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Depolymerization of Waste Plastics to Monomers and Chemicals Using a Hydrosilylation Strategy Facilitated by Brookhart's Iridium(III) Catalyst

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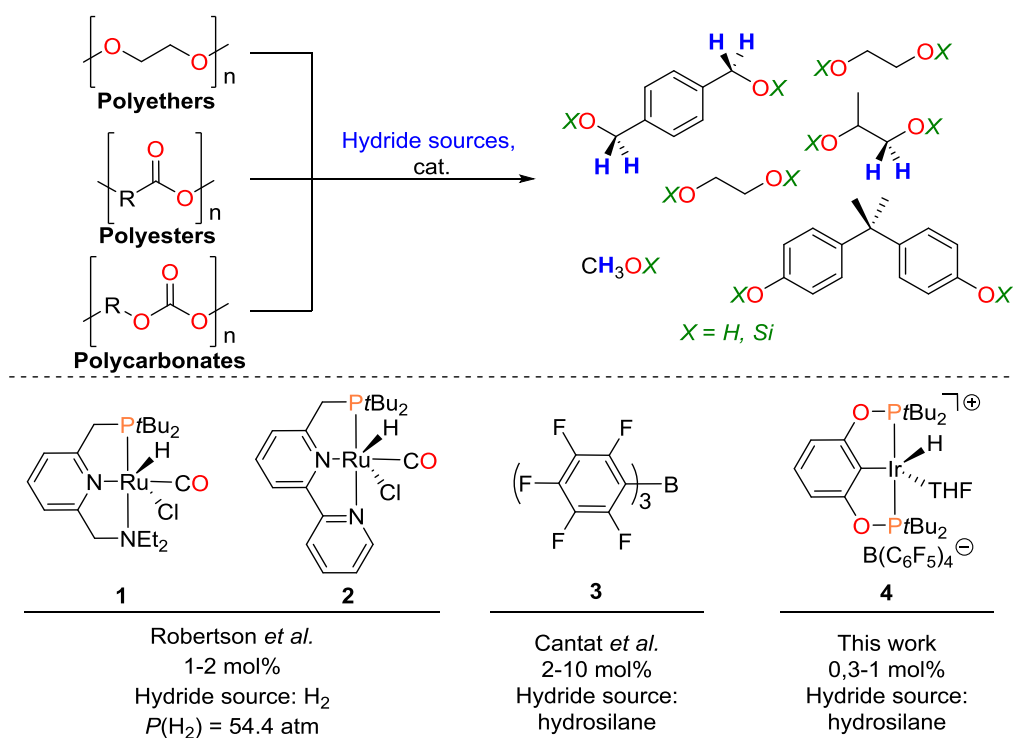
ABSTRACT: Plastic waste management is a major concern. While the societal demand for sustainability is growing, landfilling and incineration of waste plastics remain the norm and methods able to efficiently recycle these materials are desirable. Herein, we report the depolymerization, under mild conditions, of oxygenated plastics in the presence of hydrosilanes with the cationic pincer complex $[\text{Ir}(\text{PCP})\text{H}(\text{THF})][\text{B}(\text{C}_6\text{F}_5)_4]$ (PCP = 1,3-(tBu₂P)₂C₆H₃) as catalyst. The iridium catalyst, with a low loading (0.3-1 mol%), proves selective toward the formation of silyl ethers or the corresponding alkanes depending only on the reaction temperature. It is noteworthy that the depolymerization of real household waste plastics such as **PET** (from plastic bottles) and polylactic acid (**PLA**) from 3D printer filaments is not altered by the presence of dye or other plastic's additives.

Introduction

Plastics are ubiquitous in our modern society. Thanks to their lightness, their ease to be molded and their low costs, these polymers have forced their use in various applications such as electronics, packaging, medicine, etc. It is estimated that 4-6 % of the annual production of fossil resources are used to supply the 335 million tons of plastics consumed worldwide.¹ In consequence, millions of metric tons of waste are generated every year, which are either incinerated or deposited in landfills. This open cycle poses ecological problems, causing pollution issues and emissions of large quantities of the greenhouse gas CO₂.² The increasing awareness of the environmental issues associated with plastic wastes generates a public demand for sustainability and renewability in the plastic industries. In this context, a conglomerate of industries and associations³ has called for the implementation of a circular economy of plastics lying on three main axes: drastically reducing the leakage of wastes in the environment, decoupling plastic production from fossil resources and up-taking recycling processes.⁴

