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Magali Puillet, James Delorme, Delphine Crozet, Matthieu Humbert, David Gajan, et al.. Ni(II) and Co(II) bis(acetylacetonato) complexes for alkene/vinylsilane silylation and silicone crosslinking. *Catalysis Science & Technology*, 2021, 11 (14), pp.4849-4856. 10.1039/D1CY00834J . hal-03403129

**HAL Id: hal-03403129**

**<https://hal.science/hal-03403129>**

Submitted on 26 Oct 2021

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## Ni(II) and Co(II) bis(acetylacetonato) complexes for alkene/vinylsilane silylation and silicone crosslinking

Magali Puillet,<sup>‡,a</sup> James Delorme,<sup>‡,a</sup> Delphine Crozet,<sup>a</sup> Matthieu Humbert,<sup>a</sup> David Gajan,<sup>b</sup> Magali Bousquié,<sup>c</sup> Delphine Blanc,<sup>c</sup> Jean Raynaud<sup>\*a</sup> and Vincent Monteil<sup>\*a</sup>

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Commercially available Ni(II) and Co(II) complexes - M(acac)<sub>2</sub> (acac=acetylacetonate) and M(tmhd)<sub>2</sub> (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionato) - exhibit catalytic activity for alkene/vinylsilane dehydrogenative silylation (DS) and hydrosilylation (HS) with tertiary silanes without the use of any external reducing agents. Using the model compounds divinyltetramethylsiloxane *a.k.a* dtms and vinylpentamethyldisiloxane *a.k.a* vpmds, different selectivities (HS, DS, undesired non-C-Si bond-forming reactions...) are observed whether Nickel or Cobalt catalysts are employed, with Ni being DS-selective and Co yielding both HS and DS products. All four complexes are efficient at thermally inducing silicone-oil crosslinking under non-inert atmosphere, and promote metal-dependent selectivity that is slightly different from model reactions, which HR-MAS NMR spectroscopy unveils. Additional observations as well as NMR studies of [Ni(tmhd)<sub>2</sub> + reagent] mixtures suggest an activation mechanism different from SiH-promoted full reduction of the high oxidation state complex.

### Introduction

Alkene hydrosilylation is a key reaction to manufacture silicone lubricants, adhesives, rubbers, and other high-value products.<sup>1-3</sup> Platinum compounds such as Speier's<sup>4</sup> and Karstedt's<sup>5</sup> complexes traditionally serve as efficient catalysts because of their high activity, stability and selectivity for alkene hydrosilylation. However, high and volatile prices of noble metals induce an important interest in tackling hydrosilylation using earth-abundant metal complexes. Nickel, cobalt and iron catalysts have already been reported and reviewed as relatively active and selective for alkene hydrosilylation (HS) and dehydrogenative silylation (DS).<sup>6-13</sup> Two types of systems have been reported in the literature: low-oxidation state and high-oxidation state complexes. Among low oxidation state catalysts, Chirik's bis(imino)pyridine iron(0)<sup>14</sup> and cobalt (I)<sup>15</sup> are seminal examples, which are very active under strict inert conditions. More stable, high oxidation state nickel, iron and cobalt precursors have been developed to catalyze alkene HS

(or DS) after an activation *via* reduction with Grignard reagents, lithium species or borohydride.<sup>16-22</sup> New development in the field are systems which do not need external reducing agents and might harness the SiH inherent to the reaction medium for reduction of iron(II)<sup>15-17,19,24</sup> and cobalt(II)<sup>23-27</sup> precatalysts, though the exact activation mechanism remains elusive.<sup>10,27</sup>

In the 90s, Marciniac reported the use of the commercially available Ni(II) acetylacetonate Ni(acac)<sub>2</sub> without external reducing agent as a hydrosilylation catalyst.<sup>28-30</sup> It was claimed that the SiH from the used silane allowed for reduction of the precursor. This catalyst was not selective for alkene hydrosilylation (HS) and gave several other products such as dehydrogenative silylation (DS), reduction (Red) and dimerization products (Dim) (see Figure ). Note that only HS and DS establish a Si-C linkage and are thus interesting in coupling or crosslinking reactions.

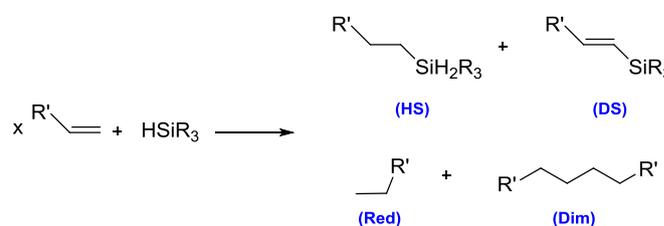


Figure 1: Products of alkene silylation with a tertiary silane of the H-SiMe(O-R)<sub>2</sub> type. HS represents the hydrosilylation product, DS the product of dehydrogenative silylation, Red the associated reduction product and Dim, the dimerization product.

