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Marie Kobylarski, Liam Donnelly, Jean-Claude Berthet, Thibault Cantat. Zirconium-catalysed hydrosilylation of esters and depolymerisation of polyester plastic waste. 2022. cea-03772514v1

HAL Id: cea-03772514

<https://cea.hal.science/cea-03772514v1>

Preprint submitted on 31 May 2022 (v1), last revised 27 Sep 2022 (v2)

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Zirconium-Catalysed Hydrosilylation of Esters and Depolymerisation of Polyester Plastic Waste

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Abstract

Schwartz's reagent, $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$, has traditionally been used as a stoichiometric reagent for the reduction of unsaturated organic molecules. Recently, methods to use $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ as a catalyst have been developed through turnover of the Zr–X intermediates, formed upon reaction with an organic substrate, with hydride reagents. Herein, we report the development of a new catalytic pathway for the reduction of esters that uses the bench-stable silane $\text{Me}(\text{OMe})_2\text{SiH}$ (DMMS) as a mild stoichiometric reductant and $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ as the catalyst. This system exploits the regeneration of Zr–H through the sigma bond metathesis of Zr–O and Si–H to achieve catalyst turnover. These reaction conditions tolerate a range of reducible functional groups (e.g. alkyne, alkene, and nitro) and give high yields of the corresponding alcohol (up to 91% isolated yield). We have also applied this methodology to the reductive depolymerisation of polyesters found in household plastic waste.

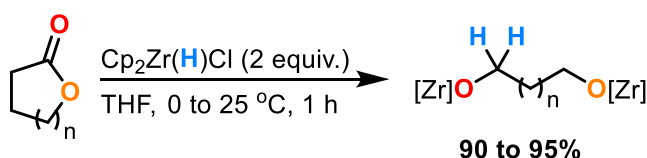
Introduction

The monohydride Zr(VI) complex Schwartz's reagent ($\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$) (**1**) was first reported by Wailes and Weigold in the 1970s.^{1–3} This complex **1** has been shown to be a versatile stoichiometric reducing agent for unsaturated organic compounds.⁴ This reactivity is enabled by the availability of an empty valence orbital on the zirconium center which allows the coordination of the substrate, followed by reduction via an hydrozirconation pathway. Stoichiometric hydrozirconation using complex **1** was demonstrated for alkenes,⁵ alkynes,³ amides,^{6,7} nitriles,⁸ imines,⁹ isocyanates,¹⁰ phosphine oxides,¹¹ and ketones.¹² In 1996, Majoral and Skowronska, developed the first stoichiometric application of complex **1** for the reductive cleavage of ester groups in lactones and cyclic anhydrides. They obtained the corresponding diol derivatives in excellent yields, at room temperature, after 1 h (Scheme 1).¹³ Although these results were limited in terms of scope and mechanistic investigation, they highlighted the efficiency of the Schwartz's reagent (**1**) as a reducing agent for ester functionalities.

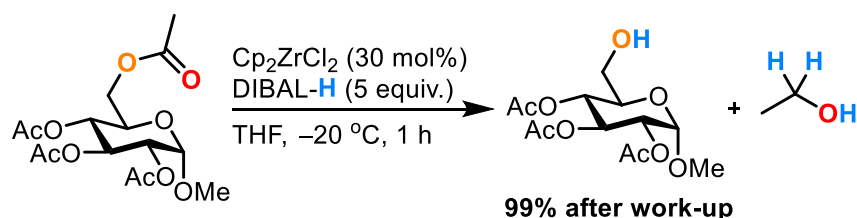
Only quite recently, there has been a growing interest in using $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (**1**) as a catalyst combined with hydride donors for the reduction carbonyl groups. In 2021, Lecourt *et al.* described the reduction of primary acetates using Cp_2ZrCl_2 as the catalyst and diisobutylaluminium hydride (DIBAL-H) as the reductant.^{14,15} However,

this required the use of superstoichiometric quantities of pyrophoric reagents, high catalyst loading (30 to 100 mol%) and cryogenic temperatures (-20 to -30 °C). In 2022, Bayeh-Romero *et al.* reported a single example of the reduction of an ester (a lactone) by the *in situ* preparation of the catalyst **1** from Cp_2ZrCl_2 and dimethoxy-(methyl)silane (DMMS) in the presence of Et_2NH .¹⁶ The desired diol was obtained in a moderate yield (55%) even after an extended reaction time (24 h).

