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Zirconium-catalysed hydrosilylation of esters and depolymerisation of polyester plastic waste†

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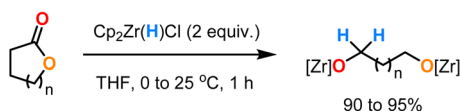
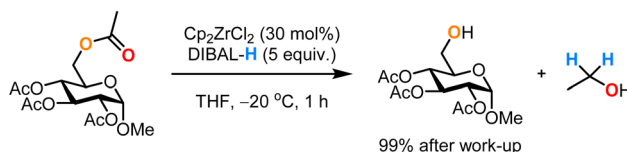
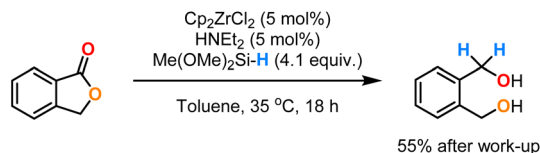
Schwartz's reagent, $\text{Cp}_2\text{Zr(H)Cl}$, has traditionally been used as a stoichiometric reagent for the reduction of unsaturated organic molecules. Recently, methods to use $\text{Cp}_2\text{Zr(H)Cl}$ as a catalyst have been developed through turnover of the $[\text{Zr}]-\text{X}$ intermediates, formed upon reaction with an organic substrate, by hydride reagents. Herein, we report the development of a new catalytic pathway for the reduction of esters that uses the bench-stable silane $\text{Me(OMe)}_2\text{SiH}$ (DMMS) as a mild stoichiometric reductant and $\text{Cp}_2\text{Zr(H)Cl}$ as the catalyst. This system exploits the regeneration of $[\text{Zr}]-\text{H}$ through the σ -bond metathesis of $[\text{Zr}]-\text{OR}$ with $[\text{Si}]-\text{H}$ 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 alcohols (up to 91% isolated yield). This methodology also proved fruitful for the reductive depolymerisation of a variety of polyesters found in household plastic waste.

The monohydride Zr(VI) complex Schwartz's reagent ($\text{Cp}_2\text{Zr(H)Cl}$) (**1**) was first reported by Wailes and Weigold in the 1970s.^{1–3} 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 centre that allows the coordination of the substrate, followed by reduction *via* a 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.¹³ They obtained the corresponding diol derivatives in excellent yields at room temperature after 1 h (Scheme 1). Although these results were limited in terms of scope and mechanistic

investigation, they highlighted the efficiency of Schwartz's reagent (**1**) as a reducing agent for ester functionalities.

Only quite recently, there has been a growing interest in using zirconocene complexes as catalysts combined with hydride donors for the reduction of carbonyl groups. In 2019 and 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 an excess of pyrophoric reagents, a high catalyst loading (30 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 $\text{Me(OMe)}_2\text{SiH}$ (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 $[\text{Zr}]-\text{H}$.

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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. The reactivity was enabled by the exquisite inherent selectivity of the catalyst and the use of hydrosilanes as mild reductants. 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 the first general and practical method for the $[\text{Zr}]\text{-H}$ catalysed 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.

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 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**. The conditions using 1 mol% of catalyst **1** led to the reaction stalling at 81% yield after 18 h (Table 1, entries 2 and 3). To study the effect of varying the reductant, we tested using 5 mol% of catalyst **1** with different hydrosilanes as reductants (Table 1, entries 4 to 7). Polymethylhydrosiloxane (PMHS), 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 a more Lewis acidic silicon centre 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 in anisole (Table 1, entries 2, 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 ester **2a** after 2 h

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

Entry	X (mol%)	Solvent	E-H	Time (h)	Yield ^a (%) 3a
1	10	$\text{THF-}d_8$	DMMS	1	>95
2	5	$\text{THF-}d_8$	DMMS	1	86
				2	>95
3	1	$\text{THF-}d_8$	DMMS	1	48
				18	81
4	5	$\text{THF-}d_8$	PMHS	7	<5
5	5	$\text{THF-}d_8$	Et_3SiH	7	n.d.
6	5	$\text{THF-}d_8$	Ph_3SiH	7	n.d.
7	5	$\text{THF-}d_8$	$(\text{EtO})_3\text{SiH}$	1	31
				2	65
				5	>95
8	5	C_6D_6	DMMS	1	>95
9	5	CD_2Cl_2	DMMS	1	72
				2	>95
10	5	Anisole	DMMS	1	85
				2	>95
11 ^b	5	C_6D_6	DMMS	1	30
				12	>95
12 ^c	5	C_6D_6	DMMS	1	70
				2	>95
13 ^c	5	C_6D_6	HBpin	2	>95
14	5	C_6D_6	HBCat	2	8

^a Yields measured by ¹H NMR against mesitylene as an internal standard. n.d. = not detected. ^b Reaction conducted at 25 °C. ^c Reaction conducted at 60 °C.

at 60 °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 while in the absence of hydrosilane, the 5 mol% of catalyst **1** reacted quantitatively with **2a** to give the alkoxyzirconocene products in trace yield (see ESI†).