Herein we developed readily available and easy-to-handle precursors for vinyl silane/alkene silylation without the use of

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

external strong reducing agent, yet promoting the curing of functional silicone oils. Our study is based on Marciniak's seminal work on Ni(acac)<sub>2</sub>.<sup>1-3,10,28-30</sup> We extended the scope of catalysts with a solubility-enhancing ligand for **Ni** – 2,2,6,6-tetramethyl-3,5-heptanedionate (tmhd) – and with Cobalt analogues.<sup>31</sup> We were particularly interested in comparing bis(acetylacetonato)Ni(II) and Co(II) complexes (see Figure 2) and their respective activities and selectivities for alkene/vinylsilane hydrosilylation and dehydrogenative silylation using industrially relevant tertiary silanes. We also implemented these precatalysts in the crosslinking of vinyl- and Si-H-functionalized PDMS chains under non-inert atmosphere (presence of O<sub>2</sub> and ambient moisture, see Experimental section).

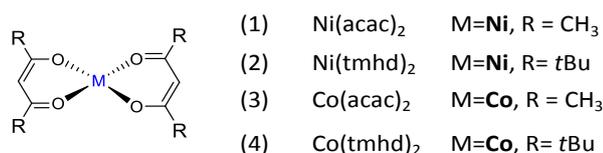


Figure 2: Precatalysts tested in this study of alkene/vinylsilane silylation with a tertiary silane.

## Results and discussion

We first studied the silylation of divinyltetramethylsiloxane (dvtms), vinylpentamethylsiloxane (vpmds) and 1-octene (see SI for all experiments, Sections 1-4 for dvtms and vpmds & 5 for 1-octene) with MD'M (1,1,1,3,5,5-Heptamethyltrisiloxane). Before quantifying the conversion and the selectivity, the major products of the reaction catalyzed by Ni(tmhd)<sub>2</sub> were identified by NMR spectroscopy. A combination of <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR, as well as GC/GC-MS analyses (for confirmation, in 1-octene case in particular) revealed the major and minor products of the reaction depicted in Figure 1 for vinyl-silane model compounds and 1-octene (see Experimental section and SI, sections 1 to 5).

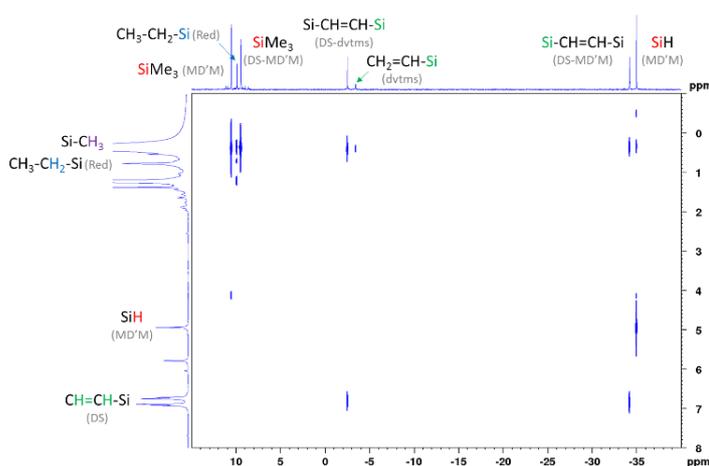


Figure 3: 2D <sup>29</sup>Si-<sup>1</sup>H NMR spectra (700 MHz, methylcyclohexane (MCH) d14) using INEPT sequence to attribute all signals to the various reaction products. This example uses Ni(tmhd)<sub>2</sub> as precatalyst (see Table 1 for conditions), selective for dehydrogenative silylation (DS).

Harnessing NMR spectroscopy, the starting substrates were characterized using <sup>1</sup>H and <sup>29</sup>Si nuclei. Then, the reaction medium was analyzed with <sup>1</sup>H and <sup>29</sup>Si NMR thanks to a 2D <sup>29</sup>Si-<sup>1</sup>H INEPT. Using the 2D spectra (Figure and SI, sections 2&3), we could identify the various Si moieties, and in particular the characteristic signals of the dehydrogenative silylation (DS) and reduction products (Red). Thus, we can conclude that Ni(tmhd)<sub>2</sub> is selective for dehydrogenative silylation and concomitant/subsequent reduction, as reported in the literature.<sup>1-10</sup> On the contrary, **Co** proved to yield both HS and DS products, even slightly favouring the former. <sup>1</sup>H-NMR was particularly helpful in the case of **Co**, to evidence all products of catalytic silylation (see SI, sections 1-4).

To further exemplify as well as compare **Ni** and **Co**, we summarized the catalytic performances of the precatalysts (1) to (4) in Table . Reactions took place at 90°C in neat substrates using 0.5 mol% of catalysts and with a ratio of SiH:SiVi = 1:1 (mol ratio of MD'M:dvtms = 2:1 and for ratio of MD'M:vpmds = 1:1). All catalysts mainly yield alkene/vinyl silane dehydrogenative silylation (DS) giving also reduction products (Red) (entry 1,3,5 and 7 in Table 1 for dvtms), for both dvtms and vpmds substrate (comparison with entries 2, 4, 6 and 8 in Table 1 for vpmds). Cobalt catalysts yield some hydrosilylation product, which sets them apart from DS-selective Nickel catalysts (entries 5-8 for **Co** compared to 1-4 for **Ni**), in particular for dvtms as substrate. However, only the Co(tmhd)<sub>2</sub> precatalyst **4** is active for the silylation of vpmds. The acac-counterpart is likely quickly deactivated through formation of **Co** black (black residues are quickly observed in that case during catalysis).

