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Martin Jakoobi, Anthony Vivien, Clément Camp, Chloé Thieuleux. Co<sub>2</sub>(CO)<sub>8</sub> and unsaturated epoxides as unexpected partners in generating functionalized siloxane oils and cross-linked materials. *Catalysis Science & Technology*, 2021, 11 (14), pp.4714-4718. 10.1039/D1CY00920F . hal-03357171

**HAL Id: hal-03357171**

**<https://hal.science/hal-03357171>**

Submitted on 29 Sep 2021

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## COMMUNICATION

## Co<sub>2</sub>(CO)<sub>8</sub> and unsaturated epoxides as unexpected partners in generating functionalized siloxane oils and cross-linked materials

Received 00th January 20xx,  
Accepted 00th January 20xx

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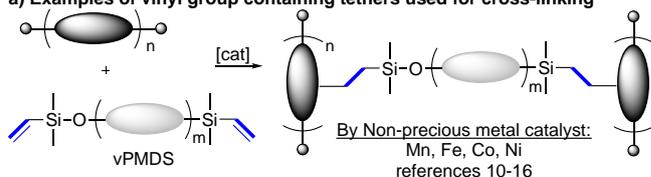
DOI: 10.1039/x0xx00000x

Herein, we describe the unexpected ring opening of the epoxide group of allyl glycidyl ether and 4-vinylcyclohexene oxide in polymethylhydrosiloxane (PMHS) hydrosilylation reaction using 0.1 mol% of Co<sub>2</sub>(CO)<sub>8</sub> as catalyst. This results in the cross-linking of PMHS via newly formed Si-C, Si-O-C and Si-O-Si bonds. Our studies also demonstrate the need for intramolecular proximity of Si-H bonds within the polysilane compound to trigger the cross-linking process.

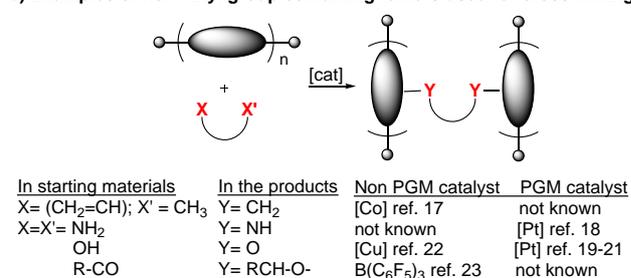
Polysiloxanes or just silicones in layman's terms, are semi-inorganic polymers composed of alternating silicon-oxygen backbone. Since their first commercial appearance in the 1940s, these materials have found their way to our everyday lives as lubricants, electrical insulators, sealants, cosmetic additives to say the least.<sup>1,2</sup> Their increasing use can be exemplified by the fact that, in 2016, >2 million metric tons of silicone based materials were produced to satisfy the ubiquitous needs of our society, while the current projections estimate the global market to increase to 3 million metric tons by 2022.<sup>3</sup> Currently, platinum group metal (PGM) complexes and more specifically Pt-based complexes are the most widely used catalysts in alkene hydrosilylation for the preparation of polymeric siloxane fluids and cross-linked materials.<sup>2,4</sup> While ppm levels of these PGM catalysts are used for the process, their recyclability is viable only in the production of simple organofunctional silanes whereas, in siloxane curing process, the catalyst is lost in the final cross-linked product.<sup>5</sup> From an industrial point of view, the use of cheap, environmentally benign and active first-row metal catalyst for the synthesis of polysiloxane products would be highly beneficial. While the advances made in the first-row transition metal catalyzed alkene hydrosilylation reaction with small-size molecular silanes have highlighted the applicability of such catalysts in

otherwise Pt-dominated domain,<sup>6-9</sup> the same statement cannot be made for reactions involving polysiloxane cross-linking with alkenes. At this stage, the use of small diolefinic compounds as tethers for polymethylhydrosiloxane (PMHS) cross-linking with PGM catalysts has been well established and covered in literature.<sup>2,4,5</sup> Currently, there are only few examples depicting the use of non-precious metals, such as Mn,<sup>10</sup> Fe,<sup>11,12</sup> Co<sup>13-15</sup> and Ni<sup>16</sup> for the cross-linking of PMHS with polymeric diolefinic derivatives, such as polydimethylsiloxanes containing terminal or internal vinyl groups (vPDMS) (Scheme 1a). When linkers other than standard diolefinic compounds are considered for PMHS cross-linking, the number of available examples for first-row metals can be counted on one hand (Scheme 1b). An interesting alternative to diolefins was published by Chirik and coworkers who demonstrated the possibility of using a simple terminal alkene