To investigate the mechanism of this catalytic system, we first studied the elementary steps by a series of stoichiometric reactions (Fig. 1). The 1 : 1 reaction of complex **1** with ester **2a** in C_6D_6 resulted in almost 50% conversion (47%) of the ester **2a** to the alkoxyzirconocene products **3a^{Zr}** and **4a^{Zr}** after 2 h at 80 °C. This ratio in **3a^{Zr}** and **4a^{Zr}** did not change upon heating for a further 16 h and at this stage, complex **1** was fully consumed. The addition of 1.1 equiv. of DMMS to this mixture gave full conversion of ester **2a** with the formation of the two alkoxyzirconocene products **3a^{Zr}** (36%) and **4a^{Zr}** (21%) and the two 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. The potential over reduced products (*p*-xylene and ethane) resulting from exhaustive deoxygenation were not detected during this experiment.

As only 1.1 equiv. instead of 2 equiv. of DMMS were used, the yields in **3a^{Si}** and **4a^{Si}** cannot reach 100% and thus the presence of both zirconium- and silicon-alkoxides is expected. In line with the relative oxophilicities of Si and Zr,²² the com-

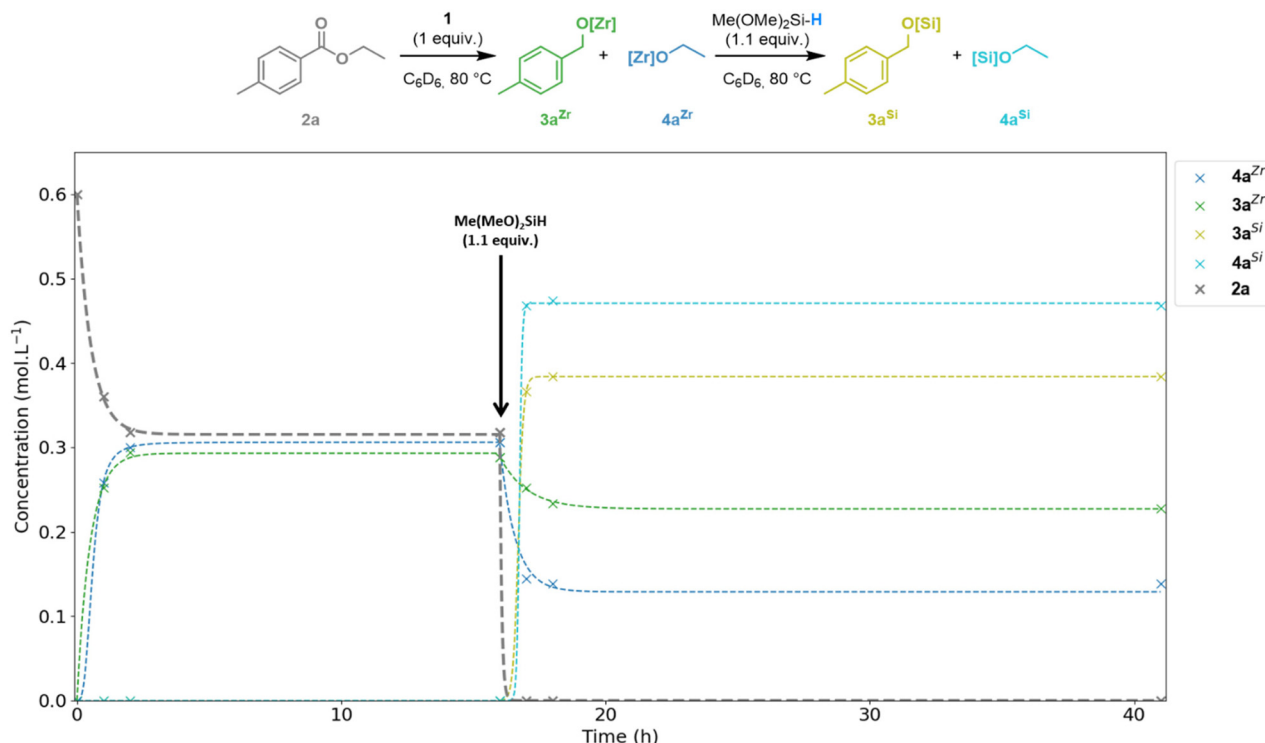
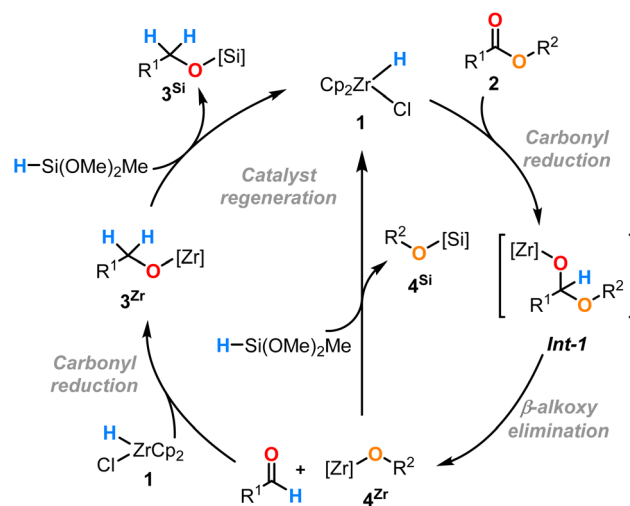