The reuse of manufactured polymers remains challenging because of the high density of chemical functionalities in the polymer matrix, the presence of additives in plastics and/or the blend of different materials. Besides incineration and landfilling, physical and chemical recycling technologies are appealing approaches to improve the conservation of carbonaceous materials.⁵ The former processes consist of melting and remodeling the plastic, although the second generation plastics have more limited usages because of the presence of impurities. In contrast, chemical processes can afford the recovery of pure chemicals, useful for the production of recycled virgin quality plastics as well as new chemicals.⁶ In this respect, the development of new depolymerization systems recently emerged in the scientific community.⁴⁻⁶ Classical

aminolysis, hydrolysis or transesterification reactions have been widely repurposed in the catalytic depolymerization of polyesters⁷⁻⁹ and polycarbonates.^{10, 11} Alternatively, the cleavage of C–O bonds can be achieved through reduction methods.¹² Robertson and co-workers tackled the recycling of waste plastics via the catalytic hydrogenation of oxygenated polymers with the soluble Ru(II) pincer complexes **1** and **2** (Scheme 1).¹³ Selective deconstruction of a wide range of polycarbonates and polyesters into the corresponding valuable alcohols or carboxylic acids was achieved with excellent yields. Hydrogenation of the polymers proceeded in relatively harsh conditions (54 atm H₂, 160°C). Taking advantage of the kinetically and thermodynamically favored hydrosilylation of carbonyl functions, our group recently reported the efficient catalytic reduction of a range of natural and manufactured oxygenated polymers, at room temperature, with B(C₆F₅)₃ (**3**) as a catalyst.¹⁴ Nonetheless, this Lewis acid catalyst is incompatible with a number of solvents and its price is close to precious metal (B(C₆F₅)₃ ~ 110 €/mmol, [Ir(COD)Cl]₂ ~ 40 €/mmol of Ir, COD = 1,5-cyclooctadiene [Sigma-Aldrich]). It is also poorly selective, and demands high loadings (2-10 mol%). These drawbacks call for more stable, efficient catalysts.



Scheme 1: Catalysts for the reductive depolymerization of plastics and polymers

The cationic Ir(III) complex **4** is a well-known hydrosilylation catalyst exhibiting similar chemical behavior as borane **3**¹⁵ (Scheme 1). The electrophilic activation of hydrosilanes by Lewis acid **4** favors reduction of oxygenated functions such as carbonyl¹⁶ or carboxyl¹⁷ groups as well as ethers,^{18, 19} leading to the corresponding silylated alcohols or alkanes.²⁰ While complex **4** proved to be very efficient in hydrosilylation reactions with organic substrates, its utilization in the reduction of poly-functional materials is scarce^{21, 22} and Brookhart *et al.* reported the unique example of depolymerization of polyethylene glycol (**PEG**) into silylated ethylene glycol with **4** within 4 h at 65°C.¹⁸ Here we report the efficient use of the Brookhart's complex in the catalytic depolymerization of polyesters and polycarbonates with hydrosilanes. Silyl ethers or hydrocarbons are formed selectively by controlling the temperature of the reaction, thus

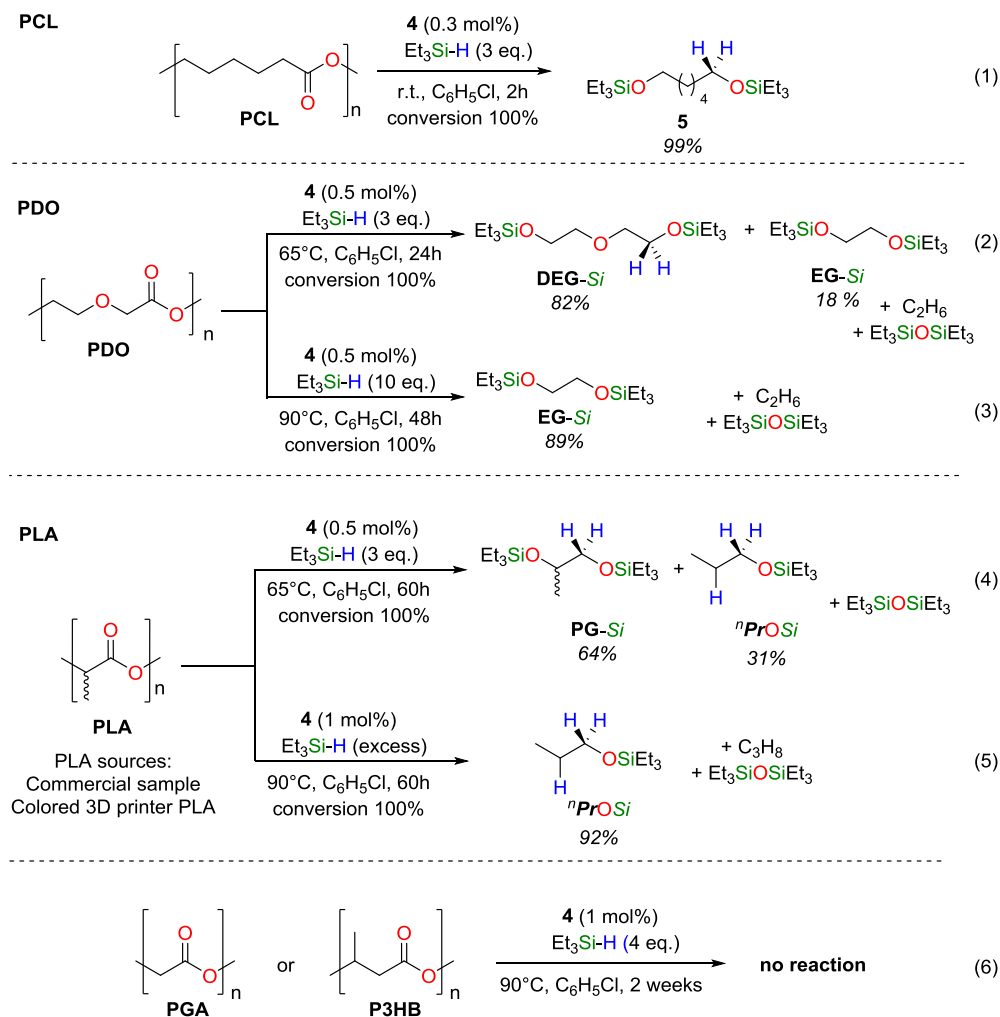
demonstrating the wide applicability of the iridium(III) catalyst in the depolymerization of oxygenated polymers.