### a) Examples of vinyl group containing tethers used for cross-linking



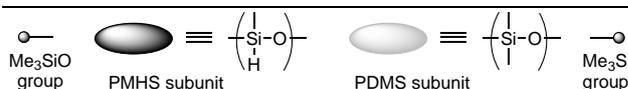
### b) Examples of non-vinyl group containing tethers used for cross-linking



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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

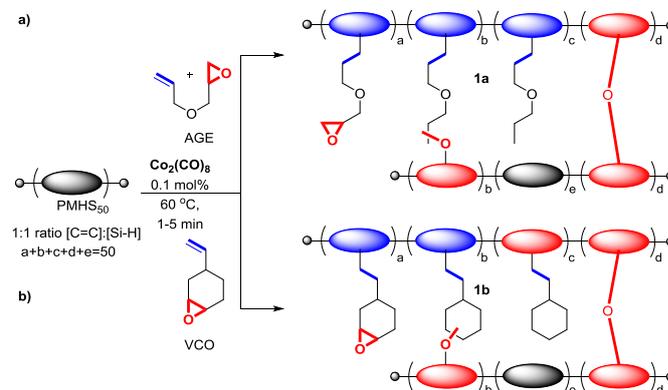


**Scheme 1.** Current scope of tethers used for non-precious metal catalyzed silicone oil cross-linking.

as a cross-linker in Fe-catalyzed dehydrogenative silylation, which was then followed by isomerization and further hydrosilylation at the terminal position to form cross-linked PMHS *via* two Si-C bonds.<sup>17</sup> Besides olefins, the use of diaminoalkanes as cross-linkers is known for Pt-catalysts<sup>18</sup> but, to this date, no precedent was published with abundant metal based catalysts. While the cross-linking of PMHS through the formation of hydrolysable Si-O-C bonds offers a wider selection of substrates to start from, this does not translate into a large number of available examples. Currently, diols and hydroxyacids have been used in the PMHS cross-linking *via* double OH group dehydrogenative silylation using Pt-catalysts,<sup>19-21</sup> while for non-PGM catalysts there is only one example based on a Cu-catalyst.<sup>22</sup> An interesting alternative to form new Si-O-C bonds between PMHS chains was published in 2019 by the Hawker's group, who demonstrated the potential of using  $\alpha$ -diketones as suitable cross-linkers in a tris(pentafluorophenyl)borane ( $B(C_6F_5)_3$ ) catalyzed reaction.<sup>23</sup> Very recently, we also showed that  $Co_2(CO)_8$  was capable of forming new Si-C, Si-O-C and Si-O-Si bonds between PMHS chains using unsaturated carbonyl compounds as unconventional tethers.<sup>24</sup>

Building on the newly discovered reactivity of  $Co_2(CO)_8$ , we report here the use of unsaturated epoxides as effective tethers in PMHS cross-linking and the necessity of block Si-H bonds in the polyhydrosiloxane for this process. Our initial attempts using simple and commercially available  $Co_2(CO)_8$  at 0.1 mol% loading demonstrated that the reaction between industrially relevant allyl glycidyl ether (AGE) and PMHS (internal Si-H content  $\sim 45.5$  wt%) did not lead to the expected hydrosilylation product as obtained with Pt catalysts,<sup>25-27</sup> but instead to a gel **1a** in <5 min both at room temperature (Scheme 2a) and at 60 °C (See ESI, Table S3). According to solid-state  $^{13}C$  NMR spectra (see Figure S1 and S2 in ESI for details), C=C bond hydrosilylation occurred as shown by the disappearance of olefinic signals. Additionally, the epoxide ring has undergone cleavage, which is exemplified by the disappearance of the epoxide ring  $^{13}C$  NMR signals and formation of new Si-O-R bonds leading to cross-linking (see solid-state  $^{29}Si$  spectrum in ESI). Subsequent reduction by another Si-H bond leads to the formation of dehydroxylated sidechains (RH) in the functionalized PMHS material and further cross-linking of the PMHS chains through the formation of Si-O-Si bridges (see Figure S3 in ESI). According to  $^{29}Si$  NMR (see ESI) new peaks at -58.1 and -66.0 ppm have appeared, indicating the presence of  $MeSi(OSi\equiv)_2(OR)$  ( $R=alkyl$ ) subunits and Si-O-Si bridges (for an overview of  $^{29}Si$  chemical shifts in polysiloxane materials see Scheme S1). These spectral features further cement the confirmation that the cross-linking of PMHS occurred *via* concomitant hydrosilylation of the C=C bond and epoxide ring opening, leading to the formation of new Si-C, Si-O-C and Si-O-Si bonds. To expand the scope of this newly found reactivity we tested 4-vinylcyclohexene oxide (VCO) under the same reaction conditions (Scheme 2b). Gel **1b** was formed in <1 min at 60 °C (Scheme 2) and within 10 min at

