

# Polydimethylsiloxane Chains as Solubilisers of Metal Complexes in Supercritical Carbon Dioxide.

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Polydimethylsiloxane chains are effective solubilising groups for pyridine-type ligands and their corresponding copper-complexes in supercritical carbon dioxide. The use of these complexes as precursor catalysts in the homogeneous oxidation of aromatic alcohols in supercritical carbon dioxide is described.

## INTRODUCTION

Supercritical carbon dioxide (scCO<sub>2</sub>) is a relatively green alternative to commonly used organic solvents and research into its use as a reaction solvent is therefore desirable [1]. Although metal catalysed homogeneous reactions in scCO<sub>2</sub> would be attractive [2], the low solubility of many catalysts is a barrier to their use in such processes. Enhancing the solubility of such catalysts in supercritical media is therefore an important research target. In recent years, a number of methodologies have been developed to improve solubility, including the use of “CO<sub>2</sub>-philic” ligands, especially fluorinated ligands [3,4,5]. Drawbacks to their use include the effect that the strongly electron-withdrawing fluorine can have on the activity of the catalyst [6] and the difficulty, danger and expense involved in synthesizing ligands of this sort. For these reasons, the design of new, easily prepared solubilisers, that do not alter the chemical properties of the catalyst, is highly desirable. In previous work we have successfully used trimethylsilyl groups [7] and carbosilane dendrons [8] attached to the ligands as effective solubilisers.

The aim of the work described here was: (i) to confirm experimentally the increased solubility in scCO<sub>2</sub> of metal complexes incorporating pyridine ligands with solubilising polydimethylsiloxane chains (PDMS); and (ii) to investigate the use of these complexes as precursor catalysts in a selected catalysed process, the copper assisted oxidation of aromatic alcohols using TEMPO as co-catalyst and molecular oxygen as terminal oxidant. Using a similar approach, Kerton and co-workers showed recently that PDMS tagged arylphosphines could be satisfactorily used as ligands in homogeneous catalysis [9].

## I - MATERIALS AND METHODS

All preparations and other operations were carried out under dry oxygen-free nitrogen atmosphere following conventional Schlenk techniques. Hydride terminated polydimethylsiloxane ([H]<sub>2</sub>[SiMe<sub>2</sub>(OSiMe<sub>2</sub>)<sub>n</sub>], **I**), 4-vinylpyridine, TEMPO (2,2,6,6-tetramethyl-piperidinyloxy), nitrobenzyl alcohol and Kardstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylenes) were obtained from Aldrich and used as supplied. The average molecular weight of **I** was determined by <sup>1</sup>H NMR integration of Si-CH<sub>3</sub> versus Si-H (n = 10). Copper acetate was prepared from copper sulphate and acetic acid via a commonly known synthesis. Solvents were dried and degassed before use. Infrared spectra were recorded on Perkin-Elmer Model 883 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were run on Bruker AMX-300 spectrometer. UV/Visible spectra were recorded using a Perkin-Elmer Lambda 25 UV/VIS Spectrometer. Microanalyses (C, H, N) were carried out by the Microanalytical Service of the University of Sevilla.

## Preparation of pyridine terminated polydimethylsiloxane, [PyC<sub>2</sub>H<sub>4</sub>]<sub>2</sub>[SiMe<sub>2</sub>(OSiMe<sub>2</sub>)<sub>n</sub>] (II)

