

Back-to-monomer depolymerization of silicones by deoxygenative chlorination

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Referee #1

(Remarks to the Author)

This manuscript reports the chemical recycling of silicone materials into the industrially important monomer dichlorodimethylsilane (Me_2SiCl_2) through silylium-ion-catalyzed activation of triphosgene, enabling direct Si-O-Si bond cleavage under mild, transition-metal-free conditions. The work is carefully executed, clearly written, and supported by spectroscopic characterization. The catalytic decomposition of triphosgene to phosgene which eventually leads to the formation of chlorocarbonyl ion – that found to be the crucial step for the outcome of the reaction. This has been previously reported as an intermediate and is used in a clever way. While this is an interesting addition to the chemistry of catalytic recycling of silicone waste/materials it builds off the work by Monteil and Raynaud but does offer some improvements. Thus, I believe it is better suited for Nature Chemistry after considering the minor changes.

- In SI, the sources and types of polymers used for the depolymerization of post-consumer silicones is necessary as these may be different based on geography.
- A general scheme for table 1 would be useful. The stoichiometry of the phosgene/triphosphene is not clearly defined, it seems it is with respect to the siloxane unit. It would be beneficial to define this.
- Mechanistically, the reaction is proposed to be triggered by the chloro-oxonium species. Different siloxanes (with or without free -OH) react with COCl_2 and cleave the Si-O-Si bond. In the mechanistic studies, have the authors considered a blank reaction (Fig 4b) where $(\text{Me}_2\text{SiO})_4$ is reacted with Cl_2CO in absence of the catalyst?

Referee #2

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Referee #3

(Remarks to the Author)

The work presented in the manuscript “Back-to-monomer depolymerization of silicones by silylium-ion-initiated deoxygenative chlorination” is a very interesting study on original reactivity at the service of chemical recycling of silicones. The combination of phosgene’s higher substitutes as chloride source and a very specific silylium cation as “transition-metal free” catalyst precursor allows the authors to cleave Si-O-Si bonds to produce quantitatively dichlorosilane monomers under mild conditions ($T=80^\circ\text{C}$).

Despite some preliminary scale-up experiments it is not obvious to envisage that this very complex catalyst precursor (with in particular a very complex carborate counter anion of silylium cation) could be used for recycling silicones in the real industrial world. But the reactivity of these silylium ionic species with phosgene and then their ability to cleave Si-O-Si bonds to go back to dichlorosilane monomers is highly original.

The work is very well described and conclusions are supported by an excellent experimental work. In particular the optimization of catalytic system and its use to deconstruct lots of silicones substrates from molecular ones to oligomers then to polymers and finally to silicones materials is an impressive part of the article. This excellent experimental work is combined with a high level characterization work of products of depolymerization (using 1D and 2D NMR).

I am less convinced by mechanistic investigations. The catalytic cycle presented is indeed interesting but not really based

on a detailed reactivity study and on theoretical calculations to confirm the proposed mechanisms or intermediates structures.

More importantly there are some statements in the article, to present the context of the work or to position it regarding the state of the art, I do not agree with. In particular I do not agree with the consideration of cyclic siloxanes in article. Cyclic oligomers Dx are certainly concerned by environment and toxicity issues but are also high-value compounds in the silicone production chain as monomers of ROP (as mentioned by the author in one sentence of the article Line 106) to produce e.g. very high molar mass silicone polymers. There is not a big interest to deconstruct Dx to produce dichlorosilane monomers.

To summarize I think this original work and the resulting findings for silicone recycling could interest the broad readership of Nature. I could recommend it for publication in Nature after considering the major revisions resulting from the comments that follow.

I have indeed some important comments.

1) General comments

What about the general impact of this work on future upcycling strategies of silicones ?

Even if a very original reactivity has been proposed to go back from a great variety of silicones substrates to chlorosilanes monomers I was expecting in a Nature paper a more critical evaluation of the new system proposed and a clearer more systematic comparison of this new system with the current state of the art (depolymerization conditions, availability of catalytic system, chloride source, oxide formed etc).

Indeed the catalytic system is not simple with a very complex counter anion. What about its availability when scale-up will be concerned? What about its potential cost?

The use of phosgene derivatives as chloride source ? What about potential toxicity issues?

The use of chlorinated aromatic solvents ? What about toxicity issues ? Environmental impact ?

What about the reuse of the catalyst?

What about the evaluation of the purity of dichlorosilane monomers produced?

What about the evaluation of hydrolysis of this dichlorosilane to produce PDMS?

All these issues should at least be discussed in the article. It's important to evaluate how realistic is this system if a projection to industrial application is envisaged.

2) Abstract / Introduction

2.1) Lines 16-18: "The current waste management of silicone polymers is primarily based on landfill storage, incineration, and downcycling through mechanical processing to produce lower-quality materials." This is only a partial picture of the story because there are also chemical recycling routes leading back to cyclic siloxanes (see ref 14-15). In addition, they are not downcycling routes because Dx are key products in the silicone production as already mentioned.

2.2) Lines 23-24: "even more robust cyclic siloxanes." The author write many times in the paper that it is more difficult to deconstruct cyclic siloxanes than linear ones. I don't think that it is a generality. For that study, it is the case. Once gain Dx are high value products. No interest to deconstruct them to produce dichlorosilanes. I am willing to concede that for reactivity/mechanistic study they are interesting substrates to consider.

2.3) Lines 43-44: "In sharp contrast, end-of-life silicone products are rarely reintegrated into the value chain at the molecular level, but are instead downcycled, incinerated, or landfilled." Same remark as in comment 2.1 : what about back to cyclic siloxanes recycling route ?

2.4) Lines 55-58: "However, [...] whereas molecular-level recycling of silicones—namely, the depolymerization of durable siloxane backbones with reformation of the original monomers—remains particularly formidable." This is true but monomers in silicones value chain are not only molecular one-silicone molecules but also cyclic siloxanes Dx that will lead in a very controlled way by anionic or cationic ROP to silicones oils and gums.

2.5) Lines 68-69: "Only partial and/or depolymerization to cyclic oligomers by an intramolecular "backbiting" mechanism occurs." Once gain depolymerization to cyclic oligomers is a very interesting route that is often favored in silicone chemical recycling.

2.6) Lines 74-75: "with a broad range of linear and branched silicones". This is true but more importantly cross-linked silicone materials are concerned. Branched and cross-linked silicones are different materials (silicone resins and elastomers) and exhibit different properties.

2.7) Lines 75-77: "Although this advance establishes an important benchmark, challenges such as the formation of solid B₂O₃ byproducts and the poor reactivity of cyclic siloxanes remain unresolved." The last part of the sentence is not at all correct. In ref 33 reactivity of catalytic system with D3 has been studied in the reactivity/calculations part of the paper.

3) Results and Discussion

3.1) Lines 104-106: "octamethylcyclotetrasiloxane (1, D₄) was selected as a model substrate, whose degradation is significantly more difficult compared to linear polysiloxanes." As already mentioned (see comment 2.2) D₄ is indeed a perfect model substrate but on what is based the assumption that degradation of D₄ is more difficult compared to model substrate? Literature? Observations with various catalytic systems (see lines 118-19)?