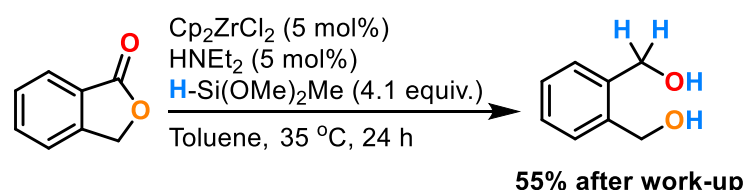
Skowronska and Majoral, 1996:



Lecourt *et al.*, 2021:



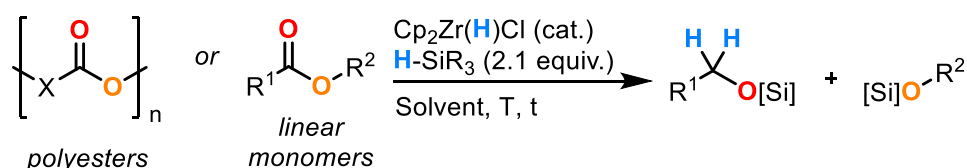
Bayeh-Romero *et al.*, 2022:



Scheme 1. Limited previous examples of ester reduction mediated/catalysed by Zr-H.

Recently, we proved that $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (**1**) could also catalyse the partial reduction of secondary amides to imines.¹⁷ This reaction proceeded with high chemoselectivity, avoiding over reduction to amine products, and the reactivity was enabled by the exquisite inherent selectivity of the catalyst and the use of hydrosilanes as mild reductants.⁴ Given that amides with their poor carbonyl electrophilicity are more difficult to reduce than esters, and inspired by the previous examples of Zr-catalysed/mediated ester reduction, we herein describe a general and practical method for the hydrosilylation of linear monomeric esters into their alcohol derivatives (Scheme 2). To demonstrate the robustness of our methodology, we expanded the substrate scope to include a range of polyester plastic materials. By overcoming the inherent low reactivity of these polymer materials due to their lack of solubility, inhomogeneity and relatively low purity, we provide an example of chemical upcycling by transforming waste materials into value-added monomer products.^{18–20}

This work - catalytic reduction of linear esters and polyesters



Scheme 2. Development of a general procedure for Zr-catalysed ester hydrosilylation.

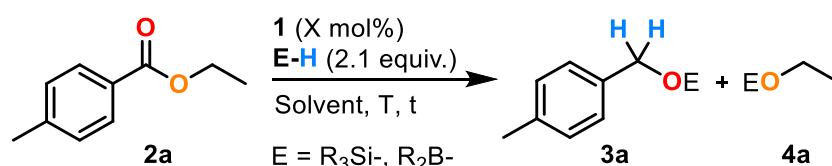
Results & Discussion

Based on the work of Bayeh-Romero *et al.* and our previous work on the reduction of secondary amides,^{16,17} initial conditions were applied to the reduction of ethyl 4-methylbenzoate **2a**, using 10 mol% of $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (**1**) with 2.1 equiv. of dimethoxy(methyl)silane (DMMS) in $\text{THF-}d_8$ at 80 °C (Table 1, Entry 1). After only 1 h, the corresponding 4-methylbenzyl silylated ether **3a**^{Si} was obtained in a yield of >95%. Reducing the catalyst loading to 5 mol% required an extended reaction time of 2 h to reach a similar yield in **3a** and the conditions using 1 mol% of **1** led to the reaction stalling at 81% yield after 18 h (Table 1, Entries 2 and 3).

