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METHYL- AND PHENYL-BIS(TERTIARY PHOSPHINE) HYDROXO COMPLEXES OF PLATINUM(II): REACTIONS WITH WEAK ACIDS AND HYDRATION OF NITRILES CATALYSED BY HYDROXO AND *N*-BONDED CARBOXAMIDO COMPLEXES OF PLATINUM(II)

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Summary

Methyl- and phenyl-hydroxo complexes of platinum(II), $Pt(OH)RL_2$ (R = Ph, L = Pcy_3, P-t-Bu_2Me, P-t-$BuMe_2$, PEt_3, $PMePh_2$, PMe_2Ph; R = Me, L = P-t-Bu_2Me, P-i-Pr_3) * have been prepared by the action of KOH on cationic acetone complexes $[PtR(OCMe_2)L_2]^+$ generated in situ. All have mutually *trans*-phosphine ligands, except for $Pt(OH)Ph(PMe_2Ph)_2$, which was isolated in an impure state as a *cis-trans* mixture. The hydroxo complexes behave as strong bases and react with nitromethane, acetone or *p*-cresol to give, respectively, *C*-bonded nitromethyl-(CH_2NO_2), *C*-bonded acetonyl-(CH_2COMe) and *O*-bonded *p*-cresolato-(*p*-MeC_6H_4O) platinum(II) complexes. Complexes in the first two of these classes can also be obtained in lower yield by reaction of $PtClRL_2$ with nitromethane or acetone in the presence of silver oxide. Methyl cyanoacetate, $NCCH_2CO_2Me$, reacts with $Pt(OH)PhL_2$ (L = PEt_3, P-t-Bu_2Me) to give *N*-bonded methoxycarbonyl-keteniminato complexes $Pt(N{=}C{=}CHCO_2Me)PhL_2$, but with Pt(OH)Me(dppp) the product is the *C*-bonded cyano(methoxycarbonyl)methyl complex Pt[CH(CN)(CO_2Me)]Me(dppp). Both hydroxo complexes and *N*-bonded acetamido complexes $Pt(NHCOMe)RL_2$ catalyse hydration of acetonitrile to acetamide at 80°C, but are less efficient than trialkylphosphine platinum(0) complexes. The order of activity for R = Ph is L = PEt_3 > P-t-$BuMe_2$ > PPh_3 ~ PMe_2Ph > P-t-Bu_2Me >> Pcy_3, while for a given tertiary phosphine the order of activity is R = Ph > Me. Hydration of acrylonitrile under similar conditions generally gives a mixture of acrylamide, β-cyanoethanol and β,β-dicyanoethyl ether, the last two products arising in irreprodu-

* Abbreviations: Me, methyl; Et, ethyl; i-Pr, isopropyl; t-Bu, t-butyl; cy, cyclohexyl; C_6H_8, cyclohexyne; C_6H_9, 1-cyclohexenyl; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; vpp, *cis*-vinylene-1,2-bis(diphenylphosphine); COD, 1,5-cyclooctadiene; acac, acetylacetonato.

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cible amounts by addition of water to the olefinic double bond. The mechanisms of these reactions are discussed in the light of the observed trends.

Introduction

The Pt—OH bond in neutral hydroxoplatinum(II) complexes containing σ-carbon and tertiary phosphine ligands is remarkably reactive. Complexes such as $Pt(OH)RL_2$ (R = Me, Ph, C_6H_9, CH_2CN; L_2 = dppe, vpp, 2 PPh_3) [1—6] react with a variety of weak acids, in particular carbon acids, under mild conditions (equation 1):

$$Pt(OH)RL_2 + HX \rightarrow PtXRL_2 + H_2O \quad (1)$$

HX = *p*-MeC_6H_4OH, CH_3COCH_3, CH_3NO_2, PhC_2H, CH_3CONH_2, $PhNHCH_3$ etc.

The reversibility of these reactions enables hydroxoplatinum(II) complexes to catalyse hydrogen—deuterium exchange with D_2O at activated methyl and methylene carbon atoms [7]. Hydroxoplatinum(II) complexes also catalyse homogeneously the addition of water to nitriles (R'CN) to give carboxamides, probably via *N*-bonded carboxamido complexes [1,8,9]. The most active catalysts for both reactions are two- or three-coordinate platinum(0) complexes, e.g. $Pt(P\text{-}i\text{-}Pr_3)_n$, ($n$ = 2, 3) and $Pt(PEt_3)_3$, which oxidatively add water to generate unstable hydrido-hydroxo complexes $PtH(OH)L_2$ [7]. In the presence of potentially coordinating solvents, the hydroxide ligand *trans* to H^- is displaced to give tight ion-pairs such as $[PtH(solvent)L_2]OH$ or $[PtHL_3]OH$, which are probably the active catalysts. Similar entities $[PtR(solvent)L_2]OH$ can be envisaged as intermediates in the corresponding reactions catalysed by $Pt(OH)RL_2$. In the series *trans*-$Pt(OH)R(PPh_3)_2$, the reactivity of the Pt—OH bond increases with increasing electron-donating ability (or increasing *trans*-influence) of the anionic ligand R [2]. We have prepared a series of hydroxoplatinum(II) complexes $Pt(OH)RL_2$ containing a range of monodentate tertiary phosphines L to see if variation of L affects the reactivity of the Pt—OH bond, particularly in the catalytic hydration of nitriles.

