

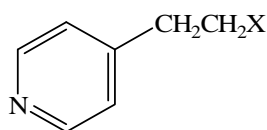
Specially Functionalised Ligands and Coordinating Supports which Facilitate Dissolution of Catalytic Transition Metal Species in Non-Polar “Green” Solvents, such as scCO_2

M. Herbert, A. Galindo, F. Montilla.* *Dpto. de Química Inorgánica, Universidad de Sevilla, Apto. 1203, 41071 Sevilla, Spain.*
E-mail: montilla@us.es. Fax: +34 954557153.

INTRODUCTION

For environmental, economic and moral reasons, the chemical industry is increasingly seeking to engage cleaner, sustainable processes where appropriate, in place of older more polluting technologies. In some cases, a means by which this might be achieved is via the substitution of organic solvents, which present a variety of environmental hazards, for “green” solvents. Non-toxic, largely inert supercritical carbon dioxide (scCO_2) which contributes zero net VOC emissions is an example of such a solvent [1]. In spite of some highly successful applications of scCO_2 , in general it is an extremely poor solvent, very non-polar and lacking the ability to dissolve all but the smallest molecules of any significant polarity. Dissolution of inorganic salts and the vast majority of metal complexes is therefore difficult and consequently homogeneous catalysis employing such compounds is not possible in the same way as in more conventional solvents. One strategy for improving the solubility of catalysts is the functionalisation of ligands with non-polar substituents [2]. Such groups include trimethylsilyl groups [3], carbosilane dendrimers [4] and polydimethylsiloxane (PDMS) [5].

We have previously employed 4-(polydimethylsiloxanyl-ethyl) pyridine, **1**, in the solubilisation of copper(II) acetate [6], a useful oxidation catalyst. In the work described here, we present selected results from our continued study of this ligand, investigating the isolation and characterisation of new supported metal complexes of palladium, rhenium and molybdenum and their possible application in homogeneously catalysed model oxidation processes.



MATERIALS AND METHODS

Unless stated, operations were carried out under dry oxygen-free nitrogen atmosphere employing conventional Schlenk techniques. All chemicals were obtained from Aldrich and used as supplied. Compound **1** was prepared as previously reported [6]. Aqueous $[\text{Mo}(\text{O})(\text{O}_2)_2]$ was prepared by reaction of MoO_3 and 30% $\text{H}_2\text{O}_2(\text{aq})$ and is hereon denoted $[\text{MoO}_5]$. Solvents were dried and purified with a suitable drying agent followed by distillation

carried out under nitrogen. A simple high-pressure apparatus, described elsewhere [7], was used to carry out reactions in scCO₂. Reaction conditions are noted aside relevant results in the Results and Discussion section. Pressurised reactions in conventional solvents employed a specially equipped tube reactor. Infrared spectra were recorded on Perkin-Elmer Model 883 spectrophotometer. NMR spectra were run on Bruker AMX-300 spectrometer. Gas Chromatography was run on a Varian CP-3800 gas chromatograph. Atomic absorption and elemental analysis were provided by the Microanalytical Services (CITIUS) of the University of Seville. Full characterisation of the new compounds **2-4** will be reported elsewhere [8].

Preparation of 4-(2-polydimethylsiloxanyl-ethyl)-pyridyl complexes (2-4).

di-{4-(2-polydimethylsiloxanyl-ethyl)-pyridyl} palladium diacetate (2). Palladium acetate (50.0 mg, 0.223 mmol) and **1** (225 mg, 0.45 mmol, 2 equiv.) were mixed in dry acetone (10 mL) and left stirring overnight. The acetone was then evaporated and to the resulting dark brown oil was added hexane (15 mL). The hexane was filtered off and the resulting yellow solution was left to stand for a week. During this time a beige sediment precipitated from which the solution was filtered and the hexane was then evaporated to leave the product as a yellow oil. *Elemental analysis* – Calculated: C = 36.11 %, H = 7.59 %, N = 1.30 %. Experimentally: C = 35.13 %, H = 7.59 %, N = 1.35 %. *Atomic absorption* – Pd = 4.47 %.

