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The catalytic hydration of nitriles to amides using a homogeneous platinum phosphinito catalyst

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Abstract

New homogeneous catalysts for the hydration of nitriles to amides are described. The catalyst precursors are coordination compounds of Pt(II) with secondary phosphine oxides. They contain a hydrogen bridged mono-anionic didentate phosphinito group, together with a third phosphine oxide ligand and a monodentate anionic ligand, either hydride or chloride. Reacting the chloride with silver ion, or the hydride with water gives a cationic species which is the active catalyst. On coordination to the cation the nitrile becomes susceptible to nucleophilic attack. The hydrolysis gives the amide as the sole product, and there is no tendency towards further hydrolysis to the acid. The effects of substituents on phosphorus are investigated, and a reaction mechanism is suggested. The most active catalyst, $[PtH(PMe_2OH)(PMe_2O)_2H]$, **2a,** is derived from dimethylphosphine oxide, and this precursor catalyses the hydration of acrylonitrile to acrylamide with a turnover number of 77,000, without addition to the C=C double bond.

Keywords: Amides; Homogeneous catalysis; Nitrile hydrolysis; Platinum phosphinito complexes

1. Introduction

The vast increase in knowledge of organometallic chemistry over the last 50 years has inspired a sustained interest in the homogeneous catalysis of organic reactions using transition metal compounds [1,2]. Some reactions, such as olefin metathesis [3,4], are almost inconceivable without the intervention of a transition metal: however others, such as the polymerisation of olefins, can be brought about by other means [5]. The hydrolysis of nitriles when catalysed by a base, generally leads to the carboxylate salt, because the rate constant for the hydrolysis of the amide to the carboxylate salt is usually greater than that for the hydrolysis of the nitrile to the amide. The successive rate constants at 25°C for the alkaline hydrolysis of acetonitrile giving acetamide and then acetate ion are 1.6×10^{-6} and 7.4×10^{-5} M^{-1} s^{-1} [6] (for a general account of the chemistry of nitriles and amides see Ref. [7]). Recent work at 250–300°C in water under pressure has shown that autocatalysis occurs under these conditions [8]. In acid solution the situation is often more complicated, and the ratio of the rates can be concentration dependent. In dilute acidic solutions the second step is generally faster than the first, but in concentrated acid the relationship is reversed

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[9]. This can be used preparatively, so that treatment of a nitrile with concentrated acid followed by work up with ice can give good yields of amides [10]. The hydration of nitriles to amides may also be carried out using alkaline hydrogen peroxide [11], or metals [12,13] (such as copper) or metal oxides (such as manganese dioxide) [14]. These methods go some way to avoiding the further hydrolysis to the acid or carboxylate ion. A less well-known method for hydrolysing nitriles to amides involves the reaction with formic acid with the simultaneous formation of carbon monoxide [15,16].

Transition metal coordination compounds have been used as catalysts for nitrile hydrolysis and give good selectivity to the amide [17,18]. We report here our work involving phosphinito complexes of platinum which have proved to be extremely effective catalysts for the hydration of nitriles to amides without further hydrolysis, and perform well in the presence of other functional groups. A preliminary report of this work has appeared [19] and the application of this catalyst to the synthesis of the cardiovascular drug atenolol has been described elsewhere [20]. Very recently a report on the use of the catalyst in the preparation of tertiary amides has appeared [21].

Early work with platinum salts and acetonitrile was carried out by Hofmann and Bugge [22,23] in the first decade of the twentieth century, and led to the formation of platinum blue. It was realised at the time that platinum blue contained acetamide, and later Gillard and Wilkinson [24] suggested a polymeric structure with acetamido bridges for platinum blue, and X-ray diffraction studies on related systems have confirmed this [25]. This is an early example of a coordinated ligand undergoing nucleophilic attack, but under the conditions used, the amide is not released from the coordination sphere. A similar situation arises with d^6 Co(III) ions, which cause a large increase in the rate of nucleophilic attack, but only give low catalytic turnover numbers as the ions undergo substitution very slowly [26]. However, tertiary phosphine complexes of platinum(II) release acetamide from their coordination spheres and so provide the basis for catalysis. Several catalysts of this type have been reported [17].

On coordination to a transition metal, secondary phosphine oxides are converted to hydroxy phosphines [27], and a considerable number of compounds are known which contain such ligands [28,29]. A common occurrence when two such ligands are present is the loss of a proton to give a hydrogen bonded phosphinito chelate, such as those in **1a–4**. We decided to investigate the possibility that the oxygen of a coordinated hydroxy phosphine might behave as a nucleophile.

2. Experimental

All reactions were performed in air unless otherwise stated. The starting materials dimethylphosphine oxide [30], diphenylphosphine oxide [31], $Pt(PPh_3)_4$ [32] and the catalyst precursors $[PtH(PPh_2OH)(PPh_2O)_2H]$, **1a** [33] and $[PtCl(PPh_2OH)(PPh_2O)_2H]$, **1b** [34] were synthesised by published procedures. ^1H NMR spectra were recorded on a Bruker AM 360 (360.13 MHz) spectrometer, and all chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. ^{31}P NMR spectra were recorded either on a Bruker WM 250 (101.26 MHz) spectrometer or on a Bruker AM 360 (145.785 MHz) spectrometer, using 85% phosphoric acid as external reference.

The hydration reactions were performed in air. GLC analyses were performed on a Perkin-Elmer 8310 Gas Chromatograph, which was fitted with a 1-m column packed with Porapak Q 80/100.