To study the efficiency of Schwartz's reagent (**1**) as a new catalyst for the reduction of esters, we tested using 5 mol% with different hydrosilanes as reductants (Table 1, Entries 4 to 7). Polymethylhydrosiloxane (PMHDS), Et_3SiH and Ph_3SiH only gave trace yields of **3a**, whereas $(\text{EtO})_3\text{SiH}$ gave >95% yield after 5 h. This highlights the importance of having at least two alkoxy substituents on the hydrosilane, as noted previously for the reduction of secondary amides.¹⁷

A solvent screen showed a rate increase in C_6D_6 , with >95% yield of **3a** already after 1 h (Table 1, Entry 8). Similar reactivity to that in $\text{THF-}d_8$ was observed in CD_2Cl_2 and also in anisole (Table 1, Entries 9 and 10), which is regarded as a non-toxic and biodegradable solvent according to the CHEM21 guide.²¹ The influence of the temperature was investigated and full conversion was achieved at 25 °C after 12 h and at 60 °C after 2 h (Table 1, Entries 11 and 12).

Exchanging DMMS for pinacolborane (HBpin) resulted in the efficient reduction of **2a** after 1 h at 80 °C, demonstrating that reductants based on boron are also applicable to this system, although only sluggish reactivity was observed using catecholborane (HBCat) (Table 1, Entries 13 and 14). The reaction did not proceed in the absence of the catalyst and only gave trace conversion in the absence of silane (see ESI).



Entry	Cat. X (mol%)	Solvent	Reductant	T (°C)	Time (h)	Conversion ^a (%)	Yield ^a (%) in 3a
1	10	$\text{THF-}d_8$	DMMS	80	1	>95	>95

2	5	THF- <i>d</i> ₈	DMMS	80	1	86	86
					2	>95	>95
3	1	THF- <i>d</i> ₈	DMMS	80	1	48	48
					18	80	81
4	5	THF- <i>d</i> ₈	PMHDS	80	7	<5	<5
5	5	THF- <i>d</i> ₈	Et ₃ SiH	80	7	n.d.	n.d.
6	5	THF- <i>d</i> ₈	Ph ₃ SiH	80	7	n.d.	n.d.
7	5	THF- <i>d</i> ₈	(EtO) ₃ SiH	80	1	31	31
					2	65	65
					5	>95	>95
8	5	C ₆ D ₆	DMMS	80	1	>95	>95
9	5	CD ₂ Cl ₂	DMMS	80	1	72	72
					2	>95	>95
10	5	Anisole	DMMS	80	1	85	85
					2	>95	>95
11	5	C ₆ D ₆	DMMS	25	1	34	30
					12	>95	>95
12	5	C ₆ D ₆	DMMS	60	1	72	70
					2	>95	>95
13	5	C ₆ D ₆	HBpin	80	2	>95	>95
14	5	C ₆ D ₆	HBCat	80	2	8	6

Table 1. Optimisation of reaction conditions for the reduction of ester **2a**.

^aYields measured by ¹H NMR against mesitylene as an internal standard. n.d. = not detected.

To investigate the mechanism of this catalytic system, we first studied the elementary steps by a series of stoichiometric reactions (Figure 1). The 1:1 reaction of complex **1** with ester **2a** in C₆D₆ resulted in 47% conversion of the ester **2a** to the alkoxyzirconocene products **3a^{Zr}** and **4a^{Zr}** after 2 h at 80 °C. This ratio did not change upon heating for a further 16 h. The addition to this mixture of 1.1 equivalent of DMMS gave full conversion of ester **2a** and the formation of a mixture of alkoxyzirconocene products **3a^{Zr}** (36%) and **4a^{Zr}** (21%) and silyl ethers **3a^{Si}** (61%) and **4a^{Si}** (78%) after 1 h at 80 °C. The ratio between these products did not change significantly upon heating for a further 25 h, suggesting that the system reaches an equilibrium state. The potential over reduced products (*p*-xylene and ethane) resulting from exhaustive deoxygenation were not detected during this experiment. These results confirm that

under these conditions the complexes **3a^{Zr}** and **4a^{Zr}** can be converted to the silyl ethers **3a^{Si}** and **4a^{Si}** by exchange of the Zr–OR and Si–H bonds, in line with the relative oxophilicities of Si and Zr.²¹ This transformation also results in the regeneration of Cp₂Zr(H)Cl (**1**) which facilitates further conversion of ester **2a**. This is consistent with the mechanism proposed by Bayeh-Romero for the hydrosilylation of ketones and aldehydes and in agreement with our observations for the reduction of secondary amides.^{16,17}