Hydride terminated polydimethylsiloxane (1.40 cm<sup>3</sup>, 1.30 g, 1.62 mmol) and 4-vinylpyridine (0.60 cm<sup>3</sup>, 0.585 g, 5.28 mmol) were mixed and air removed by vacuum. Under a nitrogen atmosphere, dry dichloromethane (5 cm<sup>3</sup>) and the catalyst, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylenes (0.85 μL) was added. The mixture was heated to 60°C and allowed to react for 24 hours. The solvent was removed by vacuum to give the crude product, a clear dark orange oil. This was dissolved in hexane (15 cm<sup>3</sup>) and washed with deionised water (3 x 5 cm<sup>3</sup>), dried with MgSO<sub>4</sub>, filtered and evaporated to give the product **II** as a clear, slightly amber oil (0.89 g, 0.88 mmol, 54%). <sup>1</sup>H NMR analysis of compound **II** indicated that it was a mixture of isomers corresponding to the Markonikoff (**II-M**) and anti-Markonikoff (**II-AM**) addition in a ratio of approximately 1:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.02-0.15 (s, -[CH<sub>3</sub>]<sub>2</sub>SiO-), 0.91 (m, 2H, PyCH<sub>2</sub>CH<sub>2</sub>Si, **II-AM**), 1.38 (q, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 1H, PyCHCH<sub>3</sub>Si, **II-M**), 2.22 (d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 3H, PyCHCH<sub>3</sub>Si, **II-M**), 2.65 (m, 2H, PyCH<sub>2</sub>CH<sub>2</sub>Si, **II-AM**), 7.01 (d, <sup>3</sup>J<sub>HH</sub> = 5.7 Hz, 2H, Py, **II-M**), 7.14 (d, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz, 2H, Py, **II-AM**), 8.41 (d, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, 2H, Py, **II-M**), 8.48 (d, <sup>3</sup>J<sub>HH</sub> = 5.7 Hz, 2H, Py, **II-AM**). Average molecular weight determined by NMR: 1010 (n = 10). Anal. Calc. for C<sub>36</sub>H<sub>82</sub>N<sub>2</sub>O<sub>10</sub>Si<sub>11</sub> (n = 10): C, 42.73; H, 8.17; N, 2.77. Found: C, 43.56; H, 8.36; N 3.23%.

## Preparation of Cu<sub>2</sub>[AcO]<sub>4</sub>[ViPy]<sub>2</sub> (III)

Copper Acetate (0.61 g, 1.52 mmol) was charged to a Schlenk tube and dissolved in ethanol (30 cm<sup>3</sup>). The solution was flushed with nitrogen and heated to 80°C. Then, 4-vinylpyridine (0.34 g, 3.05 mmol) was added and the solution was allowed to react for 10 minutes. Upon addition of the vinylpyridine precipitation of the product as green microcrystals could be observed almost instantly. The solution was cooled to room temperature and then refrigerated before the product was filtered off. The product was washed with cold ethanol and dried (0.74 g, 1.29 mmol, 85%). Calc. Anal. for Cu<sub>2</sub>C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>O<sub>8</sub>: C, 46.07; H, 4.57; N, 4.88%. Found: C, 44.97; H, 4.18; N 4.82%

## Preparation of {Cu<sub>2</sub>[AcO]<sub>4</sub>[(PyC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(SiMe<sub>2</sub>(OSiMe<sub>2</sub>)<sub>n</sub>)]<sub>m</sub> (IV)

Copper acetate (0.38 g, 0.95 mmol) and **II** (0.89 g, 0.88 mmol) were dissolved in ethanol (15 cm<sup>3</sup>), heated to 40°C and left to react for 21 hours. The solvent was removed under vacuum to leave a dark sludge which was extracted with hexane, filtered and fine solids then removed by centrifugation. The hexane was removed under vacuum to leave the crude product, a cloudy blue green oil. This was again dissolved in hexane, remaining sediment was removed by a second centrifugation and the solvent again evaporated leaving **IV** as a clear blue green oil (0.70 g). The product was kept refrigerated and under vacuum.

*Cu-content determination in IV:* The copper content in complex **IV** can be easily calculated by UV-Vis spectroscopy using the Beer-Lambert law from a calibration plot of standard solutions of the complex **III** in dichloromethane. Complex **III** is taken to exhibit approximately the same extinction coefficient as the analogous PDMS-tagged derivate **IV**. The spectrum of Cu<sub>2</sub>[AcO]<sub>4</sub>[ViPy]<sub>2</sub> (**III**) for which the copper content by weight is known to be 22.16 %, was recorded in dichloromethane and the maximum absorbance was found to occur at 721 nm. Next solutions of concentrations between 0.3 and 6.5 % Cu by weight were used to create a calibration graph. Absorbance measurements for known weights of compound **IV** in dichloromethane were taken and the copper content of the product was determined to be variable between 4 and 6 % by weight of the product. Iodometric titration confirmed the results obtained by the spectroscopic determination.

## Experiments in supercritical carbon dioxide.

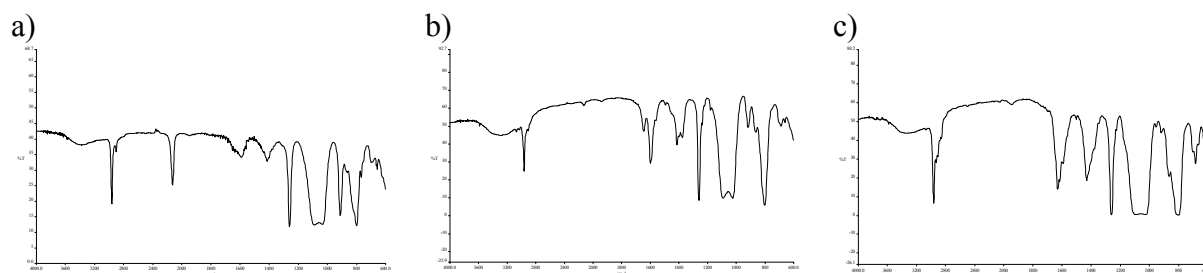
A simple high-pressure apparatus, described elsewhere [10], was used to carry out the solubility measurements and the reactions in scCO<sub>2</sub>.

