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Synthesis and theoretical analysis of palladium complexes of polydimethylsiloxane functionalised pyridine and their catalytic activity in alcohol oxidations under low polar conditions

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ABSTRACT

Palladium(II) complexes of polydimethylsiloxane (PDMS)-functionalised pyridine (**1**), $[Pd(OAc)_2(\mathbf{1})_2]$ (**2**) and $[PdCl_2(\mathbf{1})_2]$ (**3**), were synthesised and characterised. The *cis*/*trans* isomerism of models of complex **3** was investigated using DFT calculations. Models of complex **2** were also theoretically analysed, to identify any possible C–H···O interactions. Complex **2** was investigated as a catalyst for selective alcohol oxidations both under solventless conditions and in supercritical carbon dioxide ($scCO_2$). In $scCO_2$ the presence of **1** was found to stabilise the palladium complex, inhibiting its decomposition to Pd(0), a stabilisation not witnessed with non-PDMS functionalised pyridine analogues.

1. Introduction

The use of solubilising polymer substituents in catalysis is a strategy with numerous precedents [1]. However, the incorporation of light polysiloxanes, such as polydimethylsiloxanes (PDMS), into catalyst structures to facilitate catalysis in non-polar media was not reported until relatively recently [2]. PDMS is chemically and thermally very stable, non-volatile and possesses high gas permeability. Besides these properties, these polymers display relatively good solubility in nearly all organic solvents including even very non-polar media such as $scCO_2$ [3], which due to its advantageous properties, is attracting increasing interest as a media for homogeneous catalysis [4]. However, $scCO_2$ shows generally poor solvent properties and is very non-polar [5], which often complicates its use as a reaction solvent. The solubilities of reaction components, in particular transition metal catalyst complexes, are often too low to permit any kind of efficient reaction. In this regard, the past few years have now seen a number of publications on PDMS solubilisation in catalytic systems [6] including incorporation of Jacobsen [7] and Grubbs [8] catalysts in PDMS membranes. The functionalisation of phosphine ligands with PDMS has been used to solubilise a metal complex in $scCO_2$, facilitating homogeneous catalysis [9]. Similarly our own research group has described ligand functionalisation with trimethylsilyl [10a–c] and carbosilane dendron groups [10d] producing soluble metal complexes that were active catalysts in $scCO_2$.

Additionally, some of our more recent work has begun to investigate the use of PDMS functionalised ligands in the solubilisation of catalyst complexes in $scCO_2$. This work has centred on our investigations of the PDMS functionalised pyridine ligand 4-(polydimethylsiloxanyl-ethyl)pyridine (**1**) (Scheme 1) and we have prepared complexes of rhenium [11a], copper [11b,c] and molybdenum [11d] incorporating **1** which showed novel catalytic properties.

A wide range of catalytic organic transformations facilitated by palladium compounds have been developed and extensively studied [12]. PDMS functionalised complexes with high solubilities in very non-polar media might therefore have applications in a range of catalytic processes and indeed, while this work was in progress, Mizoroki-Heck reactions catalysed by soluble polysiloxane-supported palladium catalysts were described [13]. Consequently, the preparation of palladium(II) complexes of ligand **1** is reported here, including our observations and some results from catalytic studies of alcohol oxidation in apolar media. Due to the capacity of $scCO_2$ to mix perfectly with gaseous reagents, such as dioxygen, there are obvious additional advantages to its use in this reaction [14].

2. Results and discussion

2.1. Synthesis of PDMS functionalised palladium(II) complexes

Palladium(II) acetate [15] possesses good solubility in the majority of organic solvents, including halocarbons and toluene.

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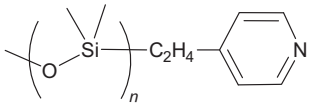


Scheme 1. Polydimethylsiloxane functionalised pyridine **1**.