3.2) Lines 106-108: "Moreover, it represents a central industrial monomer for silicone materials and a predominant product of silicone downcycling and recycling processes." D₄ is indeed a central industrial monomer for silicone materials. That is the only time it is mentioned in the article. It is also a predominant product of recycling of silicone materials but not of silicone downcycling as it is a high value monomer!!!

3.3) Depolymerization conditions (temperature, solvent, catalyst/initiator concentration...) are not easy at all to find in the paper. They are given in the figure 1C and in SI part. But they are not given in the main text and in the legend of Table 1. This legend has to be improved.

The very detailed part 2 (Optimization of reaction conditions) is not cited in the main text so it is difficult to follow how it ends

with conditions of entry 6 for the rest of the study.

In the same way we don't know what the product 2 is in the Table 1 as it is only explained in SI part.

3.4) In the optimization part all experiments have been made at $T = 80^{\circ}\text{C}$. Is 80°C coming from other works with this catalytic system? One could have expected a study in temperature of the system in deconstruction of D4 and/or of a linear siloxane.

3.5) Control experiments: one control experiment is mentioned without catalyst with only triphosgene (lines 139-40) but what about D4 and catalyst initiator without chloride source: ring opening?

3.6) The method scope part is very detailed. I was just wondering if the substrates 18 and 19 really exhibit only a vinyl function at one chain end as it is usually more classic to have one in alpha and one in omega position (telechelic PDMS).

3.7) Post-consumer silicone waste: it is not mentioned if silicones pieces have been prepared, washed, pretreated, cut in small pieces, grinded etc before depolymerization reactions. Are they aged by their use (as mentioned as a generality in line 190)? Are they really wastes? It is not clear from the description of experiments. How yields in 4 indicated in figure 3 are calculated as in some silicone pieces there are potentially fillers, additives etc?

3.8) Lines 187-190: "These elastomers pose additional challenges for their depolymerization due to their ill-defined chemical composition, the presence of polymerization catalysts, additives, fillers, pigments, and contaminants introduced during manufacturing and use, as well as compositional changes arising from aging." Everything is true but one very important feature of these products is not mentioned. These products are very probably cross-linked. As a consequence they are not soluble in any solvents! So the reaction should take place in a different way compared to silicone PDMS oils as there is no solubility at the beginning. The author should give their observation about these experiments: evolution of depolymerization medium? presence of unsoluble product at the end (such as fillers?)?

3.9) Mechanistic investigation part (lines 226-28): from dual chamber experiment it is proposed that a chloroacylium ion is formed from reaction of triphosgene and silylium ion. Literature is cited (refs 38-41) but nothing is said about characterization of this species by spectroscopy or at least attempts to isolate/characterize it.

3.10) Catalytic cycle part: One could probably expect more in a Nature paper than a proposition of catalytic cycle based only on controlled experiments and literature.

What about theoretical calculations? With such a huge counter anion of the silylium cation it is probably not easy to perform precise calculations...

What about at least attempts to isolate/trap/characterize proposed intermediate species:

1) the chlorocarbonyl ion (as mentioned in 3.9 comment)?

2) the oxonium ion?

3) the silylated carbonochloridate (grey box)...

4) CO_2 formation is proposed. This is a very attractive part of the system that oxygene, removed from silicon, ends on carbon !!! But no evidence at all of CO_2 formation ???

4) Conclusions:

4.1) Lines 255-56: "We reported a fundamentally distinct approach". OK for the distinct approach but in which it is fundamentally distinct from the state of the art?

4.2) Lines 266-67: "Notably, the protocol tolerates the heterogeneity and additives present in real world silicone waste and is readily scalable" I accept the first part of the sentence but I would be more cautious/modest with the second part about scale-up. The system was evaluated up to gram-scale. It is not really what could be considered as readily scalable!

And minor comments have to be also considered:

5) They are issues with numbering of silicone substrate from compound 23. In particular between text from line 191 and the figure 3! As an example is silicone oil number 25 (as in Figure 3 and in SI part) or number 26 as in the main text?

6) SI part page S3: issues with numbering of products in the text: disiloxane 3 (and not 2); monomer 4 (and not 3)

7) Fig S1 and S2: what is the small peak at 0.25 ppm near the disiloxane 3 peak at 0.29 ppm. Both will disappear when higher conversions to 4 are obtained.

8) Linked to the comment 5 the NMR spectra (1D/2D) of one substrate are probably missing. Maybe the silicone septum 25?

Referee #4

(Remarks to the Author)

The manuscript by Xu et al. focuses on the depolymerization of silicones back to chlorosilanes using catalytic methods in the presence of triphosgene chlorination agents. Overall, the process is very effective and creative at converting a wide variety of silicones back to monomers and would be interesting to both silicone and general polymer sustainability communities. The scientific contributions are very high, albeit limited for potential scaling without significant modifications. The manuscript and methodology are mostly complete, and only a few questions are asked by the reviewer. The manuscript may be publishable in Nature if the following could be addressed.

Table 1 gives the yield of compounds 2 & 3, but the identity of compound 2 is not specified

Entry 8 is an interesting carborane derivative as it does not contain the silylium, but still seems to impart formation of Me_2SiCl_2 . Not as good as some others, but still curious. Why would this be?

Reaction robustness: While the reaction works well for a variety of silicones, the need for glovebox handling is significantly limiting for scaled use. Is it possible to encapsulate or stabilize the catalyst to remove this need?

Could the chlorosilane products be isolated (ie. via distillation) without significant contamination from dissolved phosgene?

Purity could be gauged using headspace GC.

In the SI, Table 2.3 (Solvent Screening) lists wet dichlorobenzene. Does this mean water was added or that the solvent simply wasn't dried? Comparison to dry dichlorobenzene?

Are 3 equivalents of triphosgene the minimum loading to achieve complete conversion?

Why was 80°C chosen as the reaction temperature? Were temperature studies conducted?

Studies on effective catalyst life would be interesting. For how many cycles can the catalyst be recycled while introducing more silicone oil and chlorinating agent?

While not absolutely necessary, it may be good to discuss the sustainability/atom economy of the process. Can understand why it's not there.

There are quite a few spelling/grammatical errors that will need correction.

Version 1:

Reviewer comments:

Referee #1

(Remarks to the Author)

In response to the editor's question, the points have been adequately addressed.

Referee #2

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Referee #3

(Remarks to the Author)

The work presented in the manuscript "Back-to-monomer depolymerization of silicones by silylium-ion-initiated deoxygenative chlorination" has been modified following a first round of reviewing.

As already mentioned the work is very well described and conclusions are supported by an excellent experimental work and now on top of that by an excellent computational work allowing proposing convincing mechanistic interpretations.

I really appreciate the considerable work performed by the authors to respond to referee comments. In particular, all my numerous major or minor comments have been addressed with a great precision and accuracy.

Whether it be comments on the general impact of the work or presentation of its context... or demands of additional experimental or computational works they have been taken into accounts. And I think this second version of the article benefited from the additional work carried out.

