# Aerobic Oxidation of 1-Phenylethanol Catalyzed by Palladaheterocycles

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Received: October 10, 2003; Accepted: February 10, 2004

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de.

**Abstract:** Cyclometallated palladium compounds with pyridine were shown to serve as more efficient catalysts for the aerobic oxidation of 1-phenylethanol than a previously investigated analogue with an oxazoline ring. Substituents with different electronic properties in the phenyl ring were shown to exhibit an only minor influence on the reactivity of the catalytic system. The first step in the reaction consists of the splitting of the acetate bridge in the dimeric starting complex and coordination of a ligand to palladium. By *ab initio* calculations it was shown that, in the presence of solvent, a complex with pyridine was more stable than that with the alcohol, whereas the opposite situation was found in the gas phase. The complex with coordinated alcohol was stabilized by hydrogen bonding. Good agreement was found between the computed structure and the X-ray structure of the initial palladaheterocycle **1**.

**Keywords:** alcohols; computer chemistry; heterocycles; oxidation; palladium; X-ray diffraction

## Introduction

The oxidation of alcohols to carbonyl compounds is one of the most important organic chemical transformations. Traditionally stoichiometric inorganic reagents, usually with high toxicity, have been employed as oxidants.[1] The need for more economic and environmentally benign processes has stimulated the development of green catalytic methods.[2] Recently various protocols where oxygen serves as the stoichiometric oxidant have been developed.[3] Catalysts based on palladium have been most commonly employed,[4] but complexes based on other metals also work. Of particular interest are those which use oxygen from air at ambient pressure as the oxidant; some examples are provided by catalysts containing Fe,[5] Os/Cu,[6] Cu,[7] Ru,[8] Ru in ionic liquids,[9] and Pt.[10]

For palladium-catalyzed reactions $Pd(OAc)_2$/DMSO/$O_2$[11] and $Pd(OAc)_2$/pyridine/$O_2$[12] have been most commonly employed as starting complexes. The reactions usually occur at about 80 °C. Replacing pyridine by triethylamine in the latter type of system yielded a catalyst which was active even at ambient temperature.[13] The mechanism of the $Pd(OAc)_2$/pyridine/$O_2$ process has been suggested to involve formation of a palladium-alkoxide complex and β-elimination as the key steps.[14] Sparteine, used in place of pyridine, was shown to have a dual role and serve both as a base and as a ligand.[15]

We recently discovered that primary and secondary alcohols are oxidized to aldehydes and ketones, respectively, when stirred in an open flask in the presence of dimeric palladium complex **1** (Figure 1) and pyridine.[16] Here we present new results concerning conditions of importance for this reaction, an extension to other more robust catalysts and catalytic systems, and theoretical calculations to improve the understanding of the initial steps of the catalytic cycle. To give credence to the calculations, we also report a crystal structure from an X-ray diffraction study.

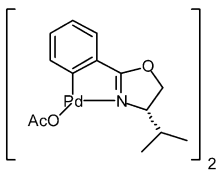


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**Figure 1.** Palladacycle **1**.

 DOI: 10.1002/adsc.200303166  

## Results and Discussion

### Scope and Limitations with Palladium Catalyst 1

*Role of the Base*

Typically, the aerobic oxidation of *rac*-1-phenylethanol (1.0 mmol) was run in toluene (10 mL) at 80 °C in the presence of palladium catalyst **1** (5 mol % Pd) and a base (20 mol %). The base of choice, as in most palladium-catalyzed oxidations, was pyridine. To find out the role of the base, a variety of bases was tried for the oxidation. As seen from Table 1, inorganic bases, ranging from weak to strong, appeared unsuitable and so did $sp^3$-hybridized nitrogen bases such as triethylamine, Hünig's base (*N,N*-diisopropylethylamine) and 4-dimethylaminopyridine. Pyridine and 4-isopropylpyridine seemed the best, leading to complete conversion of *rac*-1-phenylethanol within 24 hours, and 4-methoxypyridine exhibited only slightly lower reactivity. Sterically hindered 2,6-dimethylpyridine appeared unsuitable for the reaction. Together, these circumstances suggest that pyridine acts not only as a base but also as a ligand during critical step(s) in the catalytic cycle. It is worth noticing that the initial reaction rate was the same whether 1, 2 or 4 equivalents of pyridine were added, but catalyst survival increased with higher concentrations of pyridine.

