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Chemoselective Ruthenium-Catalyzed Reduction of Acid Chlorides to Aldehydes with Dimethylphenylsilane

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Abstract: A variety of aromatic and alkyl acid chlorides can be selectively converted into aldehydes using dimethylphenyl silane ($HSiMe_2Ph$) as the reducing reagent in the presence of the cationic ruthenium catalyst $\{Cp[(i\text{-}Pr)_3P]Ru(NCMe)_2\}^+[PF_6]^-$. The reactions proceed under very mild conditions and are tolerant to many functional groups.

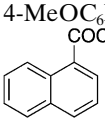
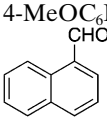
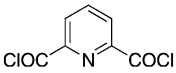
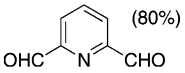
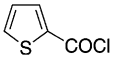
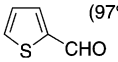
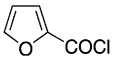
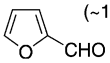
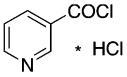
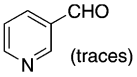
Keywords: acid chlorides; chemoselectivity; hydrosilylation; ruthenium

Reduction of carbonyl substrates is a fundamental organic reaction allowing for their interconversion (e.g., esters to aldehydes) and preparation of a variety of other organic products (e.g., alcohols from ketones).[1] Reductions of aldehydes, ketones and imines by silanes have been in the spotlight for a long period of time, whereas the development of catalytic reduction methods for less reactive substrates has received attention only recently.[2–6] On the contrary, acid chlorides are very reactive compounds but their transformation into aldehydes presents a serious chemoselectivity problem. In addition to the classical Rosenmund reduction by hydrogen, acid chlorides are usually converted to aldehydes by different alumo- and borohydrides (such as DIBALH),[1,7] tin hydrides,[8] transition metal hydrides,[9] or active metals.[10] These methods have serious issues of cost, toxicity, safety, sensitivity to reaction conditions and/or incompatibility with functional groups. In this regard, catalytic reduction by silanes, which have little toxicity, are air-stable and cheap, is a very attractive but surprisingly little studied alternative.[11–13] Earlier studies with group 9 and 10 metals required harsh conditions,[12] but recently Maleczka et al. reported the PMHS reduction of a series of aromatic acid chlorides to aldehydes under mild conditions.[12e] However, the latter method utilizes a Pd catalyst and fails for electron-poor benzoyl chlorides and aliphatic acid chlorides.

We have recently reported the Ru-catalyzed hydrosilylation of carbonyls[14] and developed methods for the chemoselective hydrosilylation of nitriles[5c] and pyridines.[15] Here we extend these studies towards the reduction of acid chlorides by silanes, which is (i) chemoselective towards the formation of aldehydes, (ii) works equally well for aromatic and aliphatic substrates, (iii) goes under mild conditions, (iv) shows excellent tolerance to the presence of several common functional groups, (v) works "on bench" and (vi) the catalyst is recyclable.

Complex $\{Cp[(i\text{-}Pr)_3P]Ru(NCCH_3)_2\}^+[PF_6]^-$ (**1**) effectively catalyzes the chemoselective reduction of a variety of acid chlorides to the corresponding aldehydes by using $HSiMe_2Ph$ as the reducing agent (Table 1).[16] The use of *t*-BuCN (10–20% mol) is crucial for the success of this reaction, as this nitrile stabilizes the catalyst without concomitant nitrile hydrosilylation.[15,17] The reaction proceeds in various solvents (CH_2Cl_2, acetone, acetonitrile[18]), with acetone being the best. Under these conditions, PhCOCl can be quantitatively reduced to PhCHO within only 1 h at room temperature (Table 1, entry 1). Gratifyingly, we observed that aliphatic acyl chlorides (entries 2–8) also can be reduced as easily as aromatic derivatives (entries 1 and 10–13). Chlorine substituents in the α- and β-positions are tolerated and the corresponding aldehydes were obtained with high selectivity (entries 5–7), but only traces of aldehyde are observed for the more reactive bromide derivative $BrCH_2CH_2COCl$ (entry 8). The less substituted substrates (entries 2 and 3) react faster than sterically loaded ones (entry 4). The reduction of some substrates containing α-protons resulted in the formation of a mixture of target aldehydes and silyl enols (e.g., entries 2 and 7). But the latter compounds can be easily converted into aldehydes by a simple aqueous work-up.[19]

