

Cite this: *Chem. Commun.*, 2012, **48**, 10514–10516

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## Selective switchable iron-catalyzed hydrosilylation of carboxylic acids†

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Received 7th August 2012, Accepted 30th August 2012

DOI: 10.1039/c2cc35727e

Selective reduction of carboxylic acids either to aldehydes or alcohols is achieved using a one pot procedure based on iron-catalyzed hydrosilylations. Using phenylsilane and (COD)Fe(CO)<sub>3</sub> catalyst under UV-irradiation at rt, alcohols were obtained specifically in good yields, whereas aldehydes were selectively obtained using TMDS and (*t*-PBO)Fe(CO)<sub>3</sub> catalyst under thermal activation.

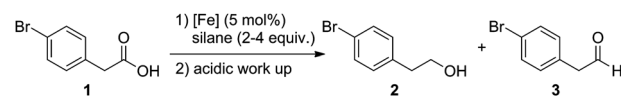
One of the most difficult tasks in organic and total synthesis is the chemoselective reduction of carboxylic acids to either the corresponding alcohols or aldehydes. Indeed, the classical selective direct reduction of carboxylic acids to aldehydes is tedious due to the higher reactivity of aldehydes in comparison with acids, which usually lead to the corresponding alcohols.<sup>1</sup> The classical methodologies to access aldehydes from acids proceed in two steps: (i) the reduction using stoichiometric or catalytic hydride species, followed by (ii) the selective oxidation of the obtained primary alcohols using stoichiometric oxidants.<sup>2</sup> Alternative two step procedures involved a catalytic hydrogenation or hydride reduction of modified more reactive carboxylic acid derivatives such as activated esters,<sup>3</sup> acyl halides<sup>4</sup> or anhydrides.<sup>5</sup> Some effective one-pot procedures involved thexylborane-dimethyl sulfide,<sup>6</sup> alane reagents,<sup>7</sup> isobutyl Grignard reagents *via* titanocene catalyzed reactions<sup>8</sup> and thermal decomposition of activated amino silyl carboxylate.<sup>9</sup> Using transition metal complexes, only scarce examples were described. Recently Nagashima *et al.* have reported an elegant ruthenium catalyzed selective reduction of carboxylic acids to aldehydes using 1,2-bis(dimethylsilyl)benzene.<sup>10</sup> On the other hand, during the last decade, iron-catalyzed reactions,<sup>11</sup> and particularly for reduction,<sup>12</sup> were intensively studied. However, while iron-catalyzed hydrosilylation of carboxylic derivatives such as amides<sup>13</sup> and esters<sup>14</sup> have been recently reported, no example with carboxylic acids was described in the literature. Based on these results and our background on iron-catalyzed hydrosilylation,<sup>13–17</sup> we describe the first general hydrosilylation of carboxylic acids catalyzed by carbonyl iron based catalysts.

Initial studies focused on the reduction of carboxylic acids with several iron catalyst precursors and silanes (Table 1 and

Table S1 in ESI†). Preliminary studies on the catalytic activity of [CpFe(CO)<sub>2</sub>L][X] complexes<sup>15,16</sup> (L = phosphine, *N*-heterocyclic carbene) led to disappointing results as no or low conversions were observed due to degradation of the catalysts. Based on results in hydrosilylation of carboxylic derivatives,<sup>13</sup> we then decided to investigate carbonyl iron precursors for the hydrosilylation of 2-(*p*-bromophenyl)-acetic acid **1**.