*Catalyst Survival*

After complete conversion of *rac*-1-phenylethanol, another equivalent of the alcohol (1.0 mmol) could be oxidized, but now with a slower rate. When a third equivalent of alcohol was added, complete conversion could not be obtained, but the reaction terminated after a turnover number (TON) of about 43 (Table 1, entry 1). The same turnover of the catalyst was observed with an initial excess of alcohol (5 mmol) in the reaction mixture. Optimal conditions turned out to be slow addition with a syringe pump and further addition of molecular sieves. In this case a TON of 58 was realized (entry 2). In conclusion, the catalyst had a limited survival under the reaction conditions in the presence of the alcohol.

*Novel Catalytic Systems*

Due to the limitations with complex **1**, we synthesized the dimeric complexes **6**–**10** according to Figures 2 and 3. We anticipated that these complexes based on a pyridine skeleton would be more robust than the original 4,5-dihydro-1,3-oxazole complex **1**. Of these complexes, **7** and **10** are new compounds. They were synthesized in reasonable yields and were fully characterized.

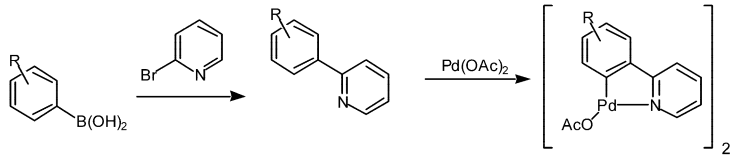
Complex **6** showed a behavior similar to that of **1** and complete conversion with pyridine or 4-methoxypyri-

**Table 1.** Oxidation of *rac*-1-phenylethanol catalyzed by palladacycle **1**.

| Entry | Base[a] | Conversion[b] after 2 h [%] | Conversion[b] after 4 h [%] | Conversion [b] after 24 h [%] | TON[b, c] |
|---|---|---|---|---|---|
| 1 | Pyridine | 57 | 73 | 100 (< 21 h) | 43 (5 d) |
| 2 | Pyridine[d] | – | – | – | 58 (3 d) |
| 3 | 4-*i*-Pr-Pyridine | 52 | 71 | 100 (< 21 h) | [e] |
| 4 | 4-MeO-Pyridine | 19 (1 h) | 43 | 87 | 48 (8 d) |
| 5 | 2,6-$Me_2$-Pyridine | * | 15 | 57 | [e] |
| 6 | 4-$Me_2$N-Pyridine | * | * | 6 | [e] |
| 7 | 2,6-$Br_2$-Pyridine | * | * | * (10 after 6 d) | [e] |
| 8 | NaOH | * | 20 | 43 | [e] |
| 9 | *t*-BuOK | * | * | 32 | [e] |
| 10 | $Cs_2CO_3$ | * | * (3 h) | 37 | [e] |
| 11 | NaOAc | * | * | 24 | [e] |
| 12 | LiOAc | * | * | 12 | [e] |
| 13 | $Et_3N$ | * | * | 17 | [e] |
| 14 | Hünig's base | * | * | 20 | [e] |
| 15 | – (No base) | * | * | 19 | [e] |

[a] Method: 1-phenylethanol (1 mmol), palladacycle **1** (5 mol % Pd), base (0.20 mmol), toluene (10 mL), 3 Å MS (500 mg), 80 °C.
[b] Conversion was determined with GC using naphthalene as internal standard.
[c] TON after loss of catalytic activity.
[d] After oxidation was started, more alcohol was added by syringe pump (10 μL/h). More molecular sieves were also added to the mixture twice a day.
[e] Oxidation was not continued till the loss of catalytic activity.
* No product formed.