However, its solubility in highly apolar media, such as hexane is demonstrably poor. Preparation of the complex of ligand **1** was therefore interesting, since the PDMS functionalisation would be anticipated to improve the solubility in this type of media. 4-(Polydimethylsiloxanyl-ethyl)pyridine (**1**) was prepared by the hydrosilylation of 4-vinylpyridine with hydride terminated polydimethylsiloxane catalysed by Karstedt's catalyst, following the procedure previously described by us [11]. Preliminary spectroscopic data and a more detailed characterisation of **1** have already appeared and therefore this will not be discussed again here [11]. Ligand **1** consists of a 2:1 mixture of the β and α addition products of the hydrosilylation reaction. Reaction of palladium(II) acetate with **1** yields the corresponding coordination complex of diacetatopalladium, **2**. This compound was characterised as $[Pd(OAc)_2(\mathbf{1})_2]$ (Scheme 2), taking the form of a yellow oil. The product workup requires extraction with hexane, confirming solubility of the product in such low polar solvents. Analysis of the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **2** demonstrated that complexes with a low *n* value (*n* = the number of PDMS monomer units $\{Si(CH_3)_2\text{-}O\}_n$ per terminal pyridine) and those of the α-addition isomer of **1** had been eliminated during the product workup. In the ^1H NMR spectrum of **2** shown in Fig. S1 (Supplementary data), only signals corresponding to the β-addition isomer of **1** are present, the $CHCH_3$ peaks observable at 1.29 and 1.85 ppm in the spectrum of **1** now absent, with only one peak each for the protons of the pyridine ring, indicating the presence of only one isomer. Similarly in the $^{13}C\{^1H\}$ NMR spectrum (see Fig. S2), only signals corresponding to the β-addition isomer are visible. From the peak integrals of the ^1H NMR spectrum the value of *n* was calculated to be 13, whilst $n \approx 5$ had been calculated for the sample of **1** from which **2** was prepared, indicating that the part of **2** formed from fractions of **1** with lower *n* were eliminated during the workup, presumably due to poorer solubility in the very low polar hexane used to extract the product. Evidence supporting this was obtained in the synthesis of the dichloro analogue, **3**, discussed below, and similar β isomeric purification and *n* increase was observed in the synthesis of methyltrioxorhenium analogues [11a].

Pure dichloropalladium adopts a polymeric structure with μ_2-chloride bridges and displays very poor solubility in most media; typically it is dissolved by refluxing in a coordinating solvent such as acetonitrile or benzonitrile forming the corresponding monometallic coordination complex which can then undergo substitution reactions. The synthesis of the dichloropalladium complex of **1**, namely **3**, was achieved by heating the two components at 80 °C in ethanol overnight, followed by hexane extractions of the product. Complex **3** was obtained as a yellow oil and identified as $[PdCl_2(\mathbf{1})_2]$ (Scheme 2). Similar to the diacetato counterpart **2**, only complexes formed from the β-addition complex of **1** were present in the final isolated sample of **3**, there was no observable trace of the α-addition product of **1**. Also in common with **2**, **3** possessed a far higher value of *n*, approximately 15, than the sample of **1** from which it was prepared (again $n \approx 5$). It was assumed that **3** complexes formed from the lower *n* fractions of **1** were being eliminated during the workup, due to their insolubility in hexane. Evidence that this was the case was obtained from ^1H NMR analysis of the last solid fraction from which **3** was separated. Examination of the integrals showed an *n* value of 4, indicating that the lower polymer lengths in this sample were insufficient for solubilisation in hexane.

2.2. Theoretical analyses of complexes 2, 3, $[PdCl_2(py)_2]$ and $[PdCl_2(4VP)_2]$ (4VP = 4-vinylpyridine)

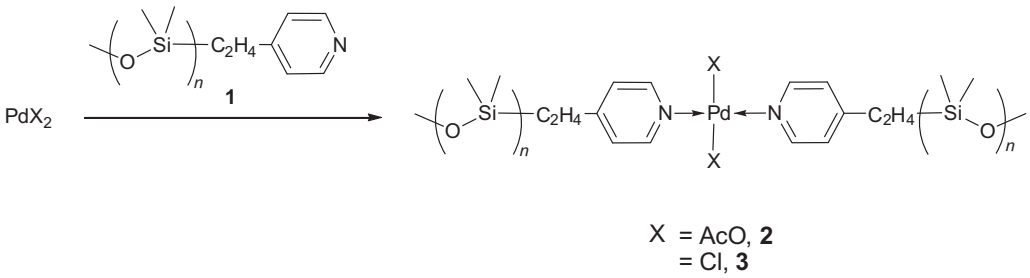
In a previous work, *trans*/*cis* isomerism in related $[PdCl_2(P)_2]$ complexes, with P representing a phosphine species with a carbosilane dendron function, was analysed [10d]. A similar theoretical study has now been carried out for the complexes discussed here. Scheme 2 shows the *trans*-configuration for complexes **2** and **3**. Experimentally this is the most stable configuration that $[PdCl_2(N)_2]$ compounds can adopt (N representing a monodentate N-donor ligand). In some cases, the *cis* isomer is isolable, but will convert to the thermodynamically favourable *trans* isomer when heated. All *cis*-dichloropalladium complexes with pyridine-type coligands to have been X-ray characterised have a bidentate ligand (usually bipyridine or related) which forces the geometry.[1] To confirm that the *trans* isomer is the most stable for complexes **2** and **3**, a theoretical DFT type analysis was conducted for several model compounds representing complexes **2** and **3** (Scheme 3). The model compounds possessed two *p*-ethyl-PDMS (β isomer[2]) functionalised pyridines, the shortened ($n = 2$ or 4) PDMS functions terminating with $Si(CH_3)_3$, $(NC_5H_4\text{-}CH_2CH_2\text{-}(SiMe_2O)_n\text{-}Si(CH_3)_3)$. The $[PdCl_2(py)_2]$ and $[PdCl_2(4VP)_2]$ complexes were also computed for comparative purposes.