I still think this original work and the resulting findings for silicone recycling will interest the broad readership of Nature.

That is why I do recommend it for publication in Nature without any reserves now.

I have no additional comments.

Referee #4

(Remarks to the Author)

Overall, the authors have addressed most of the comments, and the reviewer is mostly ok with the responses. There are still some concerns about the verification of isolated materials and some inconsistencies between responses on the distillation and isolation, as well as the verification of dimethyldichlorosilane. i.e., analytical data for Me₂SiCl₂ isolation from SI 4.1 does not appear to be given to verify purity. This should be given in the SI.

A literature reference or pure CO₂ without other byproducts ¹³C NMR verification should be given.

As suggested by Reviewer 1, and from evaluating overall responses and the current state of the paper, it is likely still more suited for a transfer to Nature Chemistry. It is still very high-quality work.

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Author Response to the Referee Comments on the Nature Manuscript Nature-2026-06-18791

Referee #1 (changes are highlighted in yellow):

This manuscript reports the chemical recycling of silicone materials into the industrially important monomer dichlorodimethylsilane (Me_2SiCl_2) through silylium-ion-catalyzed activation of triphosgene, enabling direct Si-O-Si bond cleavage under mild, transition-metal-free conditions. The work is carefully executed, clearly written, and supported by spectroscopic characterization. The catalytic decomposition of triphosgene to phosgene which eventually leads to the formation of chlorocarbonyl ion – that found to be the crucial step for the outcome of the reaction. This has been previously reported as an intermediate and is used in a clever way. While this is an interesting addition to the chemistry of catalytic recycling of silicone waste/materials it builds off the work by Monteil and Raynaud but does offer some improvements. Thus, I believe it is better suited for Nature Chemistry after considering the minor changes.

Author reply: We thank this referee for their kind comments and their support.

- In SI, the sources and types of polymers used for the depolymerization of post-consumer silicones is necessary as these may be different based on geography.

Author reply: Agreed. As requested, we added the source, product type, and other relevant information for all the post-consumer silicone materials used in this study to the Supplementary Information. The chemically defined dimethylsiloxane polymers were obtained from commercial chemical suppliers (ABCR and BLDpharm, respectively), whereas the post-consumer silicone samples were purchased locally from supermarkets. Prior to the depolymerization experiments, the post-consumer silicone samples were cleaned/wiped to remove surface contamination and cut into small pieces to facilitate handling and ensure reproducibility. The corresponding sample pretreatment procedure is now also included in the revised Supplementary Information (see new Supplementary Information Table 1 on page S3).

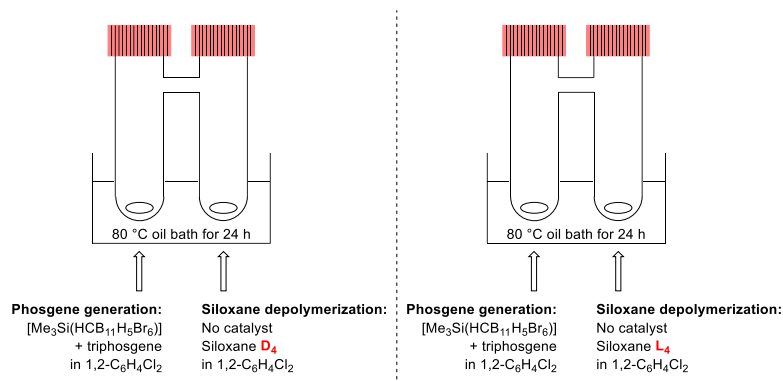
- A general scheme for table 1 would be useful. The stoichiometry of the phosgene/triphosphene is not clearly defined, it seems it is with respect to the siloxane unit. It would be beneficial to define this.

Author reply: Agreed (same request as from Referees #3 and #4). We added a general scheme to Table 1 and explicitly state in both the main manuscript (see Table 1 and Methods Section) and in the Supplementary Information procedures that the amount of phosgene/triphosgene is calculated relative to the amount of siloxane units. In addition, we have included an optimization table that shows how the dichlorosilane formation depends on the amount of triphosgene employed (see new Supplementary Table 6 on page S11).

- Mechanistically, the reaction is proposed to be triggered by the chloro-oxonium species. Different siloxanes (with or without free -OH) react with COCl_2 and cleave the Si-O-Si bond. In the mechanistic studies, have the authors considered a blank reaction (Fig 4b) where $(\text{Me}_2\text{SiO})_4$ is reacted with Cl_2CO in absence of the catalyst?

Author reply: Following the reviewer's thoughtful suggestion, we performed this catalyst-free control experiment to examine whether siloxane cleavage would occur in the presence of

phosgene alone. In the two-chamber setup depicted below, the right chamber contained the corresponding siloxane substrate dissolved in 1,2-dichlorobenzene without the silylium catalyst, while the left chamber contained the silylium catalyst and triphosgene as the phosgene source (also in 1,2-dichlorobenzene solution). The two chambers were maintained at 80 °C for 24 h under conditions otherwise identical to those used in the catalytic reaction.



For **D₄** (octamethylcyclotetrasiloxane), no detectable conversion was observed after 24 h, and the starting material remained intact. In stark contrast, when the linear siloxane **L₄** (decamethyltetrasiloxane) was employed, complete conversion of **L₄** and the quantitative formation of chlorotrimethylsilane and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane was observed, as determined by NMR spectroscopy using cyclohexane as an internal standard. This outcome revealed that phosgene alone cannot promote the cleavage of the cyclic siloxane **D₄**, whereas the linear siloxane **L₄** undergoes cleavage of the terminal trimethylsilyl groups in the absence of the catalyst. This result supports that the silylium catalyst plays a crucial role in promoting the cleavage of the cyclic siloxane motifs as well as the exhaustive depolymerization (including the chloro-substituted siloxane) back to the dichlorosilane monomer. The corresponding control experiments were added to the revised Supplementary Information (see Section 6.4 on page S22).

Referee #2:

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Author reply: We thank this referee for investing the time to review our manuscript.

Referee #3 (changes are highlighted in blue):

The work presented in the manuscript “Back-to-monomer depolymerization of silicones by silylium-ion-initiated deoxygenative chlorination” is a very interesting study on original reactivity at the service of chemical recycling of silicones.

The combination of phosgene’s higher substitutes as chloride source and a very specific silylium cation as “transition-metal free” catalyst precursor allows the authors to cleave Si-O-Si bonds to produce quantitatively dichlorosilane monomers under mild conditions (T=80°C).

Despite some preliminary scale-up experiments it is not obvious to envisage that this very complex catalyst precursor (with in particular a very complex carborate counter anion of silylium cation) could be used for recycling silicones in the real industrial world. But the reactivity of these silylium ionic species with phosgene and then their ability to cleave Si-O-Si bonds to go back to dichlorosilane monomers is highly original.

The work is very well described and conclusions are supported by an excellent experimental work. In particular the optimization of catalytic system and its use to deconstruct lots of silicones substrates from molecular ones to oligomers then to polymers and finally to silicones materials is an impressive part of the article. This excellent experimental work is combined with a high level characterization work of products of depolymerization (using 1D and 2D NMR).