Table 1. Evaluation of catalytic activity for dvtms and vpmds hydrosilylation with MD'M

Entry	Catalyst	Vinyl-silane	Conversion (%)		Selectivity (% Vinylsilane)			
			MD'M	Vinyl silane	HS	DS	Red	Dim
1	(1)	Dvtms	53	100	0	53	47	0
2		Vpmds	52	100	0	45	40	15
3	(2)	Dvtms	52	100	0	52	48	0
4		Vpmds	47	100	0	43	43	14
5	(3)	Dvtms	35	73	14	48	38	0
6		Vpmds	0	0	0	0	0	0
7	(4)	Dvtms	35	73	14	48	38	0
8		Vpmds	30	45	70	15	15	0

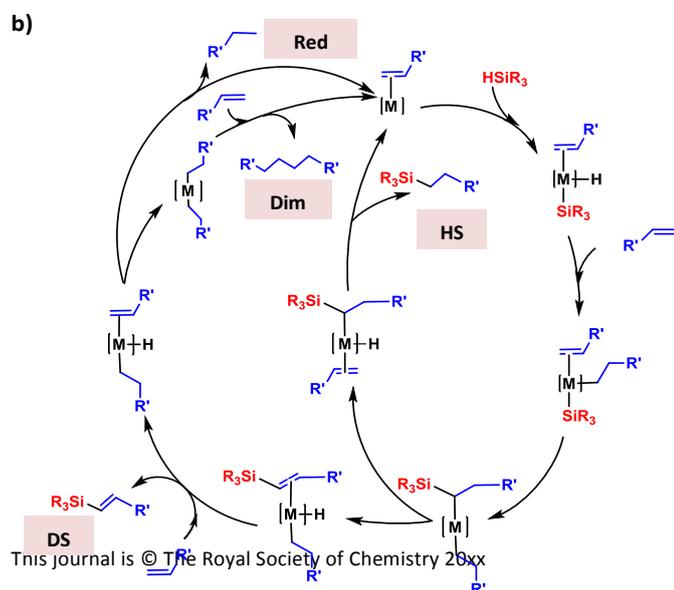
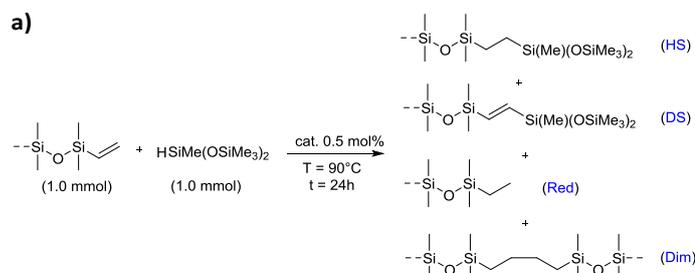
Reaction conditions: 90°C, neat, 0.5mol%, ratio SiH/SiVi =1:1, 24h reaction time. Conversion and selectivity determined by NMR analysis (see SI, Sections 1-5).

The catalytic activity for the hydrosilylation of 1-octene with MD'M was also investigated (SI, section 5) and all **Ni** and **Co** catalysts are mainly selective for isomerization. Notably, observed selectivities are different from Shimada and co-workers' publication<sup>22</sup> where Ni(acac)<sub>2</sub> is active for hydrosilylation with the use of NaHBET<sub>3</sub> as external reductant. Active-catalyst generation mechanism is thus probably different when the system is activated with a stronger external

reducing agent than the inherent tertiary silane featuring H-SiMe(O-R)<sub>2</sub> moieties.<sup>1-10</sup>

In order to study the catalyst activation mechanism, dtms silylation was monitored *in situ* using variable temperature NMR (VT-NMR) at 90°C with 12.5 mol% of Ni(tmhd)<sub>2</sub> as catalyst and with a ratio of SiH:SiVi = 1:1 (molar ratio of MD'M:dtms = 2:1). No catalytic intermediate has been observed when the catalyst is mixed with either MD'M or dtms alone. Performing the silylation within the NMR spectrometer has allowed us to follow the kinetics of the reaction, without significant perturbation from paramagnetism (see SI, sections 4 & 8), inferring specific environments for Ni(II) (since few environments are devoid of paramagnetism)<sup>32-36</sup> and no reduction product (either paramagnetic for Ni(I) or even ferromagnetic for some nanoparticles of Ni(0)).<sup>37-39</sup> We could evidence that the reaction is occurring under these conditions and some free ligand is released (small characteristic signals for keto/enol forms of free tmhd-derived 2,2,6,6-tetramethylheptane-3,5-dione can be observed on <sup>1</sup>H-NMR spectra, see SI, sections 2, 4, 7 & 8). This was confirmed by pre-contacting the Ni complex with either Si-H or vinyl moieties under similar conditions in order to identify ligand-set alteration (see SI, section 2 & 4).