The DFT study began by investigating the chloride complexes with shorter PDMS chains ($n = 2$), model $\mathbf{3_2}$. The optimised structures calculated for *trans*-$\mathbf{3_2}$ and *cis*-$\mathbf{3_2}$ are shown in Fig. S3 (Supplementary data). Energetically, the *trans* isomer was calculated to be more stable than the *cis* by 10.0 kcal mol^{-1} (electronic energy). In order to evaluate the importance of steric factors in this difference, calculations were carried out for the analogous *cis*- and *trans*-isomers of $[PdCl_2(py)_2]$ and $[PdCl_2(4VP)_2]$ using the same computational level. Fig. S4 shows the optimised structures. Roughly the same energy difference was computed between the two isomers (ca. 12 kcal mol^{-1}). This indicates that steric influences from the PDMS chains have no significant role in stabilising the *trans* isomer with respect the *cis*. Calculations performed for the complex with longer PDMS chains ($n = 4$), model $\mathbf{3_4}$, again found the *trans* isomer to be more stable than the *cis* by 10.9 kcal mol^{-1}. The optimised structures calculated for *trans*-$\mathbf{3_4}$ and *cis*-$\mathbf{3_4}$ are shown in Fig. 1. The PDMS substituents, located relatively far away from the metal centre, have a high degree of conformational freedom and thus can easily adopt conformations which minimise steric repulsions, even in the *cis* isomer.

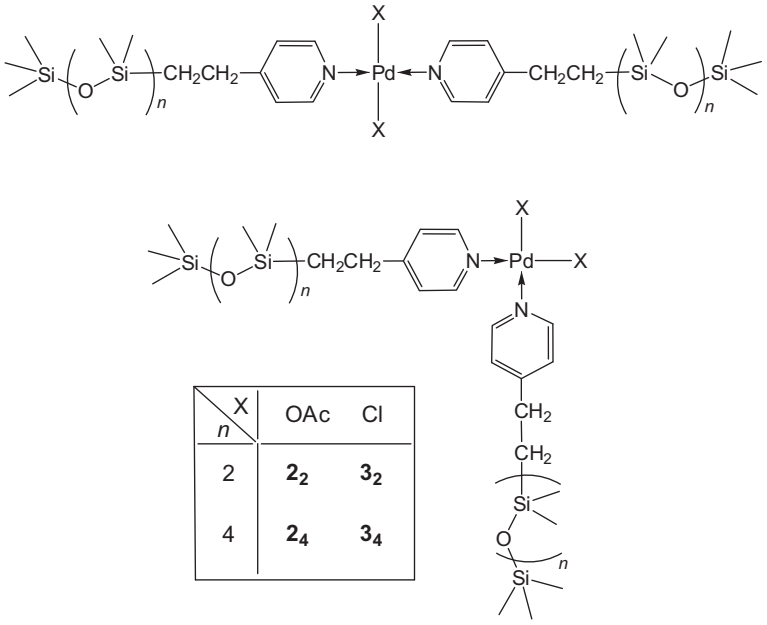
The complex subsequently studied in catalysis (see below) was the acetate derivative **2**, and the theoretical study was thus extended to the models *trans*-$\mathbf{2_2}$ and *trans*-$\mathbf{2_4}$. Fig. 2 shows the corresponding optimised structures. Previously, theoretical studies carried out for model methyltrioxorhenium (MTO) complexes of the PDMS functionalised pyridine, showed C–H···O interactions between the PDMS chains and the oxo groups of the rhenium [11a]. These interactions likely play an important role in stabilising the catalyst complex during epoxidative catalysis, leading to significantly enhanced TONs. In the palladium acetate models $\mathbf{2_2}$ and $\mathbf{2_4}$, however, no such interaction involving the PDMS chains was observable in proximity to the metal centre. Consequently, the higher stability of **2** under the catalytic conditions, compared with its unsubstituted analogue (see discussions below), is unlikely to be attributable to any C–H···O type interaction involving the PDMS chain.

[1] CSD Search. Cambridge Structural Database System, Cambridge Crystallographic data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

[2] Calculations of the α and β isomers of ligand **1** appeared in Ref. [11a].



Scheme 2. Synthesis of palladium complexes with PDMS functionalised pyridine ligands.



Scheme 3. Models used in the DFT study.