*2.1. Preparation of $[PtH(PMe_2OH)(PMe_2O)_2H]$, **2a***

Dimethylphosphine oxide (0.16 g, 2.05 mmol) was added to a stirred solution of $Pt(PPh_3)_4$ (0.50 g, 0.402 mmol) in dry toluene (10 ml), at room temperature under nitrogen. Almost in-

stantly a colourless solution was obtained which was stirred for 1 h. During this time a white powder separated. Precipitation was completed by addition of diethyl ether (20 ml) and stirring for a further hour. The product [PtH(PMe_2OH)-($PMe_2O)_2H$], **2a** (0.13 g, 75%) was filtered, washed with diethyl ether, hexane and dried in vacuo: mp 231–233°C; IR (nujol) 1989 (m) (ν_{Pt-H}) cm^{-1}. Found: C, 17.21; H, 4.79. $C_6H_{21}O_3P_3Pt$: requires C, 16.78; H, 4.93%.

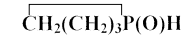
2.2. Preparation of [PtCl(PMe_2OH)(PMe_2-$O)_2H$, **2b**

Dimethylphosphine oxide (0.17 g, 2.18 mmol) in degassed ethanol (3 ml) was added dropwise over 2 h, at room temperature o a stirred solution of K_2PtCl_4 (0.30 g, 0.723 mmol) in degassed ethanol (8.5 ml) and H_2O (5 ml). The reaction mixture was then stirred under nitrogen at 40–50°C until it turned pale brown. Treatment with charcoal followed by filtration through Celite® gave a pale yellow solution, which was concentrated under reduced pressure. Addition of water gave [PtCl(PMe_2OH)-($PMe_2O)_2H$], **2b** (0.20 g, 60%) as fine white needles, which were washed with water, diethyl ether and dried in vacuo: mp 253–255°C; $^{31}P\{^1H\}$ NMR ($CDCl_3/CD_3OD$, −55°C) δ 101 ($^1J_{PtP_A}$ 2631 Hz, P_A), δ 54 ($^1J_{PtP_B}$ 3486 Hz, P_B), δ 88 ($^1J_{PtP_C}$ 2543 Hz, P_C), $^2J_{P_AP_B} \sim 20$ Hz, $^2J_{P_AP_C}$ 458 Hz, $^2J_{P_BP_C}$ 16 Hz; ^1H NMR ($CDCl_3/CD_3OD$) δ 1.8–1.85 (d, 6H), δ 1.7–0.8 (2 d, 12H), δ 1.6 (broad s, 2H); IR (nujol) 298 (w) (ν_{Pt-Cl}) cm^{-1}. Found: C, 15.46; H, 4.35. $C_6H_{20}ClO_3P_3Pt$: requires C, 15.54; H, 4.35%.

2.3. Reaction of **2a** with dilute hydrochloric acid

A suspension of **2a** (0.15 g, 0.35 mmol) in THF (2 ml) was treated with 2 M hydrochloric acid (0.2 ml) and heated under reflux for 2 h. The solvent was removed under reduced pressure to give a white residue which was taken up in acetone; addition of water gave fine white needles, which were filtered off, washed with water, diethyl ether and dried in vacuo. The product was identified as [PtCl(PMe_2OH)-($PMe_2O)_2H$], **2b** (0.11 g, 68%) by comparison with an authentic sample.

2.4. Preparation of phospholane oxide,



This procedure was performed under a nitrogen atmosphere using dry solvents throughout.

The double Grignard reagent $BrMg(CH_2)_4$-MgBr was prepared [35] by dropwise addition of $Br(CH_2)_4Br$ (21.5 g, 0.10 mol) in THF (25 ml) to a vigorously stirred suspension of activated magnesium (5.0 g, 0.21 mol) in THF (75 ml). Care was taken to ensure that the temperature did not rise above 30°C (ice-bath cooling). The addition was completed within 45 min and the mixture stirred at room temperature for a further 90 min. Diethyl phosphite (7.0 g. 0.051 mol) in THF (20 ml) was added dropwise with ice-bath cooling at such a rate that the temperature was maintained at 20–30°C. Stirring was continued for a further hour. Gradual addition of an ice-cold solution K_2CO_3 (30.0 g in 50 ml water) generated a heavy off-white precipitate of $MgCO_3$, which was rapidly filtered off in air and washed with degassed ethanol (4×25 ml). Most of the water and ethanol were removed under reduced pressure to give the crude product as a pale yellow/brown oil, which was dried by dissolving in chloroform (25 ml) and shaking with 4-A molecular sieves. Vacuum distillation through a 15-cm Vigreux column gave 2.15 g (41%) of

(bp: 105–107°C, 0.2 mm Hg) as a slightly impure colourless oil: $^{31}P\{^1H\}$ NMR ($CDCl_3$)

δ 48 (unidentified signals δ 35 and 72); ^{1}H NMR ($CDCl_3$) δ 1.95 (m, 4H), δ 1.65 (m, 4H), δ 7.35 (d, 1H), ^{1}J(P–H) 459 Hz; EI mass spectrum *m/z:* 104.0391. (Found M^+), 104.0390 (Required M^+); IR (neat) 2324 (m) (ν_{P-H}), 1181 (s) ($\nu_{P=O}$) cm^{-1}.