Under UV-irradiation (350 nm) at rt, using Fe(CO)<sub>5</sub> or Fe<sub>2</sub>(CO)<sub>9</sub> (5 mol%) as the catalyst in toluene in the presence of 4 equiv. of PhSiH<sub>3</sub>, the reduction of the carboxylic acid **1** led after an acidic work up to the alcohol **2** (65 and 41%, respectively) with trace amount (8%) of aldehyde **3** (entries 1 and 2). In order to increase the reactivity and the selectivity of the reaction, we have selected two iron complexes [Fe(CO)<sub>3</sub>L] bearing a labile bidentate ligand (L = 1,5-cyclooctadiene (COD) or *trans*-4-phenyl-but-3-en-2-one (*t*-PBO)) which should be more easily activated.<sup>18</sup> Indeed, using the complex (CO)<sub>3</sub>Fe(COD)<sup>19</sup> **A** under the same conditions, a full conversion was obtained with an alcohol/aldehyde ratio of 87/13 (entry 3). By contrast, using the complex (CO)<sub>3</sub>Fe(*t*-PBO)<sup>20</sup> **B** only moderate conversion was obtained under irradiation (entry 4). Under thermal conditions (50 °C, 16 h), none of the catalysts permitted to reach full conversions (entries 5 and 6).

**Table 1** Optimization of the conditions for the reduction of carboxylic acids with silanes<sup>a</sup>



Entry	[Fe]	Silane (equiv.)	Solvent	Conditions	Yield <sup>b</sup>
					2/3
1	Fe(CO) <sub>5</sub>	PhSiH <sub>3</sub> (4)	Toluene	UV, 24 h	65 8
2	Fe <sub>2</sub> (CO) <sub>9</sub>	PhSiH <sub>3</sub> (4)	Toluene	UV, 16 h	41 8
3	(CO) <sub>3</sub> Fe(COD) <b>A</b>	PhSiH <sub>3</sub> (4)	Toluene	UV, 24h	87 13
4	(CO) <sub>3</sub> Fe( <i>t</i> -PBO) <b>B</b>	PhSiH <sub>3</sub> (4)	Toluene	UV, 16 h	38 5
5	<b>A</b>	PhSiH <sub>3</sub> (4)	Toluene	50 °C, 16h	10 10
6	<b>B</b>	PhSiH <sub>3</sub> (4)	Toluene	50 °C, 16 h	23 7
7	<b>A</b>	PhSiH <sub>3</sub> (4)	THF	UV, 24 h	<b>99 1</b>
8	<b>A</b>	TMDS (2)	Toluene	UV, 16 h	11 89
9	<b>A</b>	PMHS (4)	Toluene	UV, 16 h	5 58
10	<b>B</b>	TMDS (2)	Toluene	UV, 16 h	4 73
11	<b>B</b>	PMHS (4)	Toluene	UV, 16 h	7 52
12	<b>B</b>	TMDS (2)	Toluene <sup>c</sup>	50 °C, 24 h	<b>2 98</b>
13	<b>B</b>	PMHS (10)	Toluene	50 °C, 24 h	2 38
14	Fe(CO) <sub>5</sub>	TMDS (2)	Toluene	80 °C, 24 h	0 0
15	Fe <sub>2</sub> (CO) <sub>9</sub>	TMDS (2)	Toluene	50 °C, 24 h	11 89

<sup>a</sup> RCO<sub>2</sub>H (0.5 mmol), silane (2–4 equiv.), iron precursor (5 mol%), solvent (2 mL). <sup>b</sup> Determined by GC. <sup>c</sup> 1 mL of toluene.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2cc35727e

Among the variety of silanes and solvents tested (see also Table S1 in ESI<sup>†</sup>), optimal conversions toward the formation of the alcohol were obtained using PhSiH<sub>3</sub> (4 equiv.), in the presence of 5 mol% of the catalyst **A** in THF at rt under UV-irradiation (350 nm) for 24 h (entry 7). More interestingly, using TMDS (1,1,3,3-tetra-methyldisiloxane) (2 equiv.) the reaction with 5 mol% of **A** at rt under UV irradiation for 16 h gave an opposite selectivity as aldehyde **3** was obtained as the major product (89%) with small amount of alcohol **2** (11%) (entry 8). Using PMHS (polymethyl-hydrosiloxane) (4 equiv.), similar selectivity was observed but with lower conversion (2/3 = 5 : 58, entry 9). With the complex **B** as the catalyst under the same conditions the reaction led to aldehyde **3** with 73% yield with 4% of alcohol **2** (entry 10). With PMHS (4 equiv.), aldehyde was obtained in 52% (entry 11). In contrast, when the reaction was performed at 50 °C, 24 h with TMDS in toluene, a full conversion was eventually observed, and aldehyde **3** was selectively obtained in 98% yield (entry 12). It must be also underlined that PMHS was less effective with complex **B** (entry 13), and that Fe(CO)<sub>5</sub> was ineffective under such conditions while Fe<sub>2</sub>(CO)<sub>9</sub> led to an 89/11 mixture of aldehyde/alcohol (entries 14 and 15).