2.3. Palladium catalysed aerobic alcohol oxidation in apolar media

The majority of palladium(II) catalysed homogeneous alcohol oxidation systems to have been reported, including those of Peterson and Larcock [16], Uemura et al. [17a,b], and Sigman et al. [18], typically employed organic solvents (e.g. DMSO, toluene and THF) as the reaction medium. Sheldon et al. introduced an aqueous system, employing a palladium catalyst with ligands possessing ionic functional groups, that was soluble in the highly polar reaction media [19]. This system is highly effective in the conversion of smaller more polar alcohols with sufficient solubilities in water, which form a biphasic reaction system with the "green" aqueous reaction solvent. This system is a good example of a catalyst being designed to function well in a specific reaction environment. In a similar vein the work described here aimed to facilitate active catalysis in very apolar media, such as "green" $scCO_2$ and solventless conditions. Having developed palladium complexes with good solubilities in low polar media, their catalytic efficacy in the selective oxidation of alcohol substrates in such reaction conditions was thus examined.

The oxidation mechanism requires deprotonation of the alcohol substrate, a step which cannot be catalysed by non-specialised dichloro complexes, rendering them inactive as catalysts in this particular transformation [17c]. The dichlorocomplex **3** would therefore not be expected to be catalytically active in this transformation, and thus it was not investigated. Carboxylate complexes, however, are quite capable of facilitating the oxidation mechanism and thus the diacetatopalladium complex **2** has potential as a catalyst for this process. The principle objective of the ensuing catalytic study was to demonstrate advantages stemming from the solubility of the catalyst in very non-polar media, which might permit homogeneous catalysis under conditions where it would be impossible to use a non-PDMS functionalised analogue to obtain decent product yields. The activity of **2** in the catalytic oxidation of alcohols to their corresponding carbonyl products was thus investigated both in solventless conditions and in $scCO_2$.

2.4. Oxidation of 2-octanol under solventless conditions

In a previous publication we presented a highly efficient solventless epoxidation system employing ligand **1** in conjunction with methyltrioxorhenium as catalyst and we hoped to observe a similar enhancement using palladium in alcohol oxidations [11a]. Since the objective of this study was to demonstrate whether **2** would display enhanced activity compared to non-PDMS functionalised analogues in very low polar conditions, a low polar alcohol substrate, 2-octanol, was chosen for the study of activity in a solventless system. A more polar substrate, e.g. benzyl alcohol, would likely dissolve unfunctionalised analogues of **2** very efficiently, with there thus being no necessity to enhance the solubility of the catalyst complex. Under some standard conditions [17a,b] a study of the solventless oxidation of this substrate catalysed by

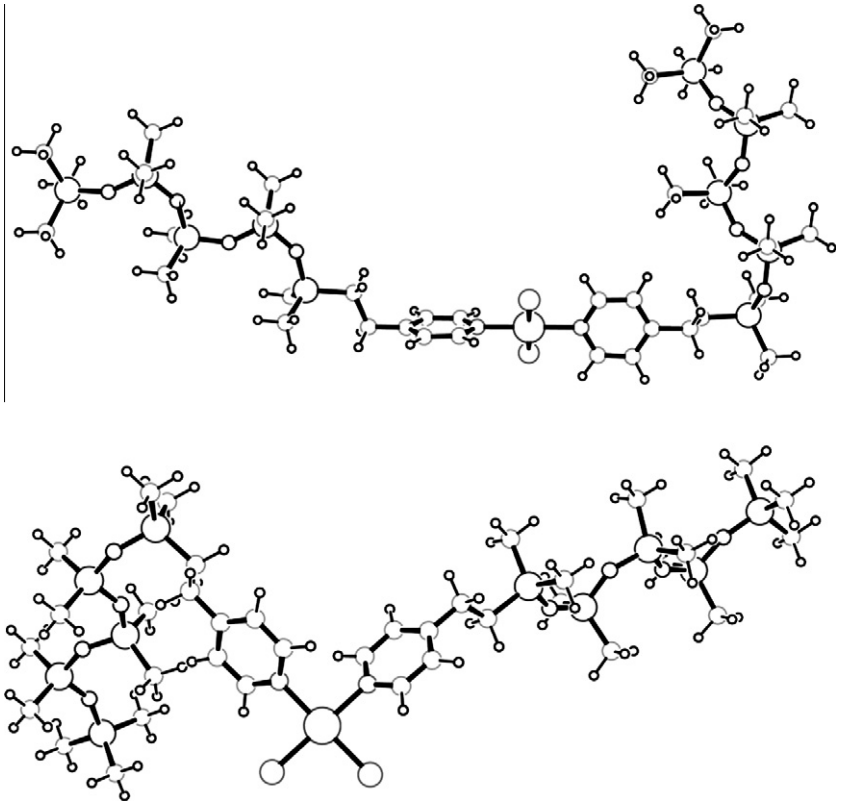


Fig. 1. Optimised structures of model compounds *trans*-$\mathbf{3_4}$ and *cis*-$\mathbf{3_4}$.