2.5. Preparation of

$$[PtCl(\overline{CH_2(CH_2)_3POH})(\overline{CH_2(CH_2)_3PO)_2H}],\ 3$$

Phospholane oxide (0.26 g. 2.50 mmol) in degassed ethanol (3 ml) was added dropwise over 2 h to a stirred solution of K_2PtCl_4 (0.3 g, 0.723 mmol) in degassed ethanol (10 ml) and H_2O (10 ml). The reaction mixture was then stirred under nitrogen at 40–50°C for 5 h. The resulting pale yellow solution was concentrated under reduced pressure to ca. 5 ml. Addition of water gave $[PtCl(PC_4H_8OH)(PC_4H_8O)_2H]$ (0.22 g, 56%) as a cream powder, which was washed with water, diethyl ether and dried in vacuo: mp 226–228°C; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 74 ($^1J_{PtP_B}$ 3601 Hz, P_B), δ 112 ($^1J_{PtP_A/P_C}$ 2565 Hz, P_A/P_C); ^{1}H NMR ($CDCl_3$): δ 1.6–2.4 (m, 24H); IR (nujol*):* 297 (w) ($\nu_{Pt\ Cl}$) cm^{-1}; (Found: C 26.56, H 4.58. $C_{12}H_{26}ClO_3P_3Pt$ requires C 26.62, H 4.84%).

2.6. Preparation of $PtCl(PMe_2Ph)(PMe_2O)_2H]$, **4**

A suspension of **2b** (0.15 g, 0.324 mmol) in dry CH_2Cl_2 (20 ml) was treated with dimethylphenylphosphine (0.05 g, 0.362 mmol) and stirred at room temperature under nitrogen for one hour. The clear pale yellow solution was then concentrated under reduced pressure to ca. 5 ml. Addition of diethyl ether/60–80 petroleum ether precipitated $[PtCl(PMe_2Ph)(PMe_2O)_2H]$, (0.14 g, 83%) as a white powder, which was filtered off, washed with diethyl ether and dried under suction: mp 196–198°C; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 81, ($^1J_{PtP_A}$ 2770 Hz, P_A), δ 45, ($^1J_{PtP_B}$ 3499 Hz, P_B), δ −5, ($^1J_{PtP_c}$ 2041 Hz, P_C), $^2J_{P_AP_B}$ 16 Hz, $^2J_{P_AP_C}$ 408 Hz, $^2J_{P_BP_C}$ 17.5 Hz; ^{1}H NMR ($CDCl_3$): δ 1.9 (2 × d. 12H, $^2J_{PH}$ 2.4 Hz), δ 1.45 (d 6H, $^2J_{PH}$ 1.4 Hz, $^3J_{PtH}$ 31 Hz), δ 7.5–7.75 (m, 5H); IR (nujol): 281 (w) (ν_{Pt-Cl}) cm^{-1}; (Found: C 27.71; H 4.41. $C_{12}H_{24}ClO_2P_3Pt$: requires C, 27.52; H 4.62%).

2.7. Control experiment: attempted hydration of acetonitrile with diphenylphosphine oxide

A vigorously stirred mixture of diphenylphosphine oxide (0.019 g, 0.10 mmol), acetonitrile (7.86 g, 0.192 mol) and water (5.0 ml, 0.27 mol) was heated under reflux for 15 h. After cooling to room temperature, the reaction mixture was analysed by GLC. This showed that no acetonitrile had been hydrated to acetamide.

2.8. Attempted hydration of methyl benzoate

A vigorously stirred mixture of **2a** (0.0052 g, 0.012 mmol), methyl benzoate (2.2 g, 0.016 mol), THF (8 ml) and water (0.6 ml, 0.03 mol) was refluxed at 90°C for 4 h. After cooling, the solvent was removed under reduced pressure and the starting material recovered.

2.9. The catalytic hydration of various nitriles with $[PtH(PMe_2OH)(PMe_2O)_2H]$, **2a**

2.9.1. Catalytic hydration of acetonitrile

A vigorously stirred mixture of **2a** (0.0127 g, 0.0296 mmol), acetonitrile (7.86 g, 0.192 mol) and water (5.0 ml, 0.27 mol) was refluxed for 15.5 h. After cooling, the excess water was removed under reduced pressure to give acetamide (10.35 g, 91%), which was dried in vacuo: mp 79–81°C (lit [36] 79–81°C); 1R (nujol) 3346, 3167 (s) (ν_{N-H}) cm^{-1}, 1676 (s) ($\nu_{C=O}$) cm^{-1}.

2.9.2. Catalytic hydration of 3-cyanopyridine

A vigorously stirred mixture of **2a** (0.005 g, 0.0117 mmol), 3-cyanopyridine (3.0 g, 0.029 mol) and water (5 ml, 0.277 mol) was refluxed at 90°C for 5 h. After cooling, the excess water was removed under reduced pressure to give nicotinamide (3.20 g, 91%), which was dried in vacuo. The purity of the product was checked by t.l.c.(silica) using a 1:1 ethyl acetate/toluene mixture as the eluent: mp 129–130°C (lit. [37] 128–131°C); IR (nujol) 3366, 3163 (s) (ν_{N-H}) cm^{-1}, 1676 (s) ($\nu_{C=O}$) cm^{-1}.

2.9.3. Catalytic hydration of acrylonitrile

A vigorously stirred mixture of **2a** (0.0068 g, 0.0158 mmol), acrylonitrile (20.15 g, 0.38 mol), ethanol (15 ml) and water (15 ml, 0.83 mol) was refluxed at 100°C for 15 h. After cooling, the solvent was removed under reduced pressure to give acrylamide (25.05 g, 93%), which was dried in vacuo: mp 84–85°C (lit. [38] 84.5°C); IR (nujol) 3341, 3173 (s) (ν_{N-H}) cm^{-1}, 1669 (s) ($\nu_{C=O}$) cm^{-1}.

2.9.4. Catalytic hydration of benzonitrile

A vigorously stirred mixture of **2a** (0.0054 g. 0.0126 mmol), benzonitrile (3.5 g, 0.034 mol), ethanol (5 ml) and water (1.5 ml, 0.083 mol) was refluxed for 4.5 h. After cooling, the solvent was removed under reduced pressure to give benzamide (3.55 g, 86%), which was dried in vacuo: mp 130°C (lit. [39] 130°C); IR (nujol) 3369, 3171 (s) (ν_{N-H}) cm^{-1}, 1653 (s) ($\nu_{C=O}$) cm^{-1}.