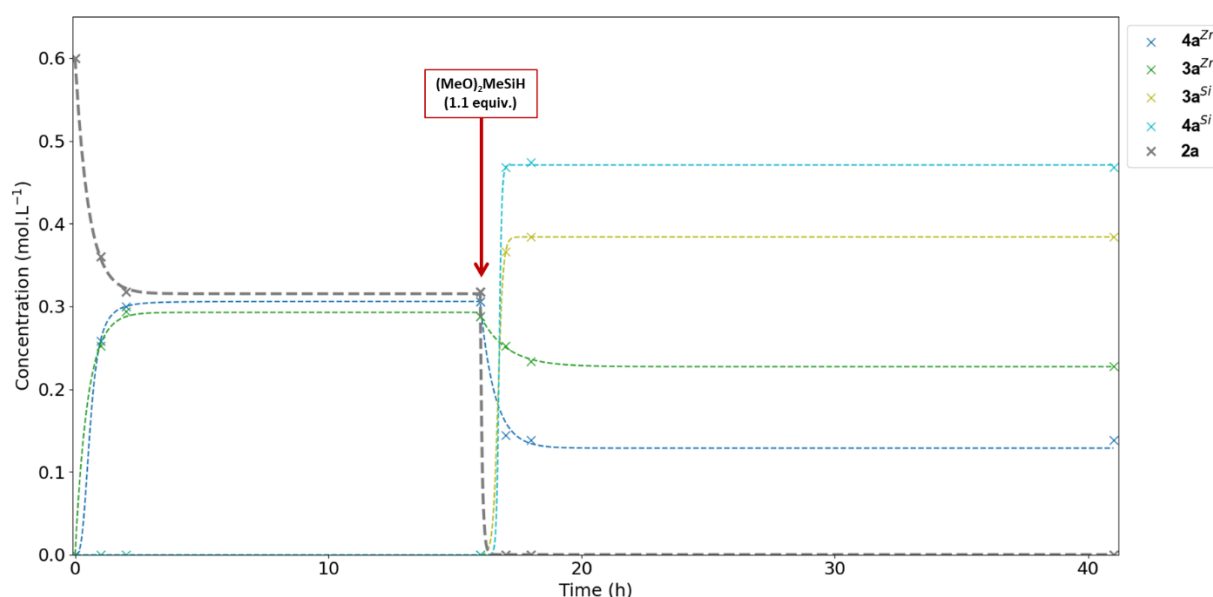
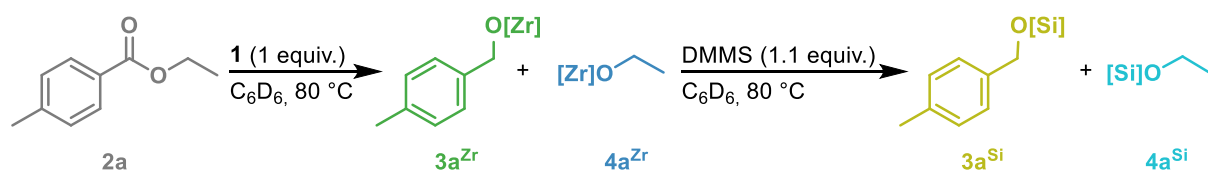
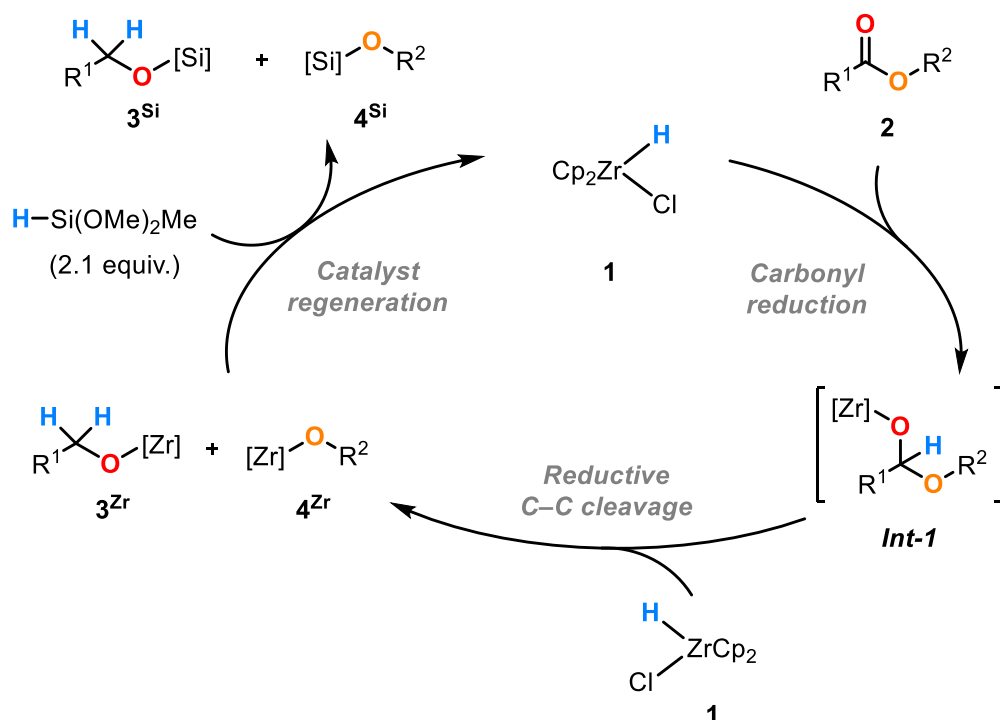