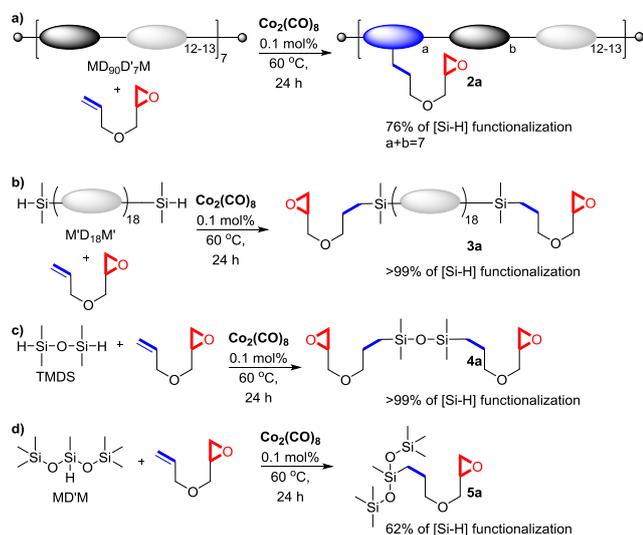
room temperature (See ESI, Table S3) *via* epoxide ring opening and further Si-O-Si bond formation evidenced by similar solid-state NMR features as in **1a**. While the concomitant hydrosilylation



**Scheme 2.** Cross-linking of PMHS with AGE and VCO. Reaction conditions: alkene (3.75 mmol, 1.0 eq), PMHS (3.75 mmol, 1.0 eq),  $Co_2(CO)_8$  (0.1 mol% compared to [Si-H]) in toluene. The samples were further post-cured at 60 °C until the end of 24 h of reaction time.

and epoxide ring-opening of AGE has never been reported with cobalt or any other transition-metal based complexes, it is worth mentioning that there is one example where the epoxide ring opening of AGE-functionalized PMHS (prepared by classical hydrosilylation of the AGE olefinic part using Pt-catalysts) and cross-linking was induced in presence of diamines.<sup>28</sup> While the cross-linking of PMHS chains by the Si-C and Si-O-C bonds derived from C=C bond hydrosilylation and epoxide ring opening is unknown for VCO, the formation of gelous material can occur in presence of VCO, PMHS and a Pt based complex (the Ashby's catalyst).<sup>29</sup> In that example, VCO has undergone C=C bond hydrosilylation, followed by epoxide ring opening and polymerization to give linear polyethers. The unexpected activation of the epoxide groups in unsaturated epoxides under our reaction conditions contrasts with the previously mentioned examples and could arise from the combination of the catalyst,  $Co_2(CO)_8$ , and the intramolecular proximity of Si-H bonds in PMHS. To investigate the necessity of block Si-H groups to trigger the activation of epoxide group towards PMHS cross-linking, we carried out hydrosilylation reactions of AGE with polymeric silanes featuring diluted Si-H bonds (i.e. isolated Si-H units within the polymethylhydrosiloxane compound). When MD<sub>90</sub>D'M, which is a polysiloxane containing Si-H subunits separated from each other by 12-13 PDMS subunits on average, is used instead of PMHS (Scheme 3a), only the C=C bond hydrosilylation product **2a** is observed with 76% of Si-H bonds functionalization. Similarly, when another more diluted version of PMHS, namely M'D<sub>18</sub>M', which contains only terminal Si-H bonds, was used (Scheme 3b), the reactivity of AGE is limited to C=C bond hydrosilylation in **3a** (>99% of respective Si-H bond functionalization). Additionally, to probe the necessity of polymeric Si-H bonds in the silane, we conducted experiments between AGE and TMDS (1,1,3,3-tetramethyldisiloxane, a molecular analogue of block [Si-H] bonds in PMHS), and AGE

