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# Catalytic conversions in water. Part 10.† Aerobic oxidation of terminal olefins to methyl ketones catalysed by water soluble palladium complexes

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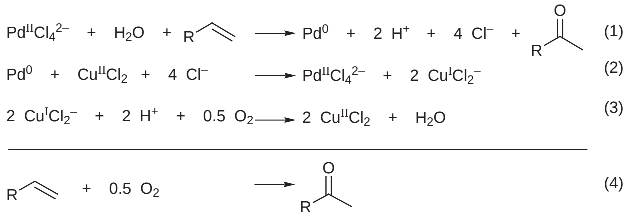
**Water soluble palladium(II) complexes of bidentate diamine ligands, such as bathophenanthroline disulfonate, are stable, recyclable catalysts for the selective aerobic oxidation of terminal olefins to the corresponding alkan-2-ones in a biphasic liquid–liquid system.**

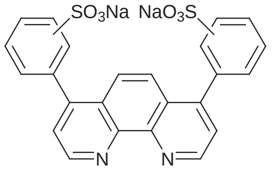
The aerobic oxidation of ethylene to acetaldehyde and terminal olefins to the corresponding alkan-2-ones [eqn. (1)–(4)] catalysed by an aqueous solution of palladium(II) and copper(II) salts are collectively known as Wacker oxidations.[1] The function of the copper co-catalyst is to mediate the reoxidation of palladium(0).



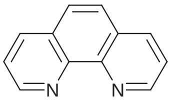
Although commercially successful, this process has several drawbacks. Substantial concentrations of copper salts (*ca*. 1 M) and chlorides (*ca*. 2 M) are added to achieve favourable redox potentials of the $Pd^{II}/Pd^0$) and $Cu^{II}/Cu^I$ couples and to solubilise $Cu^I$ as $Cu^ICl_2^-$. Acid (HCl) is required to circumvent clustering of transient atomic palladium. This not only renders the system highly corrosive, but also reduces the catalyst activity, since the rate[2] is inversely proportional to $[H^+]$ and $[Cl^-]^2$. Furthermore, the presence of large amounts of chloride leads to the formation of chlorinated by-products. Hence, much effort has been devoted[1] to the development of alternative co-catalysts, notably the heteropolyacid, $H_3PMo_6V_6O_{40}$, which still requires chloride, albeit in much lower amounts than the conventional Wacker process,[3] and two-component systems involving benzoquinone in combination with iron(II) phthalocyanine[4] or heteropolyacid.[5]

The oxidation of higher olefins introduces additional complications. Rates are much lower owing to their low solubilities in water and raising the temperature results in palladium black formation. Moreover, the products are contaminated with chlorinated by-products and isomerised olefins. Rates can be improved by using water-miscible cosolvents, *e.g.* DMF,[6] or phase transfer catalysis with tetraalkylammonium salts[7] or polyethylene glycols[8] or modified cyclodextrins[9] as inverse phase transfer catalysts. Immobilised catalysts have also been described, *e.g.* palladium-on-vanadium pentoxide,[10] organic polymer-anchored palladium[11] and supported aqueous phase catalysts.[12] However, these systems employ copper/chloride combinations and/or exhibit poor activities and selectivities. There still remains a definite need, therefore, for a system which avoids the use of copper ions, chloride ions and polar organic solvents and which is active, selective and recyclable. We report here a new catalytic system, based on water soluble palladium diamine complexes, which appears to meet these criteria.

Our approach was to stabilise $Pd^0$ *via* complexation with oxidatively stable (di)amine ligands. In an initial screening we tested ligands **1**–**5** in the oxidation of hex-1-ene at 100 °C.



**1**



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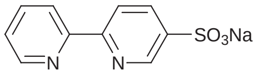

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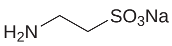

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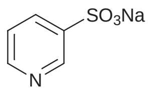

**5**

Promising results were observed with the chelating diamines **1**–**3**, while the monodentate ligands **4** and **5** were less effective (Table 1). The best results were observed with bathophenanthroline disulfonate **1**. The catalyst solution was prepared by stirring $Pd(OAc)_2$ (0.0224 g; 0.1 mmol) and **1** (0.0546 g; 0.1 mmol) overnight with 42.5 g of water to afford a clear orange solution. In a typical procedure a 175 ml autoclave was cooled to 0 °C and charged with the catalyst solution, olefin (10 mmol) and internal standard (n-alkane). The autoclave was pressurised with air, heated to 100 °C (30 bar) and kept at this temperature for 10 h. After reaction the autoclave was cooled to 0 °C and depressurised, collecting any volatile material in a liquid nitrogen trap. The mixture was extracted with $Et_2O$, the extract

