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# Synthesis and chemistry of 2-pyridyl(phosphine) complexes of platinum(0) *

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## Abstract

The complexes tetrakis[tri(2-pyridyl)phosphine]platinum(0), **1**, and tris[2-(diphenylphosphino)pyridine]platinum(0), **2**, are synthesized, and characterized by $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopy. The reactions of **1** and **2** with olefins (ethylene, maleic anhydride, diethyl maleate, and olefinic nitriles) are studied and some square-planar $Pt(PR_3)_2(\eta^2\text{-olefin})$ species isolated ($PR_3$ = the pyridylphosphine). No olefin hydration products are observed on heating the olefin complexes in aqueous solution. Oxidative addition of MeI to **1** and to **2** gives the *trans*-$PtI(Me)(PR_3)_2$ species. However, the *trans*-$Pt(H)Cl(PR_3)_2$ species is isolated only from reaction of **2** with gaseous HCl; the hydride reacts with acrylonitrile to form *cis*-$PtCl(CH_2CH_2CN)(PR_3)_2$.

## Introduction

In 1969, studies from this laboratory reported on the catalytic hydration of fluoroolefins and acetylenes using aqueous acid solutions containing chlororuthenate(II) or chlororhodate(III) species [1,2]. Interest in such catalysis has been rejuvenated and, following reports on olefin hydration catalyzed by $Pt(PR_3)_n$, $n = 2$ or 3, R = alkyl [3,4], and *trans*-$Pt(H)Cl(PMe_3)_2$ [5,6], we decided to initiate studies on corresponding Pt complexes containing pyridylphosphines.

The coordination chemistry of the pyridylphosphines $PPh_{3-n}py_n$, where $n = 1$–3 and py represents the 2-pyridyl moiety, has developed noticeably in the last decade (see for example, refs. 7–14), while reports on catalysis using pyridylphosphine complexes include: hydroformylation of olefins and the water-gas-shift reaction catalyzed by Rh species [14,15], conversion of methanol to ethanol using Ru species [16], and conversion of propyne to methylmethacrylate using Pd species [17]. The increased water solubility on successive substitution of the phenyl groups of $PPh_3$ by the 2-pyridyl group [18] appears an attractive feature in the use of pyridylphosphine ligands in systems for catalytic hydration.

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* Dedicated to the memory of Professor Piero Pino.

In this paper, we report on the synthesis of the complexes $Pt(Ppy_3)_4$, **1**, and $Pt(PPh_2py)_3$, **2**, and their reactions toward some olefinic compounds, HCl, and MeI, and note the lack of activity of some derived $\eta^2$-olefin complexes toward water. None of the species isolated catalyzes the hydration of acrylonitrile.

## Experimental

All nondeuterated solvents were distilled from drying agents under $N_2$ prior to use. The deuterated solvents, acetone-$d_6$, chloroform-$d_1$, toluene-$d_8$, dichloromethane-$d_2$, and benzene-$d_6$, were degassed by six freeze-pump-thaw cycles for NMR experiments. Gaseous HCl (BDH) and $C_2H_4$ (Matheson) were used without purification; $PPh_2Cl$ (Aldrich) and $PCl_3$ (Mallinckrodt) were distilled under $N_2$; 2-bromopyridine (Aldrich) was purified by stirring with NaOH pellets overnight at room temperature and then distilling from CaO under vacuum prior to use. The Aldrich products acrylonitrile, methacrylonitrile, crotonitrile, diethyl maleate, and diethyl fumarate were distilled from CaO under reduced pressure and kept in the refrigerator. n-Butyllithium (Aldrich), hydrazine hydrate (MCB) and maleic anhydride (Aldrich) were used without purification. $K_2PtCl_4$ was obtained on loan from Johnson Matthey, Ltd.

The $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer using 5-mm tubes. An external reference of 85% $H_3PO_4$ is used for reporting $^{31}P$ shifts, while the $^{195}Pt\{^1H\}$ shifts are referenced to the absolute resonance frequency of $^{195}Pt$, which itself is relative to the $^1H$ resonance of TMS at 300 MHz, $\Xi = 64.2$ MHz [19,20]; within both spectra, downfield shifts are positive. Infrared spectra were recorded on a Nicolet 5DX-FT spectrophotometer, using Nujol mulls between KBr plates, samples being prepared using degassed Nujol under $N_2$ in a glove-bag. All reactions and manipulations were performed under anaerobic conditions, except when otherwise stated.

*Pyridylphosphines* $Ppy_3$ was synthesized according to a literature procedure involving addition of $PCl_3$ to 2-lithiopyridine formed *in situ* at low temperature from $^nBuLi$ and 2-bromopyridine [14]; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): $\delta$ $-0.05$. $PPh_2py$ was prepared in the same manner but using $PPh_2Cl$ instead of $PCl_3$; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): $\delta$ $-3.28$.