Fig. 1 Time-step analysis by ^1H NMR spectroscopy of the stepwise stoichiometric reduction of **2a** by complex **1** and DMMS.

plexes **3a^{Zr}** and **4a^{Zr}** are converted to the silyl ethers **3a^{Si}** and **4a^{Si}** by σ -bond metathesis of $[\text{Zr}]-\text{OR}$ with $[\text{Si}]-\text{H}$ with concomitant formation of $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (**1**). The newly formed complex **1** then reacts with the remaining $\sim 50\%$ of **2a**. The distinct percentages in **3a^{Zr/Si}** and **4a^{Zr/Si}** mentioned above evidence that the metathesis reactions of the two Zr-alkoxide complexes **3a^{Zr}** and **4a^{Zr}** with the hydrosilane do not proceed at the same rate. The conversion from **4a^{Zr}** to **4a^{Si}** is faster than **3a^{Zr}** to **3a^{Si}** due to the greater affinity for the silicon atom of the more electron rich alkoxide EtO^- . Buchwald and co-workers reported the use of Cp_2TiCl_2 in combination with hydrosilanes and *n*-BuLi as an activator for the selective reduction of esters.^{23,24} A ‘self-activating’ system was also developed using $\text{Ti}(\text{OiPr})_4$ as the catalyst which was proposed to proceed by σ -bond metathesis of the Ti–OiPr bond with the Si–H bond of the silane to generate a reactive Ti–H species.²⁵ However, these methods can require high catalyst loadings (stoichiometric in some cases) and suffer from the potential generation of the flammable and toxic gas SiH_4 depending on the hydrosilane used.^{25,26} We have now shown that Schwartz’s reagent exhibits similar reactivity to these Ti^{IV} catalysts and related d^0 catalysts in the hydrosilylation of esters.

Based on these results and the previous work in this area, we can propose a catalytic cycle (Scheme 3) which is similar to that proposed by Buchwald and co-workers for the catalytic hydrosilylation of esters with $\text{Ti}(\text{OiPr})_4$.²⁵ After the addition of the Zr–H bond of the catalyst **1** to the carbonyl $\text{C}=\text{O}$ bond of the ester **2**, the hemiacetal intermediate (**Int-1**) (not detected)



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

degrades rapidly into the zirconium alkoxide **4^{Zr}** and aldehyde via a β -alkoxide elimination in a similar fashion to classical stoichiometric ester reduction reagents (e.g. LiAlH_4). Under the catalytic conditions, the aldehyde (not detected) is immediately reduced by complex **1** to the Zr alkoxide complex **3^{Zr}**.¹⁶ The two alkoxyzirconocene complexes **3^{Zr}** and **4^{Zr}** perform a σ -bond metathesis with the hydrosilane to form the desired silyl