di-{4-(2-polydimethylsiloxanyl-ethyl)-pyridyl} palladium dichloride (3). PdCl₂ (52.0 mg, 0.293 mmol) and an ethanol solution (15 mL) of **1** (300 mg, 0.59 mmol, 2 equiv.) were left stirring at 80°C overnight. A dirty yellow solution, obviously containing a quantity of palladium black resulted. This solution was first filtered, giving a clear yellow solution, and then evaporated, leaving a clouded yellow oil. This was extracted with hexane and the solution then decanted off. Suspended sediments were removed by centrifugation and the solution again separated. Over the following week, the solution again became cloudy and the suspended solids were again removed by centrifugation and decantation before the solution was evaporated leaving the product as a clear yellow paste (16.8 mg). *Elemental analysis* – Calculated: C = 34.26 %, H = 7.59 %, N = 1.11 %. Experimentally: C = 36.01 %, H = 7.95 %, N = 0.99 %. *Atomic absorption* – Pd = 1.97 %.

4-(2-polydimethylsiloxanyl-ethyl)-pyridyl methyltrioxorhenium (4). A solution of **1** (37 mg, 0.73 mmol) and methyltrioxorhenium (17.9 mg, 0.072 mmol) in dry dichloromethane were stirred together resulting in dissolution of the metal compound to give a pale yellow solution. A static vacuum was applied and the solution was stirred at 40°C for 4 hours. The solvent was then evaporated, leaving a brown oil containing some solids. Dry ethanol was then added to dissolve these components and the solution again stirred at 40°C for 4 hours. The solvent was evaporated, again leaving a brown oil and some dark solids. This mixture was extracted with hexane, which dissolved the oil well but not the solids. The hexane solution appeared clear with a strong red-brown colour. The product was evaporated to leave the product, a brown oil (47.3 mg). Analysis of ¹H NMR integrals (see data below) indicated a ratio of 16.5 Si(CH₃)₂ to every pyridine, with ~75% of pyridines coordinated to methyltrioxorhenium. *Elemental analysis* – Calculated: C = 32.44 %, H = 7.28 %, N = 0.95 %. Experimentally: C = 36.54 %, H = 7.846 %, N = 1.453 %.

RESULTS AND DISCUSSION

Synthesis of the compounds.

The capacity of pyridyl compounds functionalised with PDMS-substituents, **1**, to facilitate homogeneous catalysis through solubilisation of catalytic complexes was investigated. Coordination compounds were prepared by appropriate reaction between the ligand and metal precursors (Table 1) and characterised by conventional methods [8]. The properties of the new compounds in scCO₂ were subsequently evaluated, studying two homogeneous catalysed oxidation models; the selective oxidation of benzyl alcohol catalysed by palladium, and cyclooctene epoxidation catalysed by molybdenum or rhenium. Catalytic activity in scCO₂ was evaluated and compared with that observed in conventional solvents.

Table 1. Synthesised complexes.

| Ligand (L) | Metal precursors | | | |
|---------------|--|---|--|---|
| | Pd(OAc) ₂ | PdCl ₂ | Re(CH ₃)O ₃ | [MoO ₅] |
| 1 | [Pd(OAc) ₂ (L) ₂] (2) ^a | [PdCl ₂ (L) ₂] (3) ^{a,b,d} | [Re(CH ₃)O ₃ (L)] (4) ^a | [Mo(O)(O ₂) ₂ (L) _x] (5) ^{c,d} |

^a metal complex isolated; ^b free ligand also present in product; ^c metal complex prepared *in-situ* in reactor; ^d proposed formula.

Catalytic reactions.

As shown in Table 1, palladium compounds of the PDMS substituted pyridyl ligand (**2** and **3**), were isolated and characterised. Both of these compounds are soluble in even very non polar solvents such as hydrocarbons. In previous work, with the analogous copper acetate compound, we were able to visually observe dissolution of the metal compound in scCO₂ [6], using a high pressure view cell. However, in the case of **2** we were unable to observe obvious dissolution at 150 bar and 40°C, leading to the conclusion that solubility was no better than fairly poor. This observation is supported by the results for the alcohol oxidations (Table 2).