**Table 1** The palladium catalysed oxidation of olefins[a]

| Olefin | Ligand | Olefin conversion (%) | Selectivity to alkanone (%) |
|---|---|---|---|
| Hex-1-ene | **1** | 48 | 99 |
| Hex-1-ene | **2** | 42 | 99 |
| Hex-1-ene | **3** | 36 | 97 |
| Hex-1-ene | **4** | 12 | 40[b] |
| Hex-1-ene | **5** | 2 | 50[b] |
| Pent-1-ene | **1** | 50 | 99 |
| Oct-1-ene | **1** | 25 | 99 |
| Cyclopentene | **1** | 2 | 47[c] |
| Cyclohexene | **1** | 2 | 50[d] |
| Cyclooctene | **1** | 30 | 100 |

[a] Conditions: 0.1 mmol $Pd(OAc)_2$, 0.1 mmol ligand, 10 mmol olefin, 10 mmol NaOAc, 10 h at 100 °C and 30 bar in 42.5 g $H_2O$. [b] Main by-products were hex-2-ene and hex-3-ene. [c] Main by-products were cyclopent-2-en-1-ol and cyclopent-2-en-1-one. [d] Cyclohex-2-en-1-ol, cyclohex-2-en-1-one, benzene and cyclohexane were detected as by-products.

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† For Part 9, see G. Verspui, G. Papadogianakis and R. A. Sheldon, *Chem. Commun.*, 1998, 401.

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**Table 2** Recycling of the catalyst[a]

| Cycle | Hex-1-ene conversion (%) with NaOAc | Hex-1-ene conversion (%) without NaOAc |
|---|---|---|
| 1st | 48 (99%) | 47 (99%) |
| 2nd | 44 (96%) | 28 (97%) |
| 3rd | 40 (95%) | 15 (96%) |

[a] Conditions as in Table 1, with and without NaOAc (10 mmol).

dried over $MgSO_4$ and analysed by GC using a Varian Star 3400 instrument equipped with a CP Sil 5-CB column (50 m × 0.53 mm).

Under these conditions hex-1-ene underwent 48% conversion to give hexan-2-one in $>99\%$ selectivity. No isomerisation of hex-1-ene and no palladium black formation was observed. Up to 50% conversion (50 turnovers) the rate was independent of [hex-1-ene], indicative of saturation kinetics. Thereafter, the reaction became first order in [hex-1-ene]. When the substrate/catalyst ratio was increased from 100 to 200 the reaction was zero order in hex-1-ene up to 100 turnovers.

Similarly, various terminal and cyclic olefins were oxidised using $Pd(OAc)_2$–**1** under the same conditions (Table 1). Terminal olefins were oxidised selectively, whereas oxidation of cyclopentene and cyclohexene underwent competing allylic oxidation and tended to stop after a few turnovers. At higher temperatures (150 °C) cyclohexene was dehydrogenated into benzene in *ca*. 90% selectivity, in the presence of ionol, as a radical scavenger.

The catalyst could be recycled as is shown in Table 2. The addition of sodium acetate was necessary to stabilise the catalyst. Without NaOAc, formation of palladium black was observed after the second and third cycles. The beneficial effect may be due to preventing the formation of inactive dimers,[13] giant palladium clusters,[14] or even colloidal palladium.[15] Thus, when a solution of the orange complex was heated at 120 °C in the absence of NaOAc the solution became brown–black, indicative of giant cluster or colloidal palladium formation.

In the experiments described in Table 1 stoichiometric amounts of NaOAc were added, but in separate experiments with hex-1-ene it was shown that several equivalents with respect to palladium were sufficient for maintaining stability. The turnover frequency of hex-1-ene was measured as a function of the temperature in the range 70–120 °C. From these data the activation energy was calculated to be 90.2 kJ $mol^{-1}$. In the presence of sodium acetate the selectivity to hexan-2-one was *ca*. 99% even at 120 °C.

In conclusion, the water soluble bathophenanthroline palladium complex is an effective catalyst for the aerobic oxidation of terminal olefins to the corresponding alkan-2-ones. Catalyst recycling is simple, and due to the absence of $CuCl_2$ and acid, chlorinated and isomerised side products are completely avoided. We are currently investigating the scope of this system, *e.g.* in intramolecular oxypalladation reactions.[16]

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