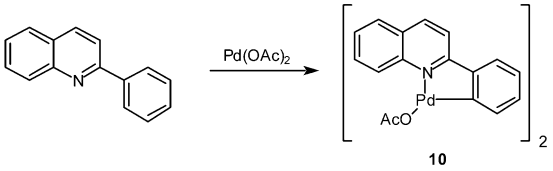
  




**2**: R = H
**3**: R = 4-$CF_3$
**4**: R = 2-Me
**5**: R = 4-OMe

**6**: R = H
**7**: R = 4-$CF_3$
**8**: R = 2-Me
**9**: R = 4-OMe

**Figure 2.** Preparation of palladacycles **6**–**9**.




**10**

**Figure 3.** Preparation of palladacycle **10**.

dine as additives was observed after less than 22 hours (Table 2, entries 1 and 2). Again, sterically hindered 2,6-dimethylpyridine and Hünig's base afforded lower yields. The advantage of palladacycle **6** over the original complex **1** lies in catalyst survival. With **6** as catalyst and 4-methoxypyridine as additive, the oxidation could be continued for several days when *rac*-1-phenylethanol was added portionwise (Table 2, entry 2). The reaction proceeded with a rather constant rate yielding a TON of 124 after 13 days. After around 14 days, it was evident that the catalyst was not active any longer. When a syringe pump was used for the addition of alcohol, a TON of 130 was observed after 5 days (entry 3).

Some control experiments were performed. The addition of 250 μL of water to the reaction mixture did not affect the initial rate of reaction, but the catalyst lost its activity more rapidly. When complex **6** was dissolved in toluene and heated at 80 °C for 5 days under air and in the absence of alcohol, some black precipitate appeared. NMR showed only minor parts of remaining **6**. Addition of molecular sieves and pyridine did not improve survival of **6** under these conditions. If complex **6** was heated to 80 °C in the presence of *rac*-1-phenylethanol, but under an atmosphere of nitrogen, these conditions also destroyed most of the complex. In none of the cases was free 2-phenylpyridine (**2**) detected. When the reaction was run for a short time at 80 °C and then left at room temperature for a week, no further oxidation was achieved. Upon resumed heating the oxidation continued. These control reactions indicate that the complex is stable in the reaction mixture at room temperature, but decomposes slowly at 80 °C.

When subjected to the same reaction conditions as those used for complex **6**, the series of complexes **7**–**10** also showed catalytic activity (Table 3). The differences in activity were rather small. Electron-poor **7** exhibited a slightly higher initial activity, whereas sterically more demanding **10** had a lower activity compared to all the other catalysts. However, no clear conclusions can be drawn about the influence of different substituents on the phenyl ring in the palladacycles **7**–**9**.

**Table 2.** Oxidation of *rac*-1-phenylethanol catalyzed by palladacycle **6**.

| Entry | Base[a] | Conversion[b] after 2 h [%] | Conversion[b] after 4 h [%] | Time [h] for 100% conversion [b] | Conversion[b] after 2d [%] | TON[b, c] |
|---|---|---|---|---|---|---|
| 1 | Pyridine | 60 | 80 | < 22 | 100[d] | 53 (3 d) |
| 2 | 4-MeO-Pyridine | 28 | 44 (3 h) | < 21 | 89[d] | 124 (14 d) |
| 3 | 4-MeO-Pyridine[e] | – | – | – | – | 130 (6 d) |
| 4 | 2,6-$Me_2$-Pyridine | * | * | – | 86 | [f] |
| 5 | Hünig's base | * | * | – | 35 | [f] |

[a] Method: 1-phenylethanol (1 mmol), palladacycle **6** (5 mol % Pd), base (0.20 mmol), toluene (10 mL), 3 Å MS (500 mg), 80 °C. More 1-phenylethanol (1 mmol at a time) was added to the mixture in entries 1 and 2 after the previous mmol was oxidized.
[b] Conversion and turnover number (TON) were determined with GC using naphthalene as internal standard.
[c] TON after loss of catalytic activity.
[d] Conversion of 2 mmol of 1-phenylethanol (1 mmol added after 100% conversion of the first mmol).
[e] After oxidation was started, more alcohol was added by syringe pump (10 μL/h). More molecular sieves were also added to the mixture twice a day.
[f] Oxidation was not continued till the loss of catalytic activity.
* No product formed.