Results and discussion

One of the major drawbacks in the chemical treatment of polymers is generally their insolubility in classical organic solvents which can prevent reactions or considerably slow down their kinetics. The first attempt at hydrosilylation of plastics was thus undertaken with low melting point polymers, such as the aliphatic polycaprolactone (**PCL**) (mp = 60°C), to form homogeneous or biphasic solutions by heating. Surprisingly, at room temperature, insoluble commercial pellets of **PCL** (diameter \approx 0.4 cm) rapidly reacted in presence of the mild reductant triethylsilane (Et₃SiH, 3 eq) and of the iridium catalyst **4** (0.3 mol%) in chlorobenzene. After 2 hours, no residual solid remained, ¹H NMR and DEPT 135 ¹³C NMR as well as GC-MS analyses of the clear solution revealed a complete and selective depolymerization of **PCL** into the silylated 1,6-hexanediol (**5**), obtained as the unique product in quantitative yield (Scheme 2, eq. 1). Compound **5** was isolated pure in a preparative scale (94% from 3 mmol of PCL).

Successful depolymerization of **PCL** under these mild conditions led us to consider a variety of aliphatic and aromatic polyesters which differ by the nature of the spacer between the carboxyl groups and with higher melting points than **PCL**. Though **PCL**, poly(dioxanone) (**PDO**), and poly(lactic acid) (**PLA**) are biodegradable polymers, their chemical recycling remain relevant to conserve the raw carbonaceous materials as well as to avoid, upon degradation, the release in the environment of CO₂ (or CH₄ in anaerobic conditions)^{23, 24} and the additives present in the plastic matrix. **PDO** was found inert in reduction conditions used for **PCL** but further heating to 65 °C proved sufficient to successfully depolymerize **PDO** into a mixture of

the two silylethers **DEG-Si** and **EG-Si** along with gaseous ethane and the siloxane Et₃SiOSiEt₃ (Scheme 2, eq. 2). While **DEG-Si** was the major product (82%), a complete selectivity could not be achieved suggesting that the hydrosilylation of **PDO** and **DEG-Si** are concomitant. Formation of **EG-Si** was reached in excellent yield (89%) under forcing conditions, when using an excess of the hydrosilane (10 equiv.) with higher temperature and prolonged reaction time (90 °C, 48 h) (Scheme 2, eq. 3).



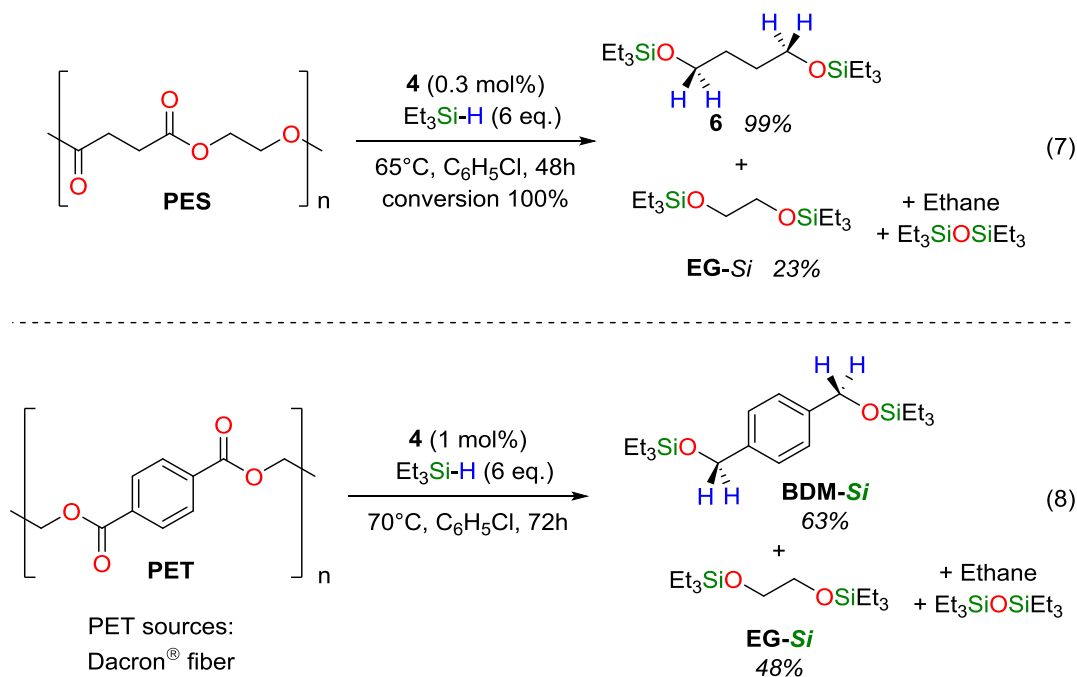
Scheme 2: Reduction of **PCL**, **PDO** and **PLA** into silylated alcohols with Et₃SiH and **4**.