In his study, Marciniec assumed that Ni(acac)<sub>2</sub> was reduced by the SiH from the silane before the Chalk-Harrod mechanism.<sup>1-3,28-30</sup> From our study, it seems that the catalytic mechanism might be different, either needing both the silane and the alkene to reduce minute amounts of the precatalyst before either conventional or modified Chalk-Harrod mechanisms occurs (see Scheme 1) or going through a concerted mechanism with no fully reduced species and subsequent oxidative addition as suggested in recent reports,<sup>7-10</sup> or that binuclear Ni(I) species might be at play.<sup>39</sup>



Scheme 1. a) Silylation of vinylsilane moieties: various reactions products are observed with M(acac)<sub>2</sub>-type precatalysts; b) Global putative mechanism explaining the formations of various products. The oxidation state of the metal and the generation of active species is omitted voluntarily since subjected to speculation (adapted from Marciniec<sup>1-3</sup>).

Very interestingly, monitoring color – in light of the absence of paramagnetism suggested by NMR spectroscopy – could suggest the formation of non-octahedral Ni(II) species via  $\sigma$ -bond metathesis, with release of acetylacetonate-type ligand (as clearly evidenced by <sup>1</sup>H NMR for the tmhd ligand, see SI, sections 4, 7 & 8). The green Ni(acac)<sub>2</sub> (due to octahedral geometry [paramagnetic] in the more favorable trimeric structure) and pink Ni(tmhd)<sub>2</sub> (due to a monomeric square-planar geometry [diamagnetic] in that case)<sup>32-36</sup> both rapidly turn bright orange, and NMR spectra do not display paramagnetic features (broad peaks or wide range of isotropic chemical shifts) even at high catalyst loading. This could suggest the formation of either square-planar, square-pyramidal trigonal or bipyramidal geometries with coordination of Si-H and vinyl moieties and subsequent release of one tmhd ligand as already suggested in the literature for such acetylacetonate-type ligands.<sup>1-10,28-30</sup> The release of the acac ligand seems less clear in our study, which could be explained by a higher propensity towards hydrosilylation of the released acetylacetonate in the mixture making the detection complicated. This could also suggest a much easier nanoparticle formation (*via* complete reduction)<sup>37,38</sup> in the case of Ni(acac)<sub>2</sub>, that could be detrimental to the reaction. That could explain the highest catalytic efficiency of the tmhd counterpart, whose role would then not be limited to an enhanced solubility. It is likely that the increased sterics from the *tert*-butyl group play a role in the bidentate ligand release, and potentially hindered subsequent hydrosilylation, making its detection possible (see SI, sections 4, 7, 8 & 9 for pictures). Co catalysis seems more difficult to rationalize, all systems are paramagnetic no matter the geometry and the darkening of the solution (see SI, section 9 – miscellaneous) could suggest reduction to Co(0) or Co(I) species, as previously proposed.<sup>10-12,40,41</sup>

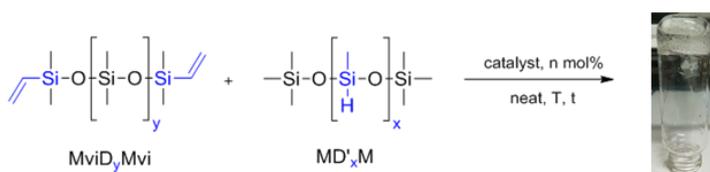
In the second part of our study, we monitored the activity of these catalysts for the crosslinking of Si-H and Si-vinyl functionalized silicone oils. Harnessing alkene (hydro)silylation to cure silicone formulations is the cornerstone of silicone materials' manufacturing: multiple applications heavily rely on this reaction.<sup>1-10</sup> The crosslinking is conventionally catalyzed by platinum complex that remain trapped in the final product, representing a large fraction of the cost of the material. As evidenced in Marciniec work,<sup>1-3,10,28-30</sup> a catalyst which is selective for dehydrogenative silylation can become active for hydrosilylation as well when it reacts with functional polymeric chain, suggesting a selectivity switch that is substrate-dependent.

