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Cobalt-catalysed selective synthesis of aldehydes and alcohols from esters[†]

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Efficient and selective reduction of esters to aldehydes and alcohols is reported in which a simple cobalt pincer catalyst catalyses both transformations using diethylsilane as a reductant. Remarkably, the reaction selectivity is controlled by the stoichiometry of diethylsilane.

Alcohols and aldehydes are important building blocks in chemical synthesis and bulk industrial feedstocks. They are widely used in the preparation of agrochemicals, cosmetics, various bioactive molecules and pharmaceutics. Reduction of carboxylic acids using hydride reagents such as DIBAL-H and LiAlH₄ is one of the main synthetic methods for the preparation of alcohols.¹ Such synthesis suffers from the sensitivity of pyrophoric reagents, noncompatibility with other functional groups and poor selectivity.¹ Alcohols can also be obtained from the hydrogenation of esters, which often requires high temperature and pressure.²⁻⁴ In this direction, eminent research groups have developed cobalt catalysed hydrogenation of esters (Scheme 1a).⁵ Alternatively, selective hydroboration and hydrosilylation of aldehyde, ketone and carboxylic acid functionalities and subsequent acidic or basic workup provided primary and secondary alcohols.⁶ Reduction of carboxylate esters using silanes leads to the formation of silylacetal and silvl ether intermediates, which can be converted to aldehydes and alcohols upon hydrolysis.7-14

Selective reduction of esters to aldehydes and alcohols using silanes is becoming a topic of interest and method of choice over the hydrogenation of esters due to the operational simplicity.^{15–18} In particular, hydrosilylation of esters is attractive to implement in synthetic transformations of targeted molecular synthesis as chemo and regioselectivities can be attained. Using transition metals and Lewis acids, controlled synthesis of acetal intermediates from esters and their further conversion to aldehydes have been reported.^{7–10} Notably, earth

abundant metal based catalysts have been developed for hydrosilylation of esters.^{8,18} Cobalt catalysed hydrosilylation of esters to alcohols and aldehydes is limited to one recent report, which used two cobalt salts and the reaction proceeded under heterogeneous conditions (Scheme 1b).¹⁹

We have reported the cobalt catalysed selective synthesis of disiloxanes, monohydrodisiloxanes and oxidation of alcohols to carboxylic acids in which the reactions proceeded with liberation of molecular hydrogen.²⁰ In continuation of our interest in hydroelementation reactions^{6c-e,21} herein we report the cobalt pincer complex [NNN^{H^tBu}CoBr₂] **1** catalysed selective synthesis of aldehydes and alcohols using hydrosilylation of esters. Interestingly, the same catalyst catalyses both transformations and the complete selectivity was attained by stoichiometry of diethylsilane (Scheme 1c).

Using methyl benzoate as a benchmark substrate the reaction conditions for the catalytic hydrosilylation of esters to aldehydes was optimized. Thus, reaction of methyl benzoate and diethylsilane in the presence of catalyst **1** (1 mol%) and KO^{*t*}Bu (2 mol%) was performed at 50 °C, which resulted in 24% conversion of methyl benzoate (Table 1). Increase of the base load to 4 mol% resulted in 99% conversion of methyl benzoate and benzaldehyde was isolated in 89% yield upon acidic workup (entry 3, Table 1). While performing the reaction at room temperature failed to occur, decreasing the catalyst load resulted in diminished conversion and yields (entries 4 and 5, Table 1). No reaction was observed in the absence of catalyst (entry 6, Table 1).

Using the optimised reaction conditions various esters were subjected to the cobalt catalysed hydrosilylation reactions, which transformed the esters to their corresponding aldehydes under mild conditions (Table 2). When butyl benzoate and benzyl benzoate were reacted with diethylsilane, benzaldehyde was obtained in good yields (entries 2 and 3, Table 2). Electrondonating group substituted esters provided the aldehydes **2b** and **2c** in 78% and 91% yields, respectively. The cobaltcatalysed hydrosilylation reaction is chemoselective to the ester functionality and the presence of a nitrile group on the aryl

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Scheme 1 Advances in cobalt catalysis for the conversion of esters to aldehydes and alcohols.