*Solubility measurements:* The solubility of the copper compounds was measured spectroscopically in scCO<sub>2</sub>. Experiments were performed in a 4.4 ml stainless steel high-pressure cell equipped with 2 sapphire windows. A sufficient amount of solute was charged the cell, to give a saturated solution in scCO<sub>2</sub> at 40°C and the utilised pressure. Before performing any measurement, the mixtures were efficiently stirred in order to guarantee that the saturation of the complex in the supercritical phase had been achieved, after which the ultraviolet-visible (UV-Vis) absorbance spectrum between 300 and 1000 nm was recorded. The absorbance in scCO<sub>2</sub> was calculated by subtracting an absorbance value at a non-absorbing region of the spectrum (e.g. 550 nm) from an absorbance value at a peak maximum (approximately 720 nm for the copper complexes). The concentration of the copper complexes in scCO<sub>2</sub> was determined using the Beer-Lambert law from a calibration plot of standard solutions in hexane. Hexane can be taken to have approximately the same polarity as scCO<sub>2</sub>, resulting in only negligible solvchromatic shifts and exhibiting similar extinction coefficients [11].

*Catalytic Reactions:* All catalytic reactions in scCO<sub>2</sub> were carried out in a in a 28 ml stainless steel high-pressure cell. The alcohol was first charged to the reactor along with a stirrer flea. The catalyst and TEMPO were then introduced in a separate vial also containing a small stirrer flea and the reactor was then sealed. The pressure in the reactor was reduced to vacuum and subsequently brought to the specified pressure of O<sub>2</sub>, warmed to the specified temperature and then CO<sub>2</sub> was introduced up to 150 bar before stirring was initiated. After depressurisation, products were extracted with diethyl ether and filtered before being evaporated to give the reaction product. Reaction yields were calculated from the NMR spectra of the products in CDCl<sub>3</sub>, using the ratios of the integrals of the aromatic peaks of the alcohol and aldehyde.

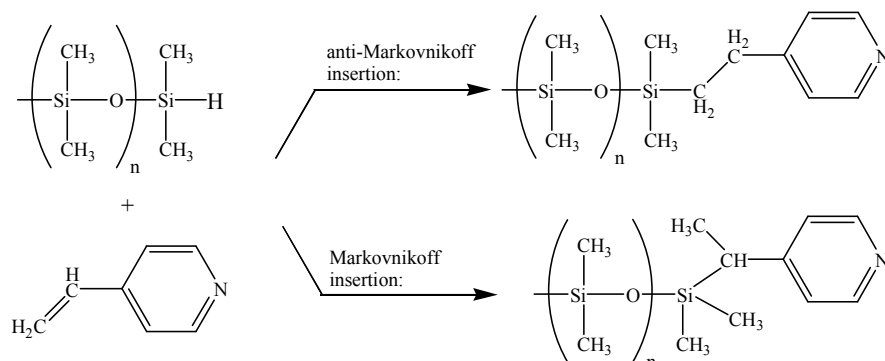
## II – RESULTS AND DISCUSSION

**Ligand Syntheses and Characterization.** The pyridine ligand **II** was prepared in good yields from a commercially available hydride terminated polydimethylsiloxane, [H]<sub>2</sub>[SiMe<sub>2</sub>(OSiMe<sub>2</sub>)<sub>n</sub>] (**I**), and 4-vinylpyridine, in the presence of the Kardstedt's catalyst. In-situ IR spectra of the reaction mixture allows the progress of the hydrosilylation reaction to be monitored. In **Figure 1a**, the IR spectrum of **I** shows the presence of the Si-H peak. Hydrosilylation of vinylpyridine to form **II** results in the loss of this peak and the appearance of the peaks corresponding to the pyridine group (**Figure 1b**).



