcyclododecatriene epoxide remain unaffected by the reduction conditions (Table 9, entry 5).

Table 9. Reduction of Epoxides[a,b]

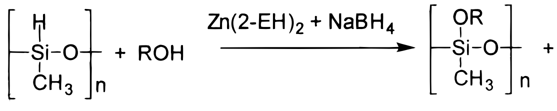
Entry	Epoxide	Alcohol	Conv. (%)	Sel (%)
1	 **30a**	 **30b**	80	100
2	 **31a**	 **31b**	90	100
3	 **32a**	 **32b**	50	100
4	 **36a**	 **36b**	40	100
5	   		No reaction	

[a] Reaction conditions: epoxide = 100 mmol, $Zn(2\text{-}EH)_2$ = 4 mmol, $NaBH_4$ = 4 mmol, PMHS = 110 mmol, solvent = diisopropyl ether (20 mL), 70 °C (reflux), 4–6 h. [b] Isolated yields.

Other Substrates. Carboxylic acids such as 2-ethylhexanoic acid are not or only slightly reduced by PMHS in the presence of $Zn(2\text{-}EH)_2$ + $NaBH_4$ catalyst, since they are first hydrosilylated by PMHS with evolution of hydrogen. Anhydrides such as butyric anhydride and maleic anhydride are also inert.

Nitriles such as benzonitrile, lactams such as *N*-methylpyrrolidone or succinimide, and nitro compounds such as nitrobenzene are unreactive under these conditions. Also, phosphine oxides such as Ph_3PO, for which we screened many combinations of metal carboxylates + $NaBH_4$ catalysts, are not reduced to the corresponding phosphines.

Dehydrogenative Silylation of Alcohols by PMHS in the Presence of Zinc Hydride Catalysts. We have previously mentioned that, in contrast to the catalysis by tin compounds,[3,4] the ZnH-catalyzed reduction of carbonyl compounds cannot be operated in protic solvents such as alcohols and carboxylic acids. A considerable effervescence of hydrogen occurs when PMHS is added to the carbonyl compound dissolved in alcohol in the presence of $Zn(2\text{-}EH)_2$ + $NaBH_4$ catalyst. We have observed that this hydrogen evolution results from the dehydrogenative silylation of the alcohol by PMHS, affording the corresponding alkoxylated polysilyl ethers according to eq 4.

 (4)

$$\left[-\overset{H}{\underset{CH_3}{Si}}-O-\right]_n + ROH \xrightarrow{Zn(2\text{-}EH)_2 + NaBH_4} \left[-\overset{OR}{\underset{CH_3}{Si}}-O-\right]_n + H_2 \quad (4)$$

Silylation is a well-known procedure for the protection of alcohols,[28] but the present method is rapid, quantitative, inexpensive, forms no salts, and does not generally require any solvent or aqueous workup.[29] The reaction is easily carried out by first dissolving 1 mol % of $Zn(2\text{-}EH)_2$ and 1 mol % of $NaBH_4$ in the alcohol. Then 1 equiv

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(27) Noveck, K.; Ridder, H. *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; 1987; Vol. A11, p 277.

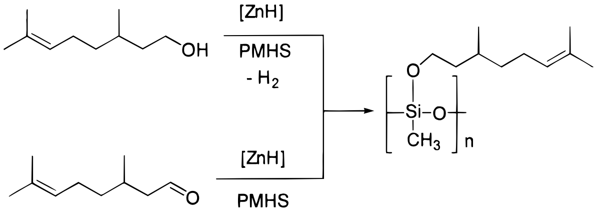
(28) Green, T. W.; Wuts, P. G. M. *Protective groups in Organic Synthesis*, 2nd ed.; John Wiley & Sons: New York, 1991; pp 68–87.

(29) Mimoun, H. Patent WO 96/28497 (1996) to Firmenich S.A.

of PMHS is slowly added at room temperature (exothermic reaction!) and the mixture is stirred until no more hydrogen is evolved. The amount of evolved H_2 exactly corresponds to the expected stoichiometry of eq 4, and we have used this volumetric method to evaluate the available SiH bonds in PMHS. The resulting liquid, semiviscous, polysiloxane resulting from the addition of 1 mol of PMHS to 1 mol of alcohol can be removed from the zinc catalyst by thermal treatment at 150 °C for 1 h and filtration of the gray precipitate through Celite. No silylation of the alcohol is observed if the zinc carboxylate is not activated by $NaBH_4$. The reactivity of the alcohols is in the order primary > secondary ≫ tertiary.