A similar behavior has been observed with **PLA** (Scheme 2, eq. 4). Although the depolymerization of **PLA** required longer reaction times than **PDO** (60 h vs 48 h), the reaction occurs in presence of the iridium complex **4** (0.5 mol%) and Et₃SiH (3 equiv.) to yield the silylated propylene glycol **PG-Si** (64%) and the over-reduced product ⁿ**PrOSi** (31%). As for the deconstruction of **PDO**, the reduction of **PLA** and **PG-Si** seems to be kinetically competitive and **PG-Si** and ⁿ**PrOSi** were observed simultaneously during the progressive reduction of **PLA** (see SI, section II.5). Nonetheless, 1 mol% of the Ir catalyst and an excess of the hydrosilane (10 equiv.) were sufficient to yield to ⁿ**PrOSi** in 92% yield along with ethane and Et₃OSiEt₃ at 90 °C (Scheme 2, eq. 5). Interestingly, strictly similar results have been obtained from the treatment of a soluble ground powder of commercial **PLA** as well as large insoluble pieces of coloured **PLA** from 3D printer plastic (white, blue and red; ≈0.4x0.3x0.3 cm), showing the high tolerance of the Ir catalyst **4** towards the contaminants present in these **PLA** plastics (dyes and additives).

Despite the structural similarities between polyglycolic acid (**PGA**) and poly-3-hydroxybutyric acid (**P3HB**) with **PLA**, these materials were left untouched in the presence of **4** and Et₃SiH regardless the quantity of reductant, the temperature and the reaction times (up to 2 weeks) (Scheme 2, eq. 6). These distinct behaviours in hydrosilylation are obviously not related to different steric congestions nor to the solubility of the polymers (soluble **PLA** vs insoluble **PCL**).

We then investigated the depolymerization of **PES** (polyethylene succinate), an aliphatic biodegradable copolymer of ethylene glycol and butanedioic acid. In presence of excess Et₃SiH (6 equiv.) and a 0.3 mol% **4**, **PES** was readily depolymerized at 65 °C to the silylated butanediol **6** and ethylene glycol **EG-Si** (Scheme 3, eq. 7). Interestingly, the disilylether **6** was produced almost quantitatively (99%). **EG-Si** was obtained in lower yield (23%) due to its further

reduction to ethane and siloxane $\text{Et}_3\text{SiOSiEt}_3$. **PET** from commercial Dacron[®] fibers or small chunks of Evian[®] bottles were finely ground and dried. The powders were then converted at 70°C, using slight excess Et_3SiH (6 equiv.) and 1 mol% of the iridium complex **4**, into two silylethers: silylated 1,4-benzenedimethanol (**BDM-Si**) and **EG-Si** in 63% and 48% yield (Scheme 3, eq. 8).



Scheme 3: Reductive depolymerization of **PES**, and **PET** with Et_3SiH and catalyst **4**