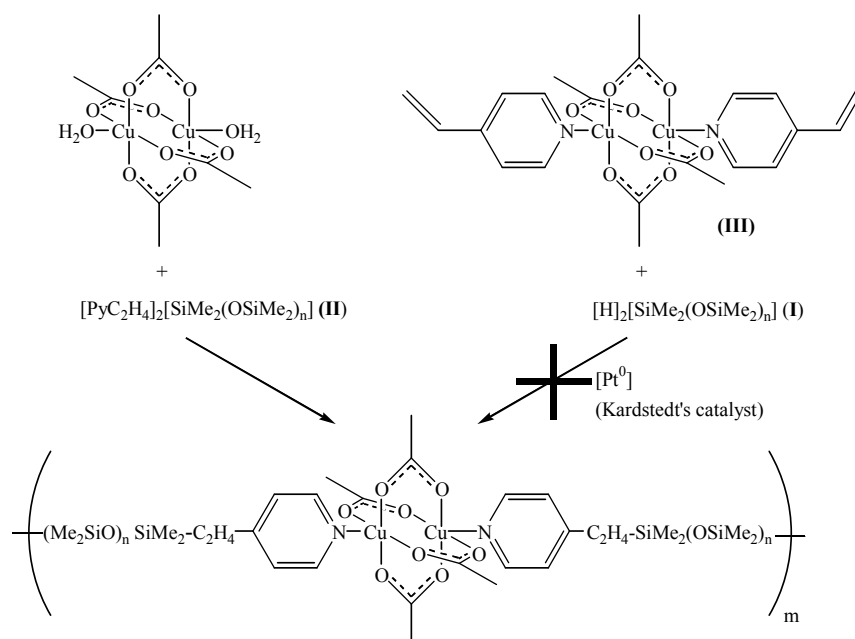
**Figure 1.** IR Spectra of PDMS compounds **I**, **II** and **IV**.

**Figure 2** illustrates the general reaction scheme for PDMS attachment by hydrosilylation reaction.  $^1\text{H}$  NMR analysis of compound **II** indicated that it was a mixture of isomers resulting from the Markovnikoff (**II-M**) and anti-Markovnikoff (**II-AM**) addition in a ratio of roughly 1:2. Modification of the reaction conditions did not result in any significant difference in the composition of the isomer mixture. Chromatographic separation of the isomers was attempted but always gave unsatisfactory results.



**Figure 2.** Hydrosilylation reaction for attachment of PDMS to vinylpyridine.

**Preparation of copper complex IV.**  $\{\text{Cu}_2[\text{AcO}]_4[(\text{PyC}_2\text{H}_4)_2(\text{SiMe}_2(\text{OSiMe}_2)_n)]\}_m$  (**IV**), a green air-stable oil, was prepared by reacting **II** with  $\text{Cu}_2[\text{AcO}]_4[\text{H}_2\text{O}]_2$  in ethanol. Direct hydrosilylation of  $\text{Cu}_2[\text{AcO}]_4[\text{ViPy}]_2$  (**III**), obtained by reaction of  $\text{Cu}_2[\text{AcO}]_4[\text{H}_2\text{O}]_2$  and vinylpyridine, with the Si-H precursor **I** is not possible, probably due to the deactivation of the Pd catalyst in the presence of the copper complex (see **Scheme 1**).



The IR spectrum of complex **IV** demonstrates the presence of polydimethylsiloxane with the pyridine and acetate fragments (**Figure 1c**). It appears that the carboxylate group is bridging, giving the typical  $\text{Cu}_2(\text{AcO})_4$  core, rather than being in a monodentate coordination mode, as suggested by the difference ( $\Delta\nu = 199\text{ cm}^{-1}$ ) observed between the asymmetric and symmetric C-O stretches ( $\nu = 1628$  and  $1429\text{ cm}^{-1}$ , respectively) in the IR spectrum [12].

Elemental analysis did however suggest a deficiency in the  $\text{Cu}_2(\text{AcO})_4$  fragment compared to the stoichiometric prediction. Coordination of the ligand **II** to the copper complex was evident from the different behaviour of **IV** relative to a dispersion of  $\text{Cu}_2(\text{AcO})_4(\text{Py})_2$  (**V**) in polydimethylsiloxane. Whilst polydimethylsiloxane and **IV** are both soluble in hexane, **V** is not. A sample of **IV** can thus be wholly dissolved in hexane, whereas for a dispersion of **V** in polydimethylsiloxane (prepared by solvent stripping a dichloromethane solution of the two components to dryness) only the polymer dissolves, leaving behind a suspension of **V**. Compound **IV** should therefore be considered a complex mixture containing the ligand **II** (an isomers mixture) both as free ligand and coordinated to the  $\text{Cu}_2(\text{AcO})_4$  core.