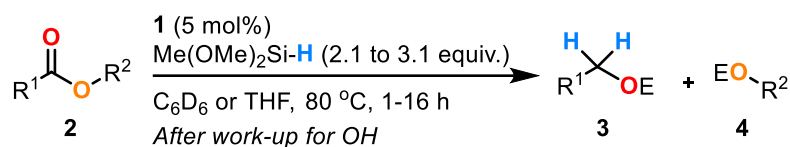
Figure 1. Time-step analysis by ¹H NMR spectroscopy of the stepwise stoichiometric reduction of **2a** by complex **1** and DMMS.

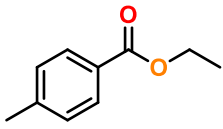
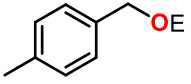
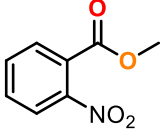
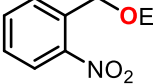
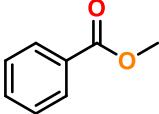
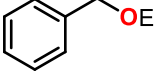
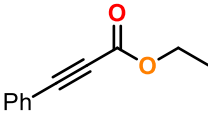
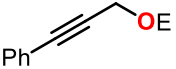
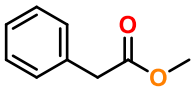
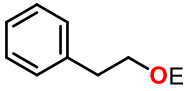
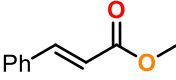
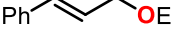
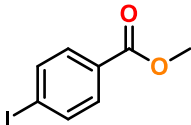
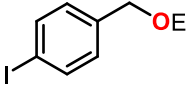
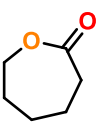
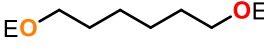
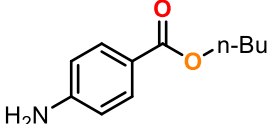
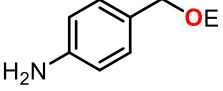
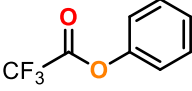
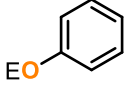
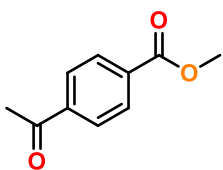
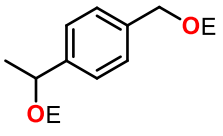
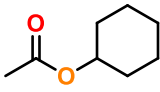
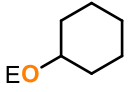
Based on these results and the previous work in this area, we propose the following catalytic cycle (Scheme 3). After the addition of the Zr–H bond of the catalyst **1** to the carbonyl C=O bond of the ester **2**, the intermediate species (**Int-1**) undergoes rapid reductive cleavage of the C–O bond, facilitated by a second equivalent of complex **1**. The resulting alkoxyzirconocene complexes (**3^{Zr}** and **4^{Zr}**) perform a σ -bond metathesis with the hydrosilane to form the desired silyl ether products (**3^{Si}** and **4^{Si}**), with concomitant regeneration of the Zr–H catalyst **1**.