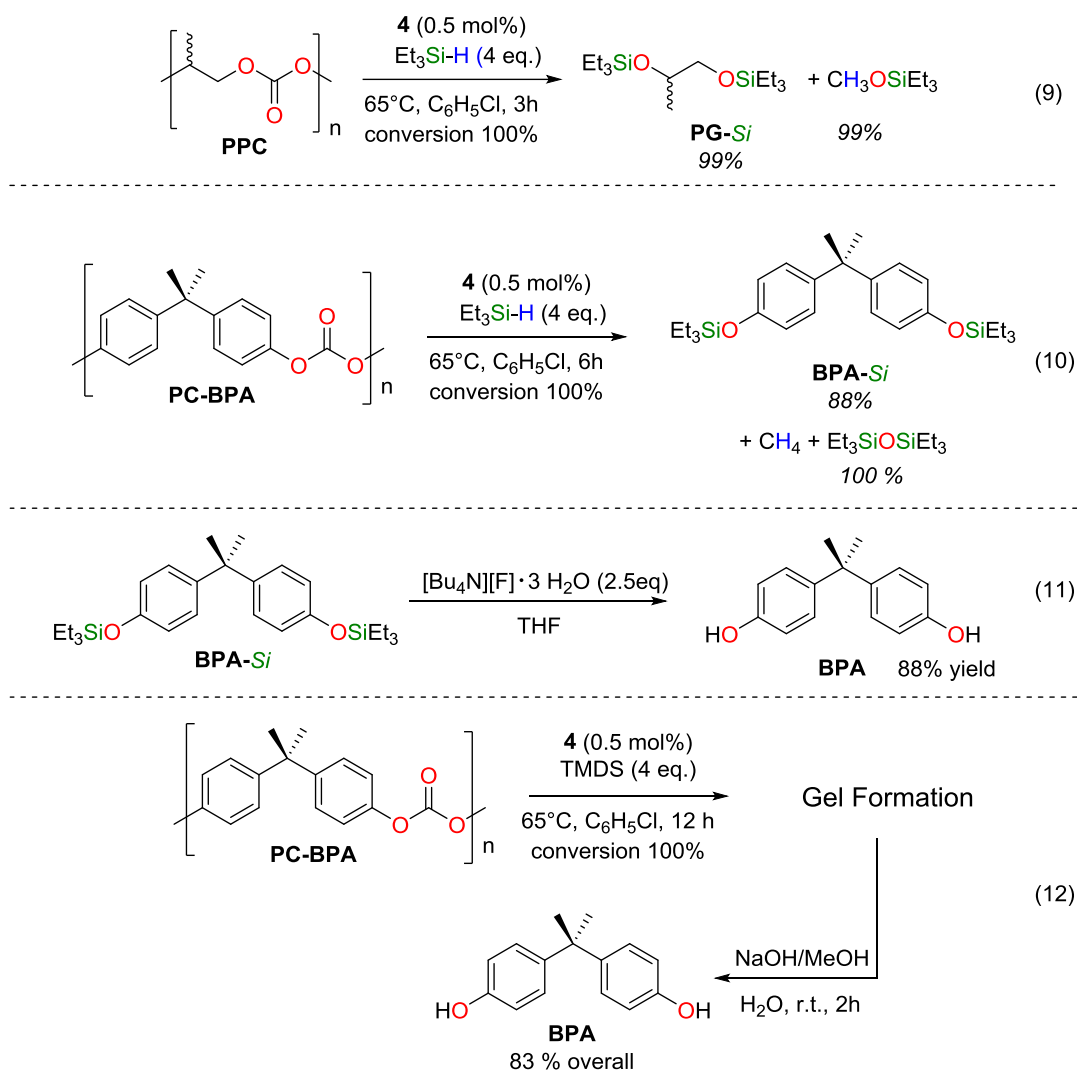
Ethane and $\text{Et}_3\text{SiOSiEt}_3$ were also present as products of the reduction of **EG-Si** and prolonged heating (2 weeks at 90 °C) led to para-xylene (1,4-Me-benzene) and ethane. The formation of such silyl ethers is attractive as these products can be used as sources of alkoxide groups in Ullman's coupling reactions to prepare ethers.²⁵⁻²⁸ Alternatively, the useful alcohols could be obtained through hydrolysis of the silyl ethers. In the case of **PET**, hydrolysis of **BDM-Si**

affords the diol 1,4-benzenedimethanol (**BDM**) which is a valuable building block for the production of pesticides, perfumes or dyes (see SI, section IV.1).^{29,30}

Interestingly, the reduction of **PET** required harsher conditions than **PLA** with the present hydrosilylation system, which is consistent with the chemical behavior noted by Robertson and co-workers under hydrogenation conditions.¹³ However, we observed a different behavior with the organoborane $B(C_6F_5)_3$ (**3**) and 16 h were needed to depolymerize **PLA** with a slight excess of Et_3SiH and 5 mol% **3** at room temperature, while the same reaction was achieved within 3 h with **PET**.¹⁴ As already observed with natural polymers,²² catalyst **4** proved less reactive than $B(C_6F_5)_3$ requiring longer reaction times and higher temperatures for both **PLA** and **PET**. Nevertheless, $B(C_6F_5)_3$ in presence of excess silane favored rapid (24 h) cleavage of all the C-O bonds at room temperature with formation of alkanes and siloxane as the sole products. The iridium catalyst **4** exhibits a higher selectivity allowing the conservation of functionalities, such as silylethers. Moreover, when 5 mol% of the borane **3** are required to treat **PLA**, the iridium catalyst completed the deconstruction of this polymer with only 0.5 mol% demonstrating a higher stability.