The crosslinking activity of the four precatalysts  $\text{Ni}(\text{acac})_2$ ,  $\text{Ni}(\text{tmhd})_2$ ,  $\text{Co}(\text{acac})_2$  and  $\text{Co}(\text{tmhd})_2$  was studied, and some curing parameters were changed to monitor the influence on the crosslinking time and on the final material properties. Crosslinking time is determined with a stop-stirring test (SST) consisting of mixing di-vinyl and poly-SiH silicone-oils with the catalyst heating in an oil bath and measuring time when the magnetic stirrer stops (see Experimental Section). Here, we performed this test under non-inert atmosphere (presence of  $\text{O}_2$  and ambient moisture).<sup>31</sup>

Crosslinking of dvtms with poly-SiH oil  $\text{MD}'_{50}\text{M}$  was first evaluated. The catalytic activity of complexes (1) to (4) is summarized in Table 1 (Entries 1 to 4). Reference reactions were performed at  $90^\circ\text{C}$  using 0.5 mol% of catalysts and with a ratio of  $\text{SiH}:\text{SiVi} = 1:1$ . Nickel catalysts are sluggish for the crosslinking of dvtms. On the contrary, cobalt catalysts are very efficient, and more particularly  $\text{Co}(\text{acac})_2$  which allows a crosslinking in less than 15 minutes at  $90^\circ\text{C}$ .

The crosslinking of di-vinyl PDMS oil with poly Si-H oil was also surveyed and results are compiled in Table 1. Reference reactions were done at  $110^\circ\text{C}$  using 1 mol% of catalyst and with a ratio of  $\text{SiH}:\text{SiVi} = 3:1$ , to ensure efficient crosslinking even through undesired reactions. All four catalysts are active for the crosslinking of di-vinyl and poly-SiH oil under non-inert atmosphere (Entries 5 to 8, Table 2). Contrary to the results with dvtms ( $y=0$ ), nickel catalysts are more active than cobalt catalysts for more viscous silicone oils. Dvtms possesses a specific chelating structure and is the bidentate ligand of choice for Karstedt's type catalysts.<sup>5,42</sup> Difference between **Co**- and **Ni**-based catalyst activities may arise from a variation of dvtms coordination on the active center, precluding activity in the case of **Ni**.<sup>3,42</sup> It is possible that the chelating nature of dvtms is detrimental to the reactivity of **Ni** catalysts, maybe suggesting the formation of a stable octahedral  $\text{Ni}(\text{II})$  complex, no longer able to interact efficiently with the Si-H moiety.

Table 1. Evaluation of catalytic activity for divinyl and poly-SiH silicone oils crosslinking



Entry	y	Catalyst	Mol%	SiH:SiVi	T	SST
1	0	(1)	0.5	1	90	3 h
2	0	(2)	0.5	1	90	3 h
3	0	(3)	0.5	1	90	15 min
4	0	(4)	0.5	1	90	40 min
5	20	(1)	1	3	110	30 min
6	20	(2)	1	3	110	15 min
7	20	(3)	1	3	110	25 min
8	20	(4)	1	3	110	40 min

To evidence that crosslinking is really occurring, and to evaluate further crosslinking kinetics and compare gel properties, rheology was performed for Si-H and Si-vinyl PDMS oil curing. The catalytic crosslinking of di-vinyl and poly-SiH PDMS oils with complexes (1) to (4) is presented in Figure 4. Reactions took place at  $110^\circ\text{C}$  using 1 mol% of catalyst and with a selected ratio of  $\text{SiH}:\text{SiVi} = 3:1$ . First, we systematically observed an intersect of  $G'$  and  $G''$  suggesting that crosslinking is effective, with gel times apparently shorter than observed during SST measurements. **Ni** catalysts are more active under this set of conditions and yield materials with slightly higher  $G'$  moduli (close to  $10^5$  Pa for a reference formulation of Table 2, see also SI, sections 7 & 8).  $\text{Co}(\text{acac})_2$  is less active as expected from SST, probably due to higher air instability leading to catalyst degradation, and gives lower modulus gel ( $\sim 10^3$  Pa).  $\text{Co}(\text{tmhd})_2$  has a gel time in accordance with SST and modulus higher than  $10^4$  Pa and consistently close to  $10^5$  Pa. Premature oxidation might be detrimental to **Co** catalysis. Adventitious contaminants in silicone oils might also be responsible for the lower efficiency of a slightly more sensitive **Co** catalysis, which could also explain the delay in crosslinking observed by rheometry.

Interestingly DSC can be used to monitor these crosslinking reactions. Thermal kinetics of the catalyzed crosslinking of di-vinyl and poly-SiH PDMS oils was monitored using DSC analysis. Crosslinking of dvtms with poly-SiH oil  $\text{MD}'_{50}\text{M}$  was first studied. Reference reactions were heated at  $8^\circ\text{C}/\text{min}$  rate, using 0.5 mol% of complexes (1) to (4) with a ratio of  $\text{SiH}:\text{SiVi} = 1:1$  (see SI, section 6-Figure S21).