### *Tetrakis[tri(2-pyridyl)phosphine]platinum(0), 1*

(a) A saturated aqueous solution of $K_2PtCl_4$ (0.50 g, 1.2 mmol; in 5 mL) was added to a refluxing THF solution (20 mL) containing KOH (0.13 g, 2.4 mmol) and five equivalents of $Ppy_3$ (2.92 g, 11 mmol). The mixture was refluxed for about 10 min, and the resulting orange solution cooled to room temperature (r.t.). The THF was pumped off, and the yellow precipitate that formed in the aqueous layer was extracted with $CH_2Cl_2$ (10 mL); this $CH_2Cl_2$ solution was transferred via a cannula tube to another flask where the extract was dried over $MgSO_4$ for 2 h. The drying agent was filtered off, and hexane introduced until the precipitate reformed again; the solid was collected, washed thoroughly with hexane, and recrystallized from $CH_2Cl_2$/hexane (v/v 1 : 1) to give a yellow solid, which was dried *in vacuo* at 20 °C; yield up to 0.65 g, 43%.

(b) A benzene suspension of *cis*-$PtCl_2(Ppy_3)_2$ [21,22*] (0.30 g, 0.38 mmol; in 30 mL) and $Ppy_3$ (0.30 g, 1.14 mmol) was refluxed, and hydrazine hydrate in benzene (10% by vol.) was added dropwise to the mixture with vigorous stirring until all white precursor complex had dissolved. The resulting yellow solution thus formed was refluxed for another 10 min and then cooled to 5°C. The yellow solid that formed upon concentration of the solution to 10 mL was collected by filtration and redissolved in $CH_2Cl_2$ (15 mL). Compound **1**, obtained by a reprecipitation procedure using hexane (~ 20 mL), was then collected and dried *in vacuo*; yield 0.19 g, 40%.

Anal. Found: C, 59.38; H, 3.80; N, 13.49. $C_{60}H_{48}N_{12}P_4Pt$ calcd.: C, 57.37; H, 3.85; N, 13.38%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, −45°C [23*]): $\delta$ 30.1 (s, $^1J(PtP)$ 3829 Hz). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, −45°C): $\delta$ −538.3 (qn, $^1J(PtP)$ 3840 Hz).

### *Tris[2-(diphenylphosphino)pyridine]platinum(0), 2*

A saturated aqueous solution of $K_2PtCl_4$ (1.0 g, 2.4 mmol; in 10 mL) was added to a refluxing EtOH solution (20 mL) containing KOH (0.27 g, 4.8 mmol) and 3.5 equivalents of $PPh_2py$ (2.3 g, 8.5 mmol). The mixture was refluxed for 20 min, and the resulting yellowish-orange solution cooled to r.t. and then concentrated to 15 mL. A yellow solid that formed was collected by filtration and washed with cold EtOH (5 mL) thrice. This product was then redissolved in $CH_2Cl_2$ (12 mL), reprecipitated by the addition of hexane (20 mL), and then dried *in vacuo*; yield of $Pt(PPh_2py)_3$ 1.7 g (72%).

Anal. Found: C, 62.63; H, 4.49; N, 3.90. $C_{51}H_{42}N_3P_3Pt$ calcd.: C, 62.19; H, 4.30; N, 4.27%. $^{31}P\{^1H\}$ NMR (toluene-$d_8$, −70°C): $\delta$ 57.02 (s, $^1J(PtP)$ 4444 Hz). $^{195}Pt\{^1H\}$ NMR (toluene-$d_8$, −70°C): $\delta$ −300.3 (q, $^1J(PtP)$ 4433 Hz).

### $Pt(PPh_2py)_2[\eta^2\text{-}CH(R)=C(R')CN]$ ($R = R' = H$ (**3**); $R = H$, $R' = CH_3$ (**4**); and $R = CH_3$, $R' = H$ (**5**))

A solution of excess cyanoolefin (acrylo-, methacrylo-, and crotonitrile, respectively; distilled, ~ 1 mL) in $Et_2O$ (5 mL) was degassed by 3 freeze-pump-thaw cycles, and then added dropwise to a suspension of **2** (93 mg, 0.094 mmol) in $Et_2O$ (20 mL) until a colourless solution resulted. This was left at −20°C overnight: the deposited white solid was collected. These compounds **3**–**5**, which were obtained in ~ 75% yields as air-dried products, gave unambiguous NMR data (see below), but the elemental analyses were unsatisfactory because of loss of the cyanoolefin during evacuation procedures. For example, pumping on **3** resulted in reformation of **2**. The crotonitrile used was close to a 1 : 1 mixture of *cis* and *trans* isomers, and **5** was formed as a corresponding mixture of isomers **5a** and **5b** (see below).