The successful reductive depolymerization of polyesters with **4** and Et_3SiH led us to consider the reduction of more oxygenated polymers. The reduction of polycarbonates is of interest as organic carbonates are classically more difficult to reduce, compared to esters, because of the delocalization of the oxygen lone pairs over the CO_3 group.³¹ Catalytic reductive hydrosilylation of polycarbonates (and plastics in general) was only reported in 2015 by our group with the organocatalyst $B(C_6F_5)_3$,¹⁴ while Robertson and co-workers reported in 2014 the catalytic hydrogenation of polycarbonates (and polyesters) with Ru(II) complexes (*vide supra*)¹³.

We first considered polypropylene carbonate (**PPC**) viewed as the assemblage of the two monomers, propylene oxide and CO₂. Surprisingly, reductive depolymerization of **PPC** using the hydrosilylation conditions of **PLA** (0.5 mol% of **4** and 4 equiv. Et₃SiH) at 65 °C proceeded more rapidly and more selectively than what was observed with **PLA** (3 h versus 60 h) affording MeOSiEt₃ and disilylether **PG-Si** in quantitative yield (Scheme 4, eq. 9). MeOSiEt₃ results from the reduction of the carbonate groups and no other by-products, such as Et₃SiOSiEt₃, CH₄ or ⁿPrOSi, were detected. The selectivity of the reaction indicated that the hydrosilylation of the polycarbonate was faster than deoxygenation of **PG-Si** (see scheme 4). This difference in reactivity could be exploited for the selective depolymerization of a mixture containing pieces of **PPC** (insoluble) and a fine powder of **PLA** (soluble), suspended in chlorobenzene. In contrast to what expected from their respective solubility, **PPC** reacted faster than **PLA**. The ¹H and ¹³C NMR spectra unveiled the formation of **PG-Si** from **PPC** which rapidly disappeared in the medium while soluble **PLA** was left untouched (see SI, section V.3). This comparative experiment highlights that the reactivity of polymers is not necessarily related to their solubility. While the reduction of carbonyl groups usually follows the order of reactivity ketones > esters > carbonates,³¹ Brookhart's catalyst **4** exhibits a different reactivity. In fact, when a mixture of propylene carbonate and *rac*-lactide are exposed to 1 mol% **4** and an excess Et₃SiH, the mono-functional carbonate is reduced before the lactide monomer (see SI, section V.2). The selective hydrosilylation of **PPC** over **PLA** hence translates a difference in reactivity between mono-functional carbonates and esters. Yet, this observation should not be taken as a general rule (*vide infra*).



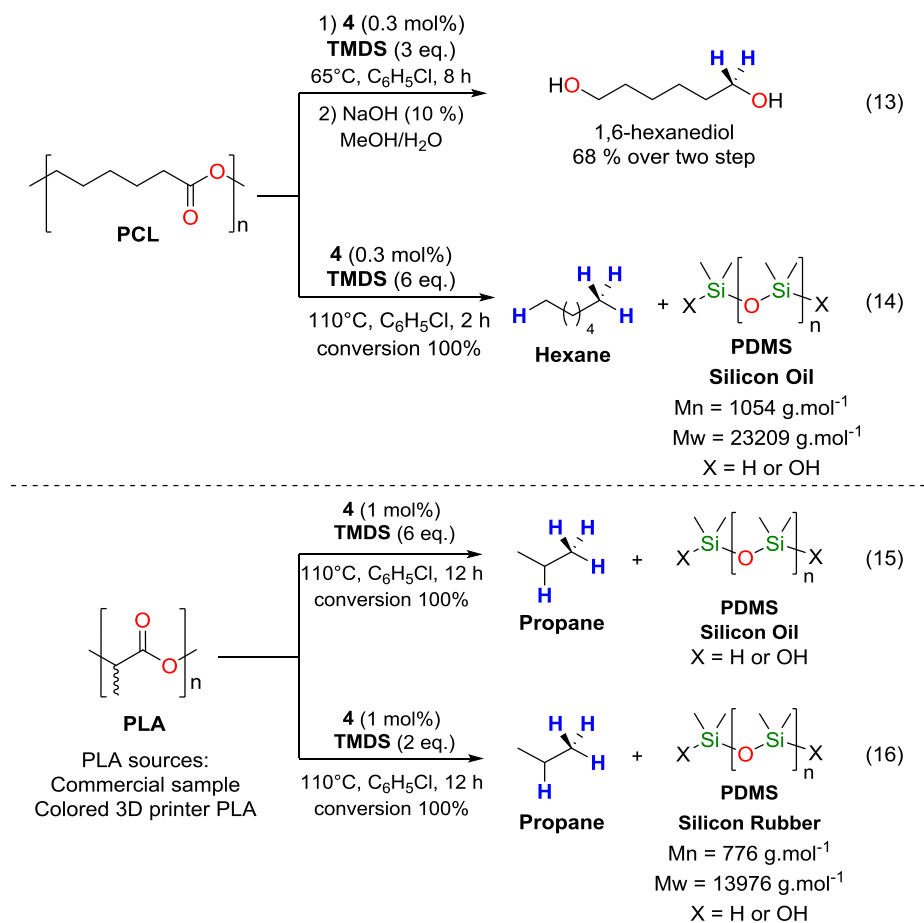
Scheme 4: Selective reduction of **polycarbonates** to their corresponding silylated alcohols with the **4**/hydrosilane system