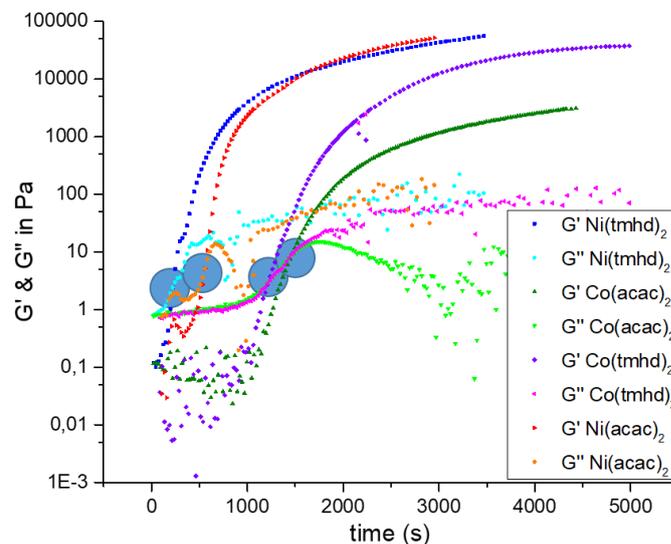


Figure 4: Rheology curves following crosslinking of di-vinyl and poly-SiH PDMS oil. Reaction conditions:  $110^\circ\text{C}$ , 1 mol%, ratio  $\text{SiH}:\text{SiVi} = 3:1$ . Blue disks mark the intersects between  $G'$  &  $G''$ , characteristic of crosslinking.

Crosslinking catalyzed by cobalt complexes starts at a lower temperature comparing to nickel complexes, and this is in accordance with the crosslinking time measured with SST (see Experimental section and SI-section 8 for values of SST for crosslinking at  $90^\circ\text{C}$ ). Catalysts bearing the acac ligand set have sharper reaction profile than with tmhd ligands, whose reaction profile is broad. This activation could be linked to the

removal of the acetylacetonate molecule during activation with the Si-H substrate in the presence of Si-vinyl moieties; with the ligand substitution being easier with the less bulky analogue.

Crosslinking of di-vinyl PDMS oil with poly-SiH oil MD'50M was also surveyed. Reference reactions were performed at a heating rate of 8°C/min, using 1 mol% of complexes (1) to (4) with a ratio of SiH:SiVi = 2:1 and thermograms are presented in Figure S22 (see SI). Under these conditions, crosslinking catalyzed by Co(acac)<sub>2</sub> starts at a lower temperature but the enthalpy is less important than with the other catalysts, suggesting incomplete reaction and possible catalyst decomposition due to air exposure. Overall, and contrary to dtms crosslinking, Ni pre-catalysts seem to outperform Co counterparts for longer oil-based formulations. This could also be a consequence of the increased sensitivities of Co complexes.

DSC thus unveils that Co is more reactive at lower temperatures than Ni for dtms formulations (see SI, section 6), probably due to the aforementioned chelating nature of dtms, deactivating Ni (pre)catalysts. However, this statement does not hold true for longer oil-based industrial formulations with spaced-apart vinyl moieties.

These DSC results are consistent with rheology experiments with the observed G' modulus is lower in the case of Co(acac)<sub>2</sub> than with the other catalysts. Initiation temperatures are then lower for Ni catalysts than for Co(tmhd)<sub>2</sub> for crosslinking (see SI, Figure S22) and reaction profiles are very similar for these three catalysts confirming the rheology findings. These observations are in agreement with what was suggested by Marciniak:<sup>1,3-28-30</sup> reaction kinetics and selectivities are strongly substrate-dependent and (hydro)silylation model reactions behave differently than crosslinking of silicone-based oils.<sup>3,43</sup> Model reactions are thus interesting to rationally design regio- and stereoselective catalyst for silylation reactions, but crosslinking of polyfunctional oils might yield different product selectivities due to unique sterics and diffusion constraints. Therefore, another method is necessary to assess the different products when crosslinking is considered.

High-Resolution Magic Angle Spinning NMR (HR-MAS NMR) spectroscopy can advantageously characterize gels displaying satisfactory mobility, bridging the gap between liquid NMR and solid-state NMR. It consists in running liquid-like sequences in a rotor spun at high frequency at the magic angle to retain proper resolution (see SI, sections 7 & 8).

Very interestingly, HR-MAS NMR of crosslinking formulations allowed us to get a better understanding of the selectivities taking place in these 3D- polymer networks. If Ni still promotes DS linkage as a major crosslinking knot, Co displays a higher propensity towards HS linkage in the crosslinking of functionalized-polymer oils (see Figure 5 and SI – [HR-MAS NMR analyses of crosslinking of di-vinyl PDMS and poly-SiH oils], section 7).

More specifically, Figure 5 clearly depicts a very selective Co(tmhd)<sub>2</sub> pre-catalyst yielding species promoting hydrosilylation of vinylsilane moieties from the functional silicone oil. Co(acac)<sub>2</sub> seems a bit less selective, since some DS

product can be identified. Moreover, its lesser activity, probably due to premature deactivation precludes an efficient use in such systems. This ligand dependency could suggest that the active species might retain one acetylacetonate-type ligand, akin postulated species for Pt(acac)<sub>2</sub>-based precatalytic systems.<sup>43,44</sup> It could also be the result of Co-based nanoparticles/colloids (Co(0)/Co(I) reduced species) formed in the case of Co(acac)<sub>2</sub> that would induce a different catalytic pathway.<sup>11,12,38,40,41</sup>

On the contrary, Ni pre-catalysts still promote the DS pathway, with identifiable characteristic olefinic protons (Figure 5a) and carbons (Figure 5b) as well as Red associated products (aliphatic regions on both overlays). Noteworthy is that Ni(tmhd)<sub>2</sub> and Ni(acac)<sub>2</sub> seem to be leading to very similar selectivities, in agreement with the model reactions (see Table 1), with the obvious solubility edge of the tmhd-based analogue in silicone formulations.