Table 1. Catalytic hydrosilylation of acid chlorides with $HSiMe_2Ph$.[a]

Entry	Substrate	Conversion[b] (time)	Products (yield)[b]
1	C_6H_5COCl	100% (1 h)	C_6H_5CHO (~100%)
2	CH_3COCl	>90% (2 h)	CH_3CHO (70%); CH_2=$CHOSiMe_2Ph$ (20%)
3	CH_3CH_2COCl	100% (1 h)	CH_3CH_2CHO (~100%)
4	$(CH_3)_3CCOCl$	100% (4 h)	$(CH_3)_3CCHO$ (~100%)
5	$ClCH_2COCl$	100%[c] (1 h)	$ClCH_2CHO$ (90%)
6	$CH_3CHClCOCl$	100% (24 h)	$CH_3CHClCHO$ (95%)
7	$ClCH_2CH_2COCl$	100% (5 h)	$ClCH_2CH_2CHO$ (80%); ClCH=$CHOSiMe_2Ph$ (20%)
8	$BrCH_2CH_2COCl$	80% (24 h)	$BrCH_2CH_2CHO$ (traces)
9	PhCH=CHCOCl	70%[c] (18 h)	PhCH=CHCHO (18%); $PhCH_2CH$=$CHOSiMe_2Ph$ (82%)
10	4-BrC_6H_4COCl	100% (3 h)	4-BrC_6H_4CHO (~100%)
11	4-$O_2NC_6H_4COCl$	90%[c] (5 h)	4-$O_2NC_6H_4CHO$ (85%)
12	4-$MeOC_6H_4COCl$	>90% (24 h)	4-$MeOC_6H_4CHO$ (83%); 4-$MeOC_6H_4CH_2OSiMe_2Ph$ (17%)
13		100% (20 h)	 (95%)
14		100%[c,d] (3 h)	 (80%)
15		>97% (24 h)	 (97%)
16		100% (24 h)	 (~100%)
17		100%[c,d,e] (24 h)	 (traces)
18	EtOOC-COCl	100%[c,f] (20 h)	EtOOCCHO (65%)

[a] In a general procedure to a solution of acid chloride in acetone-d_6 was added 1.5 equiv. of $HSiMe_2Ph$, 10–20 mol% of *t*-BuCN, and 5% mol of **1** at room temperature.
[b] Based on ^1H NMR data.
[c] 2 equiv. of CH_3CN were added instead of *t*-BuCN.
[d] 2.5 equiv. of $HSiMe_2Ph$ were added.
[e] Conversion of silane is given.
[f] Reaction in chloroform.

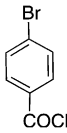
Chemoselectivity is lost, however, in the case of a conjugated acid chloride, PhCH=CHCOCl (entry 9), as a mixture of the corresponding aldehyde (13%) and the product of the formal silane 1,4-addition to the aldehyde (57%) is observed. Interestingly, the hydrosilylation of PhCH=CHCHO under similar conditions is very sluggish, which suggests that $PhCH_2CH$=$CHOSiMe_2Ph$ does not stem from the direct addition of silane to aldehyde.

