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ARTICLE

Co₂(CO)₈ as an efficient catalyst for the synthesis of functionalized polymethylhydrosiloxane oils and unconventional cross-linked materials

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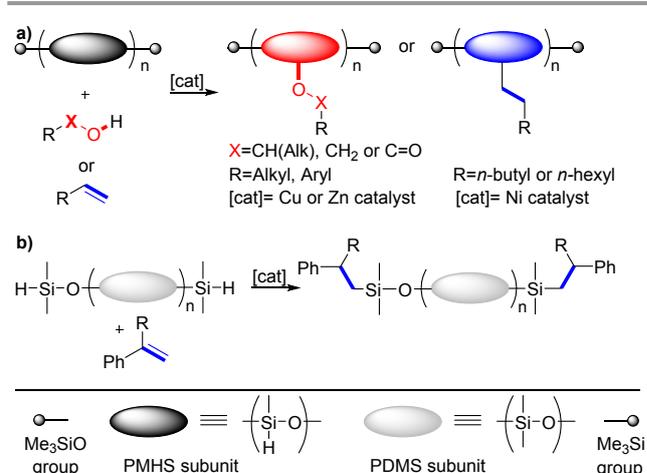
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We report here the use of Co₂(CO)₈ as a cheap and structurally simple alternative to precious metals for the functionalization of polymethylhydrosiloxane (PMHS) with terminal alkenes. This catalytic system at 0.1 mol% loading was found capable of hydrosilylating PMHS with one or two different alkenes in up to >99% efficiency under mild conditions. More importantly, we investigated the synthesis of cross-linked PMHS materials and found that both traditional dienes and unconventional tethers (such as esters and 5-hexen-2-one) led to fast and effective cross-linking of PMHS via hydrosilylation of C=C and C=O bonds, and further formation of Si-O-Si bridges between the PMHS chains. Additionally, we demonstrate here the potential of using renewable resources such as oleic acid derivatives as suitable cross-linkers to prepare bio-sourced cross-linked silicone materials.

Introduction

Polyorganosiloxanes, commonly known as silicones, are semi-inorganic polymers, which have found a wide use in many applications (for example elastomers, coatings, sealants etc.) due to their unique physical and chemical properties. To date, platinum-based complexes are the most widely used catalysts in siloxane hydrosilylation and cross-linking reactions involved in the preparation of silicone materials.^{1,2} Although Pt-catalysts are highly effective at very low ppm levels for the functionalization of polysiloxanes, these processes lead in the end to the large scale loss of valuable precious-metal based catalyst which cannot be recycled.³ Consequently, from an economical and environmental point of view, the use of platinum and other noble metal catalysts should be avoided in the modern-day synthesis of siloxane materials.⁴ Therefore, the development of environmentally benign catalytic systems should be on the forefront of silicone science. While currently, the dominance of Pt-based catalysts is still undisputed in the functionalization of silicone Si-H bonds, first row transition metal complexes have more and more contested their use. The applicability of the latter complexes in alkene hydrosilylation with small-size molecular silanes has been well covered by recent reviews,⁴⁻⁶ however the functionalization of long-chain polysiloxane oils by non-precious catalysts is still under-explored.² To the best of our knowledge, the current types of

functionalization of polysiloxane Si-H bonds are limited to the formation of new Si-O-R (R=alkyl, aryl, acyl) and Si-R (R=alkyl) bonds (Scheme 1) in polysiloxane oils. For example, Cu⁷ and Zn⁸ based catalysts, and tris(pentafluorophenyl)borane (B(C₆F₅)₃)⁹ are known to catalyze the synthesis of functionalized PMHS (polymethylhydrosiloxane) via dehydrogenative coupling using alcohols or carboxylic acids (Scheme 1a). However, when the formation of new Si-C bond is preferred, there is only one example in the literature where a non-precious metal Ni complex was successfully used to functionalize PMHS with 1-hexene or 1-octene (Scheme 1a).¹⁰ Additionally, there are examples from the Nagashima's group where Co and Fe isocyanide complexes have found use in functionalization of terminal SiMe₂-H groups of polydimethylsiloxanes (PDMS) with α -methylstyrene and styrene with yields up to 99% (Scheme 1b).¹¹



Scheme 1. Current examples of functionalization of polysiloxane oils using non-precious metal catalysts.