Table 2. Palladium catalysed oxidation of benzyl alcohol.^a

| Solvent ^b | Catalyst | Yield (%) ^c | Conversion (%) |
|----------------------|--|------------------------|----------------|
| scCO ₂ | Pd(OAc) ₂ + C ₅ H ₅ N | 50,1 | 79,2 |
| | Pd(OAc) ₂ + 1 | 40,5 | 44,1 |
| | [Pd(OAc) ₂ (C ₅ H ₅ N) ₂] | 78,4 | 91,0 |
| | 2 | 95,0 | 100,0 |
| Toluene | Pd(OAc) ₂ + C ₅ H ₅ N | 92,1 | 100,0 |
| | Pd(OAc) ₂ + 1 | 88,1 | 98,1 |
| Hexane | Pd(OAc) ₂ + C ₅ H ₅ N | 38,2 | 36,2 |
| | Pd(OAc) ₂ + 1 | 32,3 | 34,8 |

^a Conditions: 80°C, 15 h, benzyl alcohol (1 mmol), O₂ (1 bar), catalyst (0.05 mmol, 5 %), free ligand (where appropriate) (0.2 mmol, 20 %). ^b Solvent: CO₂ (150 bar)/organic solvent (5 mL). ^c Yields calculated by GC using dodecane as internal standard.

Negligible difference was observed between PDMS substituted pyridine **1** and unsubstituted pyridine when the reaction was carried out in toluene and hexane, a likely explanation being that the reaction is proceeding via the same mechanism in both cases, most probably a homogeneous and heterogeneous one respectively. In scCO₂, the activity of compound **2** was observed to be slightly superior to the analogous palladium compound

containing pyridine, $[\text{Pd}(\text{OAc})_2(\text{C}_5\text{H}_5\text{N})_2]$, and yield and conversion were similar to those seen in toluene employing pyridine (where a homogeneous mechanism is likely). However, when the substituted and unsubstituted pyridine compounds were allowed to form *in-situ* results were actually better for unsubstituted pyridine. An overall analysis would seem to indicate that any increased scCO_2 solubility that **2** has over its unsubstituted pyridine analogue has little bearing on the rate of catalysis, that a largely heterogeneous mechanism was predominant for all reactions in hexane and scCO_2 , and consequently that scCO_2 solubility of **2** is at best very low.

Also studied were cyclooctene epoxidations, catalysed by molybdenum or rhenium, employing **1** to aid solubility of the catalysts (Table 3). The preliminary results obtained in scCO_2 were all negative with no conversion. This is in contrast to the results in Cl_3CH for molybdenum and hexane for rhenium where improved conversions were seen compared to pyridine analogues.

Table 3. Catalysed cyclooctene epoxidation.^a

| Solvent ^b | Catalyst | Conversion (%) ^c |
|------------------------|--|-----------------------------|
| scCO_2 | $\text{MoO}_5 + \mathbf{1}$ | 0.0 |
| | 4 | 0.0 |
| Cl_3CH | $\text{MoO}_5 + \text{C}_5\text{H}_5\text{N}$ | 2.0 |
| | $\text{MoO}_5 + \mathbf{1}$ | 85.3 |
| Hexane | $\text{Re}(\text{CH}_3)_3\text{O}_3(\text{C}_5\text{H}_5\text{N})$ | 21.8 |
| | 4 | 99.2 |

^a Conditions: 60°C, 18 h, cyclooctene (1 mmol), catalyst (0.025 mmol, 2.5 %), ligand (0.05 mmol, 5 %), 30% aqueous H_2O_2 (1.25 mmol 125 %). ^b Solvent : CO_2 (150 bar)/Liquid solvent (10 mL). ^c Conversions calculated by GC using dodecane as internal standard.

CONCLUSIONS

Coordination compounds of a PDMS substituted pyridinyl ligand (**1**) were prepared and characterised. Novel solubility properties were observed for PDMS functionalised compounds, but though scCO_2 solubility was previously demonstrated for an analogous compound, compounds **2-5** showed little evidence of this or improved performance as oxidation catalysts.

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