The HR-MAS methodology could further be harnessed to identify new systems amenable to selectively yield new silicone networks from anti-Markovnikov & Markovnikov products,<sup>45</sup> or develop new catalysts based on these platforms.<sup>46,47</sup>

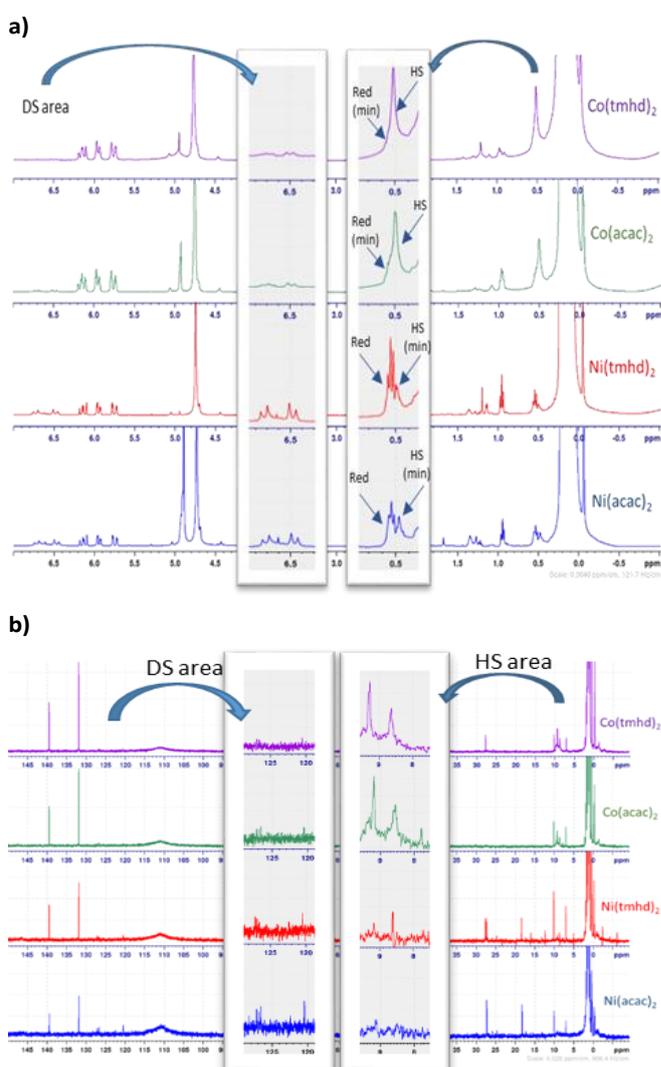


Figure 5: HR-MAS NMR spectroscopy: comparison for all catalysts of a)  $^1\text{H}$ -NMR-HR-MAS spectra and b)  $^{13}\text{C}$ -NMR-HR-MAS spectra. Gels swollen with  $\text{CDCl}_3$  (see HR-MAS section 7, Figures S43 & S44 for overlays, SI).

## Conclusions

We have evaluated the activity and selectivity of nickel and cobalt acetylacetonate-based complexes as precatalysts for silylation and crosslinking using Si-H and Si-vinyl functionalized substrates without external reducing agents and under non-inert atmosphere. Those complexes promote the in-situ formation of competent catalysts featuring different activities/selectivities depending on the chosen metal and ligand set. This choice consequently affects the crosslinking kinetics/efficiency and the mechanical properties of the final materials. **Ni** complexes promote dehydrogenative silylation selectively. **Co** complexes yield both hydrosilylation and **DS** products for model compounds, whereas the **HS** product is favored for crosslinking of functionalized oils, which was evidenced harnessing HR-MAS NMR spectroscopy. **Co** acetylacetonate-based complexes also tend to display activity at lower temperatures than **Ni**, while being more sensitive to non-inert conditions. When silicone curing formulations are employed,  $\text{Ni}(\text{tmhd})_2$  is the most active precatalyst for crosslinking of silicone oils under non-inert atmosphere, probably due to an enhanced solubility in silicone media. The activation of these high-oxidation state complexes does not seem to proceed *via* Si-H-promoted reduction. Further investigations are currently underway to pinpoint the active-catalyst generation mechanism. Finally, these thermally-induced crosslinking reactions could prove key to develop efficient “one-pack” formulations, stable at room temperature for extended shelf lives and that could be triggered to form the silicone mastics/putties when heated.