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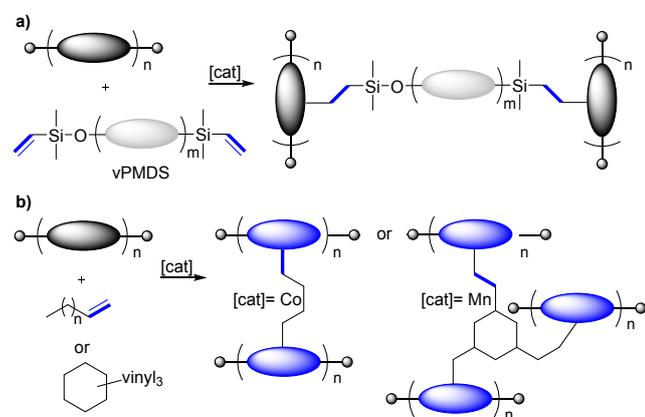
Electronic Supplementary Information (ESI) available: Detailed experimental procedures for preparation of the functionalized siloxane materials, NMR and DRIFT spectra. See DOI: 10.1039/x0xx00000x

The current number of examples describing the cross-linking of PMHS (or its ethyl analogues) with non-precious metal catalysts are also limited, as most of them involve the hydrosilylation of polydimethylsiloxanes containing terminal or internal vinyl groups (vPDMS) (Scheme 2a).^{11–16} It should be noted that only two examples in the literature report the use of non-precious metal catalysts for the cross-linking of PMHS with short alkenes (Scheme 2b). The first one employs a Co catalyst to cross-link PMHS chains with short alkenes (1-octene and dodecene) *via* dehydrogenative hydrosilylation followed by hydrosilylation.¹⁷ The second example uses a Mn(II) catalyst to hydrosilylate 1,2,4-trivinyloxyhexane with PMHS to form cross-linked polymers.¹⁴

In search for an efficient earth-abundant transition metal catalyst for the hydrosilylation process, our group previously described the preparation and use of simple cobalt nanoparticles (NP) as effective catalysts for the synthesis of silicone oils *via* alkene hydrosilylation with MD^{VI}M (1,1,1,3,5,5,5-heptamethyltrisiloxane).¹⁸ These cobalt NPs were derived from Co₂(CO)₈, which has previously been used in alkene hydrosilylation with monomeric silanes,⁴ but examples with polymeric silanes are scarce as only one example where cross-linking of polymethylphenylvinylsiloxane with polymethylphenylhydrosiloxane is described using Co₂(CO)₈.¹⁹ We therefore investigate here the use of Co₂(CO)₈ for the synthesis of functionalized PMHS oils and cross-linked materials in attempt to step closer to the goal of using active non-precious metal complexes in the silicone industry.

Results and discussion

Throughout this study, all the reactions were carried out with Co₂(CO)₈ (0.1 mol% compared to Si-H units in PMHS) at 60 °C unless stated otherwise and all the products depicted in various Tables and Schemes represent simplified structures of (poly)functionalized siloxane materials which do not correspond to block-polymers. The absence of trace amount of Pt in Co₂(CO)₈ was verified by ICP-MS (inductively coupled plasma mass-spectrometry) analysis and the Pt content (if any) was below the 0.05 ppm detection limit of the apparatus.



Scheme 2. Current examples of cross-linking of polysiloxane oils using non-precious metal catalysts.