2.9.5. Catalytic hydration of 2,6-difluorobenzonitrile

A vigorously stirred mixture of **2a** (0.0052 g, 0.0121 mmol), 2,6-difluorobenzonitrile (2.0 g, 0.0143 mol), THF (5 ml) and water (0.5 ml, 0.027 mol) was refluxed at 90°C for 4.5 h. After cooling, the solvent was removed under reduced pressure to give 2,6-difluorobenzamide (1.75 g, 78%), which was dried in vacuo: mp 144–146°C (lit. [40] 144.5–145.5°C); IR (nujol) 3400, 1201 (s) (ν_{N-H}) cm^{-1}, 1653 (s) ($\nu_{C=O}$) cm^{-1}.

2.9.6. Catalytic hydration of 1,4-dicyanobenzene

A vigorously stirred mixture of **2a** (0.0062 g, 0.0144 mmol), 1,4-dicyanobenzene (1.0 g, 0.0078 mol), THF (15 ml) and water (1.0 ml, 0.017 mol) was refluxed at 95°C for 3 h. After cooling, the solvent was removed under reduced pressure to give 1,4-dibenzamide (1.23 g, 96%), which was dried in vacuo: mp 322–324°C (lit. [41] 320.5°C); IR (nujol) 3367, 3173 (s) (ν_{N-H}) cm^{-1}, 1653 (s) ($\nu_{C=O}$) cm^{-1}.

2.9.7. Catalytic hydration of 4-hydroxybenzonitrile

A vigorously stirred mixture of **2a** (0.0073 g, 0.0170 mmol), 4-hydroxybenzonitrile (1.0 g, 8.40 mmol), THF (5 ml) and aqueous NaOH (1.0 ml, 0.1 M) was refluxed at 95°C for 5 h. After cooling, the solvent was removed under reduced pressure to give a white residue. The crude product was chromatographed (silica gel column) using first 1:1 ethyl acetate/toluene to elute 4-hydroxybenzonitrile and then ethyl acetate to give 4-hydroxybenzamide (0.78 g, 63%), which was dried in vacuo; mp 163°C (lit. [42] 161–162°C); IR (nujol) 3415, 3339 (s) (ν_{N-H}) cm^{-1}, 1647 (s) ($\nu_{C=O}$) cm^{-1}.

2.9.8. Catalytic hydration of adiponitrile

A vigorously stirred mixture of **2a** (0.0084 g, 0.0196 mmol), adiponitrile (0.95 g, 0.0088 mol), THF (5 ml) and water (0.5 ml, 0.028 mol) was refluxed at 95°C for 8 h. During this time the monoamide $NC(CH_2)_4CONH_2$ started to precipitate out of solution. The reaction mixture was kept homogeneous by adding just enough water to dissolve the intermediate. After cooling, the solvent was removed under reduced pressure to give adipamide (1.23 g, 97%), which was dried in vacuo; mp 226–228°C (lit. [43] 227°C); IR (nujol) 3379, 3181 (s) (ν_{N-H}) cm^{-1}, 1653 (s) ($\nu_{C=O}$) cm^{-1}.

*2.9.9. Inhibition of catalytic activity of **2a** by potassium iodide and catalyst regeneration (monitored by GLC)*

2a (0.0065 g, 0.015 mmol) was added to a preheated solution of acrylonitrile (8.0 g, 0.152 mol), water (6.0 ml, 0.33 mol) and ethanol (10 ml). The mixture was then refluxed at 90°C and the progress of the reaction followed by withdrawing 0.05-ml aliquots every hour and analysing them by GLC. After 2.5 h potassium iodide (0.006 g, 0.036 mmol) was added and the effect monitored by GLC. After 2 h a large excess of $AgBF_4$ (0.042 g, 0.216 mmol) was added to the mixture and the reaction monitored to completion by GLC. A plot of percentage acrylamide produced versus time showed rapid formation of acrylamide, until the addition of potassium iodide when the rate of formation was slowed down. The rate of production of acrylamide increased on adding $AgBF_4$ to the quenched mixture.

*2.9.10. The **2b** / $AgBF_4$ catalysed hydration of acrylonitrile (monitored by GLC)*

Silver tetrafluoroborate (0.0055 g, 0.0282 mmol) was added to a vigorously stirred mixture of **2b** (0.0066 g, 0.014 mmol), acrylonitrile (8.08 g, 0.151 mol), ethanol (8 ml) and water (5 ml, 0.28 mol). The reaction was monitored every half hour by removing 0.05 ml aliquots, which were analysed by GLC. The reaction was monitored this way to completion.

*2.9.11. Regioselectivity of acrylonitrile hydration catalysed by **2a***

2a (0.0094 g, 0.0219 mmol) was added to a vigorously stirred preheated (95°C) mixture of acrylonitrile (4.0 g, 0.076 mol, ethanol (4 ml) and water (3 ml, 0.166 mol). The reaction was monitored by removing 0.1-ml aliquots every hour, and analysing them by GLC. The reaction was allowed to proceed to completion. After cooling, the solvent was removed under reduced pressure to give acrylamide (5.12 g, 95%), which was dried in vacuo.

*2.9.12. Homogeneity of a hydration solution using **2a** as catalyst*

A vigorously stirred mixture of **2a** (0.0132 g, 0.0306 mmol), acrylonitrile (8.0 g, 0.152 mol), ethanol (10 ml), water (6 ml, 0.166 mol) and elemental mercury (2 drops) was refluxed at 90°C for 3.5 h. After cooling, the mercury was removed and the product isolated by evaporation under reduced pressure to give acrylamide (10.1 g, 94%), which was dried in vacuo.