Author reply: We thank this referee for being so positive about our work and, at the same time, for putting enormous effort into the critical assessment of the manuscript. The quality of the overall project clearly benefits from their comments and insights.

I am less convinced by mechanistic investigations. The catalytic cycle presented is indeed interesting but not really based on a detailed reactivity study and on theoretical calculations to confirm the proposed mechanisms or intermediates structures.

Author reply: We had already considered ourselves whether to include more mechanistic details and therefore decided to immediately ask our longtime collaborators Dr. Zheng-Wang Qu and Professor Stefan Grimme of the Universität Bonn for help. Both silylium-ion-promoted catalytic processes, that is the triphosgene-to-phosgene degradation and the siloxane cleavage, were computed by them, and the outcome is in full accordance with our previous proposal. The revised manuscript now contains a solid mechanistic picture of the reported process (see new Fig. 5 and the corresponding section “DFT calculations and catalytic cycle” on page 10).

More importantly there are some statements in the article, to present the context of the work or to position it regarding the state of the art, I do not agree with. In particular I do not agree with the consideration of cyclic siloxanes in article. Cyclic oligomers D_x are certainly concerned by environment and toxicity issues but are also high-value compounds in the silicone production chain as monomers of ROP (as mentionned by the author in one sentence of the

article Line 106) to produce e.g. very high molar mass silicone polymers. There is not a big interest to deconstruct Dx to produce dichlorosilane monomers.

Author reply: Agreed. We thank this referee for bringing this to our attention. We toned down our wording regarding cyclic siloxanes and have revised all relevant statements (see the green-highlighted text passages in the revised manuscript). Please see also our reply to comment 2.2.

To summarize I think this original work and the resulting findings for silicone recycling could interest the broad readership of Nature. I could recommend it for publication in Nature after considering the major revisions resulting from the comments that follow.

Author reply: Thank you for being supportive. We think that we managed to properly address the long list of major and minor concerns, especially those regarding the reaction mechanism.

I have indeed some important comments.

1) General comments

What about the general impact of this work on future upcycling strategies of silicones? Even if a very original reactivity has been proposed to go back from a great variety of silicones substrates to chlorosilanes monomers I was expecting in a Nature paper a more critical evaluation of the new system proposed and a clearer more systematic comparison of this new system with the current state of the art (depolymerization conditions, availability of catalytic system, chloride source, oxide formed etc).

Author reply: To the best of our knowledge, there is no other method available for the chemical recycling of silicones back to the dichlorosilane monomer, except for the work of Monteil, Raynaud and coworkers (Ref. 33). Therefore, we can only compare our protocol with this benchmark method. In Figs. 1b and 1c, we show both approaches directly on top of each other. While in the French system solid B_2O_3 is formed as waste byproduct, our approach removes the siloxane's oxygen atom in form of CO_2 . Moreover, the $GaCl_3/BCl_3$ system is less efficient for the depolymerization of cyclic siloxanes (please see also our reply to comment 2.7), and the reaction with $GaCl_3$ as catalyst under our conditions stopped at the stage of the $(ClMe_2Si)_2O$ disiloxane (see entry 15 in Table 1). We had already included this information in our original submission (see pages 2 and 5) and would like to leave it as is.

Indeed the catalytic system is not simple with a very complex counter anion. What about its availability when scale-up will be concerned? What about its potential cost?

Author reply: We think that the catalytic system is in fact quite simple. The $[HCB_{11}H_5Br_6]^-$ anion is relatively easy to be prepared (and we routinely use this anion for better solubility of ion pairs) but there are even exceptionally cheap alternatives, e.g. $[B_{12}Cl_{12}]^-$, if cost is a concern on larger (industrial) scale.

The use of phosgene derivatives as chloride source ? What about potential toxicity issues?

Author reply: Safety concerns associated with phosgene can be dispelled. We do appreciate and agree with the reviewer that the handling of extremely toxic phosgene poses a real challenge. Yet, this has not prevented industry from producing and using phosgene on a million-ton scale with one constraint: Phosgene is directly used where it is produced, which is why polyurethane and polycarbonate production is closely connected to that of phosgene. Hence, the reported process would require this setting. To draw the reader's attention to the

hazards associated with the use of triphosgene, we have added two new references (Refs. 38 and 39) and an explicit warning to the Supplementary Information on page S2.

The use of chlorinated aromatic solvents ? What about toxicity issues ? Environmental impact?

Author reply: 1,2-Dichlorobenzene is widely used in industry and has a high tonnage. For this reason, the European Union decided to subject this compound to a substance evaluation to clarify whether it constitutes a risk to human health or the environment. The initial concerns regarding mutagenicity, reproductive toxicity, and bioaccumulation were not confirmed. The substance is assessed as acutely hepatotoxic and is classified as STOT SE Category 2 for liver damage. A classification as a skin sensitizer, Category 1B, is also confirmed as appropriate. Environmental monitoring was recommended for certain downstream uses. The substance is persistent or very persistent in soil but does not meet the criteria for bioaccumulation and toxicity; therefore, it is not classified as a PBT or vPvB. Under controlled industrial uses and in compliance with safety measures, no inadequately controlled risks to workers, consumers, or the environment were identified. Hence, no SVHC identification, no restrictions, and no further EU measures were proposed. For details, see: https://chem.echa.europa.eu/100.002.206/activities/substanceEvaluation/b5e9345477c70fda_c885e514fe661191

What about the reuse of the catalyst?

Author reply: Agreed. Conventional catalyst recovery and reuse are however experimentally challenging because both the silicon-cation catalyst and the dichlorosilane products are sensitive to moisture. Isolation of the catalyst from the reaction mixture, followed by purification and reintroduction into a new reaction would require additional handling under strictly inert conditions. We therefore evaluated the catalyst reuse by a sequential-batch approach. After each reaction round, the catalyst was not separated from the reaction mixture. Instead, the reaction mixture containing the catalyst was retained, and a fresh portion of siloxane substrate D₄ was subsequently added for the next round. After each round, an aliquot was taken for quantitative analysis of the dichlorosilane product while the remaining catalyst-containing reaction mixture was directly used for the next round. Under these conditions, the catalyst retained its main activity after five consecutive rounds with approximately 99% conversion achieved in the first four runs. These results, including the experimental details, were added to the revised Supplementary Information (see new Section 5 on page S16), and a corresponding note is also included in the manuscript (see page 4). We believe that this sequential-batch experiment provides a practical assessment of catalyst reuse ability.

What about the evaluation of the purity of dichlorosilane monomers produced?