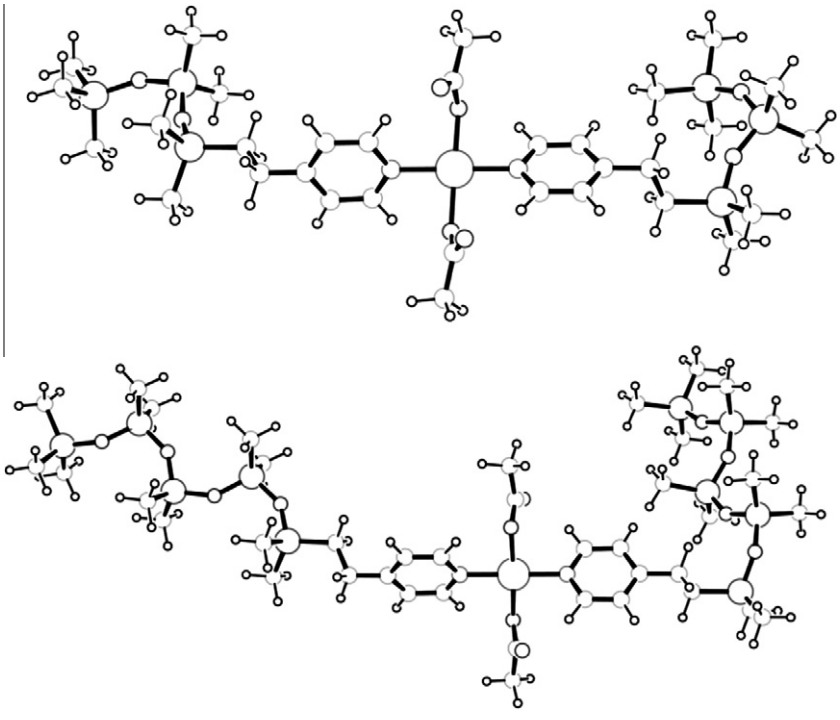


Fig. 2. Optimised structures of model compounds *trans*-$\mathbf{2_2}$ and *trans*-$\mathbf{2_4}$.

$[Pd(OAc)_2]$ was conducted, examining the influence of both unfunctionalised pyridine and **1** on the reaction. Dioxygen was used as oxidant. The results are shown in Table 1.

Both base species were found to inhibit the rate of the oxidation reaction (compare entries 2 and 3 with entry 1, Table 1). When no base species was employed a markedly higher yield was obtained whilst pyridine and **1** both reduced the level of conversion to around a third. This is in common with observations made even in early examples of Pd(II) catalysed alcohol oxidations where coordinating bases were observed to prevent catalyst decomposi-

Table 1
Solventless oxidation of 2-octanol.[a]

Entry	Ligand	Alcohol substrate	Yield (%)
1	–	2-Octanol	69
2	Pyridine	2-Octanol	28
3	**1**	2-Octanol	23

[a] $t_{reaction}$ = 18 h, T = 80 °C, alcohol substrate (5.0 mmol), [$Pd(OAc)_2$] (0.05 mmol, 1%), ligand (0.25 mmol, 5%), and O_2 (1 bar).

tion but also reduce the reaction rate. There was little difference in the yields obtained using **1** (entry 3, Table 1) or unfunctionalised pyridine (entry 2, Table 1), seemingly indicating that using the former did not result in any enhancement of the catalytic system. However, in the reactions which employed base species, the catalyst was observed to retain its yellow orange colour at the end of the reaction time, whilst in the reaction run in the absence of base the palladium had apparently converted completely to palladium black. These observations are in common with those regularly observed in Pd(II) catalysed alcohol oxidations [17a,b,20], where coordinating bases inhibit the mechanism of the oxidation by competing with the substrate for coordination sites, but also inhibit decomposition of the catalyst by preventing agglomeration of the Pd(0) complex which forms during the catalytic cycle. There are two possible reasons for the higher yield observed here when no base species was employed. It may be that the oxidation by the [$Pd(OAc)_2$] proceeded very quickly for a short period with a relatively high yield produced before the catalyst was deactivated by its reduction to palladium black. In this case the less active catalyst species were not able to reach a higher level of conversion during the reaction time despite the greater stability and thus much higher catalyst lifetime in these systems. The other possibility is that the reaction was actually efficiently catalysed by the palladium black formed from the catalyst decomposition when no base was employed and that this catalytic system was actually more active than the [$Pd(OAc)_2$]-base systems [21].