*2.10. The catalytic hydration of various nitriles with $[PtCl(PMe_2OH)(PMe_2O)_2H]$, **2b**, and $AgBF_4$*

2.10.1. Catalytic hydration of acetonitrile

2b (0.010 g, 0.022 mmol) was dissolved in a vigorously stirred mixture of acetonitrile (3.9 g, 0.096 mol) and water (3.5 ml, 0.194 mol). To this was added an excess of $AgBF_4$ (0.0057 g, 0.029 mmol) and the reaction mixture refluxed for 3 h. After cooling, it was filtered to remove the precipitated AgCl. The solvent was then removed under reduced pressure to give acetamide (4.35 g, 77%), which was dried in vacuo.

2.10.2. Catalytic hydration of acrylonitrile

2b (0.0052 g, 0.0112 mmol) was dissolved in a vigorously stirred mixture of acrylonitrile (4.0 g, 0.076 mol), ethanol (4 ml) and water (3 ml, 0.166 mol). To this was added an excess of $AgBF_4$ (0.0062 g, 0.032 mmol) and the reaction mixture refluxed for 3 h. After cooling, it was filtered to remove the precipitated AgCl. The solvent was then removed under reduced pressure to give acrylamide (4.50 g, 93%), which was dried in vacuo.

2.10.3. Catalytic hydration of benzonitrile

2b (0.0045 g, 0.0097 mmol) was dissolved in a vigorously stirred mixture of benzonitrile (3.5 g, 0.034 mol), ethanol (7 ml) and water (2 ml, 0.06 mol). To this was added an excess of $AgBF_4$ (0.0045 g, 0.023 mmol) and the reaction

mixture refluxed at 90°C for 5 h. After cooling, it was filtered to remove the precipitated AgCl. The solvent was then removed under reduced pressure to give benzamide (3.60 g, 87%), which was dried in vacuo.

The same methods were also used to investigate the activity of catalysts generated by reaction of $AgBF_4$ with the complexes $[PtCl(PPh_2OH)(PPh_2O)_2H]$, **1b,**

$$[PtCl(\overline{CH_2(CH_2)_3POH})(\overline{CH_2(CH_2)_3PO)_2H}],$$

3, and $[PtCl(PMe_2Ph)(PMe_2O)_2H]$, **4**.

2.10.4. Preparation of $[Pd(\mu\text{-}Cl)(PMe_2O)_2H]_2$

A suspension of $PdCl_2(PhCN)_2$ (0.5 g, 1.30 mmol) in dry toluene (20 ml) was treated with dimethylphosphine oxide (0.45 g, 5.77 mmol) and heated at 60°C for 2 h. The clear pale yellow solution was allowed to cool to room temperature and the solvent removed under reduced pressure to give a pale yellow oil. Recrystallisation from dichloromethane/ethanol gave $[Pd(\mu\text{-}Cl)(PMe_2O)_2H]_2$ (0.29 g, 75%) as a pale yellow crystalline solid; mp 207–209°C; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 83; ^1H NMR ($CDCl_3$): δ 1.75 (d, $^2J_{PH}$ 11 Hz); IR (nujol): 247, 274 (w) (ν_{Pd-Cl}) cm^{-1}; (Found: C, 16.13; H, 4.38, $C_8H_{26}Cl_2O_4P_4Pd_2$ requires C, 16.18; H, 4.41%).

2.10.5. Preparation of $[PdCl(PMe_2OH)(PMe_2O)_2H$

A suspension of $[Pd(\mu\text{-}Cl)(PMe_2O)_2H]_2$ (0.20 g, 0.337 mmol) in degassed acetone (20 ml) was treated with dimethylphosphine oxide (0.055 g, 0.705 mmol) and stirred at room temperature overnight under nitrogen. The reaction mixture was concentrated under reduced pressure to ca. 5 ml. Addition of water gave $[PdCl(PMe_2OH)(PMe_2O)_2H]$ (0.15 g, 59%) as fine white needles, which were filtered off, washed with water, diethyl ether and dried in vacuo: mp 184–186°C; IR (nujol): 272 (w) (ν_{Pd-Cl}) cm^{-1}. Found: C, 18.67; H, 5.22. $C_6H_{20}ClO_3P_3Pd$ requires C, 19.25; H, 5.39%).

3. Results and discussion

3.1. Catalysis of nitrile hydration

Our initial attempts to use a coordination compound containing a hydroxyphosphine for the hydrolysis of a nitrile were carried out using the hydride complex **1a**. Thus heating **1a** in aqueous acetonitrile under reflux for 16 h gives acetamide with a turnover number of ca. 390. A control experiment with diphenylphosphine oxide under similar conditions produced no acetamide as monitored by GLC, although triphenylarsine oxide has been reported [44] as a reagent for the hydrolysis of activated nitriles. Jensen and Trogler [17] found that the catalytic activity of platinum phosphine complexes increases when the steric bulk of the substituents on phosphorus is reduced. We found a similar effect with the phosphinito complexes and the turnover frequency of the methyl complex **2a** is much higher than the phenyl complex **1a** (vide infra). We also established that our system was acting homogeneously by carrying out the hydrolysis of acrylonitrile in the presence of metallic mercury as suggested by Whitesides et al. [45]. This was particularly important because heterogeneous copper catalysts have been used in the commercial production of acrylamide [12,13], and other metals are also known to catalyse the hydration of nitriles [14]. We found that addition of mercury did not affect the catalytic activity of **2a** in the hydration of acrylonitrile, and so conclude that the reaction is occurring homogeneously. A further control experiment established that **2a** does not catalyse the hydrolysis of methyl benzoate. We were initially surprised by the high activity of these catalysts derived from the neutral hydrides, **1a** and **2a**. Intuitively, we would expect that a positive charge on a nitrile complex would make