### $Pt(PR_3)_2(\eta^2\text{-}C_4H_2O_3)$ ($C_4H_2O_3$ = maleic anhydride, $PR_3 = PPh_2py$ (**6**) and $PR_3 = Ppy_3$ (**7**))

A saturated solution of maleic anhydride in $Et_2O$ (3 mL) was degassed by 3 freeze-pump-thaw cycles and added slowly to a solution of **2** (100 mg, 0.1 mmol) or **1** (125 mg, 0.1 mmol) in benzene (20 mL). The solution rapidly became pale yellow, and hexane (20 mL) was then added. The pale yellow precipitate that gradually

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* Reference number with asterisk indicates a note in the list of references.

formed upon cooling the solution to −20 °C was filtered, washed with $Et_2O$, and dried *in vacuo*; yield of **6** or **7** was 80–90%. Anal. Found for **6**: C, 55.61; H, 4.00; N, 3.19. $C_{38}H_{28}N_2O_3Pt$ calcd.: C, 55.68; H, 3.69; N, 3.42%. Anal. Found for **7**: C, 49.25; H, 3.19; N, 10.42. $C_{34}H_{26}N_6O_3Pt$ calcd.: C, 49.58; H, 3.18; N, 10.28%.

### *Pt(PPh$_2$py)$_2$[$\eta^2$-olefin] ($\eta^2$-olefin = diethyl maleate (**8**), and diethyl fumarate (**9**))*

Diethyl maleate in $Et_2O$ (1 : 5 v/v) was added dropwise to a suspension of **2** (100 mg, 0.1 mmol) in $Et_2O$ (20 mL) until a clear solution resulted; hexane (20 mL) was then added and the solution left at −20 °C for 2 d. A mixture of **8** and **9** (30% yield) formed as white microcrystals. Anal. Found: C, 55.95; H, 4.72; N, 3.37. $C_{42}H_{40}N_2O_4Pt$ calcd.: C, 56.43; H, 4.51; N, 3.13%.

### *trans-Chlorohydridobis[2-(diphenylphosphino)pyridine]platinum(II), **10***

Complex **10** was obtained by reaction of a THF solution (40 mL) of **2** (200 mg, 0.2 mmol), initially under $N_2$, with anhydrous HCl gas at 1 atm. The solution was stirred vigorously for 20 min until the yellow colour dissipated. Excess HCl was pumped off completely and an $N_2$ atmosphere was re-established. Hexane (40 mL) was then laid on top of the colourless THF solution, the mixture then being left in a freezer at −20 °C for 72 h. White crystals formed and these were collected by filtration and washed with hexanes/THF (v/v 1 : 1) and then THF alone; yield 67 mg (45%). Anal. Found: C, 54.01; H, 4.31; N, 3.34. $C_{34}H_{29}N_2ClP_2Pt$ calcd.: C, 53.87; H, 3.86; N, 3.70%. IR (Nujol): $\nu$(Pt–H) 2212 cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, r.t.): $\delta$ −16.32 (t, Pt–H, $^2J$(PH) 12.7, $^1J$(PtH) 1213 Hz). $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, r.t.): $\delta$ 30.00 (s, $^1J$(PtP) 3031 Hz).

### *trans-PtI(Me)(PR$_3$)$_2$ (PR$_3$ = PPh$_2$py (**11**), and PR$_3$ = Ppy$_3$ (**12**))*

Some **2** (100 mg, 0.1 mmol) or **1** (125 mg, 0.1 mmol) was dissolved in benzene (20 mL), four equivalents of MeI (0.035 mL, 0.40 mmol) added, and the mixture then refluxed at 80 °C for 20 min and then cooled to ~ 5 °C. A pale yellow precipitate formed when the solution was concentrated to 5 mL by evacuation at this temperature. To the solid, collected by filtration, was added water (5 mL) and the mixture then extracted with $CH_2Cl_2$ (20 mL). The colourless $CH_2Cl_2$ portion was then transferred via a cannula tube to another Schlenk flask and concentrated to 5 mL; addition of hexane (10 mL) precipitated **11** (70% yield) or **12** (60%) as a white or pale yellow solid, respectively. Anal. Found for **11**: C, 47.71; H, 3.61; N, 2.92. $C_{35}H_{31}IN_2P_2Pt$ calcd.: C, 48.68; H, 3.62; N, 3.24%. $^1$H NMR ($CDCl_3$, r.t.): $\delta$ 0.05 (t, Pt–Me, $^3J$(PH) 5.7, $^2J$(PtH) 75 Hz). $^{31}$P{$^1$H} NMR ($CDCl_3$, r.t.): $\delta$ 26.82 (s, $^1J$(PtP) 3078 Hz). Anal. Found for **12**: C, 43.45; H, 3.37; N, 9.51. $C_{31}H_{27}IN_6P_2Pt$ calcd.; C, 42.92; H, 3.14; N, 9.69%. $^{31}$P{$^1$H} NMR ($CDCl_3$, r.t.): $\delta$ 25.64 (s, $^1J$(PtP) 3133 Hz).

### *Hydration of acrylonitrile*

Complexes **1–3** and **11** were used as catalyst precursors for attempted hydration of acrylonitrile. Ampoules were charged under $N_2$ with the nitrile (0.5 mL), $H_2O$ (0.5 mL), the complex (0.02 mmol) and NaOH (0.02 mmol), sealed under vacuum, and left at 80 °C for 1 h. The organic extracts ($Et_2O$) and distillates were analyzed with a Hewlett–Packard 5890A instrument using a 6ft Porapak-Q column and a thermal conductivity detector.