2.5. Oxidation of 2-octanol in $scCO_2$

Due to the desirable sustainability credentials of the solvent, alcohol oxidations which utilised $scCO_2$ as the reaction medium would present advantages from a green perspective. Additionally, with gaseous O_2 as the oxidant, improved reaction rates and selectivities might be realised due to the perfect miscibility of the oxidant with $scCO_2$. Our previous studies with copper complexes demonstrated that PDMS substituents can confer solubility in $scCO_2$ to a catalyst precursor [11b,c] and a similar solubilisation was considered possible for the palladium complexes. Diacetatopalladium complexes of simple bases, i.e. pyridine, should possess negligible solubilities in $scCO_2$. However, the PDMS functionalisation of catalyst **2** apparently facilitates its dissolution to some extent (see Fig. S5 in Supplementary data), which is potentially crucial in activating the catalyst in a homogeneous catalytic system. A brief study investigating the catalytic oxidation of benzyl alcohol and 2-octanol by the PDMS functionalised palladium(II) acetate catalyst and some unfunctionalised analogue complexes in $scCO_2$ was thus conducted. The results are presented in Table 2.

Table 2
Oxidation of alcohols in $scCO_2$.[a]

Entry	Catalyst/ligand	Alcohol substrate	Yield (%)
1	[$Pd(OAc)_2$]/4-vinylpyridine	Benzyl alcohol	30
2	[$Pd(OAc)_2$]/**1**	Benzyl alcohol	40
3	[$Pd(OAc)_2(4VP)_2$]	Benzyl alcohol	30
4	**2**	Benzyl alcohol	35
5	[$Pd(OAc)_2$]/pyridine	2-Octanol	26
6	[$Pd(OAc)_2$]/**1**	2-Octanol	2

[a] $t_{reaction}$ = 18 h, T = 80 °C, $P(CO_2)$ = 150 bar, $P(O_2)$ = 1 bar, alcohol substrate (5.0 mmol), [Pd] (0.05 mmol, 1%), and ligand (0.25 mmol, 5%).

In the oxidation of benzyl alcohol (entries 1–4, Table 2) only negligible differences in the catalytic activity of the PDMS functionalised catalyst (entries 2 and 4, Table 2) and the unfunctionalised analogue complex of 4-vinylpyridine (entries 1 and 3, Table 2) were observed, regardless of whether the catalyst complex was previously synthesised or allowed to form *in situ*. This latter observation would seem to indicate that the coordination complex of palladium acetate and the ligand species formed fairly quickly in the reactor. In the oxidation of 2-octanol (entries 5 and 6, Table 2), when unfunctionalised pyridine was used a limited yield was recovered (entry 5, Table 2). However, when **1** was used only trace conversion to the product was witnessed (entry 6, Table 2).

From the results it can quickly be concluded that in no case did **1** confer any advantage to the catalytic system through dissolution of the palladium catalyst, as had been hoped. The study with respect to catalytic applications was therefore concluded. It is interesting, however, to make note of the state of the palladium catalyst following the oxidation in each case. When unsubstituted pyridines were employed the catalyst was completely reduced to palladium black, deposited onto all of the internal surfaces of the reactor (see vial (a) in Fig. S6, Supplementary data). In contrast, when **1** was employed the palladium apparently largely survived as a Pd(II) complex, coating the sides of the reactor as the oily orange coordination compound (see vial (b) in Fig. S6). This indicated that under the reaction conditions **2** possessed greater stability than its unsubstituted analogue. In analogous fashion, in diacetatopalladium catalysed alcohol oxidations in standard organic media, coordinating bases such as DMSO [22] and pyridine [20] are observed to prevent catalyst decomposition by stabilising intermediate Pd(0) complexes in solution, preventing coagulation as palladium black nanoparticles.

3. Experimental

3.1. General

All preparations and other operations were carried out under dry anaerobic conditions. Solvents were dried, using standard procedures. Palladium compounds and other chemicals were purchased from Aldrich and were used as supplied. Infrared spectra were recorded on Perkin–Elmer Model 883 spectrophotometer. NMR spectra were obtained using a Bruker AMX-300 spectrometer. $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si. Elemental analysis (C, H, N) were performed on an Elemental LECO CHNS 93 analyser by the Microanalytical Service of the Universidad de Sevilla (CITIUS).