Reduction of aromatic acid chlorides with electron-withdrawing groups (entries 10 and 11) proceeds as smoothly as the reduction of electro-neutral substrates (entries 1 and 13), and the reactive nitro group is tolerated (entry 11). In contrast, the reduction of an electron-rich substrate, with a donating MeO group (entry 12), is much slower and some loss of chemoselectivity is observed, leading to a mixture of the target aldehyde (83%) and its hydrosilylation product $MeOC_6H_4CH_2OSiMe_2Ph$ (17%).

A similar reactivity pattern is observed in the reactions of heteroaromatic acid chlorides. The electron-poor 2,6-pyridinedicarbonyl chloride is converted into a mixture of the corresponding mono- and bis-pyridinecarboxaldehydes, with the 2,6-bis-pyridinecarboxaldehyde becoming the predominant product (~80%) only after 3 h at room temperature (entry 14). In contrast, the reduction of electron-rich furan and thiophene derivatives goes to completion after 24 h (entries 15 and 16). Surprisingly, the course of reduction of pyridine substrates was sensitive to the position of the COCl group in the ring, as the reaction of a 3-substituted derivative gave only traces of the aldehyde product (entry 17), but this reaction might be compromised by the presence of an excess amount of HCl in the reaction mixture. Importantly, the ester functionality in the reduction of EtOOC-COCl is tolerated (entry 18).

To establish further the selectivity of this reduction method, the reaction of 4-bromobenzoyl chloride with $HSiMe_2Ph$ was studied in the presence of other potentially reactive compounds, such as alkenes, alkynes, esters, etc. (Table 2). To our delight, the presence of

Table 2. Reduction of *p*-BrC_6H_4COCl with $HSiMe_2Ph$ in the presence of other substrates.[a]

Entry	Substrate 1	Substrate 2	Conversion[b]
1		$CH_3(CH_2)_3CH{=}CH_2$	Substrate 1: ~100%; Substrate 2: 0%
2		AcOEt	Substrate 1: 90%; Substrate 2: 0%
3		EtC≡CEt	Substrate 1: 50%; Substrate 2: 50%
4		PhC≡CH	Substrate 1: 50%; Substrate 2: 5%

[a] In a general procedure to a solution of acid chloride and substrate 2 in acetone-d_6 was added 1.5 equiv. of $HSiMe_2Ph$, 2 equiv. of CH_3CN, and 5 mol% of **1**.
[b] Based on ^1H NMR data.

hex-1-ene or ethyl ester does not hamper the course of reduction of 4-BrC_6H_4COCl (entries 1 and 2). On the other hand, the hydrosilylation of an internal triple bond C≡C of alkyne proceeds as fast as the reduction of the COCl group, and a mixture of EtCH=C($SiMe_2Ph$)Et (50%) and 4-BrC_6H_4CHO (50%) was observed in the presence of hex-3-yne (entry 3). Surprisingly, no hydrosilylation of the terminal triple bond of PhC≡CH was observed. Unfortunately, the latter compound poisons the catalyst, and the reduction of 4-BrC_6H_4COCl stops at only 50% conversion (entry 4).

In order to check the practicability of this reduction method, a reaction with a representative acid chloride was performed on a preparative scale. Thus, the reaction of 4-BrC_6H_4COCl (0.5 g) with $HSiMe_2Ph$ in the presence of **1** (5 mol%) and *t*-BuCN (10 mol%) affords the corresponding aldehyde in the 80% isolated yield after recrystallization from hexanes. This procedure does not require a special set-up and can be performed on the bench in a flask pre-flushed with inert gas. Importantly, the catalyst is recyclable and can be easily separated from products by precipitation with hexane. Although there is a slow decomposition of the catalyst during the reaction, most of it can be recycled at least five times without any significant decrease in activity.