## Results and discussion

### *Platinum(0) pyridylphosphine complexes*

Complex **1**, $Pt(Ppy_3)_4$, is made from the $Pt^{II}$ precursors $PtCl_4^{2-}$ or *cis*-$PtCl_2(Ppy_3)_2$ via methods that are analogous to syntheses of $Pt(PPh_3)_4$ [24], although different solvents are required. The syntheses of **1** require THF or benzene, respectively, while EtOH is used in both corresponding methods reported for $Pt(PPh_3)_4$. Attempts to use EtOH in syntheses of **1** lead to formation of a deep red oil, solutions of which give complex $^{31}P\{^1H\}$ NMR spectra. The hydrazine reduction route in benzene to give **1** is more reproducible than the base/phosphine method in THF.

The $^{31}P\{^1H\}$ spectrum of a solution of **1** at −85 to 0°C reveals a singlet at $\delta \sim 30$ and two singlet Pt-satellites with relative intensities 1 : 4 : 1 with a $^1J(PtP)$ value ~ 3800 Hz, typical of that for tetrahedral $Pt(PR_3)_4$ complexes [25]. The quintet in the $^{195}Pt\{^1H\}$ spectrum shows the same $J(PtP)$ coupling, and confirms the tetrakis formulation. There is no evidence for dissociation of a phosphine ligand from **1** in solution at around 0°C, in contrast to the $PPh_3$ analogue which readily dissociates to $Pt(PPh_3)_3$ [25–27]. Indeed, this tris-complex is isolated from refluxed benzene solutions of $Pt(PPh_3)_4$ [24]. The $Pt(Ppy_3)_3$ species could not be isolated from refluxed solutions of **1**. The latter complex is still the major species formed when *cis*-$PtCl_2(Ppy_3)_2$ is treated with hydrazine in the absence of added phosphine [method (b) in the Experimental section]; an observed minor species with a $^{31}P$ chemical shift at 52.9 ppm ($J(PtP)$ 4435 Hz) could be $Pt(Ppy_3)_3$, these NMR data being close to those of $Pt(PPh_3)_3$ ($\delta$ 50.07, $J(PtP)$ 4449 Hz [28]) and $Pt(PPh_2py)_3$ (see below).

The synthesis of **2**, $Pt(PPh_2py)_3$, follows that described for $Pt(PPh_3)_3$ [24], but is much more dependent on the phosphine concentration used. The procedure given uses a phosphine: $Pt^{II}$ ratio of 3.5 in basic ethanol solution, and this allows for isolation of **2**, identified unambiguously by elemental analysis and the quartet in the $^{195}Pt\{^1H\}$ spectrum, with an associated $\delta$ 57.02 singlet in the $^{31}P\{^1H\}$, each with $J(PtP)$ values of ~ 4440 Hz; the NMR data are typical of a trigonal planar $Pt(PR_3)_3$ complex [25]. If $P(Ph_2py)_3$: $Pt^{II}$ ratios ≥ 4.0 are used in the synthesis, the isolated product sometimes contains small amounts of an additional species believed to be the tetrakis complex $Pt(PPh_2py)_4$, as judged solely by a $^{31}P\{^1H\}$ NMR signal at $\delta$ 25.6 with accompanying Pt-satellites ($J(PtP)$ 3910 Hz), the coupling constant being typical of $Pt(PR_3)_4$ species (see above). Attempts to isolate $Pt(PPh_2py)_4$ were unsuccessful.

Of note, the $^{31}P\{^1H\}$ coordination shifts of the pyridylphosphines within the $Pt(PR_3)_4$ species ($\Delta\delta$ ~ 30 ppm) are greater than for other tertiary phosphines ($\Delta\delta$ ~ 5–14 ppm [25]); the corresponding values within the tris(pyridylphosphine) complexes ($\Delta\delta$ ~ 53–60 ppm) are at the higher end of the range observed within other $Pt(PR_3)_3$ species [25].

Solutions of **1** and **2** are sensitive to $O_2$; indeed, **1** is very air-sensitive even in the solid state, and this may account for the unsatisfactory C analysis. As yet, pure samples of the expected peroxide complexes $Pt(PR_3)_2O_2$ have not been isolated. An impure compound, isolated from reaction of $O_2$ with **1** in $CH_2Cl_2$ at 20°C, shows a major $^{31}P\{^1H\}$ signal ($CDCl_3$, r.t.) at 18.2 ppm with Pt-satellites ($J(PtP) = 3848$ Hz), as well as an IR absorption around 815 $cm^{-1}$ ($CDCl_3$, r.t.); the spectroscopic

Table 1

$^{31}P\{^1H\}$ NMR data for the olefinic complexes 3–9 [a]