Scheme 3. Proposed catalytic cycle for the reduction of esters **2** by complex **1**.

Using the optimised conditions defined above for ethyl 4-methylbenzoate **2a** (Table 1, Entries 2 and 8), the generality of this system was explored through a substrate scope (Scheme 4). The benzoate esters **2a** and **2b** and methyl phenylacetate **2c** were cleanly reduced to the corresponding alcohols. Iodo- and amino-substituted esters **2d** and **2e** were well tolerated in this reaction with no observed hydrodehalogenation nor N–H silylation, respectively. The keto-substituted ester **2f** was reduced to the diol by addition of 3.1 equivalents of DMMS. An ester containing a nitro group **2g** required heating at lower temperature (40 °C) for an extended reaction time (24 h) to control the chemoselectivity. Alkynes and alkenes **2h** and **2i** were not reduced under these conditions with only selective ester reduction observed for these examples, although it was necessary to perform the reduction of **2h** at a lower temperature of 40 °C for 16 h. ϵ -Caprolactone **2j** was efficiently reduced to the corresponding diol. The electron-poor ester **2k** was converted to the desired products but required an extended reaction time of 16 h to reach full conversion. The sterically congested ester **2l** was also efficiently transformed to the alcohol products.



Substrate	Product	Substrate	Product
 2a	 E=[Si] >95%, E=H 66% 1 h, 3a	 2g	 E=[Si] 79%, E=H 64% 16 h, 3g ^a
 2b	 E=[Si] >95%, E=H 55% 1 h, 3b	 2h	 E=[Si] 68%, E=H 66% 16 h, 3h ^a
 2c	 E=[Si] >95%, E=H 83% 1 h, 3c	 2i	 E=[Si] 94%, E=H 82% 1 h, 3i
 2d	 E=[Si] 94%, E=H 72% 1 h, 3d	 2j	 E=[Si] >95%, E=H 66% 1 h, 3j
 2e	 E=[Si] 94%, E=H 91% 1 h, 3e	 2k	 E=[Si] >95%, E=H 27% 16 h, 4k
 2f	 E=[Si] >95%, E=H 77% 2 h, 3f	 2l	 E=[Si] >95%, E=H 62% 3 h, 4l