After having optimized the catalytic system to obtain selectively the alcohol or the aldehyde, the scope and limitations of this first selective iron-catalyzed reduction of carboxylic acids into alcohols with PhSiH<sub>3</sub> were explored using **A** (5 mol%) at rt under UV irradiation (350 nm) (Table 2). We have found that the electronic effects at the aromatic ring on phenyl-acetic acid were very limited, and the corresponding alcohols were obtained good to excellent isolated yields (entries 1–7). Of notable interest, no dehalogenation occurred during the reduction process (entry 1). The reaction proceeded also well with acetic acid derivatives bearing a 1-naphthyl or 2-thiophenyl substituent (entries 8 and 9). More hindered substrates such as 2-phenylpropanoic acid and (*R*)-mandelic acid can be also reduced selectively into their corresponding alcohols with 91 and 55% yields (entries 10 and 11). It must be underlined that under such conditions, racemic 1-phenyl-1,2-ethanediol was obtained. Linear carboxylic acid or even di-acid can also be reduced efficiently using this protocol leading the latter to the corresponding diol (entries 12–14). It is noteworthy that the reduction of fatty acids such as oleic acid was also possible, as the corresponding oleic alcohol was obtained in 72% isolated yield. It must be underlined that the reaction was chemo- and stereoselective as there is retention of the (*Z*)-geometry of the double bond (entry 15). However, the isomerisation of alkenes has been reported using Fe(CO)<sub>5</sub><sup>21</sup> or (COD)Fe(CO)<sub>3</sub><sup>22</sup> under UV irradiation. When performing such reduction with carboxylic acids bearing a terminal alkenyl moiety such as hept-6-enoic acid, the reaction was found to be less chemoselective: the corresponding alcohol hept-6-en-1-ol was obtained in 65% yield, but products resulting from the full reduction of the C=C bond and the carboxylic acid moiety (heptan-1-ol, 20%) and from the isomerisation of the C=C bond (15%) were detected (entry 16).

The reduction of benzoic acid derivatives was also possible. Starting from *p*-trifluoromethyl and 2,4-dichloro-benzoic acids, the corresponding alcohols were obtained in moderate yields (68 and 67%) (entries 17 and 18). In this last case, it must be noted that 10% of the over-reduced product, 2,4-dichlorotoluene, was also obtained. With respect to hydroxyl

**Table 2** Selective hydrosilylation of carboxylic acids into alcohols with PhSiH<sub>3</sub> using Fe(CO)<sub>3</sub>(COD) catalyst **A**