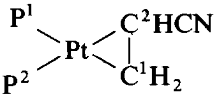
| Complexes | $\delta(P_1)$ | $\delta(P_2)$ | $^1J(PtP^1)$ | $^1J(PtP^2)$ | $^2J(PP)$ |
|---|---|---|---|---|---|
| $Pt(PPh_2py)_2(\eta^2\text{-}CH_2{=}CHCN)$, **3** | 30.7 | 31.7 | 3445 | 3969 | 34.7 |
| $Pt(Ppy_3)_2(\eta^2\text{-}CH_2{=}CHCN)$ [b] | 34.6 | 35.4 | 3406 | 3934 | 31.9 |
| $Pt(PPh_2py)_2[\eta^2\text{-}CH_2{=}C(CH_3)CN]$, **4** | 31.3 | 31.3 | 3538 | 3718 | 35.2 |
| $Pt(PPh_2py)_2(\eta^2\text{-}CH_3CH{=}CHCN)$, **5a** | 31.8 | 32.6 | 3265 | 4095 | 38.5 |
| $Pt(PPh_2py)_2(\eta^2\text{-}CH_3CH{=}CHCN)$, **5b** | 31.6 | 32.1 | 3240 | 4086 | 39.4 |
| $Pt(PPh_2py)_2(\eta^2\text{-}C_4H_2O_3)$, **6** [c] | 27.0 | | 3841 | | |
| $Pt(Ppy_3)_2(\eta^2\text{-}C_4H_2O_3)$, **7** | 32.3 | | 3836 | | |
| $Pt(PPh_2py)_2[\eta^2\text{-}cis\text{-}(CHCOOEt)_2]$, **8** | 30.0 | | 3750 | | |
| $Pt(PPh_2py)_2[\eta^2\text{-}trans\text{-}(CHCOOEt)_2]$, **9** | 28.1 | | 3815 | | |

[a] In $CDCl_3$ at 25 °C, unless stated otherwise; the $\delta$ and $J$ values are in ppm and Hz, respectively. [b] At −45 °C. [c] $^1H$ NMR data: $\delta$ 3.45 (t of d, $^2J(PtH)$ 60.0, $^3J(PH)$ 8.0 Hz).

data resemble closely those of $Pt(PPh_3)_2O_2$ [29,30]. An *in situ* $^{31}P\{^1H\}$ spectrum for a reaction of $O_2$ with **2** shows a signal at 13.00 ppm ($J(PtP)$ 3920 Hz) which could correspond to $Pt(PPh_2py)_2O_2$.

### *Olefinic complexes*

Although satisfactory chemical analyses were not obtained for complexes **3–5**, because of the loss of olefin in drying procedures, the $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopic data (Table 1) unambiguously reveal that **3–5** are essentially square-planar, $\eta^2$-olefin complexes with a *cis*-phosphine arrangement. For instance, the $^{31}P\{^1H\}$ NMR spectrum of the acrylonitrile complex **3** (Fig. 1) contains a major AB quartet with $J(PP)$ 34.7 Hz, coupling typical of *cis*-phosphorus atoms, and the corresponding Pt-satellites. The assignments given in Table 1 are illustrated tentatively in a structural diagram shown for **3**: the weaker Pt–P coupling (3445 Hz) associated with the upfield half of the AB quartet ($\delta$ 30.7) is assigned to $P^1$, assuming that the $C^1$ carbon has a stronger *trans*-influence than the $C^2$ carbon. The non-fluxional nature of **3** favours the metallocyclic structure shown, rather than the $\pi$-bonded olefin type. Strong $\pi$-back donation to the acrylonitrile is indicated also by multiplets at 2.0 and 3.8 ppm in the $^1H$ NMR spectrum of **3**, while the free nitrile shows a multiplet between 5 and 6 ppm; strong olefin–Pt $\sigma$-donation via the olefin $\pi$MO results in a downfield shift of the olefinic protons to ~ 7 ppm [31,32]. The second entry in Table 1 refers to an *in situ* species formed from **1** and excess neat acryonitrile; the data imply a structure analogous to **3**.



(3)

The methacrylonitile complex **4** shows an intense singlet at $\delta$ 31.3 in the 25 °C, $^{31}P\{^1H\}$ NMR spectrum, with symmetric AB quartet Pt-satellites; however, the accidental equivalence of the two P atoms is disrupted at −20 °C, the singlet splitting into a very close AB quartet. The smaller difference of 180 Hz in the two $J(PtP)$ values, compared to that of 524 Hz in **3**, presumably reflects more similar