## Experimental

### General considerations

Reaction were performed under non-inert atmosphere. All commercially available reagents were used as received. Silicon oils were kindly provided by Elkem Silicones®. Silicon oils were degassed under vacuum, to remove traces of volatiles from synthetic process. All reaction vials were loaded with precisely weighted (0.1 mg precision) substrate and catalyst amounts, without precautions regarding the atmosphere (presence of  $\text{O}_2$  and ambient moisture). The chemicals were obtained from the following suppliers:  $\text{Ni}(\text{acac})_2$  and  $\text{Ni}(\text{tmhd})_2$  from Strem,  $\text{Co}(\text{tmhd})_2$  from Alfa Aesar,  $\text{Co}(\text{acac})_2$  from Sigma, 1-octene from Sigma, and  $\text{CDCl}_3$  and methylcyclohexane (MCH) d14 from Eurisotop. Elkem Silicones® provided Divinyltetramethylsiloxane (dvtms), (MD'M), and all silicone oils. Vpmds was sourced from abcr.

### General procedure for catalytic silylation reactions

A 20mL reaction vial was loaded with the catalyst (0.045 mmol) together with the chosen alkene/vinyl (9mmol) and

MD'M (9mmol). Dodecane (standard) was added for GC quantification. The solution was stirred and heated to  $90^\circ\text{C}$  for 24 hours. During the course of reaction, aliquots were withdrawn for analysis. After the reaction, NMR and and/or GC/GC-MS analyses were performed.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR Spectra were recorded on a Bruker 400MHz and 700MHz spectrometers in  $\text{CDCl}_3$  and MCH d14. The mass spectra of the products were evaluated by Gas Chromatography coupled with Mass Spectrometry (GC-MS) and quantification was determined with Gas Chromatography (GC) analysis using calibration curves with appropriate substrates. GC was performed on an HP 6890 instrument using a HP5 column made of 5% of diphenyl and 95% dimethyl polysiloxane (32 m length, 0.32 mm diameter, 0.25  $\mu\text{m}$  film) and a flame ionization detector. The injection volume was 1  $\mu\text{L}$  and nitrogen was used as mobile phase with a flow of  $1\text{ mL}\cdot\text{min}^{-1}$ . The temperature program was as follow:  $40^\circ\text{C}$  plateau for 5 min; heating to  $250^\circ\text{C}$  at  $10^\circ\text{C}\cdot\text{min}^{-1}$ ;  $250^\circ\text{C}$  plateau for 5 min. GC-MS analysis was performed on an Agilent 6850 instrument equipped with a HP5 column made of 5% of diphenyl and 95% dimethyl polysiloxane (32 m length, 0.32 mm diameter, 0.25  $\mu\text{m}$  film) and an Agilent 5975C EI detector. The same temperature program as GC was used for GC-MS analysis. Alkene/vinyl silane conversions and products' selectivities are calculated from  $^1\text{H}$  NMR and double-checked using GC/GC-MS analysis (see SI, Sections 1-5) in particular for 1-octene.

### General procedure for silicone oil crosslinking

#### Stop-Stirring Time (SST)

For SST, a 20mL vial was loaded with the catalyst (0.02mmol) together with divinyl oil (viscosity 100 mPa.S, 1.58 %wt vinyl function, 4g) and poly-SiH oil (MD'50M, 46%wt SiH function, 0.3g). Catalyst loading is expressed in mol% of vinyl functional group. The medium was stirred and heated at  $90^\circ\text{C}$  or  $110^\circ\text{C}$ . The curing time was measured from the moment of placing the tube at the desired temperature until the magnetic stir bar stopped. Either extreme viscosity or actual crosslinking could be responsible for this observation. This SST was thus correlated to actual rheology measurements and good agreements between SST and effective crosslinking (intersect of  $G'$  &  $G''$ ) could be evidenced, validating the method.

#### Rheology and DSC

For rheology and DSC (differential scanning calorimetry), a 20mL vial was charged with the catalyst (0.014mmol) together with divinyl oil (viscosity 100 mPa.S, 1.58 %wt vinyl function, 3g) and poly-SiH oil (MD'50M, 46%wt SiH function, 0.25g). The medium was stirred at ambient temperature. A sample of the solution was taken for analysis. Rheometer analysis are performed on a Rheometer Thermoscientific at  $110^\circ\text{C}$  using parallel plate, 0.5 mm gap, 1s-1 frequencies and constraint starting at 3Pa, changing at 50Pa and 1000Pa after reaching 0.001mNm. 0.2mL of previous medium was injected to be tested. DSC thermograms are completed on a Mettler Toledo DSC 300+ at a heating rate of  $8^\circ\text{C}/\text{min}$  and for kinetic simulation at  $4^\circ\text{C}/\text{min}$  and  $15^\circ\text{C}/\text{min}$ . 60-80 mg of previous medium is put in aluminium 100  $\mu\text{L}$  pan.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors thank Elkem Silicones© for providing raw materials and funding for MP's and JD's PhD projects. DC thanks the FUI ECOMAT for funding her post-doctorate. JR and VM also thank Roger Spitz for enlightening discussions and Franck Collas for his DSC expertise, Sébastien Norsic for his technical support as well as Carlos Fernández de Alba Encinas for his HR-MAS NMR expertise.

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