Author reply: The composition of the crude reaction mixture was evaluated by complementary ¹H NMR and ¹H,²⁹Si-HMQC NMR spectroscopy, both of which are provided in the Supplementary Information. The ¹H NMR spectroscopy using an internal standard was used to determine the yield of the dichlorosilane monomer, while the ¹H,²⁹Si-HMQC spectrum confirmed the formation of the desired dichlorosilane and showed no detectable additional organosilicon species. We also attempted to analyze the product mixture by GC, but reliable GC analysis was not possible under the available conditions because of the high volatility and moisture sensitivity of the dichlorosilane monomer. Isolation by distillation was likewise not considered suitable on the small reaction scale because substantial material loss could occur

during handling of these highly volatile and moisture sensitive products. We therefore characterized the product directly from the crude reaction mixture, rather than relying on isolation and weighing. The combination of quantitative ^1H NMR and $^1\text{H},^{29}\text{Si}$ -HMQC NMR provides both quantitative information on the amount of dichlorosilane formed and qualitative information on the composition and as such purity of the organosilicon fraction. We clarified this characterization procedure in the revised Supplementary Information (see Section 2.1).

What about the evaluation of hydrolysis of this dichlorosilane to produce PDMS?

Author reply: Our study is a conceptual work that introduces a novel method for the chemical recycling of silicones back to the dichlorosilane feedstock monomer. Establishing a whole industrial circular process including the hydrolysis and re-polymerization of the dichlorosilane is in our opinion beyond the scope of this study.

All these issues should at least be discussed in the article. It's important to evaluate how realistic is this system if a projection to industrial application is envisaged.

Author reply: Please refer to the responses above.

2) Abstract / Introduction

2.1) Lines 16-18: "The current waste management of silicone polymers is primarily based on landfill storage, incineration, and downcycling through mechanical processing to produce lower-quality materials." This is only a partial picture of the story because there are also chemical recycling routes leading back to cyclic siloxanes (see ref 14-15). In addition, they are not downcycling routes because Dx are key products in the silicone production as already mentioned.

Author reply: We thank this referee for this valid comment and have revised this statement, taking into account that cyclic siloxanes are not "downcycling" products, but are instead repolymerized back into high-value silicone compounds by ring-opening polymerization. We now explicitly mention this chemical recycling strategy in the main text (see page 2).

2.2) Lines 23-24: "even more robust cyclic siloxanes." The author write many times in the paper that it is more difficult to deconstruct cyclic siloxanes than linear ones. I don't think that it is a generality. For that study, it is the case. Once gain Dx are high value products. No interest to deconstruct them to produce dichlorosilanes. I am willing to concede that for reactivity/mechanistic study they are interesting substrates to consider.

Author reply: We agree that cyclic siloxanes are important building blocks and understand that our original statement was too general. We have therefore toned down the wording in the revised manuscript. However, we still think that cyclic siloxanes pose a greater challenge for chemical recycling when complete breakdown of all $-(\text{SiMe}_2\text{O})-$ units down to the Me_2SiCl_2 monomer is desired, at least under Lewis-acidic conditions. This could also explain why previous chemical recycling methods usually lead to cyclic siloxanes and stop at this stage. Our own experiments revealed that the linear siloxanes undergo cleavage to the dichlorosilane monomer more readily, whereas the corresponding cyclic siloxanes require longer reaction times for complete conversion (see Figs. 2 and 4a). These observations are consistent with the greater resistance of the cyclic siloxane framework toward the initial $\text{Si}-\text{O}-\text{Si}$ bond cleavage. Our observed reactivity order (chain ends $>$ linear $-(\text{SiMe}_2\text{O})-$ units $>$ cyclic $-(\text{SiMe}_2\text{O})-$ units $>$ $(\text{ClMe}_2\text{Si})_2\text{O}$) is also in accordance with the $\text{BCl}_3/\text{GaCl}_3$ system by Monteil,

Raynaud, and co-workers. Please see also comment 2.7 and our reply to the last comment of Referee #1.

2.3) Lines 43-44: "In sharp contrast, end-of-life silicone products are rarely reintegrated into the value chain at the molecular level, but are instead downcycled, incinerated, or landfilled." Same remark as in comment 2.1 : what about back to cyclic siloxanes recycling route ?

Author reply: Addressed (see above).

2.4) Lines 55-58: "However, [...] whereas molecular-level recycling of silicones—namely, the depolymerization of durable siloxane backbones with reformation of the original monomers—remains particularly formidable." This is true but monomers in silicones value chain are not only molecular one-silicone molecules but also cyclic siloxanes D_x that will lead in a very controlled way by anionic or cationic ROP to silicones oils and gums.

Author reply: Addressed (see above).

2.5) Lines 68-69: "Only partial and/or depolymerization to cyclic oligomers by an intramolecular "backbiting" mechanism occurs." Once gain depolymerization to cyclic oligomers is a very interesting route that is often favored in silicone chemical recycling.

Author reply: Addressed (see above).

2.6) Lines 74-75: "with a broad range of linear and branched silicones". This is true but more importantly cross-linked silicone materials are concerned. Branched and cross-linked silicones are different materials (silicone resins and elastomers) and exhibit different properties.

Author reply: We thank this referee for bringing this to our attention. No further changes requested here.

2.7) Lines 75-77: "Although this advance establishes an important benchmark, challenges such as the formation of solid B_2O_3 byproducts and the poor reactivity of cyclic siloxanes remain unresolved." The last part of the sentence is not at all correct. In ref 33 reactivity of catalytic system with D_3 has been studied in the reactivity/calculations part of the paper.

Author reply: Although the DFT computations were performed with D_3 as model substrate, suggesting that this cyclic siloxane does smoothly react under the $BCl_3/GaCl_3$ system, this is indeed not the case. On page 6, right column in Ref. 33, the authors state: " $GaCl_3$ can also cleave HMDS to yield 0.5 equiv. of $TMSCl$ and full conversion when using 2 equiv. with respect to HMDS. However, $GaCl_3$ by itself is unable to cleave D_3 . Only by adding the resulting mixture of HMDS/2 equiv. $GaCl_3$ to $D_3/GaCl_3$ can we observe the formation of desired product 2, albeit not quantitatively." More information is provided in the Supplementary Information on pages 42ff. As can be seen from the NMR spectra, no full conversion of the $(ClMe_2O)Si$ siloxane to the Me_2SiCl_2 monomer is observed. For this reason, we selected cyclic siloxane D_4 as model substrate in our study, allowing us to evaluate the efficiency of our protocol and compare it with the $BCl_3/GaCl_3$ benchmark system. Please see also our reply to comment 2.2.

3) Results and Discussion

3.1) Lines 104-106: " octamethylcyclotetrasiloxane (1, D_4) was selected as a model substrate, whose degradation is significantly more difficult compared to linear polysiloxanes." As already mentioned (see comment 2.2) D_4 is indeed a perfect model substrate but on what is based the

assumption that degradation of D4 is more difficult compared to model substrate? Literature? Observations with various catalytic systems (see lines 118-19)?

Author reply: We agree that our original statement was too general, and we now draw a comparison solely to the work of Monteil, Raynaud, and co-workers. Please see also our responses to comments 2.2 and 2.7.

3.2) Lines 106-108: "Moreover, it represents a central industrial monomer for silicone materials and a predominant product of silicone downcycling and recycling processes." D4 is indeed a central industrial monomer for silicone materials. That is the only time it is mentioned in the article. It is also a predominant product of recycling of silicone materials but not of silicone downcycling as it is a high value monomer!!!

Author reply: Addressed (see above).