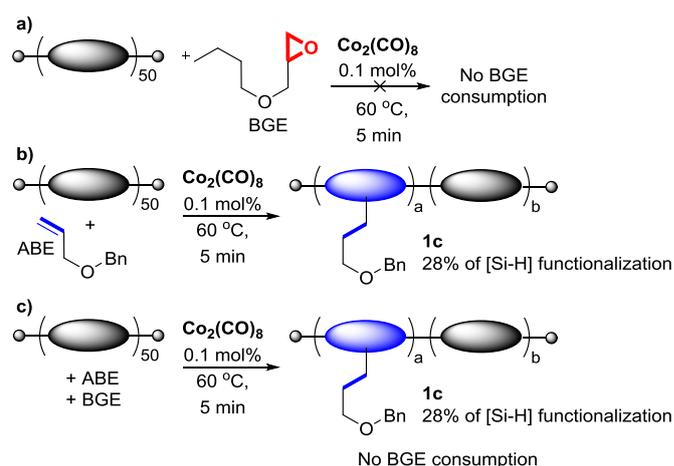
and MD<sup>V</sup>M (1,1,1,3,5,5,5-heptamethyltrisiloxane, a molecular analogue of PMHS) to hydrosilylate AGE (Scheme 3c and 3d). The reaction with TMDS (Scheme 3c) led to >99% functionalization of the Si-H bonds in **4a**, without any sign of epoxide ring opening. In presence of MD<sup>V</sup>M (Scheme 3d), the hydrosilylation of the C=C bond occurred also as the sole



**Scheme 3.** Determining the role of intramolecular [Si-H] concentration in (poly)silane towards the cross-linking of PMHS with C=O and epoxide groups.<sup>a</sup> Same reaction conditions as in Scheme 2. Reaction scale for a), b) and d): silane (0.55 mmol [Si-H], 1 equiv.), AGE (0.55 mmol 1 equiv.); for c) silane (0.55 mmol, 0.5 equiv.), AGE (1.10 mmol 1 equiv.).

reaction, leading to 62% Si-H bond functionalization in **5a**. These results with varying concentration of Si-H bonds in the silane confirm the need for block Si-H bonds in the polymethylhydrosiloxane reagent to activate epoxide groups towards PMHS cross-linking.

Furthermore, to verify the need of both the alkenyl and epoxide groups in one single substrate, we carried out the same reaction with butyl glycidyl ether (BGE) instead of AGE in presence of PMHS and  $\text{Co}_2(\text{CO})_8$  (Scheme 4a). After 5 min and even after 24 h, no reaction occurred, which lends support to the fact that alkene hydrosilylation as a first step is necessary to trigger the epoxide ring opening in AGE-functionalized PMHS and concomitant cross-linking of siloxane network. It should be noted here that the propensity of cyclic ethers to undergo ring-opening in presence of  $\text{Co}_2(\text{CO})_8$  and small hydrosilanes has been exploited in hydroformylation reaction.<sup>30</sup> Additionally,



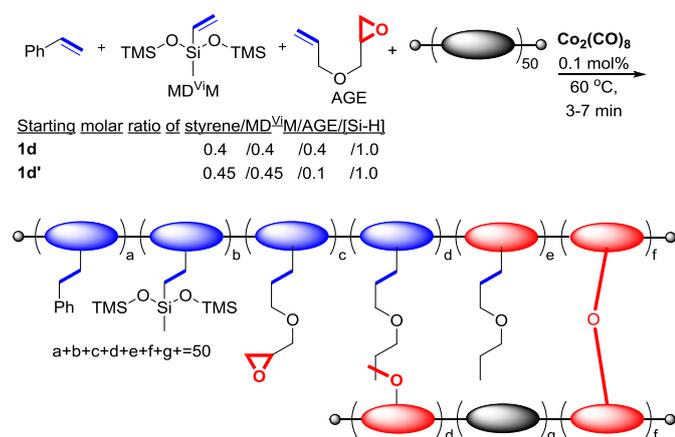
**Scheme 4.** Determining the role of allyl and epoxide groups in the PMHS cross-linking with AGE.<sup>a</sup> Same reaction conditions as in Scheme 2. Reaction scale for a)-b): PMHS (2.34 mmol [Si-H], 1 equiv.) and BGE or ABE (2.34 mol, 1 eq.). c) PMHS (2.34 mmol [Si-H], 1 equiv.), BGE (2.34 mol, 1 equiv.) and ABE (2.34 mol, 1 equiv.). Bn-benzyl.

cyclic ether, such as THF, was shown by Chalk to undergo ring-opening polymerization in presence of small hydrosilanes and  $\text{Co}_2(\text{CO})_8$ .<sup>31</sup> However, under our reaction conditions and in presence of polymeric silane, PMHS, no such reactivity was seen. Additional test reactions with allyl benzyl ether (ABE), a structural analogue of AGE, led in 5 minutes to partial functionalization (28%) of PMHS through alkene hydrosilylation, affording product **1c** (Scheme 4b), without any side reaction on the ether group. To provide further evidence for the presence of both the allyl and epoxide groups in one reagent is necessary, we conducted the reaction with equimolar amounts of ABE and BGE under our standard reaction conditions. According to Scheme 4c, partial Si-H bond functionalization occurred with ABE through classical alkene hydrosilylation leading to the same product **1c** without any epoxide ring opening of BGE.