The copper content in complex **IV** can be calculated by spectrometric determination (see Materials and Methods). In general, the copper content has been found to be variable between 4 and 6 % by weight of the product. Iodometric titration confirmed the results.

**Solubility of the copper complexes in  $\text{scCO}_2$ .** The newly synthesized PDMS-derivatised copper complex **IV** has been used to study the solubilising effects of the PDMS-tag in  $\text{scCO}_2$ . For comparison, the measurements were performed in parallel with that of the vinylpyridine derivative **III** and of the well-known pyridine derivative **V**. The solubility of the copper compounds were determined both visually and spectroscopically in  $\text{scCO}_2$  using a high-pressure cell equipped with 2 sapphire windows. Visual inspection indicates that while complex **IV** affords a green solution in  $\text{scCO}_2$ , complexes **III** and **V** have no visible solubility in the media.

The quantitative concentration of copper in  $\text{scCO}_2$  was determined by UV-Visible analysis. A concentration of  $1.7 \text{ mmol /dm}^3$  (based on  $\text{Cu}^{2+}$ ) was determined for a saturated solution of complex **IV** in  $\text{scCO}_2$  at  $40 \text{ }^\circ\text{C}$  and at 105 bar of pressure, while the analogous non-tagged derivatives **III** and **V** had no detectable solubility in the supercritical solvent.

**Applications in homogeneous catalysis.** The concentration of complex **IV** in  $\text{scCO}_2$  falls into the concentration ranges (1 mM or higher) generally adopted for homogeneous catalytic processes; therefore, this system could be used as model to test the viability of PDMS-tagged pyridine ligands in the design of new catalysts soluble in  $\text{scCO}_2$  based on conventional ones. The selective oxidation of nitro-benzyl alcohol using **IV**/TEMPO as catalyst and  $\text{O}_2$  as terminal oxidant was studied (see Materials and Methods). Complete conversion to the aldehyde was observed after 4 hours of reaction at  $60 \text{ }^\circ\text{C}$  and 150 bars. However, it is worth stressing that at the same reaction conditions, the non-substituted copper derivatives **III** and **V** catalyse the oxidation affording the aldehyde with a yield of 93 and 95 %, respectively.

**Table 1.** Oxidation reaction of 4-nitrobenzyl alcohol in  $\text{scCO}_2$ .<sup>a</sup>

Catalyst <sup>a</sup>	T(°C)	P (bar)	Conversion after 2 h <sup>b</sup>	Conversion after 4 h <sup>b</sup>
$\{\text{Cu}_2[\text{AcO}]_4[(\text{PyC}_2\text{H}_4)_2(\text{SiMe}_2(\text{OSiMe}_2)_n)]\}_m$ ( <b>IV</b> )	60	150	80	100
$\text{Cu}_2[\text{AcO}]_4[\text{ViPy}]_2$ ( <b>III</b> )	60	150	83	93
$\text{Cu}_2(\text{AcO})_4(\text{Py})_2$ ( <b>V</b> )	60	150	93	95
$\text{Cu}_2[\text{AcO}]_4[\text{H}_2\text{O}]_2$	60	150	-	34
None	60	150	2	-

<sup>a</sup>Reaction conditions: 4-nitrobenzyl alcohol 0.78 mmol, P(O<sub>2</sub>) = 1 bar, [TEMPO] 7% mol, Cu catalyst 3.5% mol. <sup>b</sup>Yield calculated by NMR integration.

## CONCLUSIONS

We conclude that polydimethylsiloxane tagged pyridine ligands can enhance the solubility of metal complexes in scCO<sub>2</sub>. Observations are similar to those in the work of Kerton et al. on transition metal catalysts studying PDMS tagged triarylphosphine ligands. The good solubility of the newly synthesised copper complex in scCO<sub>2</sub> allowed us study its activity in an oxidation reaction carried out in the supercritical media. The compound showed good catalytic activity, though strangely we observed little difference in activity using the non-substituted (and insoluble) copper derivatives. We are presently studying the solubility and the catalytic activity of other metal systems incorporating these promising PDMS chains.

## ACKNOWLEDGMENTS

The authors thank the financial support from European Commission (Contracts MRTN-CT-2004-504005) and the Spanish Ministerio de Educación y Ciencia (Ramón y Cajal Contract and research project CTQ2004-84/PPQ)

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