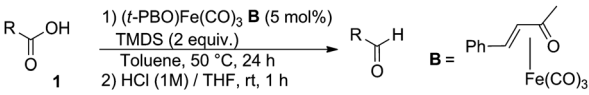
Entry <sup>a</sup>	Carboxylic acid	R	Conv. <sup>b</sup> [%]	Yield <sup>c</sup> [%]
1		R = <i>p</i> -Br-C <sub>6</sub> H <sub>4</sub>	> 97	83
2		R = <i>p</i> -F-C <sub>6</sub> H <sub>4</sub>	> 97	90
3		R = <i>p</i> -OMe-C <sub>6</sub> H <sub>4</sub>	> 97	95
4		R = <i>p</i> -OH-C <sub>6</sub> H <sub>4</sub>	> 97	74
5		R = <i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	96	82
6		R = <i>m</i> -Me-C <sub>6</sub> H <sub>4</sub>	96	88
7		R = <i>o</i> -Me-C <sub>6</sub> H <sub>4</sub>	87	79
8		R = 1-naphthyl	> 97	94
9		R = 2-thiophenyl	> 97	95
10	2-Phenylpropanoic acid		> 97	91
11	( <i>R</i> )-Mandelic acid		80	55
12	3-Phenylpropanoic acid		> 97	95
13	Hexadecanoic acid		85	82
14 <sup>d</sup>	Dodecane-1-12-dioic acid		> 97	97
15	Oleic acid		86	72
16	Hept-6-enoic acid		> 97	—
17		R = CF <sub>3</sub>	> 97	68
18		R = 2,4-Cl <sub>2</sub>	90 <sup>e</sup>	67

<sup>a</sup> RCO<sub>2</sub>H (0.5 mmol), PhSiH<sub>3</sub> (2 mmol), **A** (5 mol%), THF (2 mL) at rt under UV-light irradiation. <sup>b</sup> Determined by GC. <sup>c</sup> Isolated yields. <sup>d</sup> 10 mol% of **A** and 8 equiv. (4 mmol) of PhSiH<sub>3</sub>. <sup>e</sup> 10% of 2,4-dichlorotoluene was also detected.

and methoxy *p*-substituted benzoic acids, only over-reduced products, namely *p*-cresol and 4-methoxytoluene, were, respectively, obtained in full conversion.<sup>23</sup>

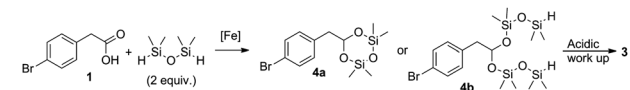
A striking difference of selectivity in the outcome of the reduction of carboxylic acids was observed when using **B** (5 mol%) with TMDS (2 equiv.), in toluene at 50 °C for 24 h leading to aldehydes (Table 3).

The electronic effects at the aromatic ring on phenylacetic acid were limited, and the corresponding aldehydes were produced in good yields (entries 1–6). The reduction of 1-naphthyl- and 2-thiophenyl-acetic acids led to the corresponding aldehydes in moderate yields (entries 7 and 8). A similar selectivity pattern was observed with linear carboxylic acids as the corresponding aldehydes were obtained selectively with good yields (72–81%) but with a slightly higher amount of alcohols as by-products (10–13%) (entries 9 and 10). Importantly, the reduction of dodecanedioic acid selectively led to the corresponding dialdehyde with good selectivity (aldehyde/alcohol: 87/13) and isolated yield (72%) (entry 11). Furthermore, this hydrosilylation reaction is tolerant towards C=C bonds as oleic acid can be transformed into oleic aldehyde in 74% yield, with low amount of alcohol and no trace of reduction of the C=C bond (entry 12). Finally, for more hindered substrates such as 2-phenylpropanoic acid more drastic conditions must be used to observe a full conversion. At 70 °C for 30 h using 4 equiv. of TMDS, the corresponding aldehyde was obtained in 92% yield (entries 13 vs. 14). For (*R*)-mandelic acid, even at higher temperature, no conversion was obtained. However, under such conditions, no conversion was observed for the reduction of benzoic acids.

**Table 3** Selective reduction of carboxylic acids into aldehydes with TMDS using Fe(CO)<sub>3</sub>(*t*-PBO) catalyst **B**<sup>a</sup>