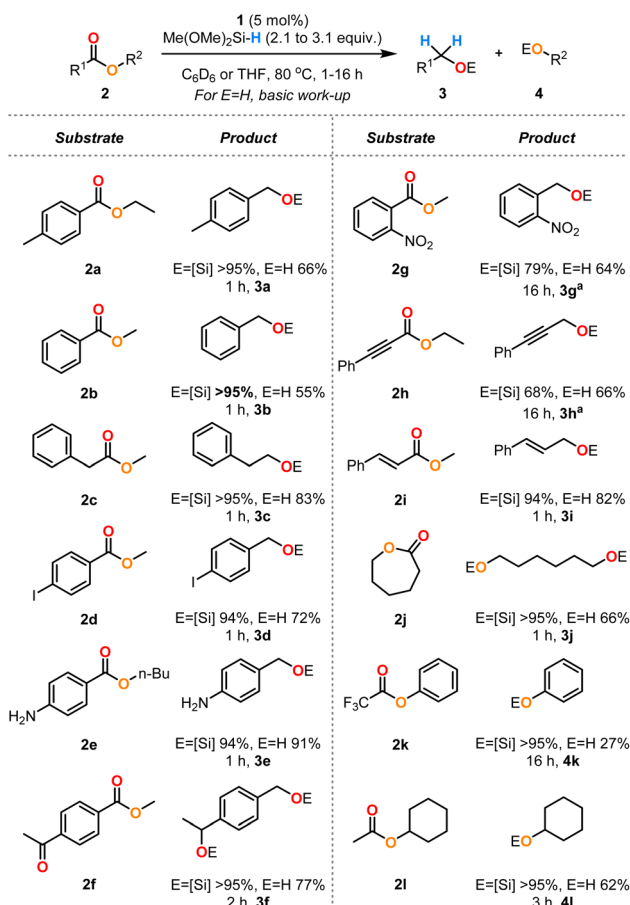
ethers **3^{Si}** and **4^{Si}**, respectively, with concomitant regeneration of the catalyst **1**.^{16,17}

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 equiv. of DMMS. An ester containing a nitro group **2g** required heating at lower temperature (40 °C) for an extended reaction time (16 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 to ensure good chemoselectivity. ϵ -Caprolactone **2j** was efficien-

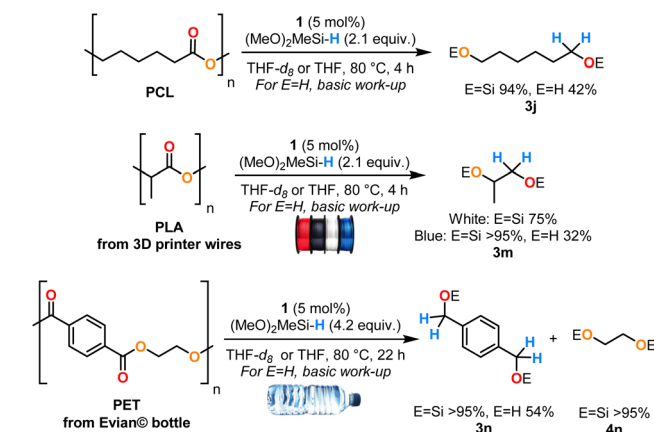
tly reduced to the corresponding diol. The electron-poor ester **2k** was converted to the desired products but required an extended reaction time of 16 h to reach full conversion. The sterically congested ester **2l** was also efficiently transformed to the alcohol products.

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.^{27,28} 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-(*t*Bu₂PO)₂C₆H₃) using hydrosilanes as hydride donors.^{29,30} 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.^{31,32} 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 depolymerise polyesters and polycarbonates in the presence of hydroboranes at low catalyst loadings (1 mol%).³³ However, this catalyst was inactive for the catalytic hydrosilylation of polyesters.

Therefore, we tested the above optimized conditions on three commonly used polyesters, the biodegradable synthetic polycaprolactone (PCL), two samples of 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



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 (see ESI†). ^aReactions conducted at 40 °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 THF-*d*₈). The yields of alcohols are isolated yields from reactions in THF after basic workup (see ESI†).

hydrolysis of the O–Si bond under basic conditions. Hydroboranes (HBpin and HBCat) were tested in this system as boron-based reductants but were poorly reactive in comparison with DMMS (see ESI†). 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 (81–84%) but required extended reaction times (38–54 h) (see ESI†). Contrary to the hydrosilylation conditions with B(C₆F₅)₃,³⁰ Ir(III),²⁹ Zn(II)³¹ and Mo(VI)³² catalysts which displayed poor chemoselectivity and were sensitive to the reaction conditions, the Cp₂Zr(H)Cl (**1**) catalyst evidenced high selectivity toward the disilyl ether derivatives without formation of over-reduced products (alkanes or monosilyl ethers), which is reminiscent of the hydroboration conditions using a La(III) catalyst.³³ 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 PET (>95% after 22 h at 80 °C vs. 73% after 24 h at 100 °C).

Conclusions

In conclusion, we have developed a robust and efficient catalytic system based on the Earth-abundant metal complex Cp₂Zr(H)Cl (**1**) 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 (alkene, alkyne, amine, etc.) coupled with excellent chemoselectivity to form alcohol derivatives exclusively. With this catalytic system, a range of polyesters obtained from commercial and household waste samples (PCL, PLA and PET) were also successfully depolymerised into their monomeric diols in high yields. Mechanistic studies suggest that catalyst turnover is achieved *via* the metathesis of Zr–O and Si–H σ -bonds. This work highlights the use of the classical organometallic reagent Cp₂Zr(H)Cl as a powerful catalyst for selective reduction reactions. New catalytic transformations using this complex are currently under investigation in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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