NH^tBu

Table 1 Optimization for cobalt catalysed synthesis of aldehydes from esters^a

	$\begin{array}{c} \begin{array}{c} \begin{array}{c} 1 \end{array} \\ \begin{array}{c} Catalyst 1/KO'Bu \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} 1 \end{array} \\ \begin{array}{c} Catalyst 1/KO'Bu \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} 0 \end{array} \\ \begin{array}{c} 0 \end{array} \\ \begin{array}{c} 0 \end{array} \\ \end{array} \\ \begin{array}{c} 0 \end{array} \\ \end{array} \\ \begin{array}{c} 0 \end{array} \\ \begin{array}{c} 0 \end{array} \\ \end{array} \\ \begin{array}{c} 0 \end{array} \\ \begin{array}{c} 0 \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 0 \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 0 \end{array} \\ \end{array} \end{array} \\ \end{array} \\ \begin{array}{c} 0 \end{array} \end{array} \\ \end{array} \\ \end{array} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \end{array} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \\$			
Entry	1 (mol%)	Base (mol%)	$\operatorname{Conv.}^{b}(\%)$	Yield ^c (%)
1	1	2	24	16
2	1	3	61	51
3	1	4	99	89
4^d	1	4	0	0
5	0.5	4	57	44
6	0	4	0	0

^{*a*} Reaction conditions: methyl benzoate (1 mmol), diethylsilane (1.5 mmol), catalyst **1**, base and toluene (1 mL) taken in a vial was heated at 50 °C under closed conditions. ^{*b*} Conversion was determined by GC using dodecane as an internal standard. ^{*c*} Isolated yield after column chromatography. ^{*d*} Reaction performed at room temperature.

Table 2 Cobalt-catalysed transformation of esters to aldehydes^a

	$\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{1}{1} \frac{1}{1} (1 \text{ mol})/\text{KO}^{\text{tB}}$			3u (4 mol%) 0 ∐		
	R ¹ ´`O´'' 2 ^{0"12} toluene, 50 °C, 12 h R ¹ ´ H 2) 1M HCI/THF, rt -R ² OH, (Et ₂ HSi) ₂ O					
Entry 1	Esters	Aldehydes	Conv. ^b (%)		Yield ^c (%)	
	° °	ОН	2a	99	89	
2	° °	Р	2a	89	81	
3	Ph O Ph	о н	2a	83	72	
4	° °	ОН	2b	86	78	
5		о Н	2c	99	91	
6	NC O	NC H	2d	91	78	
7 ^d	HO	HO	2e	89	83	
8	N C C C C C C C C C C C C C C C C C C C	N H	2f	53	39	
9	F	F	2g	84	73	
10	Br	Br	2h	63	51	
11	Ph 0	H	2i	96	81	
12	Ph O	ОН	2j	89	76	

^a Catalytic conditions: ester (1 mmol), diethylsilane (1.5 mmol), catalyst
 1 (1 mol%) and KO⁶Bu (4 mol%) were heated at 50 °C for 12 h.
 ^b Conversion was determined by GC using dodecane as an internal standard. ^c Isolated yield after column chromatography.

ester was tolerated and the *p*-cyanobenzaldehyde **2d** was isolated in 78% yield. When *p*-hydroxymethyl benzoate was reacted with excess diethylsilane, the product **2e** was isolated in 83% yield (silylation on hydroxyl group was deprotected on acidic workup). *p*-Dimethylamino, *p*-fluoro and *p*-bromo aryl esters reacted under the optimized conditions and the corresponding aldehydes **2f**-**2h** were obtained in moderate to good yields. When methylphenyl acetate and methyl cinnamate were reacted, aldehydes **2i** and **2j** were isolated in 81% and 76% yields, respectively. Notably, the α ,β-unsaturated alkene functionality was also tolerated and did not interfere in the reaction.

Further, we envisaged the hydrosilylation of esters to alcohols using the same cobalt catalyst **1**. Thus, reaction of ester with

	0 + Et₂SiH₂ 1) Catalyst 1/KO'Bu toluene, 50 °C, 20 min 2) 1M HCI/THF, rt -MeOSiEt₂H				
Entry	1 (mol%)	Base (mol%)	Conv ^b . (%)	Yield ^c (%)	
1	2	8	99	82	
2	2	10	99	96	
3	1	10	99	42	
4	1.5	10	99	65	
5	1.5	12	99	71	
6	1.5	14	99	77	
7	0	10	0	0	

 a Reaction conditions: methyl benzoate (1 mmol), diethylsilane (3 mmol), catalyst 1, base and toluene (1 mL) were taken in a vial and heated at 50 $^\circ \rm C$ under closed conditions. b Conversion was determined by GC using dodecane as an internal standard. c Isolated yield after column chromatography.