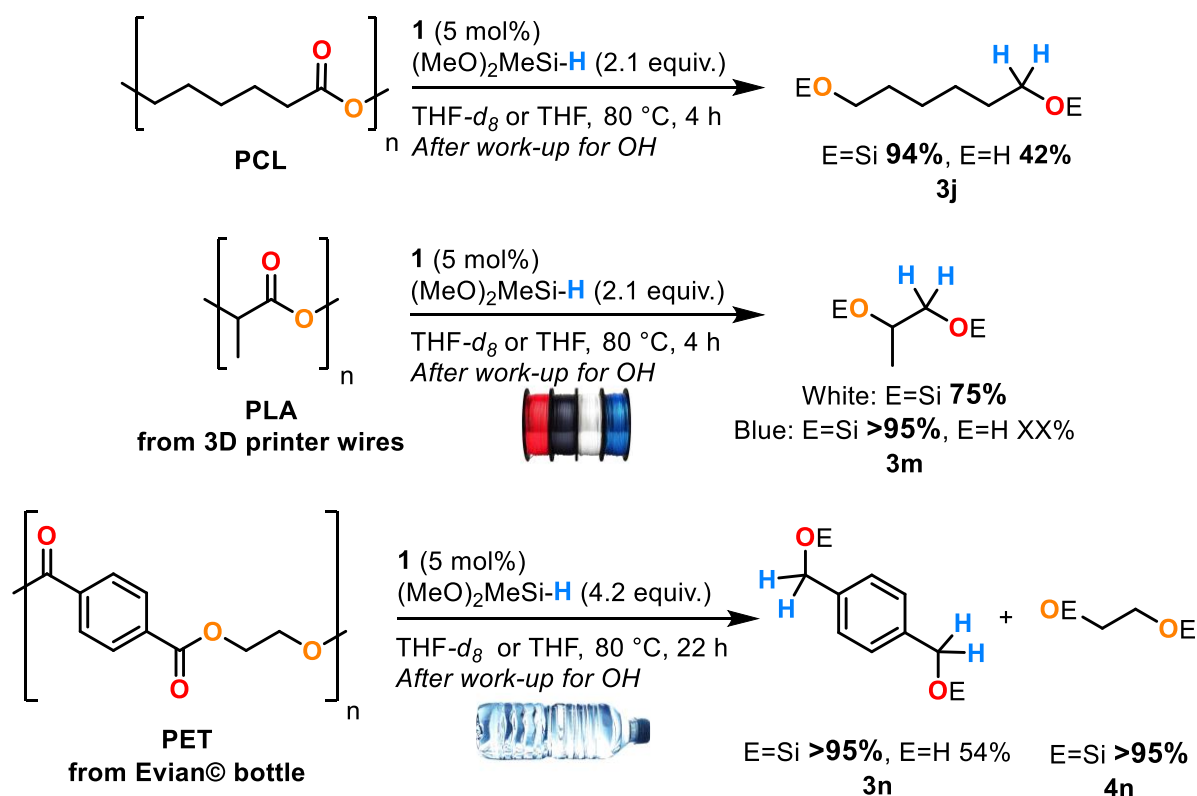
Scheme 4. Substrate scope for the hydrosilylation of monomeric esters **2** catalysed by complex **1**.

The yields of the silyl ethers were measured by ¹H NMR spectroscopy by integration against mesitylene as an internal standard (reactions conducted in C₆D₆). The yields of the alcohols are isolated yields from reactions in THF after basic workup. ^aReactions conducted at 40 °C.

Given that this catalytic hydrosilylation system could reduce monomeric esters to alcohols in high efficiency, we were encouraged to apply it to the reductive depolymerisation of polyesters found in household plastic waste. Within this growing research field, our group previously reported the catalytic reductive depolymerisation

of a variety of polyesters with the strongly Lewis acidic catalysts $B(C_6F_5)_3$ and $[Ir(POCOP)H(THF)][B(C_6F_5)_4]$ (POCOP = 1,3-(tBu_2PO) $_2C_6H_3$) and hydrosilanes as hydride donors.^{23,24} Recently, Fernandes *et al.* performed the hydrosilylation of polyesters from commercial and waste samples using $MoO_2Cl_2(H_2O)_2$ and $Zn(OAc)_2$ as catalysts.^{25–28} Related to this hydrosilylation reactivity, we have demonstrated that an f-element complex ($La(N(SiMe_3)_2)_3$) could act as a catalyst to depolymerize polyesters and polycarbonates in the presence of hydroboranes at low catalyst loadings (1 mol%).²⁹ It is noteworthy that trivalent complexes of the f-element and tetravalent group IV complexes often show similar reactivity. [REF]

Therefore, we tested the above optimized conditions on three commonly used polyesters, the biodegradable synthetic polycaprolactone (**PCL**), polylactic acid (**PLA**) from blue and white 3D printer filaments and polyethylene terephthalate (**PET**) from an Evian® bottle (Scheme 5). Excellent yields of the desired disilyl ethers from **PCL** and **PET** were obtained with 94% of **3j^{Si}** and >95% of **3n^{Si}** and **4n^{Si}** after 4 h and 22 h, respectively, at 80 °C. Interestingly, this system evidenced a high tolerance toward additives contained in the white and blue **PLA** filaments, giving **3m^{Si}** as the sole product with distinct yields due to the differing additive content (in 75% and >95% respectively, after 4 h at 80 °C). In all cases, the pure diol products **3j**, **3m** and **3n** could be readily isolated by hydrolysis of the O–Si bond under basic conditions. Hydroboranes (HBpin and HBCat) were experimented in this system as boron reductants but were poorly reactive in comparison with DMMS (see SI). In the interest of improving the sustainability of this process, anisole was tested as a solvent for the depolymerisation of the three plastics. Similar yields of the corresponding disilyl ether products were reached but required extended reaction times (see ESI). Contrary to the hydrosilylation conditions with $B(C_6F_5)_3$,²⁴ Ir(III),²³ Zn(II),²⁷ and Mo(VI)²⁸ catalysts which displayed poor chemoselectivity and were sensitive to the reaction conditions, the $Cp_2Zr(H)Cl$ catalyst evidenced high selectivity toward the disilyl ether derivatives without formation of over-reduced products (alkanes or monosilyl ethers), which is reminiscent to the hydroboration conditions with the La(III) catalyst.²⁹ Surprisingly, compared to the La(III)/HBpin system, the **PCL** depolymerisation required harsher conditions (4 h at 80 °C VS 1 h at r.t.) and under similar experimental conditions, higher yields were obtained with the **PET** (>95% after 22 h at 80 °C VS 73% after 24 h at 100 °C).