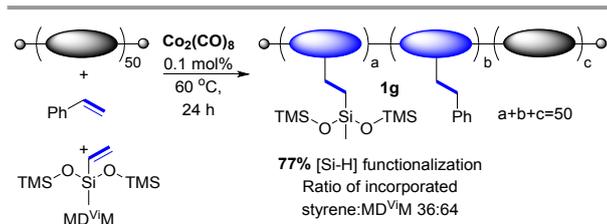
Additionally, the yields expressed throughout this work correspond to the ¹H NMR yield of Si-H bonds functionalization. In Table 1, we represent the scope of alkenes tested for PMHS functionalization under mild conditions (60 °C for 24 h) and with a molar alkene C=C/Si-H ratio of 1:1. Using 1-octene in the functionalization process gave rise to 57% of alkylated PMHS **1a** (Table 1, entry 1) and additionally to considerable amount (43%) of internal octene isomers. Switching from this linear substrate to a cyclic analogue, vinylcyclohexane (entry 2), led to an improved yield of 77% of **1b** alongside with the formation of internal isomers (23%). Notably, non-isomerizable *tert*-butyl ethylene (TBE, entry 3) was incorporated into the PMHS chain in **1c** with 79% efficiency, while styrene demonstrated quantitative hydrosilylation of Si-H bonds in **1d** (entry 4). Using the more sterically hindered heptamethyl-3-vinyltrisiloxane (MD^{VI}M) (entry 5) gave rise to 65% of functionalized product **1e**. It should be noted that all the products in entries 1-5 were formed exclusively as *anti*-Markovnikov hydrosilylated products. Additionally, we used 1,3-cyclohexadiene (entry 6) to introduce a C=C bond to the hydrosilylated product, which could offer further reactivity for the functionalized PMHS oil. The reaction between 1,3-cyclohexadiene and PMHS led to 1,2- and 1,4-addition products in approximate ratio of 6:1 (based on ²⁹Si NMR - see ESI) in **1f**, knowing that both isomers are known to occur for dienes in presence of Co₂(CO)₈.²⁰ In all examples in Table 1, ²⁹Si chemical shifts in the range of -19 to -27 ppm confirm the formation of new Si-C bonds *via* C=C bond hydrosilylation (see ESI).

To further demonstrate the versatility of this catalytic system, we performed the double functionalization of PMHS with two different alkenes in a one-pot reaction. Treatment of PMHS (1.0 eq) with styrene (0.6 eq) and MD^{VI}M (0.6 eq) in the

Table 1. Scope of alkenes for the production of functionalized silicone oils from PMHS using Co₂(CO)₈.^[a]

#	Label	Alkene	Isom. ^[b]	Yield ^[c]	State of the art ^[d]
1	1a	1-octene	43	57	>99 ¹⁰
2	1b	Vinylcyclohexane	23	77	n.r
3	1c	TBE	-	79	n.r
4	1d	Styrene	-	>99	n.r
5	1e	MD ^{VI} M	-	65	n.r
6	1f	1,3-cyclohexadiene	-	>99	n.r

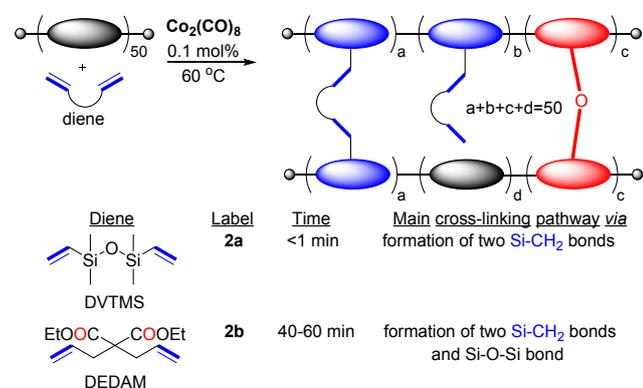
[a] Reaction conditions: alkene (0.94 mmol, 1.0 eq), PMHS (0.94 mmol, 1.0 eq of Si-H functionalities), Co₂(CO)₈ (0.1 mol% compared to Si-H functionalities) in toluene and mesitylene (as NMR standard). Conversions of starting materials and formation of product are based on ¹H NMR. [b] Isomerization (%) corresponds to the sum of formed isomers. [c] The yield refers to the % of functionalized [Si-H] bonds in the functionalized PMHS. [d] State of the art example corresponds to the highest functionalization yield of corresponding hydrosilylation product catalyzed by a non-precious metal system reported in literature. n.r – not reported. [e] 1.2 eq. of styrene was used due to formation of small amount of polystyrene at the beginning of the reaction.