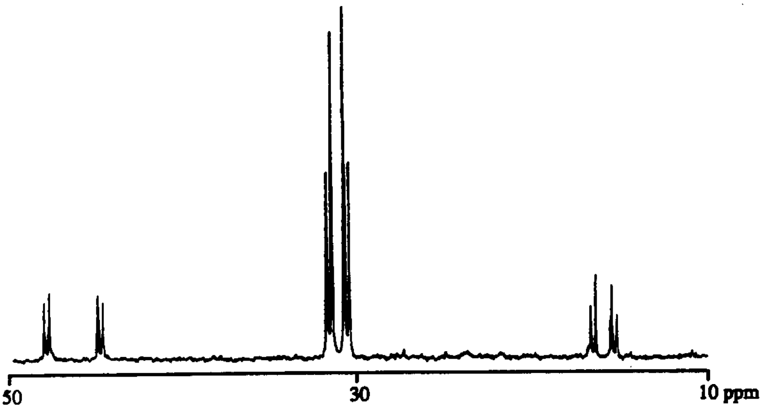


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum (121.4 MHz) at 25°C of $Pt(PPh_2py)_2(\eta^2\text{-}CH_2{=}CHCN)$, **3**, in $CDCl_3$.

electron densities at the two olefinic C atoms in **4**: the combination of the electron-withdrawing CN and electron-donating $CH_3$ groups appears comparable with the effects of the two $CH_2$ protons. In line with this type of reasoning, the difference in the *J*(PtP) coupling constants for the crotonitrile complexes **5a** and **5b** are the largest observed, 830 and 846 Hz, respectively; **5a** and **5b**, which are present in almost equal amounts, result from reaction with the roughly 1 : 1 mixture of *cis*- and *trans*-form of the crotonitrile used in the synthesis, and are inconvertible at 25°C. Species **5a** and **5b** are *syn/anti* isomers, but specific assignments are not known; $^{31}P$ NMR spectra of such Pt(0) complexes with prochiral olefins do not appear to have been reported before. *

The reactions of maleic anhydride with **1** and **2** yield **6** and **7**, respectively. The major singlet in the $^{31}P\{^1H\}$ spectrum with satellite couplings (*J*(PtP) ~ 3840 Hz) is consistent with equivalent, mutually *cis* P atoms in a square planar arrangement; complexes of the type *cis*-$Pt(halide)_2(pyridylphosphine)_2$ invariably have *J*(PtP) values in the range 3500–3900 Hz [21], while the corresponding *trans* isomers have lower couplings ~ 2500 Hz [21,33]. The olefinic protons within **6** appear as a pseudo triplet of doublets (1 : 4 : 1 intensities) centred at $\delta$ 3.45 ($^2J$(PtH) 60, $^3J$(PH) 8.0 Hz), which is a 3.65 ppm upfield, coordination shift. The metallocyclic formulation (as in **3**) is again indicated.

The isolated product from reaction of **2** with diethyl maleate analyzes correctly for $Pt(PPh_2py)_2[(CHCO_2Et)_2]$ but the $^{31}P\{^1H\}$ NMR spectrum (Fig. 2, Table 1) reveals two *cis*-square planar species, **8** and **9**. When the reaction is monitored *in situ* by solution NMR in $CDCl_3$ at 20°C, **8** (the *syn* isomer) is formed initially, but this converts over hours into **9** (the *anti* isomer); **9**, which is also formed rapidly *in situ* by reacting **2** with diethyl fumarate, does not isomerize. The isomerization of coordinated maleate to fumarate contrasts with the behaviour of coordinated crotonitrile within **5a** and **5b** (see above): differences in electronic effects presumably play a key role, and more detailed studies are required to unravel the subtleties

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* Note added in proof: A paper by Caruso et al. [F. Caruso, M. Camalli, G. Pellizer, F. Asaro and M. Lenarda, *Inorg. Chim. Acta*, 181 (1991) 167] has just appeared, describing NMR spectral and some structural data on $Pt(PPh_3)(\eta^2\text{-olefin})$ complexes.

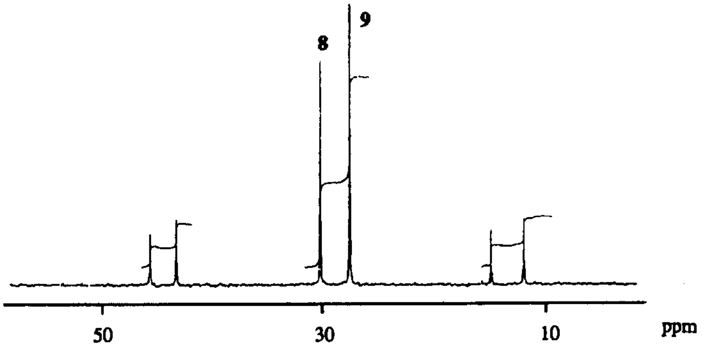


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum (121.4 MHz) at room temperature of a mixture of **8** and **9**, formed from $Pt(PPh_2py)_3$ and diethyl maleate.

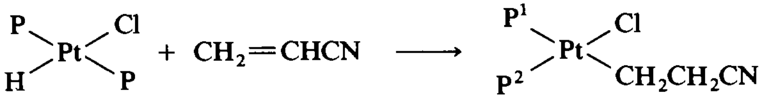
involved. Such isomerization of coordinated maleate to fumarate is not uncommon [34], and involves a rotation process around a coordinated olefinic bond of reduced bond order; a transition state 'en route' to the geometry shown in **3** above is envisioned. The olefinic protons within **8** and **9** are not clearly identified in the $^1H$ NMR spectrum, but the resonances are shifted ~ 3 ppm upfield from those of free diethyl maleate.