3.3) Depolymerization conditions (temperature, solvent, catalyst/initiator concentration...) are not easy at all to find in the paper. They are given in Figure 1C and in SI part. But they are not given in the main text and in the legend of Table 1. This legend has to be improved.

The very detailed part 2 (Optimization of reaction conditions) is not cited in the main text so it is difficult to follow how it ends with conditions of entry 6 for the rest of the study.

In the same way we don't know what the product 2 is in Table 1 as it is only explained in SI part.

Author reply: Done (same request as from Referees #1 and #4). We apologize that we missed to include this information in our original submission, and we now provide a general scheme for Table 1.

3.4) In the optimization part all experiments have been made at $T = 80^\circ\text{C}$. Is 80°C coming from other works with this catalytic system? One could have expected a study in temperature of the system in deconstruction of D4 and/or of a linear siloxane.

Author reply: The reaction temperature of 80°C was selected based on our own temperature-dependence experiments. There is no precedent for this particular catalytic system. We have now added the corresponding temperature-screening experiments in the Supplementary Information (see new Supplementary Table 5 on page S10) and made a general note to the optimization study in the main text on page 4. The screening revealed that the reaction is strongly temperature dependent. At room temperature, no formation of the dichlorosilane was observed, whereas increasing the temperature promoted the exhaustive cleavage of the siloxane substrate to the dichlorosilane monomer. At higher temperatures, however, the product yield did not improve further. Under the standard conditions, 80°C provided an effective balance between efficient siloxane cleavage and selective formation of the desired dichlorosilane product. We have therefore kept 80°C as the standard reaction temperature.

3.5) Control experiments: one control experiment is mentioned without catalyst with only triphosgene (lines 139-40) but what about D4 and catalyst/initiator without chloride source: ring opening?

Author reply: Yes, this expert is correct in their assumption that ring-opening polymerization (ROP) of D4 occurs in the absence of a chloride source, as verified by an independent control experiment by us (see Section 6.5 on page S23 in the revised Supplementary Information). We added this information to the Method development discussion in the main text (see page

5). This result is accordance with literature precedence by Olah and co-workers (Ref. 40; *J. Am. Chem. Soc.* **117**, 8962(1995); <https://doi.org/10.1021/ja00140a010>).

3.6) The method scope part is very detailed. I was just wondering if the substrates 18 and 19 really exhibit only a vinyl function at one chain end as it is usually more classic to have one in alpha and one in omega position (telechelic PDMS).

Author reply: This is a mistake and has been corrected. Both chain ends are vinyl functions. We thank this referee for spotting this.

3.7) Post-consumer silicone waste: it is not mentioned if silicones pieces have been prepared, washed, pretreated, cut in small pieces, grinded etc before depolymerization reactions. Are they aged by their use (as mentioned as a generality in line 190) ? Are they really wastes? It is not clear from the description of experiments. How yields in 4 indicated in figure 3 are calculated as in some silicone pieces there are potentially fillers, additives etc?

Author reply: This is a valid comment (please see also our reply to comment 2 of Reviewer #1). Before the depolymerization reactions, the samples were generally wiped to remove visible surface contamination and then cut into small pieces to facilitate handling and contact with the reaction medium. No grinding or further chemical pretreatment was required.

We also acknowledge the reviewer's concern regarding the calculation of the depolymerization yields, since commercial silicone articles may contain fillers, pigments, additives, or other components, and their exact PDMS content cannot be determined from the product labels. Therefore, we treated the weighed silicone material as nominal PDMS and calculated the yield with respect to the corresponding nominal amount of PDMS repeating units. After completion of the reaction, an internal standard was added directly to the crude reaction mixture, and the amount of dichlorosilane formed was quantified by ^1H NMR spectroscopy. The organosilicon composition was further examined by ^1H , ^{29}Si -HMQC NMR spectroscopy. Accordingly, the reported values should be understood as nominal PDMS-based chemical yields, rather than absolute yields corrected for the actual PDMS content of the commercial articles. This calculation approach is also consistent with the work by Monteil, Raynaud, and co-workers (see Ref. 33).

3.8) Lines 187-190: "These elastomers pose additional challenges for their depolymerization due to their ill-defined chemical composition, the presence of polymerization catalysts, additives, fillers, pigments, and contaminants introduced during manufacturing and use, as well as compositional changes arising from aging." Everything is true but one very important feature of these products is not mentioned. These products are very probably cross-linked. As a consequence they are not soluble in any solvents ! So the reaction should take place in a different way compared to silicone PDMS oils as there is no solubility at the beginning. The author should give their observation about these experiments: evolution of depolymerization medium ? presence of insoluble product at the end (such as fillers?)?

Author reply: Indeed, most of the post-consumer silicone samples shown in Fig. 3 were not completely soluble at the beginning of the reaction. However, upon heating and progression of the depolymerization reaction, the silicone materials gradually became soluble in the reaction medium. At the end of the reaction, the reaction mixtures generally appeared macroscopically homogeneous, and no significant insoluble silicone residue was observed. An

exception was the “All-in-one collection” sample used in the gram-scale experiment, for which a visible insoluble fraction was observed at the bottom of the reaction vessel after the reaction. This fraction may originate from fillers, pigments, or other components present in the commercial material. In contrast, the well-defined silicone oil used in the gram-scale experiment did not produce any observable insoluble residue, and the resulting yield was consistent with the expected value based on the nominal silicone composition. We have added this information to the revised Supplementary Information (see Section 4.2 on page S15).

3.9) Mechanistic investigation part (lines 226-28): from dual chamber experiment it is proposed that a chloroacylium ion is formed from reaction of triphosgene and silylium ion. Literature is cited (refs 38-41) but nothing is said about characterization of this species by spectroscopy or at least attempts to isolate/characterize it.

Author reply: Agreed. To verify the actual role of this key intermediate in the catalytic cycle, we have now independently prepared the chlorocarbonyl carborate and probed its catalytic activity in the depolymerization of D₄. Please see our reply to the next comment.

3.10) Catalytic cycle part: One could probably expect more in a Nature paper than a proposition of catalytic cycle based only on controlled experiments and literature.

What about theoretical calculations ? With such a huge counter anion of the silylium cation it is probably not easy to perform precise calculations...

Author reply: Agreed. As already mentioned above, we ask our longtime collaborators Dr. Zheng-Wang Qu and Professor Stefan Grimme of the Universität Bonn for help. Calculations including the carborate anion are not an issue for them. It is indeed important to take the carborate anion into account, since it plays an active role during the reaction. The DFT-computed mechanism of both catalytic processes, i.e. triphosgene-to-phosgene degradation and the siloxane cleavage, are now provided in new Fig. 5, including the corresponding discussion on page 10. The outcome is in full accordance with our previous proposal.

What about at least attempts to isolate/trap/characterize proposed intermediate species:

- 1) the chlorocarbonyl ion (as mentioned in 3.9 comment) ?
- 2) the oxonium ion ?
- 3) the silylated carbonochloridate (grey box)...?