Scheme 3. One-pot double functionalization of PMHS using styrene and MD^{VI}IM. Reaction conditions: styrene (0.56 mmol, 0.6 eq), MD^{VI}IM (0.56 mmol, 0.6 eq), PMHS (0.94 mmol, 1.0 eq [Si-H] functionalities), Co₂(CO)₈ (0.1 mol% compared to Si-H functionalities) in toluene. Formation of product is based on ¹H NMR.

presence of Co₂(CO)₈ successfully led to 77% of Si-H functionalization in **1g** (Scheme 3). Since PMHS reaction with styrene led to faster styrene incorporation when using 1.2 eq of styrene, compared to that of MD^{VI}IM when used separately (Table 1 entry 4 vs entry 5), we therefore expected a higher level of styrene incorporation into the final product. Surprisingly, the experimental result demonstrates that only 28% of Si-H bonds were functionalized with styrene and 49% with MD^{VI}IM in **1g**.⁵ This last result is a rare example of a one-pot double functionalization of a polymethylhydrosiloxane derivative and highlights the versatility and the potential of using simple non-precious metal catalysts, such as Co₂(CO)₈, in this process. Considering the lack of examples in the literature, the results in Table 1 and in Scheme 3 represent considerable expansion of the alkene scope in the functionalization of PMHS using a non-precious metal catalyst with up to >99% efficiency.

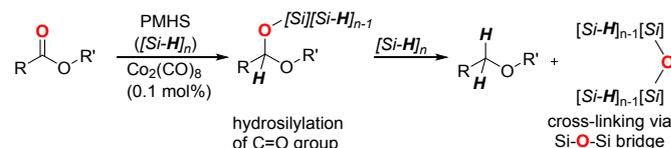
Inspired by these results, we turned our interest towards the cross-linking of polymethylhydrosiloxanes with traditional short-chain tethers containing two terminal C=C bonds. For example, the reactions between PMHS (1.0 eq of Si-H) and 0.5 eq. of the dienes (i.e. 1.0 eq of C=C), namely divinyltetramethyldisiloxane (DVTMS) or diethyl diallylmalonate (DEDAM), led to the expected cross-linking of PMHS chains in products **2a** and **2b** respectively (Scheme 4). The gelation process for both substrates occurred *via* double alkenyl group hydrosilylation, but not quantitatively as evidenced by the presence of unreacted olefin ¹H and ¹³C signals in solid state NMR spectra (See ESI). Somewhat surprisingly, the ²⁹Si CPMAS spectrum of the reaction product after DEDAM incorporation exhibits one low intensity resonance at -66 ppm, which



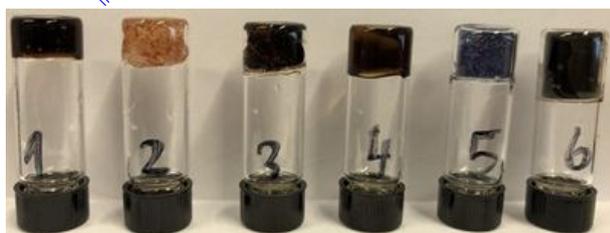
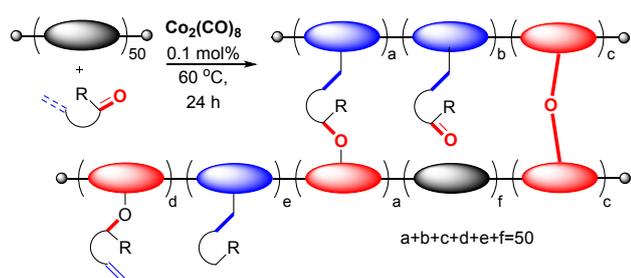
Scheme 4. Cross-linking of PMHS with conventional C=C bond containing tethers. Reaction conditions: substrate (1.17 mmol, 0.5 eq), PMHS (2.34 mmol, 1.0 eq of Si-H functionalities), Co₂(CO)₈ (0.1 mol% compared to Si-H functionalities) in toluene. The samples were further post-cured at 60 °C till the end of 24 h of reaction time.