Depolymerization of **PC-BPA** under conditions similar to **PPC** is slower (6 h vs 3 h) and afforded the disilylated phenol **BPA-Si** in excellent yield (88%) (Scheme 4, eq. 10). MeOSiEt_3 was not detected by NMR. Yet, evolution of gaseous CH_4 was observed by ^1H NMR (in a closed J-Young NMR tube) along with Friedel-Craft-like products in the form of methylbisphenol derivatives (see SI, section II.9). Of interest, hydrolysis of the hydrosilylation products from

PPC and **PC-BPA** afforded the corresponding alcohols, propylene glycol and BisPhenol A (**BPA**), respectively. They correspond to the monomers of the original polymers. For example, **BPA** was obtained in 88 % yield with 2.5 eq. of hydrated tetrabutylammonium fluoride (**TBAF**) in THF within 12 h (Scheme 4, eq. 11). An attractive alternative to **TBAF** involves the use of sodium hydroxide in methanol and water for the hydrolysis of silyl ethers.^{32, 33} Yet, hydrolysis with sodium hydroxide proved inefficient when applied to triethylsilyl ethers. In fact, such transformation requires more Lewis acidic silicon derivatives such as alkoxy silane ($[\text{RO}]_3\text{SiH}$). This finding led us to consider the silicon industrial waste 1,1,3,3-tetramethyldisiloxane (**TMDS**) as a potential reductant. Treatment of 1 mmol of **PC-BPA** with **TMDS** (4 eq) and **4** (0.5 mol%) led to the formation of a gel after 12 h at 65 °C. Notably, no Friedel-Craft product could be observed in the hydrosilylation products using **TMDS**. Hydrolysis of the crude mixture with NaOH in water/methanol enabled the formation of the monomer **BPA** in 83% yield, after 2 h (Scheme 4, eq. 12).

TMDS being a cost-efficient source of hydrides, its potential in the reductive depolymerization of plastics was further assessed. In contrast to the conditions described in eq. 1 (Scheme 2), the reduction of **PCL** does not occur at room temperature with the dihydrosiloxane. Nevertheless, in presence of 0.3 mol% of the iridium complex **4** and 3 equiv. of **TMDS** (6 equiv. of hydrides), the polymer was completely decomposed within 8 h at 65°C into numerous silyl ethers which could be further hydrolysed to 1,6 hexanediol with the NaOH/MeOH system (yield of 68 % overall, scheme 5, eq. 13). The need for a convergent depolymerization led us to consider the hydrosilylation of **PCL** at 110 °C to reduce the intermediate ethers to alkanes. In presence of 0.3 mol% **4** with 6 equiv. of **TMDS** (Scheme 5, eq.14), *in situ* ^1H NMR and DEPT ^{13}C NMR spectra revealed complete reduction of **PCL** into hexane and siloxanes in quantitative yield.

Surprisingly, after removing hexane, excess **TMDS** and the solvent under reduced pressure, a non-volatile viscous liquid was isolated. ^{13}C NMR, ^{29}Si NMR as well as FT-IR analyses confirmed the formation of polydimethylsiloxane **PDMS**.³⁴ SEC chromatography was performed to further characterize the resulting polysiloxane and unveiled a high molar weight and a high polydispersity ($M_n = 1054 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 23209 \text{ g}\cdot\text{mol}^{-1}$ and $\text{PD} = 22.0$). Chromatograms also revealed a complex distribution of the molecular weights.



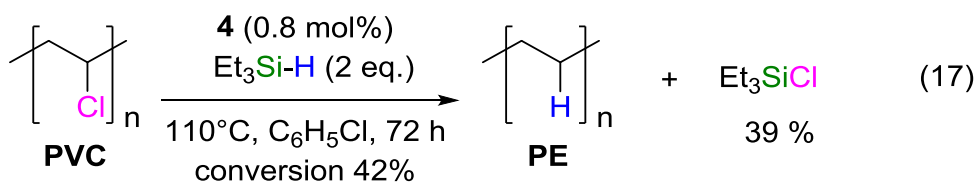
Scheme 5: Reductive depolymerization of **PCL** and **PLA** with the system **4**/**TMDS** to the corresponding hydrocarbons.