Scheme 5. Reductive depolymerisation of polyesters catalysed by complex **1**. The yields of silyl ethers were measured by ^1H NMR spectroscopy by integration against mesitylene as an internal standard (reactions conducted in $\text{THF-}d_8$). The yields of alcohols are isolated yields from reactions in THF after basic workup.

Conclusion

In conclusion, we have developed a robust and efficient catalytic system based on an Earth-abundant metal complex ($\text{Cp}_2\text{Zr(H)Cl}$) with a mild and stable reductant (DMMS) for the hydrosilylation of ester compounds and materials into their alcohol derivatives. In the case of monomeric substrates, we have demonstrated excellent functional group tolerance coupled with good chemoselectivity. With this catalytic system, a range of polyesters obtained from commercial and household waste samples were also successfully depolymerised into their monomeric diols in high yields. Mechanistic studies suggest that catalyst turnover is achieved *via* the metathesis of Zr-OR and Si-H σ -bonds. This work highlights the use of the classical organometallic reagent $\text{Cp}_2\text{Zr(H)Cl}$ **1** as powerful catalyst for selective reduction reactions. New catalytic transformations using this complex are currently under investigation in our laboratory.

Experimental

NMR-Scale Procedure for Monomer Reduction:

In a glovebox under a purified argon atmosphere, DMMS (87 μL , 0.63 mmol) was added to a mixture of ester **2** (0.30 mmol) and $\text{Cp}_2\text{Zr(H)Cl}$ (3.9 mg, 0.015 mmol) in C_6D_6

(0.5 mL) with mesitylene (20.9 μ L, 0.15 mmol) in a J. Young NMR tube. The NMR tube was sealed and removed from the glovebox and heated at 80 or 40 °C with stirring for 1–16 h. The reaction mixture was analysed by ^1H NMR spectroscopy and the yield of the silyl ether products **3^{Si}** and **4^{Si}** was determined by integration against the mesitylene signals. The identity of the product was verified by ^1H and ^{13}C NMR spectroscopic analysis and compared to NMR spectra previously reported in the literature.

NMR-Scale Procedure for PCL and PLA Reduction:

In a glovebox under a purified argon atmosphere, to a J. Young NMR tube was added pellets or chunks of a plastic polymer (0.30 mmol, 1 equiv.), $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ **1** (3.9 mg, 0.015 mmol, 5 mol%) in $\text{THF-}d_8$ (0.5 mL), DMMS (77 μ L, 0.63 mmol, 2.1 equiv.) and mesitylene as an internal standard (20 μ L, 0.14 mmol). The NMR tube was sealed and removed from the glovebox and heated at 80 °C for 4 h. The reaction mixture was analysed by ^1H NMR spectroscopy and the yield of the silyl ether products **3^{Si}** and **4^{Si}** was determined by integration against the mesitylene signals. The identity of the product was verified by ^1H and ^{13}C NMR spectroscopic analysis and compared to NMR spectra previously reported in the literature.

Acknowledgements

For financial support we acknowledge CEA, CNRS, University of Paris-Saclay, European Research Council (ERC consolidator grant agreement no. 818260) and H2020 Sun-to-X project (grant agreement no. 883264). T. C. thanks the Fondation Louis D.–Institut de France for its support.

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