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A New Homogeneous Platinum Containing Catalyst for the Hydrolysis of Nitriles.

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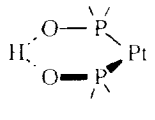
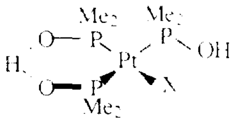
Abstract: $[(Me_2PO\cdots H\cdots OPMe_2)PtH(PMe_2OH)]$ is an extremely active homogeneous catalyst for the hydration of nitriles to amides: a mechanism involving intramolecular attack by a phosphine oxide on a nitrile within the co-ordination sphere of the platinum atom is suggested.

The hydrolysis of nitriles to amides is usually carried out in the laboratory using acid or base catalysis. A problem associated with this reaction is that it is often not possible to stop at the amide stage and further hydrolysis to the acid occurs.[1] Enzymes [2] can be used to give amides exclusively, and heterogeneous metal catalysts are used industrially, for example in the manufacture of acrylamide.[3] We report here the use of phosphinito complexes of platinum as homogeneous catalysts for the selective hydrolysis of nitriles to amides.

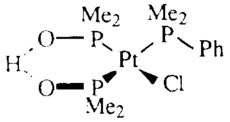
We discovered the catalytic activity of phosphinito complexes while studying the reactions of secondary phosphine complexes. We undertook the study because of the interesting reactions of secondary phosphines in the co-ordination sphere of metals, which have been summarised by Wolfsberger.[4] In common with other investigators,[5,6] we found [7] that under some conditions involving air or hydroxylic solvents, secondary phosphines form a six membered hydrogen bonded chelate of the type shown in I. Compounds of this type have been known for many years, and have been investigated as hydroformylation catalysts by van Leeuwen and co-workers.[8] Earlier work has been reviewed by Roundhill *et al.*[9] We decided to investigate these complexes as hydration catalysts.



I



IIa, X=H
IIb, X=Cl



III

We find that the phosphinito complex IIa catalyses the hydrolysis of nitriles to amides, with no detectable further hydrolysis to the acid. This selective hydrolysis is very useful synthetically, as generally the rates of hydrolysis of amides to the carboxylate ion, are greater than the rates of hydrolysis of nitriles to amides.[10] The hydrolysis is carried out by boiling the nitrile with water under reflux, or if the nitrile is not soluble in water, in aqueous tetrahydrofuran or ethanol. The most active catalyst we have found so far is derived from dimethylphosphine oxide, and the most convenient precursor is the hydride complex IIa. Generally 0.01-0.1 mole% of catalyst is sufficient to carry out the hydrolysis, which suggests possible industrial applications.[11] A comparison of the effectiveness of the new catalyst for the hydration of acetonitrile relative to some of those already reported is given in Table 1.

Table 1. Comparison of Catalytic Activities for the Hydration of Acetonitrile to Acetamide

Catalyst	Temp (°C)	Turnover Frequency mol/(mol of cat. h)	Turnover Number mol/(mol of cat.)	Reference
$[PtH(PMe_2OH)(PMe_2O)_2H]$	90	380	5,700	this work
$[PtH(H_2O)(PMe_3)_2][OH]$	78	178	5,000-6,000	12
$[PtH(H_2O)(PEt_3)_2][OH]$	78	70	not reported	12
$[PdCl(OH)(bipy)(H_2O)]$	76	29	not reported	13
$Pt[P(cC_6H_{11})_3]_2$	80	27	405	14
$Pt(PEt_3)_3$	80	3	54	14
$C_{23}H_{29}N_4O_2SPd_2$	80	not reported	4,000	15
NaOH	78	0.4		12

We have carried out hydrolyses with a range of nitriles, some of which are listed in Table 2.

Table 2. Yields and Turnover Frequencies Using IIa

Nitrile	Reaction medium at reflux temperature	Isolated yield of amide (%)	Turnover Frequency mol/(mol of cat.h)
Acetonitrile	Water	91	380
Acrylonitrile	Aqueous Ethanol	93	1485
Benzonitrile	Aqueous Ethanol	86	518
2,6-difluorobenzonitrile	Aqueous tetrahydrofuran	78	220
3-cyanopyridine	Water	91	450

Interestingly, although the catalyst is a co-ordination compound of platinum, the catalysis is not inhibited by co-ordination of the pyridine nitrogen in 3-cyanopyridine. The catalyst is especially active for the hydrolysis of acrylonitrile: 0.004 mol% of catalyst is sufficient, and the turnover number exceeds 50,000. The hydrolysis of acrylonitrile also provides a test of selectivity, as usually hydration of the carbon-carbon double bond competes with amide formation.[12] GLC analysis of the reaction mixture using IIa as catalyst shows a selectivity to acrylamide of >99%.

The active catalyst appears to be cationic as, although IIb is not active, it becomes so on reaction with Ag^+. The cationic nature of the catalytic species is also supported by the fact that the catalysis can be stopped by adding halide ion. McKenzie and Robson [15] attribute their comparatively high turnover number to an intramolecular attack by OH on a co-ordinated nitrile. In our system we find that the catalytic activity is