Regardless the further used of silyl ethers,^{25-28, 35} stoichiometric quantities of silicon by-products are formed, at the expense of a low atom economy for the whole process. In this respect, the use of **TMDS** for the complete deoxygenation of plastic wastes is more attractive than Et₃SiH, as it enables the formation of a valuable by-product, **PDMS**,³⁶ which is widely used as a lubricant, as a food additive, as silicone in breast implants³⁷, etc.³⁸ **TMDS** would be especially meaningful in the depolymerization of bio-sourced polymers, in order to produce a well-defined fuel by reduction of the bio-based carbon matrix and a silicon polymer. **PLA** was considered as the ideal candidate to test this idea. In presence of 1 mol% of the iridium catalyst **4** and 6 equiv. of **TMDS**, **PLA** was fully deconstructed at 110 °C into propane and polysiloxane **PDMS** (Scheme 5, eq. 15). Because of its volatility, the yield of propane could not be evaluated but the concentration of C₃H₈ was sufficient to detect it by ¹H and ¹³C DEPT NMR (see SI, section III.2). Decreasing the amount of **TMDS** to 2.0 equiv. did not affect the rate of the reaction leading to propane and polysiloxane, using the same conditions of loadings catalyst, temperature, and time. After removal of the volatiles, a silicon rubber of **PDMS** remained in the flask (Scheme 5, eq. 16). Similarly to the **PDMS** silicon oil obtained from **PCL** depolymerization, the silicon rubber exhibits a complex mass distribution with at least two observable peaks in SEC chromatograms and a high polydispersity. (M_n = 776 g.mol⁻¹, M_w = 13976 g.mol⁻¹, and PD = 18.0).

In addition to ethers and esters, Brookhart and co-workers demonstrated that catalyst **4** is able to reduce halogeno-alkyl compounds.^{39,40} The reduction of halogenated polymers was thus attempted with the dechlorination of poly(vinyl chloride) **PVC** (scheme 6, eq. 17). While no reaction occurs at 65 °C and 90 °C, ¹³C NMR reveals that, in the presence of 0.8 mol% **4** and 2

equiv. of Et₃SiH, insoluble pieces of **PVC** were reduced at 110 °C into soluble poly(ethylene) **PE**.⁴¹ The corresponding chlorosilane Et₃SiCl was formed in 39% yield.

When a mixture of **PVC** and **PLA** was exposed to Et₃SiH and catalyst **4**, **PLA** was left untouched at 110 °C, although its depolymerization was observed at 65 °C in the absence of **PVC** (see Scheme 2, Eq. 4). In parallel, the less reactive **PVC** was dechlorinated to **PE** and Et₃SiCl (see SI, section V.4). This reactivity trend is surprising considering that **PVC** is typically less reactive than **PLA**. More mechanistic investigations are certainly needed to decipher the origins of these unexpected selectivities. Importantly, a different behavior was observed when catalyst **4** was replaced with B(C₆F₅)₃. In this case, only the polyester (**PLA**) was depolymerized (see SI, section V.5). Overall, we can conclude that the reactivity of isolated polymers towards a depolymerization method does not transpose directly to mixtures of plastic wastes, where reactivity trends can be inverted.



Scheme 6: Reductive dechlorination of **PVC** to **PE** with the system **4**/Et₃SiH.

Conclusions

In conclusion, Brookhart's iridium(III) complex **4** has been utilized for the first time for the depolymerization of a range of oxygenated polymers, comprising household wastes. These include polyesters (**PET**, **PCL**, **PLA**, etc.) and polycarbonates (**PC-BPA**, **PPC**). In the presence of hydrosilanes, catalyst **4** cleaves C–O bonds in esters and carbonates to yield silylethers and

alkanes. A chlorinated polymer such as **PVC** was dechlorinated to **PE**, using the same protocol. Importantly, it was found that the reactivity of isolated esters, carbonates or well-defined polymers does not directly transpose to mixtures of polymers.

The method presents the advantage of regenerating the original monomers or valuable chemicals in a pure form. For instance, bis-phenol A could be isolated in 83 % yield from a sequence involving the depolymerization of **PC-BPA** with **4** and **TMDS** and the subsequent hydrolysis of the reaction products with NaOH in methanol. In addition, the reduction of bio-based polymers such as **PLA** with **TMDS** affords bio-fuels, in the form of hydrocarbons, and **PDMS** (a valuable silicon polymer), in a process that valorizes both the carbon and silicon feedstocks.

Although catalyst **4** proved very efficient in the plastic depolymerization with low catalyst loadings, its price remains a major obstacle for a scale-up process development. In addition, the energy intensive production of hydrosilanes combined with the generation of silicon by-products calls for alternative methods of reduction. In this perspective, surrogates of hydrosilanes, such as silylformates ($R_3SiOCHO$)⁴²⁻⁴⁴, may offer promising alternatives in the future by using renewable hydride sources (*e.g.* formic acid).

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Supplementary equations, detailed descriptions of experimental methods, and results are provided in the Supporting Information.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Synopsis

Several oxygenated plastics are efficiently depolymerized into valuable chemicals under mild hydrosilylation conditions with the use of molecular iridium catalyst.

TOC/Abstract Graphic