it more susceptible to nucleophilic attack. In the case of the ammine ruthenium complexes $[(NH_3)_5Ru(NCMe)]^{2+}$ and $[(NH_3)_5Ru(NCMe)]^{3+}$, the Ru(III) complex is attacked by hydroxyl anion at least a million times faster than the Ru(II) complex [46] (for a review on the reactivity of coordinated nitriles see Ref. [47]). We therefore suspected that a cationic species might be responsible for the catalysis, and obtained confirmation of this by adding potassium iodide to a solution of **2a** which was catalysing the hydration of acrylonitrile. The addition stopped the catalysis, but it could be restarted by adding silver tetrafluoroborate. We therefore suggest that under the conditions of the catalysis the hydrido complex **2a** reacts with

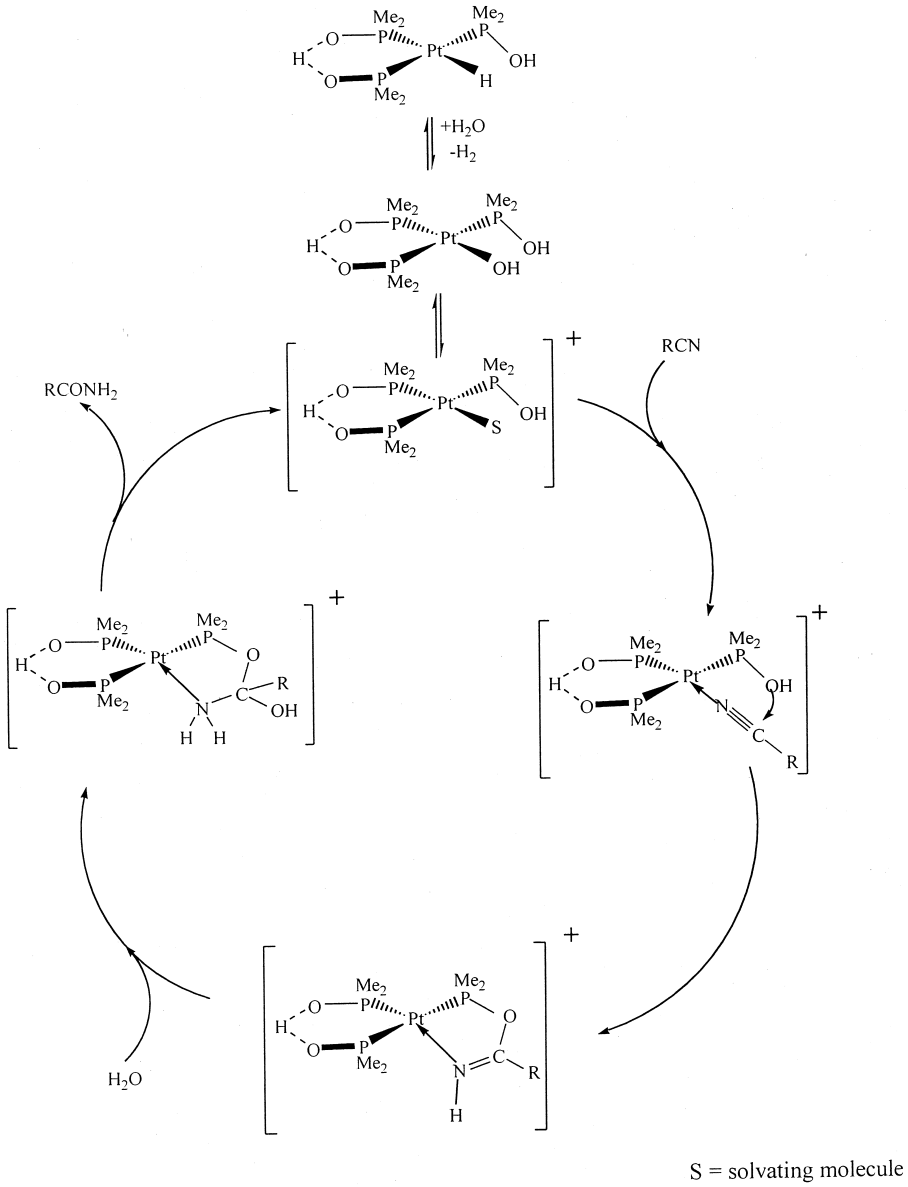


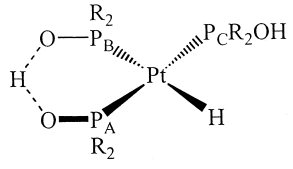
Fig. 1. Suggested mechanism for the hydrolysis of nitriles by phosphinito complexes.

water to give a cationic coordination compound, hydrogen and hydroxide similar to the reaction between $[(PAr_3)_3Rh(H)CO]$ and water [48]. It is thus possible to postulate a mechanism for the hydrolysis starting from the hydride precursor (Fig. 1).