An ethylene complex $Pt(PPh_2py)_2(\eta^2\text{-}C_2H_4)$ is readily formed *in situ* from toluene-$d_8$ solutions of **2** and 1 atm $C_2H_4$ at room temperature; the $^{31}P\{^1H\}$ NMR data at −85 °C ($\delta$ 35.5 (s, $J$(PtP) 3654 Hz)) are very similar to those of the corresponding bis(triphenylphosphine) species [26]. Low temperatures are required for the NMR measurements because of line-broadening resulting from $C_2H_4$ exchange. Of note, a solution of $Pt(Ppy_3)_4$ does not react with 1 atm $C_2H_4$ at ~ 20 °C.

### *trans*-Chlorohydridobis[2-(diphenylphosphino)pyridine]platinum(II)

The title complex **10**, isolated as white crystals, is that expected from the oxidative addition of HCl to a precursor $Pt^0$ phosphine complex [28,35,36]. The hydride appears as the expected pseudo triplet of triplets at $\delta$ −16.32 in the $^1H$ NMR, and at 2212 $cm^{-1}$ in the IR. $^1H$ NMR signals at $\delta$ 1.76 and 3.73 may result from the presence of solvated THF in the crystal lattice; their integrations correspond to 1/2 mole of THF/Pt complex, and the elemental analysis perhaps fits better the formulation $Pt(H)Cl(PPh_2py)_2 \cdot 1/2C_4H_8O$ (calcd.: C, 54.44; H, 4.19; N, 3.53%). The $^{31}P$ resonance at 30.00 ppm shows a $J$(PtP) coupling of 3031 Hz. In the synthesis, after formation of **10** in solution, as judged by the loss of the yellow colour of the precursor **2**, the excess HCl has to be pumped off immediately otherwise other hydride species are formed; one such hydride, not characterized, had the following spectral data: IR ($CDCl_3$): $\nu$(Pt–H) 2219 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, r.t.): $\delta$ −15.5 (br. s, $J$(PtH) 1173 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): $\delta$ 35.2 (s, $J$(PtP) = 3136 Hz). Complications in the HCl reaction with $Pt^0$ phosphine complexes have been noted by others [35,36], and include possible formation of ionic species and $Pt^{IV}$ dihydride species.

The *in situ* reaction of **10** with a 1 : 1 mole ratio of acrylonitrile was studied in acetone-$d_6$ at room temperature; the reaction proceeds according to eq. 1 (P = $PPh_2py$) with $t_{1/2}$ ~ 1 h.



(1)

**(10)**

The upfield hydride resonance of **10** disappears, concomitant with production of methylene multiplets at $\delta$ 2.53 and 1.19, attributable to the $\beta$-cyanoethyl product; the branched $\alpha$-cyanoethyl species is not seen, and there is no line-broadening evidence for reversibility of reaction 1 ($\beta$-hydride elimination). Studies on olefin insertion into metal-hydrides continue to appear, and the *anti*-Markovnikov net addition observed in eq. 1 is more commonly found [5,6,37,38]. Accompanying the acrylonitrile insertion is the isomerization from the *trans* precursor **10** to a *cis*-product, as shown by the low temperature $^{31}P\{^1H\}$ NMR spectrum (Fig. 3); the doublets centred at 20.22 ($P^1$) and 17.15 ppm ($P^2$) with *J*(PP) 16.5 Hz indicate *cis*-phosphines ($P^1$, *trans* to the alkyl group, is assigned the weaker *J*(PtP) coupling of 1954 Hz).

The isomerization process is readily envisioned, following hydride migration within a square pyramidal hydrido(acrylonitrile) intermediate. Of note, the room temperature $^{31}P\{^1H\}$ NMR spectrum (Fig. 3) shows collapse of the $P^1$ doublet to a broad singlet (with accompanying satellites), while the $P^2$ signal is essentially