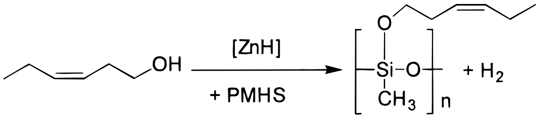
The polysiloxanes obtained by silylation of alcohols by PMHS are easily characterized by ^1H and ^{13}C NMR. The ^1H NMR spectra of the polysiloxanes show the disappearance of the PMHS Si−H signal at 4.72 ppm, similar to the ^1H NMR spectra of the alcohol precursor, with a broadening of the signals, owing to the oligomeric nature of the polysiloxane, and with a downfield shift of ca. 0.1 ppm of the $Si-OCH_2$ protons. The ^{13}C NMR spectra also resemble those of the alcohol precursor, with a demultiplication of the PMHS $Si-CH_3$ quartet from 1 ppm in PMHS to several signals for the polysiloxane between −5 and +2.5 ppm.

The ^1H and ^{13}C NMR spectra of the polysiloxane obtained by dehydrogenative silylation of alcohols are similar to those of the polysiloxane obtained by reduction of the carbonyl precursor, as shown in the case of citronellol where the resulting polysiloxane **40** is similar to that obtained from the reduction of citronellal by PMHS (eq 5 and entry 4, Table 10, Supporting Information).

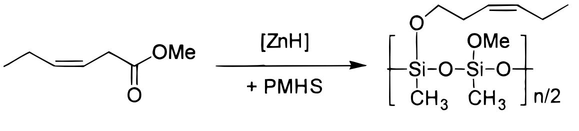


(5)

In the case of esters, the ^1H and ^{13}C NMR spectra of the polysiloxane **41** obtained by the reduction of methyl (*Z*)-3-hexenoate (eq 7) differ from that obtained by dehydrogenative silylation of (*Z*)-3-hexen-1-ol (eq 6) only by the additional presence of the signals of the $Si-OCH_3$ group resulting from the methyl ester (entry 5).



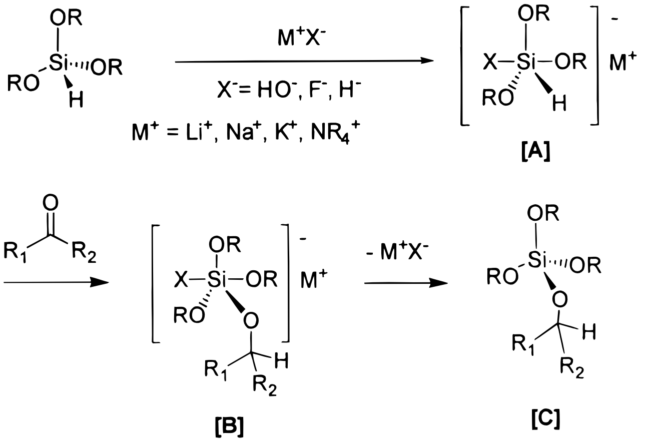
(6)



(7)

Several polysilyl ethers have been prepared from the reaction of various alcohols with PMHS in the presence of 2 mol % of $Zn(2\text{-}EH)_2 + NaBH_4$ catalyst and characterized by NMR, as shown in Table 10. As for the reduction of aldehydes, ketones, and esters, the silylation of alcohols in the presence of ZnH catalysts is perfectly tolerant of double bonds. Other metal 2-ethylhexanoates such as Mn(II) and Fe(II) activated by $NaBH_4$ were also found to be catalytically active for the dehydrogenative silylation of alcohols.

Scheme 1



Discussion

The present work illustrates various possibilities for generating active catalysts for the hydrosilylation of carbonyl compounds. Among the soluble metal carboxylates activated by hydride reducing agents, zinc has been found to be the most effective in a large scope of broad applications.