**Table 3.** Oxidation of *rac*-1-phenylethanol catalyzed by palladacycles **1** and **6**–**10**.

| Entry | Catalyst[a] | Conversion[b] after 2 h [%] | Conversion[b] after 4 h [%] | Time [h] for 100% conversion[b] | Conversion[b, c] after 2 d [%] | TON[b, d] |
|---|---|---|---|---|---|---|
| 1 | **1** | 57 | 73 | < 21 | 82 | 43 (5 d) |
| 2 | **6** | 60 | 80 | < 22 | 100 | 53 (3 d) |
| 3 | **7** | 52 | 74 (5 h) | < 19 | 94 | 59 (7 d) |
| 4 | **8** | 24 | 55 (5 h) | < 22 | 89 | 44 (3 d) |
| 5 | **9** | 43 | 67 | < 22 | 88 | 42 (3 d) |
| 6 | **10** | 51 | 77 | < 19 | 82 | 27 (3 d) |

[a] Method: 1-phenylethanol (1 mmol), catalyst (5 mol % Pd), pyridine (0.20 mmol), toluene (10 mL), 3 Å MS (500 mg), 80 °C. More 1-phenylethanol (1 mmol at a time) was added to the mixture after the previous mmol was oxidized.
[b] Conversion and turnover number (TON) were determined with GC using naphthalene as internal standard.
[c] Conversion for 2 mmol of 1-phenylethanol (1 mmol added after conversion of the first mmol).
[d] TON after loss of catalytic activity.

## Theoretical Calculations and Mechanistic Interpretations

In order to get some insight into the mechanism of the catalytic process, the structures of the dimeric acetate bridged complexes **1** and **6** were computed and that of **1** compared to an X-ray structure. The very first step of the process, the bridge-splitting reaction and coordination of a ligand, was also studied by means of quantum chemistry. Attention was focused on trends and comparison of relative binding energies of ligands for two palladium complexes, rather than on accurate calculation of absolute reaction energies.

### *Computational Details*

Calculations were performed with Jaguar 4.0 package[17] at the level of B3LYP hybrid density functional.[18] Basis sets developed at Los Alamos National Laboratory were used; an electron core potential was employed only for the palladium atom. Gas phase geometry optimization was performed with the double-ζ quality LANL2DZ basis set[19] with an additional polarization function (LACVP* keyword). This double-ζ quality basis is hereafter referred to as a *small basis set*. The triple-ζ quality basis set comprising 6–311 + G* basis and Los Alamos core potentials, LACV3P keyword, with the addition of diffuse and polarization functions (hereafter referred to as a *large basis set*) was employed for the calculation of reaction energies. Effects of bulk solvent were estimated with the help of the continuum solvent model as implemented in Jaguar 4.0. Coordinates of all optimized structures presented may be found in the Supplementary Information.

### *Crystallography*

X-Ray intensity data were collected from a yellow single crystal of **1**, using a STOE Imaging Plate Detection System, equipped with a rotating anode.[20] The net intensities were corrected for Lorentz and polarization effects. The heavy atom (Patterson) method in combination with direct methods (SHELXS[21]) yielded eight palladium positions. All remaining non-hydrogen atoms were located from difference electron density calculations, whereas the hydrogen atoms were placed in calculated positions using geometric evidence (SHELXL).[22]

The crystallographic unit cell contains four dimeric $2[(C_{12}H_{13}NO)Pd(C_2H_3O_2)]$ complex units and one chloroform ($CHCl_3$) solvate molecule. In the final refinement calculation (SHELXL[22]) the non-hydrogen atoms were treated anisotropically, whereas fixed isotropic displacement parameters [$U_{iso}(H) = 1.5/1.2\ U_{iso}$ (parent non-hydrogen) for the methyl hydrogens and remaining hydrogen atoms, respectively] were given for the hydrogen positions in order to limit the number of variables. The low value [−0.02(2)] of the Flack absolute structure parameter[22] indicates that the crystals are enantiomerically pure, containing only the *R* complex (*cf.* the crystallographic description of the structure, details of the data reduction and structure refinement calculations in the Supplementary Information).

### *Ab initio Structures of the Palladacycles **1** and **6***

The optimized geometry of the palladacycle **1** (see Figure 4A) was in good agreement with the crystal structure. The deviation of the computed bond distances between the Pd and C, O and N atoms from the experimental values was less than 3% of the bond length (absolute value of the error varied from 0.030 to 0.059 Å). The deviation of the distance between Pd atoms in the dimer from that in the crystal structure was 0.14 Å (less than 5% of the distance between atoms). Use of the large basis set for geometry optimization did not result in appreciable changes of bond distances.