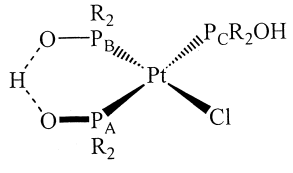
A key step in the suggested mechanism is the intramolecular nucleophilic attack of the hydroxy group attached to phosphorus on the coordinated nitrile to give a five-membered ring intermediate, (which incidentally has five different atomic types). A similar intramolecular nucleophilic attack has been established by X-ray crystallography for an iridium complex [49]. Another possibility, which has been considered by Kaminskaia and Kostic [18] in an analogous situation, is that the hydroxy group of the coordinated phosphine oxide may interact with a water molecule which attacks the coordinated nitrile. We have drawn the initial species entering the catalytic cycle in Fig. 1 with a solvating molecule, S, in one position of the coordination sphere. S could be water (particularly if the catalytic solution was prepared by boiling the hydride in water before adding the nitrile), or in catalytic cycles after the first turnover, the nitrile complex might be formed by an associative mechanism from the amide complex and a molecule of nitrile with the subsequent loss of amide product.

3.2. Preparation of the catalysts and variation of substituents on phosphorus

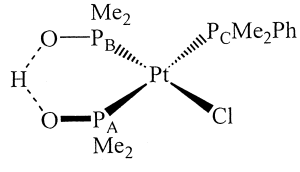
Compound **1a** was originally prepared by Beaulieu et al. [50] and was investigated for catalytic activity in hydroformylation by van Leeuwen et al. [51]. The hydride complexes are only sparingly soluble, but an X-ray structure of a triethyl phosphine derivative, $[PtH(PEt_3)(PPh_2O)_2H]$, has been reported by Han et al. [52]. In addition to the substitution of phenyl for methyl mentioned above we have carried out a systematic study of the effect of changing the substituents on phosphorus. Following the discovery that the catalytic species was cationic, we decided to prepare the catalysts from the halide precursors **1b, 2b, 3** and **4** and silver tetrafluoroborate. The halides are generally more soluble than the hydrides and so may be studied by NMR. We therefore prepared **1b**, **2b**, and **3** using the method of Dixon and Rattray [34], that is by reaction of the appropriate phosphine oxide with K_2PtCl_4. Dimethylphosphine oxide was prepared from diethyl phosphite and methyl



R = Ph, **1a**
= Me, **2a**



R = Ph, **1b**
R = Me, **2b**
R_2= -$(CH_2)_4$-, **3**



4

magnesium chloride as reported by Hays [30], but the phospholane oxide required for **3** gave some difficulty and has not been reported previously. Reaction of diethyl phosphite with the di-Grignard reagent from 1,4-dibromobutane yielded an oil which, after vacuum distillation, appeared to be somewhat impure. This was perhaps not surprising as secondary phosphine oxides are known to disproportionate to phosphines and phosphonic acids on heating [53]. Fortunately however, the phospholane oxide preferentially complexed with platinum on reaction with K_2PtCl_4, and we obtained good analytical data and NMR spectra for **3**. In order to

Table 1
Comparison of the catalytic activity of phosphinito catalysts for the hydration of acetonitrile, acrylonitrile, and benzonitrile

Turnover rate: mol/(mol of catalyst h)			
Catalyst precursor	Acetonitrile	Acrylonitrile	Benzonitrile
1b	20	68	35
2b	488	1800	610
3	90	670	140
4	186	310	230

corroborate the mechanism suggested in Fig. 1, we prepared **4** by reaction of **2b** with dimethylphenylphosphine. Substitutions of this type have been reported by Dixon and Rattray [34]. For the catalytic tests we prepared the catalysts from **1b**, **2b**, **3** and **4** with silver tetrafluoroborate and carried out the hydrolysis of acetonitrile, acrylonitrile and benzonitrile. The results are shown in Table 1, and it can be seen that the most active catalyst is that derived from dimethylphosphine complex, **2b**. A comparison of the activity of **4** with **2b**, shows that substitution of the monodentate hydroxyphosphine by the tertiary phosphine dimethylphenylphosphine, lowers the catalytic activity substantially. This adds further support to our suggestion that the reaction proceeds by internal nucleophilic attack on the coordinated nitrile.

3.3. Comparison with related systems

Following the example of Jensen and Trogler [17], in Table 2 we give a comparison of the turnover frequencies for the hydrolysis of acetonitrile to acetamide as found for **1a**, **2a** and some other catalysts previously reported. Previous work has been carried out with both palladium and platinum containing homogeneous catalysts. Although we were able to prepare the palladium analogue of **2b**, we did not observe any catalytic activity for the hydration of acetonitrile on reaction with silver tetrafluoroborate.

3.4. NMR studies

We carried out NMR studies on the catalyst precursors. Unfortunately, **2a** is insufficiently soluble and too reactive to give solution NMR spectra. **2a** reacts with chloroform or as a suspension in THF with a few drops of hydrochloric acid to give **2b**. The chloride complexes **2b**, **3** and **4** are sufficiently soluble to give reasonable NMR spectra, and the chemical shift and coupling constant data are given in Section 2, and labeling of the phosphorus atoms is given on the structural diagrams.

In the case of **2b** we examined the variation of the $^{31}P\{^{1}H\}$ NMR spectrum with temperature. At $-55°C$ the three phosphorus atoms of **2b** are distinguishable, and appearance of the spectrum is complex due to P–P and P–Pt coupling. At ambient temperature an exchange process, as shown in Fig. 2, causes the resonances due to P_A and P_C to collapse to a broad single resonance, but P_B which is always chelating, remaining as

Table 2
Comparison of various catalysts for the hydrolysis of acetonitrile

Catalyst	Temperature (°C)	Turnover frequency: mol/(mol of catalyst h)	Turnover number: mol/(mol of catalyst)	Reference
$[PtH(PMe_2OH)(PMe_2O)_2H]$, **2a**	90	380	5700	This work
$[PtH(PPh_2OH)(PPh_2O)_2H]$, **1a**	90	23	369	This work
$[PtH(H_2O)(PMe_3)_2][OH]$	78	178	5000–6000	[17]
$[PtH(H_2O)(PEt_3)_2][OH]$	78	70	Not reported	[17]
$[PdCl(OH)(bipy)(H_2O)]$	76	29	Not reported	[54]
$Pt[P(C_6H_{11})_3]_2$	80	27	405	[55]
$Pt(PEt_3)_3$	80	3	54	[55]
$C_{23}H_{29}N_4O_2SPd_2(CH_3CONH)$	80	Not reported	4000	[56]
NaOH	78	0.4	–	[17]