excess of silane was optimized to provide benzyl alcohol (Table 3). The reaction of methyl benzoate with diethylsilane in the presence of catalyst **1** (2 mol%) and KO⁶Bu (8 mol%) selectively provided benzyl alcohol in 82% yield (entry 1, Table 3) and a similar reaction with increased base load of 10 mol % leads to 96% yield (entry 2, Table 3). Lowering the catalyst load and higher loading of base provided the benzyl alcohol in lower yields (entries 3–6, Table 3). A control experiment performed in the absence of catalyst confirmed the requirement of catalyst (entry 7, Table 3).

The scope of this cobalt catalysed selective conversion of esters to alcohols was explored using various aliphatic and aromatic esters (Table 4). Under the optimized conditions the butyl and benzyl benzoate esters were selectively transformed to benzyl alcohol in good yields (entries 2 and 3, Table 4). Electron donating group substituted aryl esters provided the corresponding alcohols **3b**, **3c** and **3d** in good yields. *p*-Fluoromethyl benzoate resulted in *p*-fluorobenzyl alcohol (**3e**, 88%). Esters such as methylphenyl acetate, methylphenyl propanoate and linear aliphatic esters delivered the alcohols **3f–3i** in excellent yields. Interestingly, upon reaction of diesters such as dimethyl adipate, the corresponding hexamethylene diol (**3j**) was isolated in 86% yield.

More studies are required to understand the mechanism of this cobalt-catalysed hydrosilylation of esters to aldehydes and alcohols. However, a plausible mechanistic pathway involving the dehydro-halogenation reaction on catalyst **1** by base,²⁰ Si–H activation, perhaps involving amine-amide metal–ligand cooperation,²² subsequent hydrosilylation of esters leading to the selective formation of silyl acetal or silyl ether intermediates based on the stoichiometry of diethylsilane and acidic workup delivering the aldehydes and alcohols, respectively is proposed in Scheme S1 (ESI[†]).

In summary, we have developed an efficient and simple catalytic system for the selective reduction of esters to aldehydes and alcohols using diethylsilane as a reductant. Notably, a single cobalt pincer complex catalyses both transformations with complete selectivity without requiring any additives. Remarkably, the stoichiometry of diethylsilane controlled the selective reduction of esters to silylacetal or silylether intermediates and the subsequent Table 4 Cobalt catalysed transformation of esters to alcohols^a

	$ \begin{array}{c} 0 \\ R^{1} \swarrow_{O^{\sim}} R^{2} + El_{2}SiH_{2} \end{array} \xrightarrow{1) 1 (2 \mod\%)/KO'Bu (10 \mod\%)} toluene, 50 °C, 20 min \\ 2) 1M HC/I7HF, rt \\ -R^{2}OSIEL_{2}H \end{array} R^{1} \frown OH $				
Entry 1	Esters	Alcohols	Conv. ^{b} (%)		Yield ^c (%)
			3a	99	96
2		ОН	3a	99	92
3	Ph O Ph	ОН	3a	99	87
4	° °	ОН	3b	99	95
5	Bu	ОН	3 c	99	91
6		OH	3d	99	98
7	F O	F	3e	99	88
8		ОН	3f	99	93
9	Ph O	Phronoh	3g	99	89
10	° C	ОН	3h	99	86
11	° C	ОН	3i	99	84
12^d		ОН	3ј	99	86

^{*a*} Catalytic conditions: ester (1 mmol), diethylsilane (3 mmol), catalyst 1 (2 mol%) and KO'Bu (10 mol%) were heated at 50 °C for 20 minutes. ^{*b*} Conversion was determined by GC using dodecane as an internal standard. ^{*c*} Isolated yield after column chromatography. ^{*d*} Reaction carried out using 6 mmol of diethylsilane.

acidic workup provided the aldehydes or alcohols. Good substrate scope with many functional group tolerances was demonstrated for the synthesis of both aldehydes and alcohols from esters. The hydrosilylation of esters is proposed to proceed *via* Si–H bond activation by cobalt, facilitated by amine-amide metal–ligand cooperation and may involve Co–H intermediacy.

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Conflicts of interest

There are no conflicts to declare.

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