The gas phase structure of the palladacycle **6** (Figure 4B) was also optimized. The differences in bond

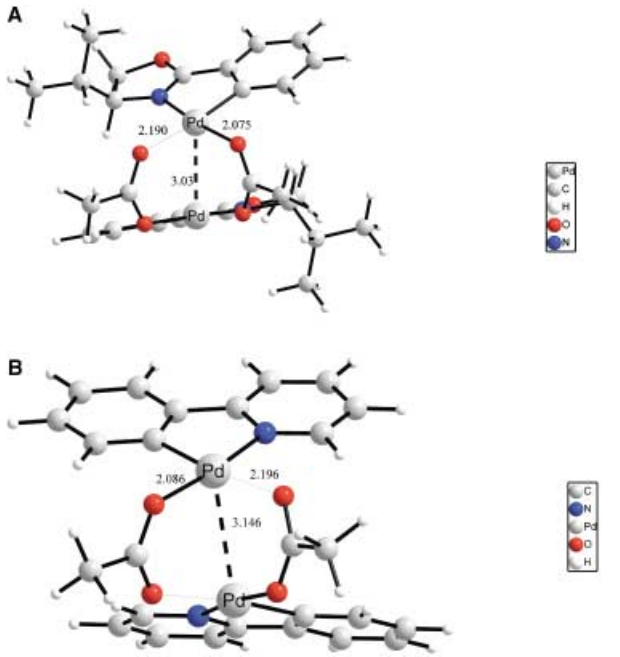



**Figure 4.** Optimized geometry of palladacycle **1** and palladacycle **6** dimers, (**A** and **B**, respectively). Bond distances are in Å. All structures are optimized at the DFT level.

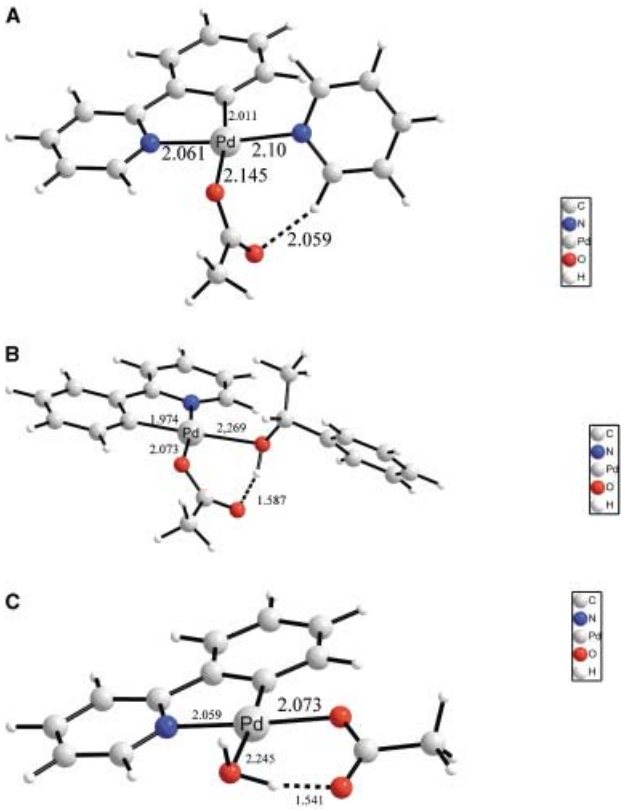



**Figure 5.** Structures of palladacycle **6** monomer coordinated with pyridine (**A**), 1-phenylethanol (**B**) and water (**C**). All structures are optimized at the DFT level. Dashed line denotes hydrogen bond. Bond distances are in Å.

distances between palladium and other atoms in **6** and **1** were very small, less than 0.008 Å, while the Pd–Pd distance in **6** was 0.11 Å longer than that in palladacycle **1**.