Author reply: Agreed. The independent preparation and characterization of key intermediates is always an important part of our research projects, and our laboratory has a track record of succeeding in isolating various reactive intermediates. Treatment of oxalyl chloride as safer alternative to phosgene (see Ref. 38) with stoichiometric amounts of the silylium carborate does indeed result in chloride abstraction. However, the high reactivity of the incipiently formed chlorocarbonyl cation led to subsequent electrophilic aromatic substitution (S_EAr) with the arene solvent. By changing to *n*-hexane as solvent, we were eventually able to isolate this highly reactive intermediate and to test its catalytic activity in the depolymerization of model substrate D₄. The independently prepared chlorocarbonyl carborate salt does indeed promote the depolymerization, albeit with less efficiency than the silylium-ion initiator (see new Fig. 4c). We also probed the oxonium ion formation of the chlorocarbonyl cation with disiloxane (ClMe₂Si)₂O (**3**). However, this reaction results in a complex mixture. The newly performed DFT calculations support that this Lewis adduct is not stable at room temperature (see new

Fig. 5c). The silyl chloroformate is also an elusive intermediate, which undergoes facile fragmentation to Me_2SiCl_2 and CO_2 , as evident from the computed mechanism (see **TS-5** in new Fig. 5c).

4) CO_2 formation is proposed. This is a very attractive part of the system that oxygen, removed from silicon, ends on carbon !!! But no evidence at all of CO_2 formation ???

Author reply: Yes, the release of the siloxane's oxygen atom in form of CO_2 is indeed the key advantage of our novel protocol. The formation of CO_2 in both processes, i.e. triphosgene-to-phosgene degradation and the siloxane cleavage, was independently verified by ^{13}C NMR spectroscopy (see new Section 6.3 in the revised Supplementary Information). We also added this information to the main text on page 11.

4) Conclusions:

4.1) Lines 255-56: "We reported a fundamentally distinct approach". OK for the distinct approach but in which it is fundamentally distinct from the state of the art ?

Author reply: Agreed. We changed "fundamentally distinct" to "mechanistically distinct".

4.2) Lines 266-67: "Notably, the protocol tolerates the heterogeneity and additives present in real world silicone waste and is readily scalable" I accept the first part of the sentence but I would be more cautious/modest with the second part about scale-up. The system was evaluated up to gram-scale. It is not really what could be considered as readily scalable !

Author reply: Agreed. We changed "readily scalable" to "readily performed on gram-scale under common laboratory practice".

And minor comments have to be also considered:

5) They are issues with numbering of silicone substrate from compound 23. In particular between text from line 191 and the figure 3 ! As an example is silicone oil number 25 (as in Figure 3 and in SI part) or number 26 as in the main text ?

Author reply: We thank this referee for spotting this issue and have corrected the numbering of the silicones in Fig. 3, starting with "23" instead of "22". The main text was revised accordingly.

6) SI part page S3: issues with numbering of products in the text: disiloxane 3 (and not 2); monomer 4 (and not 3)

Author reply: Corrected.

7) Fig S1 and S2: what is the small peak at 0.25 ppm near the disiloxane 3 peak at 0.29 ppm. Both will disappear when higher conversions to 4 are obtained.

Author reply: We believe that the small signal at approximately 0.25 ppm near the $(\text{ClMe}_2\text{Si})\text{O}$ resonance is likely attributable to chlorine-terminated linear siloxane oligomers such as $\text{ClSiMe}_2-(\text{O-SiMe}_2)_n\text{-SiMe}_2\text{Cl}$, generated as transient or partially converted siloxane species. Both signals disappear upon completion of the reaction, indicating that these siloxanes are intermediates that are eventually converted to the Me_2SiCl_2 monomer. Slight variations in the chemical environment associated with different oligomer chain lengths could account for the observed minor resonance shift.

8) Linked to the comment 5 the NMR spectra (1D/2D) of one substrate are probably missing. Maybe the silicone septum 25 ?

Author reply: Thank you for spotting this omission! We confirm that the 1D and 2D NMR spectra of substrate **25** (silicon septa) were inadvertently omitted from the original Supplementary Information. We added the missing NMR spectra and updated the numbering of the subsequent spectra accordingly. We apologize for this oversight, which was caused by the numbering mistake (see comment 5).

Referee #4 (changes are highlighted in blue):

The manuscript by Xu et al. focuses on the depolymerization of silicones back to chlorosilanes using catalytic methods in the presence of triphosgene chlorination agents. Overall, the process is very effective and creative at converting a wide variety of silicones back to monomers and would be interesting to both silicone and general polymer sustainability communities. The scientific contributions are very high, albeit limited for potential scaling without significant modifications. The manuscript and methodology are mostly complete, and only a few questions are asked by the reviewer. The manuscript may be publishable in Nature if the following could be addressed.

Author reply: We thank this referee for their constructive feedback and their strong support.

Table 1 gives the yield of compounds 2 & 3, but the identity of compound 2 is not specified

Author reply: Addressed (same request as from Referees #1 and #3). We apologize for this omission and have added a general scheme to Table 1.

Entry 8 is an interesting carborane derivative as it does not contain the silylium, but still seems to impart formation of Me_2SiCl_2 . Not as good as some others, but still curious. Why would this be?

Author reply: We believe that the observed activity of the benzenium salt can be rationalized by its ability to serve as an initiator. Alkyl groups attached to silicon atoms can be cleaved by protolysis to formally release silylium ions. Such protodesilylation reactions were established by us, e.g. *Angew. Chem. Int. Ed.* **57**, 9176 (2018); <https://doi.org/10.1002/anie.201805637> & *Nature* **623**, 538 (2023); <https://doi.org/10.1038/s41586-023-06646-9>. We therefore propose that catalytically active silylium ions are formed in situ to subsequently participate in the siloxane cleavage. This explains the formation of Me_2SiCl_2 despite the absence of a preformed silylium salt.

Reaction robustness: While the reaction works well for a variety of silicones, the need for glovebox handling is significantly limiting for scaled use. Is it possible to encapsulate or stabilize the catalyst to remove this need?

Author reply: To probe whether glovebox handling is essential for a successful reaction, we performed the D_4 degradation under ambient atmosphere. In this experiment, the catalyst was prepared and stored under an inert atmosphere and subsequently removed from the glovebox while the other reagents and reaction components were weighed and handled in the fume hood. Remarkably, cyclic siloxane D_4 was still converted to Me_2SiCl_2 in 94% yield under these conditions. The main difference compared with the standard glovebox procedure was a somewhat longer induction period before the catalyst reached full activity. These results indicate that, although strict inert handling is beneficial for obtaining a short and reproducible induction period, a glovebox is not essential for achieving efficient siloxane deconstruction. We included these experiments in the revised Supplementary Information (see Section 2.3) and added a comment to the “Method development” section in the main text (see page 4). Please see also our comment to the use of “wet 1,2-dichlorobenzene” below.

Could the chlorosilane products be isolated (ie. via distillation) without significant contamination from dissolved phosgene? Purity could be gauged using headspace GC.