Hydrosilylation catalyzed by alkali or ammonium fluorides,[5] hydroxides,[5d] and alkoxides[30] is generally thought to proceed through pentavalent anionic alkoxyhydridosilicates [**A**] which have been isolated and characterized, and which act as efficient hydrogen transfer reagents toward carbonyl compounds, including esters (Scheme 1).[31] Whether the carbonyl substrate is activated by coordination to a sixth position at silicon in the alcoxyhydridosilicates,[31a] or by the alkali cationic counterpart, as recently shown in the Li(binol)-catalyzed enantiomeric hydrosilylation of acetophenones by $(MeO)_3SiH$,[30b] is still unclear, since chiral *N*-benzylquininium fluoride having no coordination ability behaves also as an asymmetric reduction catalyst.[5d]

The coordination ability for carbonyl compounds exists for transition metals, and this will determine the particular selectivity observed in the hydrosilylation such as ability for ester reduction, 1,2 vs conjugate reduction of enones, reduction of epoxides, steric effects, etc. Titanium alkoxides are good catalysts for transesterification of esters,[32] and $Ti(OPh)_4$ forms 1:1 adducts with acetone.[33] $ZnCl_2$ forms with aldehydes 1:1 complexes which have been characterized by X-ray structure,[34] and this behavior constitutes the basis of the enantioselective

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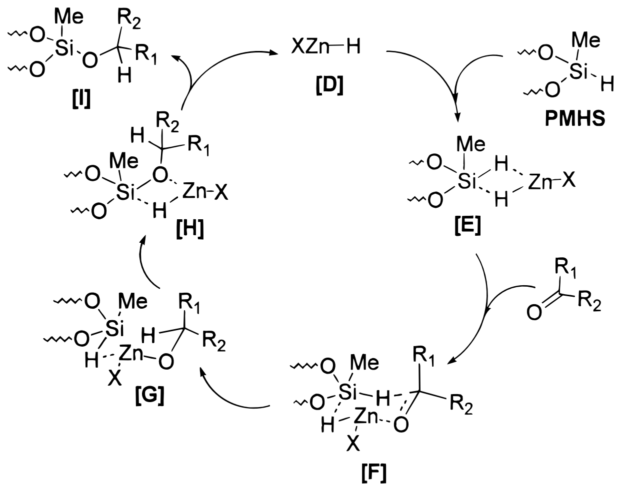
[30] (a) Hosomi, A. In *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; MYU: Tokyo, 1992; Vol. 7, p 214 and references therein. (b) Shiffers, R.; Kagan, H. B. *Synlett* **1997**, 1175.

[31] (a) Corriu, R. J. P.; Guerin, C.; Henner, B.; Wang, Q. *Organometallics* **1991**, *10*, 2297, 3574. (b) Corriu, R. J. P.; Guerin, C.; Henner, B.; Wang, Q. *J. Organomet. Chem.* **1989**, *365*, C7. (c) Corriu, R. J. P., Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 20, p 1241.

[32] (a) Otera, J. *Chem. Rev.* **1993**, *93*, 1449. (b) Siling, M. I.; Laricheva, T. N. *Russ. Chem. Rev.* **1996**, *65*, 279. (c) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807

[33] Masthoff, R.; Kohler, H.; Bohland.; Shmeil, F. *Z. Chem.* **1965**, 122.

Scheme 2

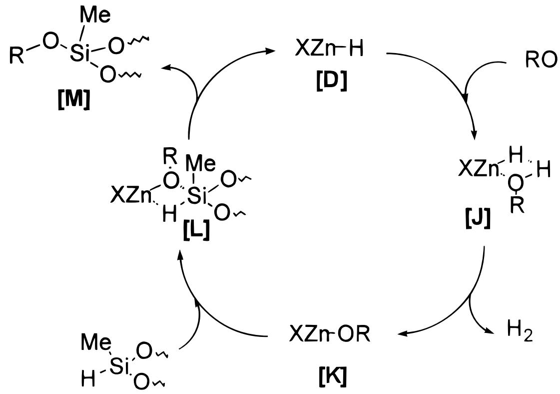


alkylation of aldehydes by dialkylzinc in the presence of chiral amino alcohols.[35] The coordinative ability of zinc toward esters probably explains why $Zn(BH_4)_2$ reduces esters while $NaBH_4$ is usually inefficient.[15]

We have illustrated here the striking properties of soluble zinc carboxylates activated by $NaBH_4$ as catalysts for the hydrosilylation of carbonyl compounds. Although we have not been able to characterize the involved active species, we assume that soluble zinc hydride complexes should be involved in the catalytic cycle. Ashby et al. have prepared a variety of zinc hydride species from the reaction of dialkylzinc and zinc salts with hydride reducing agents such as LiH, NaH, $NaBH_4$, $LiAlH_4$, etc.[36] and we have previously shown that $ZnCl_2$ reduced by 4 equiv of LiH is an efficient catalyst, while insoluble ZnH_2 is inactive (Table 1). The isolated zinc hydride complexes such as **2** and **3** were found less active than the in situ formed $Zn(2\text{-EH})_2 + NaBH_4$ combination, presumably because of their oligomeric nature preventing association with SiH bonds. To our knowledge, there are only two zinc hydride derivatives characterized by X-ray structure, $[Tp^{tBu}]ZnH$[37] and complex **3** (Table 1).[23]