corresponds to a newly formed Si-O-Si bridge (for comparison of various ²⁹Si chemical shifts in functionalized polysiloxanes see ESI pages S7-S8) in addition to the expected resonance at -21 ppm (corresponding to MeSi(OSi≡)(alkyl) subunit). Such Si-O-Si bonds could be generated through a similar mechanism than that proposed in the Ir-catalyzed deoxygenation and dehydration of carboxamides.²¹ Here, we thus hypothesize that, in the presence of Co₂(CO)₈ and PMHS the unsaturated carbonyl substrates can undergo similar deoxygenation process leading to the Si-O-Si bridges as depicted in Scheme 5. Thus, this Si-O-Si bridge could arise from the hydrosilylation of the carbonyl group of the ester RCOOR', yielding a [MeSi(OSi≡)₂(O-C(R)(OR')H)] subunit, which, after a subsequent reduction step, leads to RCH₂OR' and a newly formed Si-O-Si bridge. While carbonyl group hydrosilylation has been employed in the cross-linking of ethylene-vinyl acetate copolymer with hydride-terminated PDMS,²¹ the cross-linking of PMHS arising from deoxygenative reduction of C=O group in ester to form Si-O-Si bridge is, to the best of our knowledge, an unprecedented reactivity in the field of cross-linked siloxane materials. Previously, Nagashima's work on precious metal catalyzed amide reduction with PMHS has led to corresponding amines and insoluble cross-linked PMHS gel as a side-product.²²⁻²⁵ For comparison, the Darcel's group has reported the use of Co₂(CO)₈ and PMHS as an effective combination to deoxygenatively reduce amides to corresponding amines without mentioning the formation of gelous materials.²⁶ Very recently, B(C₆F₅)₃ catalyzed cross-linking of PMHS chains through hydrosilylation of carbonyl groups in α-diketones was demonstrated by Hawker and co-workers.²⁷ In this latter example, no Si-O-Si bridge formation from C=O group was reported.

With this additional and unconventional cross-linking capability in mind, we decided to investigate the use of unsaturated esters as promising tethers for the synthesis of functionalized polysiloxane materials. Entries 1 and 2 in Table 2 demonstrate how simple unsaturated acetates can be used as cross-linkers *via* the double reactivity of the C=C and C=O functionalities at 60 °C for **3a** and **3b**. Additionally, entry 3 indicates that the cross-linking procedure is not limited only to alkenyl acetates but can also be extended to alkyl alkenoates as demonstrated in **3c**. Furthermore, comparing the curing time for entries 1-3, we see that faster reaction occurred for substrates that have the two hydrosilylatable functionalities further apart from each other. For comparison, when the reaction between PMHS and vinyl terminated esters is catalyzed by Pt-based systems, only the vinyl moiety is hydrosilylated without reactivity on the carbonyl group.²⁸ Moving towards more industrially relevant esters, we tested methyl methacrylate (MMA) and allyl methacrylate (AMA) in the cross-



Scheme 5. Plausible mechanism of the formation of Si-O-Si bridges between PMHS chains in presence of carbonyl groups.

Table 2. Cross-linking of PMHS with unconventional C=C and C=O bond containing tethers.^[a]

#	Label	Alkene	Gelation time	Main cross-linking pathway
1	3a	Vinyl acetate	18 min	Si-CH ₂ and Si-O-C
2	3b	Allyl acetate	<2 min	Si-CH ₂ and Si-O-C
3	3c	Ethyl-4-pentenoate	<1 min	Si-CH ₂ and Si-O-C
4	3d	Methyl methacrylate	30 min	Si-CH ₂ , Si-O-C and Si-O-Si
5	3e	Allyl methacrylate	<6 min	two Si-CH ₂
6	3f	Hex-5-en-2-one	82 min	Si-CH ₂ , Si-O-C and Si-O-Si

[a] Same reaction conditions as in Scheme 3, but on two times larger scale. The numbers on the vials correspond to the entry numbers in Table 2. [b] All the gels (except 3c) contain presence of Si-O-Si bridge signals in their ²⁹Si NMR spectrum.