3.2. Synthesis of trans-[$Pd(OAc)_2(4VP)_2$]

Working always under N_2, two equivalents of 4-vinylpyridine (4VP) (113.5 μL, 1.0 mmol) were added to a solution of palladium(II) diacetate (112.2 mg, 0.5 mmol) in Cl_2CH_2 (10 mL). Immediate precipitation of the product as a yellow solid was observed and the mixture was left to stir for 6 h. Subsequently the product was separated by decantation and the solvent removed under vacuum yielding the crude product as a yellow powder. Recrystallisation from Cl_2CH_2 yielded [$Pd(OAc)_2(4VP)_2$] as a microcrystalline yellow solid (145.7 mg, 0.335 mmol, 67% yield). IR (KBr, cm^{-1}): 695, 853, 874, 925, 956, 995, 1012, 1033, 1076, 1306, 1377, 1454, 1598, 2853, 2923. ^1H NMR ($CDCl_3$): δ 1.86 (s, 3H, CH_3CO_2),

5.62 (m, 1H, Py-CHCH$_{cis}H_{trans}$, *cis*/*trans* with respect to 4-pyridyl group), 6.03 (m, 1H, Py-CHC$H_{cis}H_{trans}$), 6.65 (m, 1H, Py-C*H*CH$_2$), 7.29 (m, 2H, *m*-NC$_5$H$_4$), 8.61 (m, 2H, *o*-NC$_5$H$_4$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.3 (CH_3CO_2), 121.7 (Py-CHCH$_2$), 121.7 (*m*-NC$_5$H$_4$), 133.3 (Py-*C*HCH$_2$), 147.2 (*p*-NC$_5$H$_4$), 151.5 (*o*-NC$_5$H$_4$), 178.1 (CH_3CO_2). *Anal.* Calc. for $PdC_{18}H_{20}N_2O_4$ (434.78): C, 19.72; H, 4.64; N, 6.44. Found: C, 19.29; H, 4.76; N, 6.44%.

3.3. Synthesis of trans-[Pd(OAc)$_2$(**1**)$_2$], (**2**)

A mixture of palladium(II) diacetate (50.0 mg, 0.22 mmol) and **1** (225 mg, 0.45 mmol) in dry acetone (10 mL) was stirred at room temperature overnight. The reaction mixture was then evaporated to dryness by application of vacuum. The resulting brown oil was extracted with hexane (15 mL) affording a brownish solution, which was left for a week at room temperature. A beige precipitate was observed to precipitate, leaving a yellow solution which was separated by decantation followed by centrifugation and evaporated under vacuum to leave compound **2** as a yellow oil (40 mg, 8% yield in [Pd]). IR (NaCl, cm^{-1}): 661, 696, 801, 863, 916, 1026, 1092, 1261, 1310, 1366, 1412, 1434, 1502, 1576, 1598, 1619, 2905, 2962, 3351. ^{1}H NMR ($CDCl_3$): δ 0.06 (s, ~156H, Si(CH_3)$_2$), 0.84 (t, J_{HH} = 5.4 Hz, 4H, Py-CH$_2$CH_2-Si), 1.83 (s, 6H, CH_3CO$_2$), 2.65 (t, J_{HH} = 5.3 Hz, 4H, Py-CH_2CH$_2$-Si), 7.13 (m, 4H, *m*-NC$_5$H$_4$), 8.51 (m, 4H, *o*-NC$_5$H$_4$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.00 (Si(*C*H$_3$)$_2$), 18.60 (Py-CH$_2$*C*H$_2$-Si), 23.18 (*C*H$_3$CO$_2$), 28.81 (Py-*C*H$_2$CH$_2$-Si), 124.30 (*m*-NC$_5$H$_4$), 150.99 (*o*-NC$_5$H$_4$), 157.41 (*p*-NC$_5$H$_4$), 178.14 (CH$_3$*C*O$_2$). ^{29}Si{^{1}H} NMR ($CDCl_3$): δ −21.97 (s, O-*Si*(CH$_3$)$_2$-O), −20.80 (s, CH$_2$-*Si*(CH$_3$)$_2$-O). *Anal.* Calc. $PdC_{70}H_{176}N_2O_{30}Si_{26}$ (2362.78, formula for *n* = 13): Pd, 4.50; C, 35.58; H, 7.51; N, 1.19. Found: Pd, 4.47; C, 35.13; H, 7.59; N, 1.35%.