A plausible mechanism for the PMHS hydrosilylation of carbonyl compounds in the presence of zinc hydride catalysts is illustrated by Scheme 2. We assume that, like alkali metal hydrides,[31a] zinc hydride species [**D**] are able to coordinate to PMHS to form adduct [**E**] in which SiH bonds are activated in a reactive pentavalent dihydridosilicate associated to the zinc Lewis acid center. This four-membered adduct [**E**] is reminiscent of $LiAlH_4$ reductions in which Li^+ activates the C=O group and Al–H bonds act as hydride donors[38] and of $Zn(BH_4)_2$ in which Zn activates the carbonyl group and B–H bonds are the hydride donors. As for $LiAlH_4$, hydrogen may be transferred in a concerted way to the C=O bond coordinated to zinc in six-membered ring transition state [**F**]. The resulting zinc alkoxide [**G**] will share the oxygen atom of the alkoxide group with silicium, forming four-membered transition state [**H**] in which a pentacoordinated-activated hydridosilicate is generated. Owing to the higher bond strength of Si–O vs Zn–O, the alkoxide group is transferred to silicon in [**H**] forming the polysiloxane [**I**] and the initial zinc hydride catalyst [**D**] is regenerated, thus completing the catalytic cycle depicted in Scheme 2.

Scheme 3



Steric interaction in the transition state [**F**] between the carbonyl group and the bulky PMHS may explain the low reactivity of the encumbered formylpinane **11a** (Table 4), ketone **20a** (Table 5), and ester **28a** (Table 7), whereas $(MeO)_3SiH$ was found active as silylating agent. This difference cannot be interpreted if the hydride transfer to carbonyl occurs from ZnH separated from PMHS.

Examination of the catalytic cycle (Scheme 2) permits us to envisage two entries for the active species: the zinc hydride entry in intermediate [**E**] and the zinc alkoxide entry in intermediates [**G**] or [**H**]. Such metal hydride–metal alkoxide interchange in the hydrosilylation process has also been suggested to occur in titanium chemistry by Buchwald.[6f] Thus, the catalytic activity of several systems not involving hydride activation (Table 1) could be interpreted by their ability to generate zinc alkoxides: the $Zn(2\text{-EH})_2$–CH_3MgCl system (entry 7) could produce zinc alkoxide from the Grignard methylation of the carboxylate moiety; $ZnEt_2$–diamine systems (entries 14–15) can also alkylate carbonyl substrates and form catalytically active alkoxides species.[20]

The zinc hydride–zinc alkoxide interchange can also readily be used to interpret the dehydrogenative silylation of alcohols by PMHS, as shown in Scheme 3. Like alkali hydrides, zinc hydride species [**D**] readily react with alcohols to give zinc alkoxides with H_2 evolution,[39] presumably through the four-membered intermediate [**J**], and zinc alkoxides add to PMHS to give the four-membered intermediate [**L**] from which the polymethylsiloxane [**M**] is formed and the initial zinc hydride species is regenerated. The driving force of polysilyl ether formation from PMHS and alcohols in the presence of ZnH catalysts overrides the reduction of carbonyl compounds when these are carried out in protic solvents.

Conclusion

We have developed an economical, safe, and industrially important method for the hydrosilylation–reduction

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[34] Müller, B.; Ruf, M.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2089.

[35] Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49 and references therein.

[36] (a) Ashby, E. C.; Watkins, J. J. *Inorg. Chem.* **1973**, *12*, 2493. (b) Watkins, J. J.; Ashby, E. C. *Inorg. Chem.* **1974**, *13*, 2350. (c) Ashby, E. C.; Watkins, J. J. *Inorg. Chem.* **1977**, *16*, 2070, 2075.

[37] Looney, A.; Han, R.; Gorell., I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274. Tp^{tBu} = bis(3-*tert*-butylpyrazolyl)hydroborato.

[38] (a) Noyori, R.; Tomino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709. (b) Boone, J. R.; Ashby, E. C. *Top. Stereochem.* **1979**, *11*, 53.