According to the calculations, the difference in energy between the *syn* and *anti* configurations of the dimeric palladacycle **6** was rather small, the *anti* configuration being favored by 1.25 kcal/mole. $^1$H NMR spectroscopy showed a 13:1 ratio of the *anti* and *syn* complexes, which corresponds to an energy difference of about 1.5 kcal/mole at room temperature. Also for the other dimeric compounds, the NMR spectra displayed mixtures of *syn* and *anti* isomers (**7** 1:11; **8** 1:13; **9** 1:5; **10** 1:5). These observations are in accordance with earlier reported results from dimeric palladacycles obtained from arylimines.[23]

**Table 4.** Electronic part of the reaction enthalpy of ligand exchange reaction for palladacycle **1** in gas phase and solvent (continuum model for toluene).

| Ligand | Difference in total energies (kcal/mol) Gas phase/solvent |
|---|---|
| Water | −6/+1.5 |
| Methanol | −4.1/+2.2 |
| 1-Phenylethanol | +2.4/+5.4 |
| Pyridine | +8.2/−1.3 |

### *Thermodynamics of the Ligand Exchange*

Next the ligand exchange reaction energies for two palladium complexes (**1** and **6**) were compared. Splitting of the acetate bridge in the palladium dimer and formation of palladium complexes with a coordinated ligand, pyridine (Figure 5A), 1-phenylethanol (Figure 5B) or water (Figure 5C), were therefore studied. Only total energies (electronic contribution to the reaction enthalpy, Tables 4 and 5) without account of thermal functions and zero-point vibration energy were studied. A hydrogen bond, which varied in length from 1.54 to 1.59 Å, between the acetate oxygen atom and the hydrogen atom of the binding alcohol ligand was found to stabilize the complex. The calculations showed that without this bond the absolute energies of the monomeric complexes (palladacycles **1** and **6** with coordinated ligands) were in general 8–10 kcal/mol higher.

### *Solvent Effects*

Solvent effects were found to be quite important. One effect of the solvent on the reaction energy obviously concerns the hydrogen bond between ligands coordi-

**Table 5.** Electronic part of the reaction enthalpy of ligand exchange reaction for palladacycle **6** in gas phase and solvent (continuum model for toluene).

| Ligand | Difference in total energies (kcal/mol) Gas phase/solvent |
|---|---|
| Water | −11/−0.4 |
| Methanol | −8.6/−0.6 |
| 1-Phenylethanol | −1.7/+2.5 |
| Pyridine | +0.5/−6.0 |

nated to palladium. As a result, in the PCM model, the dimer becomes more stable with respect to the monomer with a coordinated ligand. The difference in absolute energies of two conformations (with hydrogen bond and without) of palladacycle **6** bound to 1-phenylethanol is 12 kcal/mol and 7 kcal/mol in the gas phase and in solution, meaning that solvent effects "weaken" this hydrogen bond by 5 kcal/mol. That would amount to 10 kcal/mol as the solvent effect in the reaction energy for ligand exchange reaction. Comparison with the results presented in Table 5, an energy difference of 4.2 kcal/mol, suggests that the influence of solvent effects within the hydrogen bond between palladium bound ligands is only a part of the reported total solvent effect.

Similar considerations done for the rest of the complexes indicate that solvent effects in the reaction energies are mostly due to the change in the strength of the ligand interaction around palladium.