For the hydrosilylation of pyridine and nitriles catalyzed by **1** we have previously considered an ionic mechanism, based on nucleophilic abstraction of a silylium ion by the nitrogen donor.[5c,15] Although acid chlorides are weaker nucleophiles, we were also puzzled by the observation that their reduction proceeds at rates much slower than the hydrosilylation of nitriles,[5c] but nevertheless aldehydes can be obtained in the presence of acetonitrile. To address this paradox, we first considered the possibility that the chloride may be reduced by the initial product of nitrile hydrosilylation, the imine RHC=N$SiMe_2Ph$. However, the latter was found to react with acid chlorides to give acyl imines R′C(O)N=CHR, which then undergo reduction of the imine group. Another possibility, a radical mechanism, was then ruled out as the addition of stoichiometric amounts of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl), a known radical scavenger, did not affect the rate of reduction of *t*-BuCOCl. When a 1:1:1 reaction of 4-BrC_6H_4COCl, $HSiMe_2Ph$, and **1** was followed by VT NMR, a noticeable reaction was observed at −25 °C with the formation of $\{Cp[(i\text{-}Pr)_3P]Ru(NCCH_3)(\eta^2\text{-}HSiMe_2Ph)\}^+$, a known complex.[14] However, further gentle increase of temperature to 0 °C results in the fast production of aldehyde and no further intermediates were detectable. To date, the exact mechanism of this catalytic reaction remains unknown.

In conclusion, we have discovered a new convenient and general method for the chemoselective reduction of acid chlorides to aldehydes which uses a non-toxic silane $HSiMe_2Ph$, operates under mild conditions, works equally well for aliphatic, aromatic and heteroaromatic substrates, tolerates several important functional groups, works on bench, is scalable, and allows for catalyst recycling. Finally, the catalyst has a good shelf life in air and can be easily assembled prior to use from commercially available materials.

Experimental Section

All manipulations were carried out using conventional high-vacuum or nitrogen-line Schlenk techniques. NMR spectra were recorded on Bruker (^1H, 300 MHz; ^{13}C, 75.4 MHz) and/or Bruker (^1H, 600 MHz; ^{13}C, 150.8 MHz) spectrometers. All chemicals were purchased from Sigma–Aldrich, apart from $HSiMe_2Ph$ which was purchased from Gelest. These reagents were used without purification. NMR solvents were from Cambridge Isotope Laboratories. $CDCl_3$ was dried over CaH_2 and acetone-d_6 was dried over molecular sieves (3 Å). Other solvents were dried by distillation from appropriate drying agents or using a Grubbs-type solvent purification system. Complex **1** was prepared according to the literature procedure.[20]

General Procedure for Catalytic Reaction of Acid Chlorides

In a representative procedure, to a solution of acid chloride (0.20 mmol), $HSiMe_2Ph$ (0.030 mL, 0.20 mmol), internal

standard (TMS or Cp_2Fe), and *t*-BuCN (0.002–0.004 mL, 10–20 mol%) in acetone-d_6 (0.6 mL) was added complex **1** (0.005 g, 5 mol%). The resulting mixture was stirred at room temperature and the progress of the reaction was monitored by NMR spectroscopy.

Representative Example of a Preparative-Scale Reduction with Catalyst Recycling

To a solution of 4-BrC_6H_4COCl (0.500 g, 2.28 mmol), $HSiMe_2Ph$ (0.400 mL, 2.61 mmol), and *t*-BuCN (0.025 mL, 10 mol%) in CH_2Cl_2 or acetone (30 mL) was added complex **1** (0.065 g, 5 mol%). The resulting mixture was stirred at room temperature. Full conversion of the acid chloride was observed within 3 h (in acetone) or 1 day (in CH_2Cl_2). To the resulting mixture was added hexane (30 mL) and the solution was concentrated to 5 mL under vacuum. The products were extracted with hexane (3×10 mL). The remaining catalyst was used again (4 times) with the same amounts of the starting reagents. The aldehyde was recrystallized each time from hexane solutions at −80 °C. Yields: ~70% (reactions in CH_2Cl_2) or ~90% (reactions in acetone).

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[16] No reduction happens in the absence of the catalyst.
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