Entry	Carboxylic acid	RCHO/ RCH <sub>2</sub> OH <sup>b</sup> [%]	Yield <sup>c</sup> [%]
1 <sup>e</sup>	R = <i>o</i> -Me-C <sub>6</sub> H <sub>4</sub>	96/4	77 <sup>c</sup>
2	R = <i>m</i> -Me-C <sub>6</sub> H <sub>4</sub>	98/2	95 <sup>c</sup>
3	R = <i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	97/3	83 <sup>c</sup>
4	R = <i>p</i> -OH-C <sub>6</sub> H <sub>4</sub>	88/12	80 <sup>c</sup>
5	R = <i>p</i> -Br-C <sub>6</sub> H <sub>4</sub>	98/2	87 <sup>c</sup>
6	R = <i>p</i> -F-C <sub>6</sub> H <sub>4</sub>	94/6	71 <sup>c</sup>
7	R = 1-naphthyl	96/4	45 <sup>d</sup>
8	R = 2-thiophenyl	98/2	48 <sup>c</sup>
9	3-Phenylpropanoic acid	90/10	72 <sup>c</sup>
10	Hexadecanoic acid	87/13	81 <sup>c</sup>
11 <sup>f</sup>	Dodecane-1-12-dioic acid	87/13	85 <sup>c</sup>
12 <sup>e</sup>	Oleic acid	94/6	74 <sup>c</sup>
13	2-Phenylpropanoic acid	—	9 <sup>c</sup>
14 <sup>g</sup>	2-Phenylpropanoic acid	97/3	92 <sup>c</sup>

(i) RCO<sub>2</sub>H (1 mmol), **B** (5 mol%), TMDS (2 mmol, 2 equiv.), toluene (2 mL) at 50 °C for 24 h. (ii) Acidic work up. <sup>b</sup> Ratio (%) determined by GC. <sup>c</sup> Yields of **3** determined by <sup>1</sup>H-NMR of the crude mixture using DMF as an internal standard. <sup>d</sup> Isolated yields. <sup>e</sup> 48 h. <sup>f</sup> 10 mol% of **B** and 4 equiv. of TMDS. <sup>g</sup> 4 equiv. of TMDS at 70 °C for 30 h.

**Scheme 1** Plausible silyl-acetal intermediates leading to aldehydes.

In order to rationalize the formation of the aldehyde, we have tried to isolate silylated intermediates that might lead to the formation of the carbonyl moieties after the hydrolysis step. Based on the recent work of Nagashima with ruthenium,<sup>24</sup> we have initially postulated a cyclic disilyl acetal intermediate such as **4a** (Scheme 1). However, the analysis of the crude reaction mixture using MS allows us to identify the open disilyl intermediate **4b** (M<sup>+</sup>Na<sup>+</sup> C<sub>16</sub>H<sub>33</sub>O<sub>4</sub><sup>79</sup>BrNaSi<sub>4</sub> calc. 503.0537, found 503.0545). The NMR data of the crude reaction mixture also indicate the presence of the disilyl acetal unit CH(OSi)<sub>2</sub> characterized by the chemical shift of 5.35 and 92.2 ppm, respectively, in <sup>1</sup>H and <sup>13</sup>C NMR.<sup>24</sup> Moreover, the signal of Si–H was also identified at 4.68 ppm.<sup>25</sup> The structure of **4b** is in agreement with the requirement of 2 equiv. of TMDS to get a full conversion, as with 1 equiv., even at 70 °C after 48 h, the conversion could reach only 50%. The stability of the disilyl acetal intermediates derived from TMDS is the key to obtain aldehydes chemoselectively.

In summary, we have developed the first iron-catalyzed efficient and selective switchable hydrosilylation of carboxylic acids either to alcohols or aldehydes depending on the silanes.

We are grateful to CNRS, UR1, and Ministère de l'Enseignement Supérieur et de la Recherche for support, the ministère des affaires étrangères and the fundación Gran Mariscal de Ayacucho (grant to L.C.M.C.) and the foundation Rennes1 (grant to H.L.).

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- 23 Over-reduction products were already observed for the iron-catalyzed hydrosilylation of benzoate derivatives, see ref. 14.
- 24 Disilyl acetal intermediates derived from 1-adamantanoic acid and 1,2-bis(dimethylsilyl)benzene have been characterized. See ref. 10.
- 25 In the crude mixture, the disilyl acetal derivative **4b** was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, COSY, HMBC and HMQC, see ESI†.