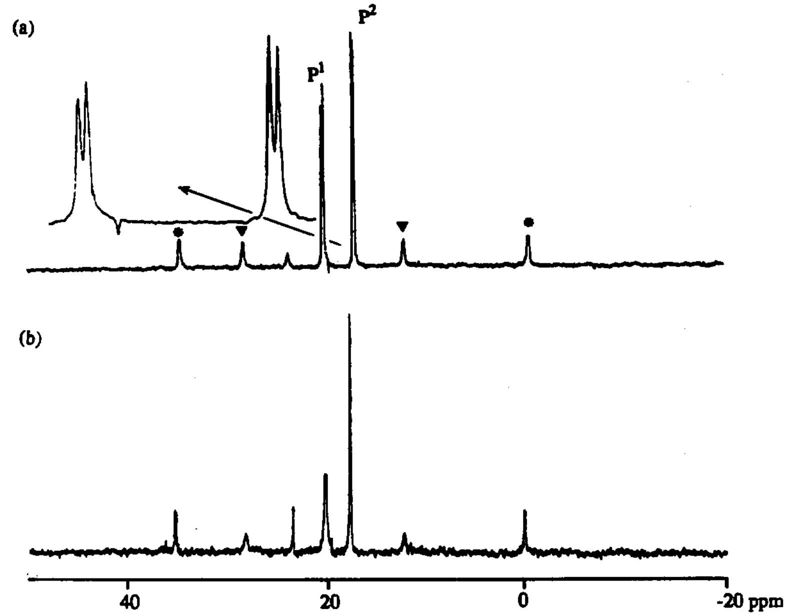


Fig. 3. $^{31}P\{^1H\}$ NMR spectra (121.4 MHz) in acetone-$d_6$ of *in situ* formed *cis*-$PtCl(CH_2CH_2CN)(PPh_2py)_2$; see eq. 1 for the assignments (▼ and • are the Pt-satellites associated with $P^1$ and $P^2$, respectively). (a) At −45 °C. (b) At room temperature. The minor peak at $\delta$ ~ 24 results from the phosphine oxide $OPPh_2py$.

Table 2

Hydration of acrylonitrile [a]

| Complex | Turnovers [b] | |
|---|---|---|
| | β-cyanoethanol | acrylamide |
| $Pt(Ppy_3)_4$, **1** | 37.8 | 3.9 |
| $Pt(PPh_2py)_3$, **2** | 40.2 | – |
| $Pt(PPh_2py)_2(CH_2CHCN)$, **3** | 42.5 | – |
| *trans*-$Pt(H)Cl(PPh_2py)_2$, **10** | – | – |
| None [c] | 42.4 | 15.2 |

[a] Conditions given in Experimental section; 1 h reaction time at 80 ° C. [b] Turnover number = mole/mole Pt/h; (–) implies non-detection. [c] No complex added; blank reaction using just NaOH.

unchanged; some reversible interaction of the CN group with the metal centre might account for the NMR phenomenon.

Attempted preparations of *trans*-$Pt(H)Cl(Ppy_3)_2$ from **1** and HCl were unsuccessful; an isolated yellow species contained hydride(s) but sharp IR bands in the 3440–3520 $cm^{-1}$ region suggest protonation at the pyridyl group(s).

### *Iodo(methyl)bis(phosphine)platinum(II) complexes*

Methyl iodide reacts with both **1** and **2** via net oxidative addition to give the *trans*-$PtI(Me)(PPh_{3-n}\ py_n)_2$ complexes ($n = 1$, **11**; $n = 3$, **12**). The corresponding reaction with $Pt(PPh_3)_3$ is well documented and has been shown to proceed via initial halogen atom abstraction and $Pt^I$ intermediates in a non-chain, radical mechanism [39]. The spectroscopic data leave little doubt about the identities of the methyl complexes, but the elemental analyses for C are not satisfactory; that for **11** is particularly poor (~ 1.0% low), and it should be noted that a recently reported synthesis of **11** from addition of $PPh_2py$ to PtI(Me)(1,5-cyclooctadiene) also gives a product 0.75% low in C content [40], while the reported spectroscopic data agree well with ours.

### *Attempted hydration of acrylonitrile using 1, 2, 3 and 11*

Table 2 summarizes the product distribution for hydration of acrylonitrile in the presence of some of the new complexes. In the absence of added NaOH, complexes **1**–**3** show no activity for hydration, and it seems clear that the observed turn-overs result solely from base (NaOH) catalysis. The turn-over number for the blank is much higher than that given by Jensen and Trogler for the same conditions [6] and, has been pointed out by others [3], purification of the acrylonitrile increases the β-cyanoethanol production.

Our findings are compatible with those of Ramprasad et al. [5] who find that hydration of acrylonitrile is not catalyzed by *trans*-$Pt(H)Cl(PMe_3)_2$. The non-activity of **1** and **2** contrasts, however, with that of $Pt(PR_3)_n$ complexes (R = alkyl, $n = 2$ or 3) [3,4]. The complexes **1**–**3** and **10** are decomposed in basic aqueous media and, in the case of **3**, no acrylonitrile hydration product is seen.

## Concluding remarks

The well known class of platinum(0) complexes $Pt(PR_3)_n$ (R = alkyl, aryl; $n = 3$, 4) has been extended to include pyridylphosphines. Such phosphines exhibit solubility in water, and their complexes have potential for homogeneous catalysis in aqueous media. Our goal of catalytic hydration of olefins using the $Pt^0$ complexes, or a derived hydridoplatinum(II) complex, has not been accomplished; however, the syntheses and diverse chemistry of the new Pt(0) complexes have been established. To a first approximation, the chemistry resembles that of $Pt(PPh_3)_n$, but there are subtle (e.g. use of different solvents) and more marked differences (e.g. non-isolation of $Pt(Ppy_3)_3$ and $Pt(PPh_2py)_4$, and non-reactivity of $Pt(Ppy_3)_4$ toward 1 atm $C_2H_4$).

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