3.4. Synthesis of trans-[PdCl$_2$(**1**)$_2$], (**3**)

A mixture of palladium(II) dichloride (52.0 mg, 0.293 mmol) and **1** (300 mg, 0.59 mmol, 2 equiv.) in ethanol (15 mL) was stirred at 80 °C overnight. The resulting mixture was then filtered to remove palladium black which had formed affording a yellow solution. The solvent was then evaporated by applying vacuum leaving a turbid yellow oil. This was extracted with hexane with the resulting yellow solution separated from the solid residues by centrifugation and left for a week at room temperature. A brown solid precipitated which was separated by centrifugation, the solution affords compound **2** in the form of a yellow gum (52.4 mg, 3.3% yield in [Pd]). IR (NaCl, cm^{-1}): 659, 689, 703, 798, 863, 954, 1097, 1261, 1413, 1430, 1617, 2905, 2963. ^{1}H NMR ($CDCl_3$): δ 0.09 (s, ~180H, Si(CH_3)$_2$), 2.68 (t, J_{HH} = 8.7 Hz, 4H, Py-CH_2CH$_2$-Si), 7.17 (m, 4H, *m*-NC$_5$H$_4$), 8.67 (m, 4H, *o*-NC$_5$H$_4$). *Anal.* Calc. $PdC_{74}H_{194}N_2O_{30}Cl_2Si_{30}$ (2612.22): Pd, 4.07; C, 34.02; H, 7.49; N, 1.07. Found: Pd, 1.97; C, 36.01; H, 7.95; N, 0.99%.

3.5. Computational details

The electronic structure and geometries of the model compounds were computed by density functional theory at the B3LYP level [23,24]. The Pd atom was described using the LANL2DZ basis set [25,26], while the 6-31G* basis set was used for the Cl, Si, C, O, N and H atoms. The optimised geometries of the compounds *trans*- and *cis*-[PdCl$_2$(py)$_2$] and *trans*- and *cis*-[PdCl$_2$(4VP)$_2$] (4VP = 4-vinylpyridine) were characterised as energy minima by the nonexistence of imaginary frequencies (NImag = 0) in the diagonalisation of the analytically computed Hessian (vibrational frequencies calculations). For the larger systems, **2$_2$**, **2$_4$**, **3$_2$** and **3$_4$**, frequency calculations were considered too expensive and were not carried out. DFT calculations were performed using the GAUSSIAN 03 suite of programs [27]. Coordinates of all optimised compounds are collected in Supplementary data.

3.6. General experimental procedure for the 2-octanol oxidation reactions

3.6.1. Solventless

Reactions were conducted in a glass Lab Crest® reactor equipped with a high pressure valve. The specified quantities (see footnote to Table 1) of catalyst and alcohol substrate were charged and the reactor sealed. O_2 (1 bar) was then applied and the reactor heated at 80 °C with stirring for the duration of the reaction. When the reaction had finished the reactor was cooled in an ice bath and de-pressurised. The products were then dissolved in an appropriate solvent and analysed by GC.

3.6.2. In $scCO_2$

Catalytic reactions in $scCO_2$ were carried out in a in a 27 mL stainless steel high-pressure cell. The 2-octanol substrate was charged to the reactor along with a stirrer flea and the specified quantity (see footnote to Table 2) of catalyst was then introduced in a separate vial also containing a small stirrer flea, in this manner preventing contact between the substrate and co-catalysts during the reaction without dissolution occurring. The reactor was sealed and air removed by application of vacuum. O_2 (1 bar) was then introduced, the reactor heated to 80 °C in a thermostatted oil bath and CO_2 was pumped until 150 bar was achieved. Stirring was then initiated. After reaction the reactor was cooled in an ice bath and de-pressurised through a solvent trap. The products were extracted from the reactor with an appropriate solvent and the extract combined with the contents of the solvent trap. The solution was then analysed by GC.

4. Conclusions

In summary, the [Pd(OAc)$_2$(**1**)$_2$] (**2**) and [PdCl$_2$(**1**)$_2$] (**3**) compounds have been synthesised via the reactions of the corresponding palladium(II) precursor with polydimethylsiloxane (PDMS)-functionalised pyridine (**1**), and adequately characterised. DFT calculations have been performed with models of **2** and **3** in order to investigate the *cis*/*trans* isomerism in such a complexes and to identify any possible C–H···O interactions in **2**. Complex [Pd(OAc)$_2$(**1**)$_2$] (**2**) has been investigated as a catalyst for selective alcohol oxidations both under solventless conditions and in supercritical carbon dioxide ($scCO_2$). The PDMS functionalised pyridine ligand **1** was thus shown not to confer significant advantages in alcohol oxidations in the apolar environments of either solventless or $scCO_2$ reactions. However, the apparent stability of **2** compared to unfunctionalised analogues under the reaction conditions may indicate that in other palladium catalysed systems where **2** was more active there could be some advantage to its use. With palladium(II) catalysts being useful in a wide range of transformations, not limited to oxidation reactions, there may well exist systems in which the functionalised complexes **2** and **3** would represent ideal specialised catalysts. Further studies in this direction are in progress.

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Appendix A. Supplementary data

Spectra of **2**, optimised structures of $\mathbf{3_2}$, $[PdCl_2(py)_2]$ and $[PdCl_2(4VP)_2]$, solubilisation of **2** in $scCO_2$, visual appearance of catalysts after the oxidation reactions in $scCO_2$ and coordinates of optimised compounds.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.09.004.

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