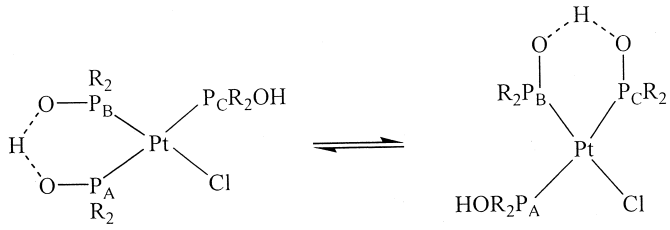


Fig. 2.

a sharp peak with a P_B–Pt coupling constant of 3486 Hz. This is typical of phosphorus *trans* to chlorine [57].

In the case of **4** the exchange process shown in Fig. 2 cannot occur and so the spectrum shows three different phosphorus atoms at ambient temperature. The lower catalytic activity found for **4** with $AgBF_4$ compared with **2b** with $AgBF_4$ as shown in Table 1 suggests that the hydroxyphosphines have formed a relatively stable hydrogen bridge which results in the hydroxy groups being less available to attack the coordinated nitrile group.

3.5. Range of application and catalyst selectivity

We have carried out the hydrolysis reaction using **2a** with a variety of nitriles. Results are shown in Table 3.

The choice of solvent does not appear to be critical, and in some cases, for example 4-hydroxybenzonitrile, addition of a small quantity of sodium hydroxide was beneficial. The reaction is particularly successful with acrylonitrile and proceeds with hydration of the nitrile group but without addition to the carbon–carbon double bond. We obtained a turnover number of 77,000 using **2a** as catalyst for this reaction, without using specially purified acrylonitrile. Previous workers using platinum containing homogeneous catalysts for the hydration of acrylonitrile have reported addition to the C=C double bond as well as hydrolysis of the nitrile group. The results of some of these studies are shown in Table 4.

Jensen and Trogler's [17] study of the hydration of acrylonitrile catalysed by $[PtH(H_2O)(PMe_3)_2]OH$ showed that the relative proportions of nitrile/alkene hydration are very temperature dependent [17] and at 80°C nitrile hydration is the minor pathway. Jensen and Trogler propose that the alkene hydration occurs by nucleophilic attack on a coordinated alkene, rather than Michael addition to the acrylonitrile coordinated through the nitrile group. We at-

Table 3
Summary of yields and conditions for nitrile hydrolysis with catalyst 2a

Nitrile	Product	Reaction medium	Isolated yield (%)	Turnover frequency mol/(mol. catalyst h)
Acetonitrile	Acetamide	Water	91	380
Acrylonitrile	Acrylamide	Aqueous ethanol	93	1485
1,4 Dicyanobutane	Adiponitrile	Aqueous THF	97	55
Benzonitrile	Benzamide	Aqueous ethanol	86	518
4-Hydroxybenzonitrile	4-Hydroxybenzamide	Aqueous THF	63	63
1,4-Dicyanobenzene	1,4-Diamidocarboxybenzene	Aqueous THF	96	173
2,6-Difluoro-benzonitrile	2,6-Difluoro-benzamide	Aqueous THF	78	220
3-Cyanopyridine	Nicotinamide	Water	91	450

Table 4
Catalytic hydration of acrylonitrile showing competition with alkene hydration

Catalyst	Temperature (°C)	Turnover frequency: mol/(mol of catalyst h)			Selectivity for nitrile (%)	Reference
		Acrylamide	β-Cyanoethanol	β,β-Dicyano ethylether		
$[PtH(PMe_2OH)(PMe_2O)_2H]$, **2a**	90	1485	–	–	> 99	This work
$[PtH(H_2O)(PMe_3)_2][OH]$	25	6.2	0.02	0.19	97	[17]
$[PtH(H_2O)(PMe_3)_2][OH]$	80	65.0	84.5	10.5	29	[17]
$[Pt(P^iPr_3)_3]$	80	1.8	2.5	20.9	7.5	[55]
$[Pt(NHCOMe)(Ph)(PEt_3)_2]$	80	2.2	0.25	2.45	45	[58]

tribute the high selectivity of **2a** to the intramolecular nucleophilic attack on the coordinated nitrile, as suggested in the mechanism given in Fig. 1. Hydration of the carbon–carbon double bond would require the unlikely formation of a seven-membered ring. The high catalytic activity of **2a** was also evident when 3-cyanopyridine was used as substrate. 3-Cyanopyridine has two donor nitrogen atoms and the ring nitrogen would be expected to coordinate strongly to Pt(II). However, we obtained a 91% yield of nicotinamide after 5 h, and so deduce that there must be sufficient cyano-coordinated complex to allow the reaction to proceed at a reasonable rate.

4. Conclusion

We have found very active catalysts for the hydrolysis of nitriles to amides, which are tolerant of some functional groups. The degree of tolerance needs to be further explored, and the application to complex molecules developed. Nitriles have been used in rhodium catalysed Michael addition to αβ-unsaturated esters [59]. The hydrolysis of nitriles obtained by cyanoethylation has been reported by Murahashi et al. [60] but the catalysts used were of low activity. The scope of these reactions is increased by the high activity of the catalysts reported here.

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