To demonstrate the applicability of this newly found reactivity with unsaturated epoxides, we carried out a one-pot reaction in which the PMHS was co-functionalized with styrene and MD<sup>V</sup>M (1,1,1,3,5,5,5-Heptamethyl-3-vinyltrisiloxane), and cross-linked with AGE. Using a styrene/MD<sup>V</sup>M/AGE ratio of 0.4/0.4/0.4 compared to 1 equiv. of PMHS Si-H bonds, we obtained a cross-linked gel **1d** in 3 min (Scheme 5a). The incorporation of alkenyl substrates and cross-linking of PMHS via Si-O-C bonds and Si-O-Si bridges were confirmed by solid-state  $^{13}\text{C}$  NMR and  $^{29}\text{Si}$  NMR, respectively (see ESI for details). The use of AGE as an effective tether was further demonstrated by lowering the AGE quantity in the starting reaction mixture to only 0.1 equiv. in the presence of 0.45 equiv. of both styrene and MD<sup>V</sup>M. Under these reaction conditions, gel **1d'** was formed in 7 min at 60 °C with similar chemical shifts in  $^{13}\text{C}$  and  $^{29}\text{Si}$  solid-state NMR spectra (see Figures S4 and S5 for comparison). Finally, to further show the versatility of our catalytic system, we explored the possibility to generate gels starting from AGE and VCO with different Co loadings at room temperature and 60 °C (see ESI Table S2). The best result was obtained using AGE where a gelous material

was obtained within 23 min at 60 °C using only 0.02 mol% of Co catalyst. To further get insight of the Co active

Nesrine Oueslati and Christine Lucas for solid-state NMR measurements.



**Scheme 5.** The use of AGE as tether for cross-linking of in-situ formed polyfunctionalized PMHS. Reaction condition: For **1d**: Styrene, MD<sup>VI</sup>M and AGE (all 0.38 mmol, 0.4 eq), PMHS (0.94 mmol [Si-H], 1.0 equiv.), Co<sub>2</sub>(CO)<sub>8</sub> (0.1 mol%) in toluene. For **1d'**: Styrene and MD<sup>VI</sup>M (both 0.526 mmol, 0.45 equiv.), AGE (0.12 mmol, 0.10 equiv.), PMHS (1.17 mmol [Si-H], 1.0 equiv.), Co<sub>2</sub>(CO)<sub>8</sub> (0.1 mol%) in toluene. Ph-phenyl. TMS-trimethylsilyl.

species in such reaction, mercury tests were carried out with AGE and VCO (further details can be found in ESI Table S3). In each case, parallel reactions without and with Hg (400 eq.) were conducted. In all reactions, gels were obtained at the exact same reaction time (see ESI Table S3) suggesting that Co NPs are probably not formed during the catalytic reaction.

To conclude, we demonstrated here the use of industrially relevant allyl glycidyl ether and 4-vinylcyclohexene oxide as unconventional tethers in polysiloxane cross-linking procedure using Co<sub>2</sub>(CO)<sub>8</sub> as a non-noble metal catalyst. The cross-linking occurred *via* the hydrosilylation of the alkenyl group of unsaturated epoxide that triggered the concomitant epoxide ring opening, leading to the formation of Si-O-C bonds that underwent, in part, further reduction and led to the formation of Si-O-Si bridges along with alkyl pendant groups. Additional tests with PMHS analogues with diluted Si-H bonds provided evidence that the novel reactivity of the epoxide group was related to the presence of block Si-H groups in PMHS. Importantly, this catalytic system was successfully employed for the synthesis of trifunctionalized cross-linked materials and demonstrated further the potential of using non-precious metal complexes in silicone chemistry for unprecedented reactivity.

## Acknowledgements

This work was in part performed in the frame of the F.U.I. project "DISCOVER" (F.U.I. standing for "Fonds unique interministériel") and we gratefully thank the Region Rhône-Auvergne, the European Union through the "Fonds Européens de Développement Régional" (FEDER) and the Momentum CNRS 2017 program for financial support. We also thank

## Conflicts of interest

There are no conflicts to declare.

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