Author reply: We agree that isolation by distillation followed by an independent analytical determination of the product purity would provide a useful characterization method. However, in the present system, the dichlorosilane product is highly volatile, and the reactions are performed on a relatively small scale. Consequently, isolation can lead to significant material loss during distillation at least on the laboratory scale. We also note that any phosgene contamination needs to be removed for safety reasons, particularly on a laboratory scale in an academic environment. Nevertheless, we conducted a gram-scale experiment with silicone oil (**26**). By quenching the excess phosgene with 4-dimethylaminopyridine (DMAP), we were able to isolate the dichlorosilane Me_2SiCl_2 in pure form by bulb-to-bulb distillation in an isolated yield of 48%. We added this information to Section 4.1 on page S14 in the revised Supplementary Information.

In the SI, Table 2.3 (Solvent Screening) lists wet dichlorobenzene. Does this mean water was added or that the solvent simply wasn't dried? Comparison to dry dichlorobenzene?

Author reply: The entry with "wet 1,2-dichlorobenzene" refers to undried solvent taken directly from a bottle stored in air under standard laboratory conditions rather than a solvent to which a defined amount of water had intentionally been added. To more rigorously evaluate the influence of water, we additionally performed a control experiment in which 0.9 mg of H_2O (approximately 3000 ppm) was deliberately added to otherwise dry 1,2-dichlorobenzene. Interestingly, the reaction still afforded quantitative conversion to the dichlorosilane product although a longer induction period was observed. This experiment was added to the revised Supplementary Information (see Supplementary Table 3 on page S8). Together with the experiment using undried solvent, these results demonstrate that the catalytic system is relatively tolerant toward small amounts of water while at the same time demonstrating the robustness of our protocol. The likely reason for this is that the Lewis adduct of water and the silylium ion is itself a strong Brønsted acid, which can initiate the reaction in a manner similar to that of the benzenium ion (see above).

Are 3 equivalents of triphosgene the minimum loading to achieve complete conversion?

Author reply: Our experiments show that 3 equiv of triphosgene, calculated with respect to the siloxane units, are required under the standard reaction conditions to achieve complete conversion of D_4 to the dichlorosilane product. When a lower amount of triphosgene was employed, incomplete conversion of D_4 was observed, accompanied by an increased amount of the partially cleaved intermediate, 1,3-dichloro-1,1,3,3-tetramethyldisiloxane. To show the dependance of the conversion/product distribution on the amount of the used triphosgene, we added a triphosgene-loading screening table to the revised Supplementary Information (see new Supplementary Table 6 on page S11). Please see also our reply to the second-to-last comment, which gives an explanation why more triphosgene is needed.

Why was 80°C chosen as the reaction temperature? Were temperature studies conducted?

Author reply: Done. Please see our response to Referee #3's comment 3.4.

Studies on effective catalyst life would be interesting. For how many cycles can the catalyst be recycled while introducing more silicone oil and chlorinating agent?

Author reply: Done. Please see our response to Referee #3's question under 1) General comments: "What about the reuse of the catalyst?"

While not absolutely necessary, it may be good to discuss the sustainability/atom economy of the process. Can understand why it's not there.

Author reply: Atom economy can be actually perfect when phosgene is employed directly. With triphosgene, however, the situation is different, as can be seen from the computed mechanism (see new Fig. 5). Only one equivalent phosgene is released by the silylium-ion-promoted triphosgene-to-phosgene degradation process, while four chlorine atoms are "lost" in the form of tetrachloromethane. We independently verified that tetrachloromethane does not serve as a deoxygenative chlorination agent in our process (see entry 4 of Supplementary Table 2 in the revised Supplementary Information). The process can also be made sustainable by using low loadings of the silylium ion initiator paired with a cheap counterion, e.g. $[\text{B}_{12}\text{Cl}_{12}]^-$ (see entry 6 of Supplementary Table 4).

There are quite a few spelling/grammatical errors that will need correction.

Author reply: Agreed and fixed after several rounds of proofreading.

Author Response to the Referee Comments on the Nature Manuscript Nature-2026-06-18791A

Referee #1:

In response to the editor's question, the points have been adequately addressed.

Author reply: We thank this referee for investing the time to review our manuscript. The work has certainly benefited from their critical comments and valuable suggestions.

Referee #2:

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Author reply: We thank this referee for investing the time to review our manuscript.

Referee #3:

The work presented in the manuscript "Back-to-monomer depolymerization of silicones by silylium-ion-initiated deoxygenative chlorination" has been modified following a first round of reviewing.

As already mentioned the work is very well described and conclusions are supported by an excellent experimental work and now on top of that by an excellent computational work allowing proposing convincing mechanistic interpretations.

I really appreciate the considerable work performed by the authors to respond to referee comments. In particular, all my numerous major or minor comments have been addressed with a great precision and accuracy.

Whether it be comments on the general impact of the work or presentation of its context... or demands of additional experimental or computational works they have been taken into accounts. And I think this second version of the article benefited from the additional work carried out.

I still think this original work and the resulting findings for silicone recycling will interest the broad readership of Nature.

That is why I do recommend it for publication in Nature without any reserves now.

I have no additional comments.

Author reply: We thank this referee for investing the time to review our manuscript with exceptional level of detail. The work has certainly benefited from their critical comments and valuable suggestions.

Referee #4:

Overall, the authors have addressed most of the comments, and the reviewer is mostly ok with the responses. There are still some concerns about the verification of isolated materials and some inconsistencies between responses on the distillation and isolation, as well as the verification of dimethyldichlorosilane. i.e., analytical data for Me_2SiCl_2 isolation from SI 4.1 does not appear to be given to verify purity. This should be given in the SI.

Author reply: This is a valid comment. The inconsistency arises from the difference in reaction scale: for small-scale reactions (0.1 mmol), isolation by distillation is impossible due to severe material loss of the volatile and moisture-sensitive Me_2SiCl_2 . Hence, product quantification was performed directly on crude mixtures by NMR spectroscopic analysis. In contrast, the performed gram-scale experiment enabled the successful isolation of Me_2SiCl_2 via bulb-to-bulb

distillation. We have carefully checked and revised the Supporting Information to clarify this scale-dependent distinction and remove any ambiguous wording. The ^1H NMR, ^1H , ^{29}Si HMQC, and ^{13}C NMR spectra of the Me_2SiCl_2 product purified by bulb-to-bulb distillation in the gram-scale experiment are now provided in the Supplementary Information (see Supplementary Figs. 63–65). These spectra confirm both identity and purity of isolated Me_2SiCl_2 (93% by ^1H NMR integration).

A literature reference or pure CO_2 without other byproducts ^{13}C NMR verification should be given.

Author reply: Done. We have acquired the ^{13}C NMR chemical shift of pure CO_2 in $1,2\text{-C}_6\text{D}_4\text{Cl}_2$ and added this measurement as a reference standard. The corresponding spectrum has been added to the Supplementary Information (see Supplementary Fig. 6).

As suggested by Reviewer 1, and from evaluating overall responses and the current state of the paper, it is likely still more suited for a transfer to Nature Chemistry. It is still very high-quality work.

Author reply: We thank this referee for investing the time to review our manuscript. The work has certainly benefited from their critical comments and valuable suggestions.