linking reaction. The former is known to polymerize in the presence of Co(OAc)₂ and to react with PMHS to give semi-interpenetrating networks.²⁹ However, in our case the reaction between PMHS and MMA (entry 4) led to the cross-linked product **3d** via the hydrosilylation of both the C=C bond and the ester functionalities (evidenced from solid-state ¹³C and ²⁹Si spectra, see ESI). On a further note, it is known in literature that when Pt-based catalysts are used instead, the reaction between PMHS and other alkyl acrylates leads to the expected alkene hydrosilylation product without the ester group reduction.³⁰ When AMA (entry 5), which contains an additional allyl group, is used in the presence of Co₂(CO)₈ and PMHS, the reduction of the ester group was suppressed and cross-linking in **3e** occurred via hydrosilylation of the two C=C bonds only (evidenced from solid state ¹³C and ²⁹Si spectra, see ESI). For comparison, allyl (meth)acrylates have previously been incorporated into PMHS chains through the exclusive hydrosilylation of the allyl group, without evidence of cross-linking through the C=C bond in the alkenoate part of the molecule nor via ester group reduction.^{31,32} This result from entry 5 suggests that, in the presence of multiple C=C and C=O bonds, the cross-linking is faster via the hydrosilylation of two C=C bonds. While

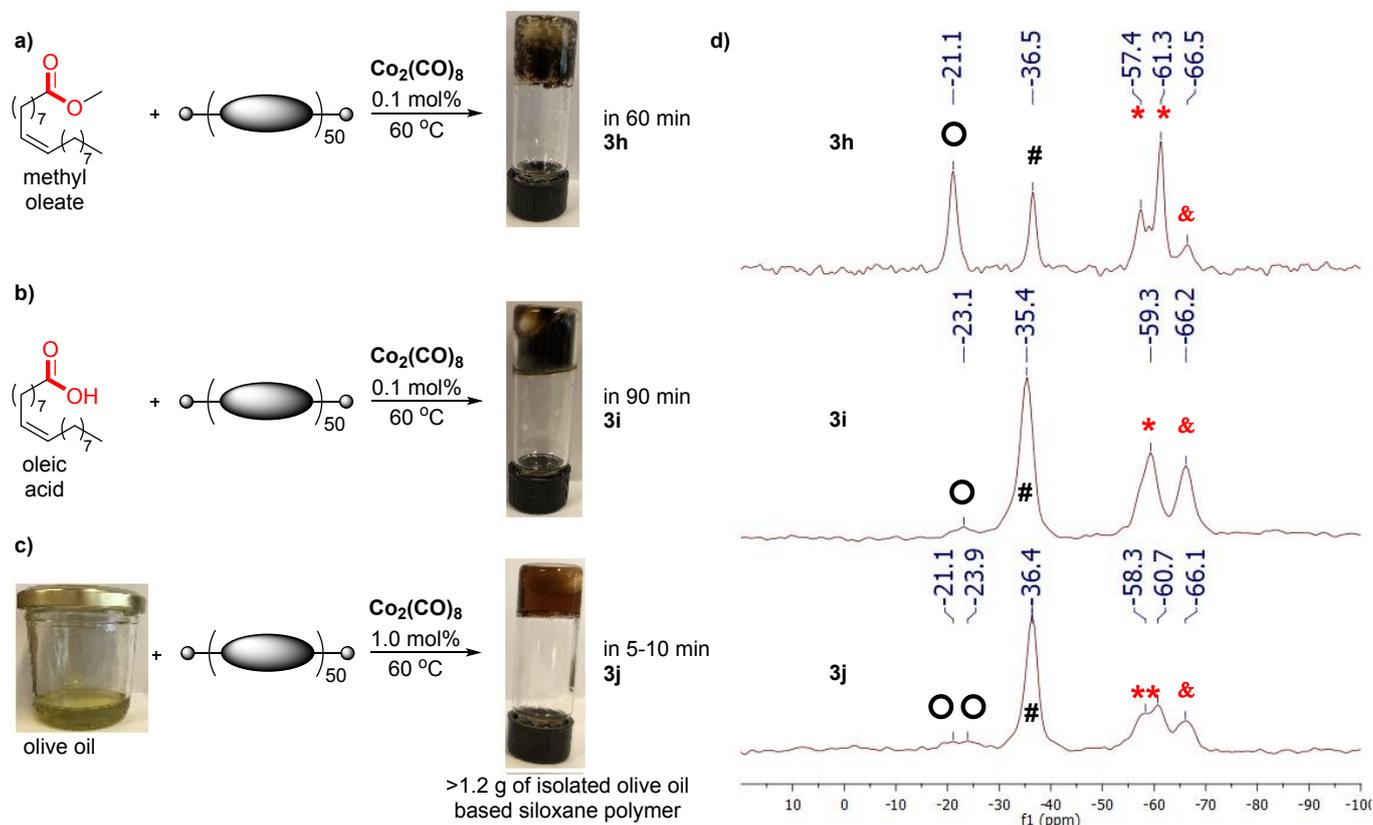
unsaturated esters (entries 1-5) have demonstrated excellent aptitude as unconventional tethers, the question about the reactivity of the carbonyl group remains to be explored further. When the same reaction was carried out with hex-5-ene-2-one (entry 6), which is a less reactive carbonyl compound, the gelation of **3f** took <90 min to cross-link PMHS chains via C=C and C=O bond hydrosilylation, and via Si-O-Si bond formation.