[39] Bell, N. A.; Kassyk, A. L. *J. Organomet. Chem.* **1988**, *345*, 245; *Inorg. Chim. Acta* **1996**, *250*, 345.

of aldehydes, ketones, esters, triglycerides, and epoxides to alcohols by PMHS in the presence of various metal hydride catalysts among which zinc hydrides, best generated from the reaction of soluble metal carboxylates with sodium borohydride, proved to be the most effective catalysts. The procedure is simple and highly selective for a large variety of carbonyl substrates and affords a cheap and safe alternative to the use of stoichiometric hazardous $LiAlH_4$ reagents. Zinc hydride also efficiently catalyzes the dehydrogenative hydrosilylation of a variety of alcohols using a simple procedure. The hydrosilylation presumably occurs via an interchange between zinc hydride and zinc alkoxide activating PMHS to pentacoordinated hydridosilicates. Further work is being carried out in order to isolate the active species and extend the scope of these reactions to enantioselective reduction.[40]

Experimental Section

General. Chemicals described in the study were all reagent grade purchased from Fluka or available in bulk quantities from Firmenich S.A. PMHS used in this study ($M_w = 2200$; specific gravity at 25 °C = 1; 1.55 wt % H) was obtained from Rhone Poulenc (trade name = Rhodorsil Hydrofugeant 68), but PMHS from other suppliers (Aldrich, Hüls, Bayer, GE, Dow-Corning) was found suitable as well. The molecular weight of PMHS was taken to be 65 for calculations of stoichiometry. The complexes $Zn(BH_4)_2$,[41] $[HZnOC_2H_4NMe_2]_2$,[42] $[PhZnH\cdot Py]_3$,[43] $[HZnN(Me)C_2H_4NMe_2]_2$,[44] and $(PhZnH)_2\cdot TMEDA$[22] were prepared according to literature procedures. Sodium borohydride was supplied by Morton Inc. Zinc, iron, manganese, tin, and cobalt 2-ethylhexanoates (metallic soaps) were commercially available from OMG-Vasset but can also easily be prepared from the reaction of metal oxide, carbonate, or acetate with 2-ethylhexanoïc acid in toluene at 120 °C, with azeotropic distillation of water or acetic acid. All compounds were characterized by GC-MS and ^1H and ^{13}C NMR.

General Reduction Procedure. Solid $NaBH_4$ (2 mol %) was added to a solution of zinc 2-ethylhexanoate (2 mol %) in diisopropyl ether (DIPE). The mixture was stirred at room temperature until all hydrogen has been evolved (ca. 15 min). The substrate (1 molar equiv) was added, and the mixture was heated at 75 °C (reflux DIPE). Then 1.1 molar equiv (for aldehydes, ketones or epoxides) or 2.2 molar equiv (for esters and lactones) PMHS was added in ca. 1 h. The reaction was followed by GC injection of the organic phase obtained after hydrolysis of aliquot samples by 10% NaOH. The mixture was maintained under reflux until all the substrate has been consumed and then was cooled at room temperature and slowly pumped onto an aqueous 30%NaOH or 45%KOH solution (1.2 equiv of OH^-/mol of initial PMHS, carefully avoiding the reverse hydrolysis). The two-phase mixture was stirred for 1 h at 40 °C until two clear phases were formed. The organic phase was concentrated in vacuo, and the resulting alcohol was bulb-to-bulb distilled in vacuo.

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Supporting Information Available: Supporting Information Available: Table 10 (dehydrogenative silylation of alcohols by PMHS) and full Experimental Section (synthesis of **4b**, **18b**, **23b**, **31b**, **37**−**43**, reduction of peanut oil; ^1H and ^{13}C NMR spectra of new compounds **37**−**43** and jojoba alcohols; MS spectra of C_{18}:1, C_{20}:1, C_{22}:1, and C_{24}:1). This material is available free of charge via the Internet at http://pubs.acs.org.

JO982314Z

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(40) Mimoun, H. International Application PCT/1B98/01378 (Sept 3, 1998) to Firmenich S.A.

(41) Crabbe, P.; Garcia, G. A.; Rius, C. *J. Chem. Soc., Perkin Trans. 1* **1973**, 810.

(42) (a) Bell, N. A.; Coates, G. E. *J. Chem. Soc. A* **1968**, 823. (b) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354.

(43) De Koning, A. J.; Boersna, J.; Van Der Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *195*, 1.

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