*Interpretation*

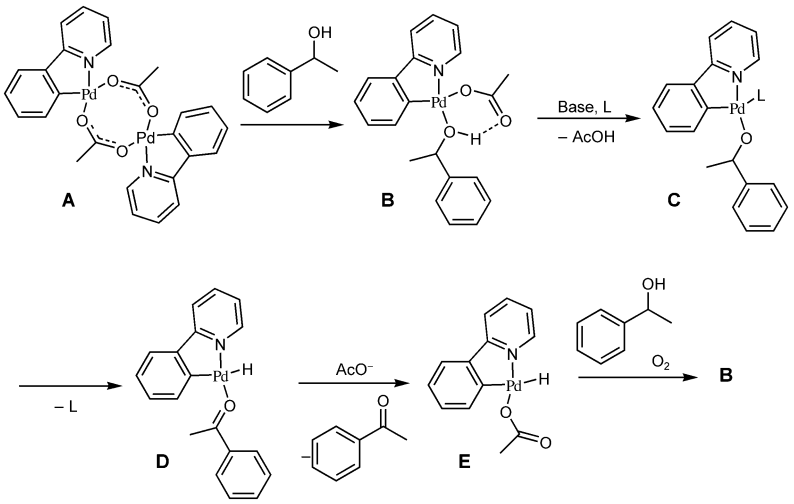
The calculations imply that there is a competition between alcohol, water and pyridine for a coordination site at the palladium atom (see Tables 4 and 5). In an efficient palladium-catalyzed aerobic oxidation designed by Sigman, the rate-determining step is a β-hydride elimination from an alkoxide.[24,25] In this case it was proposed that the coordinated acetate will promote an intramolecular deprotonation of the coordinated alcohol and at the same time afford a coordination vacancy at the metal. An observed hydrogen bond between acetate and coordinated water in the original complex was supportive within this context. It is worth noticing that our calculations also show a distinct hydrogen bond between acetate and coordinated alcohol or water. It is therefore conceivable that the deprotonation step is similar in our system. As acetate is expected to be a stronger base than pyridine in toluene, the role of pyridine is more likely as a ligand in the catalytic cycle.

A reasonable reaction mechanism, based on the present and previous findings,[24] for the palladium-catalyzed oxidations is shown in Scheme 1.

Details of the reaction mechanism will be addressed in our future work. Attempts to further improve the performance of the catalytic system will also be made.

## Conclusion

Palladacycles prepared from 2-phenylpyridines provide efficient catalysts for the aerobic oxidation of 1-phenylethanol. The first step in the reaction is the splitting of the dimeric palladium complex and coordination of a ligand, which can be the alcohol or pyridine, which also serves as a base in the reaction. The alcohol complex is stabilized by a hydrogen bond between the hydroxy proton and the carbonyl group of the acetate ligand. The reactivity of the catalytic system is insensitive to changes of the electronic properties of substituents in the phenyl ring of the palladium complex.




**Scheme 1.** Proposed mechanism (L = e.g., pyridine or toluene).

# Experimental Section

## General Remarks

Toluene and tetrahydrofuran (THF) were distilled from Na/benzophenone. Molecular sieves (MS 3 Å) were activated at 200 °C and reduced pressure. Bases, $Pd(OAc)_2$ and *rac*-1-phenylethanol were purchased and used without further purification. Acetic acid was refluxed over $KMnO_4$ and distilled. 2-Phenylpyridines (**3**, **4**, **5**) were synthesized by Suzuki coupling from 2-bromopyridine and phenylboronic acids.[26] Palladacycles **1**,[16] **6**, **8** and **9**[27] were synthesized by published methods.

## Palladacycle 7

A mixture of 2-(4′-trifluoromethylphenyl)pyridine (3; 81 mg, 0.36 mmol), $Pd(OAc)_2$ (81 mg, 0.36 mmol) and glacial acetic acid (6 mL) was heated at reflux under nitrogen. After 3.5 h, heating was turned off and the mixture was stirred overnight. The orange precipitate formed was filtered off and washed with water. The precipitate was dissolved in dichloromethane and dried over $Na_2SO_4$. After filtration and concentration, the solid was recrystallized from dichloromethane giving **7** as orange crystals. Additional **7** was obtained from the filtrate. Yield: 113 mg (41%; 11:1 mixture of isomers); decomp. > 213 °C; anal. calcd. for $C_{28}H_{20}F_6N_2O_4Pd_2$: C 43.37, H 2.60, N 3.61; found: C 43.26, H 2.67, N 3.52; $^1$H NMR (400 MHz, $CD_2Cl_2$) (major isomer): δ = 7.92 (1H, dd, *J* = 5.6 and 0.9 Hz, py-H), 7.51 (1H, td, *J* = 7.8 and 1.6 Hz, py-H), 7.21 (1H, d, *J* = 7.8 Hz, py-H), 7.08 (1H, s, Ph-H), 7.06 – 7.02 (2H, m, Ph-H), 6.74 – 6.71 (1H, m, py-H), 2.25 (3H, s, $CH_3$); (minor isomer): δ = 8.07 (1H, d, *J* = 6.6 Hz, py-H), 7.61 (1H, td, *J* = 7.8 and 1.6 Hz, py-H), 7.27 (1H, d, *J* = 7.8 Hz, py-H), 6.94 (1H, s, Ph-H), 6.90 – 6.86 (1H, m, py-H), 2.31 (1H, s, $CH_3$), (signals from two hydrogen atoms hidden under those of the major isomer); $^{13}$C NMR (125 MHz, $CD_2Cl_2$): δ = 182.47, 163.41, 152.11, 150.35, 148.35, 138.99, 129.44 ($J_{C\text{-}F}$ = 31.7 Hz), 128.48, 124.28 ($J_{C\text{-}F}$ = 312.7 Hz), 123.25, 122.71, 121.35, 118.88, 25.06.