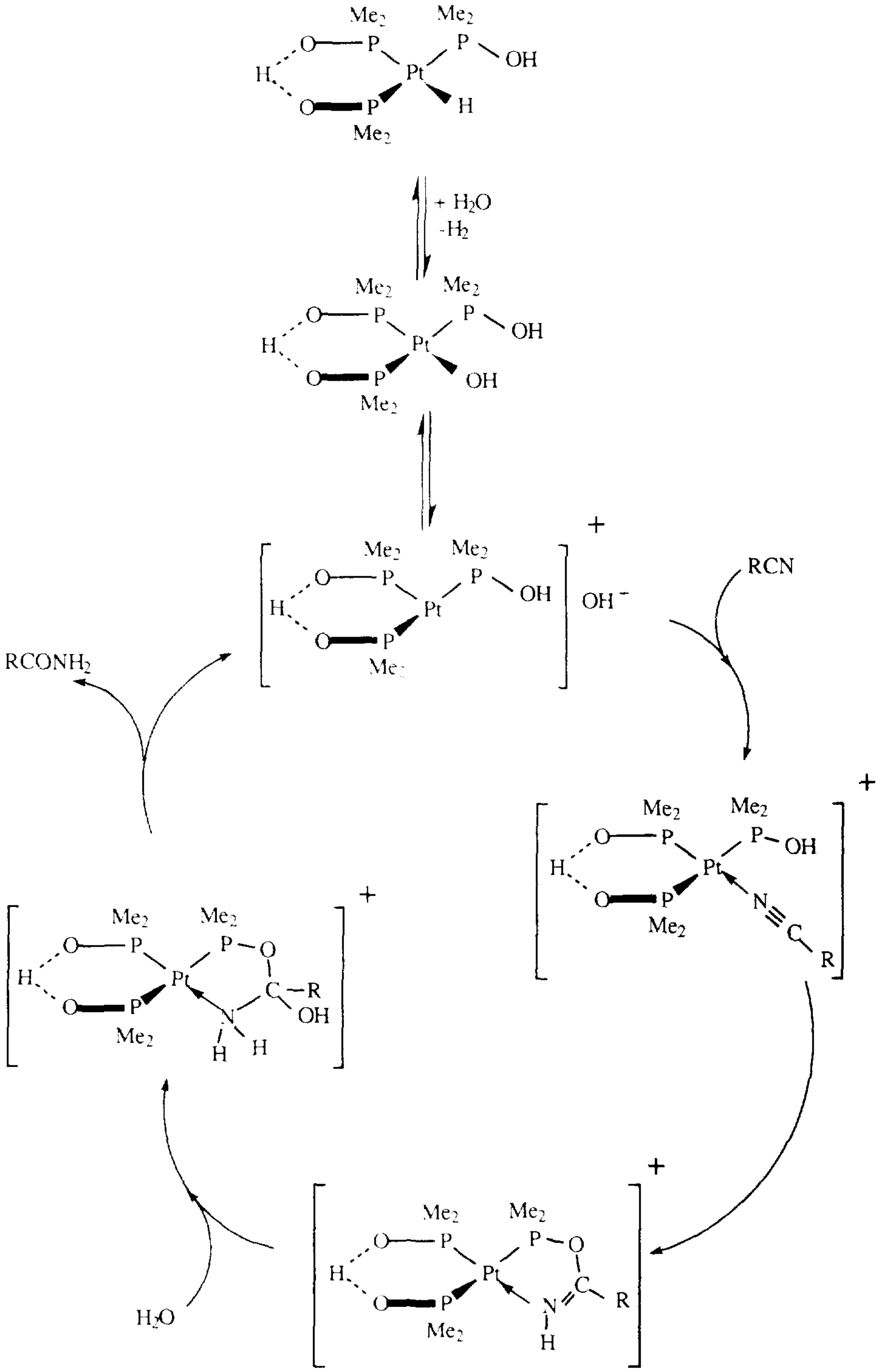


Figure. Suggested Mechanism for the Hydolysis of Nitriles by Phosphinito Complexes.

lowered when one of the phosphorus donors does not have a hydroxy substituent. Thus the catalyst derived from III and $AgBF_4$ has less than half the turnover rate of the catalyst derived from IIb and $AgBF_4$. This leads us to suggest attack by the hydroxyphosphine on the co-ordinated nitrile as shown in the catalytic cycle in the Figure. We have not found conditions under which free phosphine oxides catalyse the hydration of nitriles. Other authors have noted substantial rate increases on comparing intramolecular and intermolecular reactions, and intramolecular reactions are important in enzyme mimics.[16,17]

Experimental Procedure

The catalyst IIa was prepared as suggested by other workers [8,18] by the reaction of $(Ph_3P)_4Pt$ with an excess of dimethylphosphine oxide in toluene.

Preparation of IIa: Dimethylphosphine oxide (0.16g, 2.05 mmol) was added to a stirred suspension of $Pt(PPh_3)_4$ (0.5g, 0.402 mmol) in dry toluene (10 ml) at room temperature under nitrogen. Almost immediately a colourless solution was obtained, which was stirred for 1h, during which time the product begins to precipitate. Precipitation was completed by addition of diethyl ether (20 ml) and after stirring for a further hour the product was filtered off, washed with diethyl ether and hexane and dried *in vacuo*. Yield: 0.13g, 75%.M.p. 231-233^{0}C. ν(Pt-H) 1989 cm^{-1}. Found C,17.2, H,4.8. $C_6H_{21}O_3P_3Pt$ requires C,16.8; H,4.9%.

Hydration of 3-cyanopyridine: A vigorously stirred mixture of IIa (5.0 mg, 0.0117 mmol), 3-cyanopyridine (3.0g, 0.029 mol) and water (5ml, 0.277 mol) was heated under reflux for 5 hours. After cooling the excess of water was removed under reduced pressure to give nicotinamide (3.2g, 91%). M.p. 129-130, Litt.[19] 129-130^{0}C.

Hydration of acrylonitrile: A vigorously stirred mixture of IIa (6.8 mg, 0.0158 mmol), acrylonitrile (20.15g, 0.38 mol), ethanol (15 ml) and water (15 ml, 0.83 mol) was heated under reflux for 15h. After cooling, the solvents were evaporated to give acrylamide (25.05g, 93%) which was dried *in vacuo*. M.p. 84-85, Litt.[19] 85^{0}C.

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