On a general note, while all the examples in Table 2 show the formation of cross-linked products in <90 min, this did not result in complete hydrosilylation of all active Si-H groups, as evidenced by DRIFT, ¹H and ²⁹Si solid-state NMR spectra (see ESI). Additionally, the scheme depicting the cross-linked products in Table 2 illustrates that the formation of each new Si-O-Si bridge between the PMHS chains was accompanied by the formation of reduced sidechain after full reduction of the carbonyl group in the incorporated substrate. It should be noted that all the obtained gels were colored (Table 2) and in comparison to known colorless gels formed via non-precious metal catalyzed cross-linking^{11,16,31}, our gels did not undergo discoloration under air in 24 h. However, while the gels were colored, they yielded slightly colored or white solids after drying at 60 °C overnight.⁵⁵ Interestingly, in the case of AMA (entry 5) the product was intense blue hard glassy solid, while all the other products in Table 2 were soft gels that could easily be punctured and sliced. In order to illustrate the potential of Co₂CO₈ to catalyze the formation of gels, the reaction was carried out with DEDAM and MMA using a lower Co loading of 0.01 mol%. A gel was obtained within 2 h when MMA was used but no gel could be formed with DEDAM even after one day of reaction. These results show that the Co loading could be decreased to prepare a gel on the case-by-case basis depending on the olefinic reagent.

Examples in Table 2 have demonstrated the possibility to use various (un)saturated ester and carbonyl group containing substrates as effective tethers in polymethylhydrosiloxane cross-linking. Considering the end-product's lifetime and its eventual release to the environment, we feel that the environmental impact can be minimized³³ with the use of bio-sourced tethers, such as fatty acid derivatives. Based on the analogy of the esters used in Table 2, we believe that Si-O-C linkage formed from fatty acid derivatives would offer an ideal target for facile degradation pathway under acid- or base-catalyzed hydrolysis.^{34,35}

In Scheme 6a, we demonstrated that the reaction between methyl oleate and PMHS led to the gel **3h** within 60 min. Similar gel **3i** was formed in 90 min with the use of oleic acid (Scheme 6b). As the last example for PMHS cross-linking, we tested olive oil, which contains mostly oleic acid based triglycerides³⁶ and therefore offers high ester group density. As seen on Scheme 6c, 1 mol% of Co₂(CO)₈ catalyzed the cross-linking reaction in <10 min to yield **3j**. Excerpts of ²⁹Si NMR spectra of all three products (Scheme 6d) confirm the presence of silyl acetal groups (-57 to -62 ppm) and the formation of Si-O-Si bridges (ca. -66 ppm). However, the similarities between gels **3h-3j** end here, as the extent of C=C and C=O group hydrosilylative reduction varies between those samples. For example, methyl oleate gel **3h** has undergone full reduction of ester groups to