## Palladacycle 10

A mixture of 2-phenylquinoline (100 mg, 0.49 mmol), $Pd(OAc)_2$ (99 mg, 0.44 mmol) and glacial acetic acid (5 mL) was refluxed under nitrogen for 1 h and then allowed to reach RT overnight. The precipitate formed was filtered and washed with water and then dissolved in dichloromethane and dried over $Na_2SO_4$. Filtration, concentration and drying under vacuum gave **10** as brown solid. Yield: 186 mg (57%, 5:1 mixture of isomers); decomp. > 189 °C; anal. calcd. for $C_{34}H_{26}N_2O_4Pd_2$: C 55.23, H 3.54, N 3.79; found: C 55.03, H 3.61, N, 3.70; $^1$H NMR (400 MHz, $CDCl_3$) (major isomer): δ = 8.53 (1H, d, *J* = 8.8 Hz), 7.83 (1H, d, *J* = 8.6 Hz), 7.51 – 7.42 (2H, m), 7.36 – 7.28 (2H, m), 6.78 (1H, d, *J* = 7.3 Hz), 6.48 – 6.41 (2H, m), 6.13 (1H, t, *J* = 7.3 Hz), 2.28 (3H, s); (minor isomer): δ = 8.40 (1H, d, *J* = 8.8 Hz), 7.67 (1H, d, *J* = 8.6 Hz), 7.15 – 7.11 (3H, m), 7.05 – 7.01 (1H, m), 6.88 (1H, dd, *J* = 7.6 and 1.3 Hz), 6.73 (2H, m), 6.63 (1H, td, *J* = 7.6 and 1.3 Hz), 2.41 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) (major isomer): δ = 180.56, 165.16, 151.47, 147.94, 144.77, 139.02, 131.33, 130.37, 127.78, 127.59, 127.38, 127.18, 126.27, 123.63, 123.49, 115.92, 25.18; (minor isomer): δ = 182.20, 179.79, 165.76, 152.58, 147.50, 138.22, 132.86, 130.16, 128.53, 127.13, 126.92, 126.81, 126.07, 124.19, 123.99, 115.83, 29.91.

## General Procedure for Alcohol Oxidation

Base (0.20 mmol), MS 3 Å (500 mg) and naphthalene (1 mL of a 0.50 M solution in toluene) were added to a mixture of palladium complex (5 mol % Pd, 0.025 mmol) and toluene (3 mL) in a dry 25-mL two-neck flask equipped with cooler and drying tube. The mixture was heated at 80 °C for 15 min and then a solution of 1-phenylethanol (122 mg, 1 mmol) in toluene (4 mL) was added dropwise with a syringe. Additional toluene (2 mL) was added to rinse the syringe. The reaction mixture was stirred at 80 °C for the time indicated (see Tables 1 – 3). A sample was taken, diluted with diethyl ether and filtered before injecting into a GC-MS. The conversion and TON were calculated using a calibration curve. Additional 1-phenylethanol (1 mmol at a time) was added to the mixture in some cases.

## Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 221366. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336 – 033; e-mail: deposit@ccdc.cam.ac.uk].

Tables with the geometries (XYZ coordinates) of all computed structures. Details on the crystal structure determination and evaluation. Supplementary pictures with crystal structures and all optimized geometries.

# Acknowledgements

*This work was supported by the Carl Trygger Foundation. We thank Dr Christian Linde and Dr Andreas Fischer for valuable discussions.*

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