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Scheme 6. Functionalization and cross-linking of PMHS with renewable fatty acid derivatives. Same reaction conditions as in Scheme 3. Reaction scale for: a) Methyl oleate (1.17 mmol), PMHS (2.34 mmol [Si-H]), b) Oleic acid (technical grade 90%) (1.17 mmol), PMHS ([Si-H] 2.34 mmol), c) olive oil (1143 μL), PMHS ([Si-H] 7.03 mmol). d) ^{29}Si SSNMR excerpts (20 to -100 ppm) of 3h-3j. Si-C bond (O), Si-H bond (#), Si-O-R bond (*) and Si-O-Si bridge (&). in cross-linked material.

silyl acetal groups (99.3 ppm in ^{13}C NMR) and the complete hydrosilylation of the C=C bonds (evidenced by the lack of C=C signals in ^{13}C and formation of new Si-C bonds in ^{29}Si NMR). The C=C bond hydrosilylation of oleic acid derivatives by $\text{Co}_2(\text{CO})_8$ is somewhat unexpected, as we demonstrated recently that while cobalt NPs in solution can tandem isomerize-hydrosilylate internal C=C bonds of methyl oleate to the terminal position with MD'M (monomeric analogue of PMHS), such reactivity was not seen with $\text{Co}_2(\text{CO})_8$.¹⁸ On the other hand, the products from PMHS cross-linking using oleic acid and olive oil, 3i and 3j, have mainly reacted via the carboxylic group (formation of Si-O-C and Si-O-Si bonds in ^{29}Si NMR, Scheme 6d), while leaving the C=C bond mostly untouched (low intensity of the Si-C peak between -21 to -24 ppm in ^{29}Si NMR, Scheme 6d). We also carried out test reactions with oleic acid derivatives and MD'M under the same reaction conditions and, in all cases, no C=C, C=O or COOH hydrosilylation was observed. The different behavior of oleic acid and olive oil from that of the methyl oleate may be due to

the reactive nature of COOH group in oleic acid and the close proximity of three C=O groups in the olive oil, which leads to preferential C=O group reduction than to new Si-C bond formation after C=C bond hydrosilylation. Additionally, we would like to emphasize that the reaction with olive oil (Scheme 6c) was successfully carried out on a gram-scale, demonstrating the potential of using $\text{Co}_2(\text{CO})_8$ and possibly other non-precious metal catalysts for the synthesis of biosourced cross-linked siloxanes materials.

Conclusions

In this study, we have demonstrated the use of simple $\text{Co}_2(\text{CO})_8$ as an excellent non-noble metal catalyst for the synthesis of mono- and bi-functionalized PMHS oils in a one-pot reaction, with catalyst loadings as low as 0.1 mol%. Importantly, this catalytic system offered a unique method for the cross-linking of PMHS with traditional dienes and unconventional organic

tethers, such as (un)saturated esters. These results demonstrate that a non-precious metal catalyst can be advantageously used for the synthesis of polyfunctional siloxane materials. Finally, this study provides a germane example where a well-known but neglected non-precious metal catalyst not only provides a more sustainable alternative to currently used noble-metals but can be used with profit to promote original chemistry ultimately leading to new products.

Author Contributions

M. J. and V. D. carried out the experiments. The manuscript was written through the contributions of M. J., C. C. and C. T. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ During January 2019-January 2021 platinum price has varied 597-1079 USD per troy ounce, <https://www.nasdaq.com/market-activity/commodities/pl%3Anmx>.

§ At the beginning of the reaction, formation of polystyrene was observed. This parasitic reaction counts to some extent why we observed lower styrene incorporation than expected but does not explain the overall result.

§§ Such discoloration process is reversible when the dry gels are wetted with toluene. This observation suggests that the coloration is not related to the structure of the gels but to Co catalyst that is embedded in the gel framework.

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