Results and discussion

The complexes $Pt(OH)RL_2$ (R = Ph, Me; L = various tertiary phosphines) are prepared by reaction of *trans*-$PtClRL_2$ with silver tetrafluoroborate in acetone and immediate treatment of the resulting colourless oily solvento species $[PtR(OCMe_2)L_2]BF_4$ with aqueous potassium hydroxide. This method has been used previously to prepare the complexes $Pt(OH)R(PPh_3)_2$ (R = C_6F_5, CCl=-CCl_2, Ph, Me) [2]. Extended reaction times (>1 h) lead to the formation of σ-acetonyl complexes $Pt(CH_2COMe)RL_2$ by reaction of the hydroxo complexes with acetone. In the preparation of Pt(OH)Me(dppe) [3] and Pt(OH)Me(dppp) from the corresponding chloro complexes, the rate of this competing reaction requires that the acetone used as solvent for the chloride abstraction step be replaced completely by methanol before KOH is added. However, in the present case, use of methanol leads to an inseparable mixture of methoxo, hydroxo and

hydrido complexes, together with decomposition products.

Most of the new hydroxo complexes are colourless solids which are stable to air at room temperature, although the triethylphosphine complex Pt(OH)Ph-$(PEt_3)_2$ liquefies on exposure to moist air and is best stored at 0°C in the solid state or in n-pentane solution under nitrogen. The complexes are generally more soluble in organic solvents than the previously described triphenylphosphine complexes [2]. However, the tricyclohexylphosphine complex Pt(OH)-$Ph(Pcy_3)_2$ is only sparingly soluble in benzene and dichloromethane, and Pt(OH)-$Ph(PMePh_2)_2$ is insoluble in saturated hydrocarbons.

Spectra

Spectroscopic data for the hydroxo complexes are given in Table 1; corresponding data for previously unreported chloro complexes are in Table 2. The IR spectra of all the hydroxo complexes show a weak ν(OH) band at ca. 3660—3680 cm^{-1} in dichloromethane, but this band is undetectable in Nujol mull spectra. Similar observations have been made for other platinum(II) hydroxo complexes [1—3,6]. The complex $Pt(OH)Ph(P\text{-}t\text{-}Bu_2Me)_2$ shows a broad singlet in its ^1H NMR spectrum at δ —1.07 ppm in C_6D_6 [δ 0.13 ppm in CD_2Cl_2] which broadens further on addition of D_2O and is assigned to the OH proton. No OH resonances could be located in the spectra of the other hydroxo complexes. Although triplet OH resonances have been observed in the region δ 1.23 to —2.16 ppm for *cis*-$Pt(OH)R(PPh_3)_2$ (R = C_6F_5, CH_2CF_3) [2,6], *trans*-$Pt(OH)R(PPh_3)_2$ (R = $CCl{=}CCl_2$, $CH{=}CCl_2$, Ph, CF_3) [2] and *trans*-$Pt(OH)(CF_3)(PMePh_2)_2$ [6], they were unobservable in the cases of Pt(OH)Me(dppe) [3], $Pt(OH)(CH_2CN)L_2$ (L = vpp, dppe, dppp) [5,6] and *trans*-$PtH(OH)(P\text{-}i\text{-}Pr_3)_2$ [7].

All except one of the new complexes contain mutually *trans*-phosphine ligands, as shown by the appearance of singlet ^{31}P resonances with ^{195}Pt satellites; ^1J(PtP) is in the expected range of 2900—3100 Hz. In agreement, the ^1H NMR spectra of complexes containing methylphosphines show the characteristic 1 : 2 : 1 triplet pattern for the P—CH_3 resonances. The Pt—CH_3 resonance of the complex *trans*-$Pt(OH)Me(P\text{-}i\text{-}Pr_3)_2$ also appears as a triplet with ^{195}Pt satellites [^3J(PH) 5 Hz, $^2J(PtCH_3)$ 73 Hz], the magnitude of $^2J(PtCH_3)$ being appreciably less than that for *trans*-$PtClMe(P\text{-}i\text{-}Pr_3)_2$ (82 Hz), indicative of the higher *trans*-influence of OH^- relative to Cl^- in platinum(II) complexes. This has also been inferred from comparisons of ^1J(PtP) values in PtXMe(dppe) [3] and of ν(PtH) values in the IR spectra of *trans*-$PtHX(P\text{-}i\text{-}Pr_3)_2$ (X = Cl, OH) [7]. In the case of $Pt(OH)Ph(PMe_2Ph)_2$, which could not be isolated in an analytically pure state, the crude product is a mixture of *cis*- and *trans*-isomers. The $^{31}P\{^1H\}$ NMR spectrum of the *cis*-isomer shows a pair of doublets with ^{195}Pt satellites [^2J(PP) 15 Hz; ^1J(PtP) 1718, 3445 Hz] assignable to the phosphorus atoms *trans* to Ph and OH respectively [cf. ^1J(PtP) for Pt(OH)Me(dppe): 1804 Hz (P *trans* to Me) and 3546 Hz (*trans* to OH)] [3].

The ^1H NMR spectra of the complexes $PtXMe(P\text{-}t\text{-}Bu_2Me)_2$ (X = Cl, OH) are broad and featureless at room temperature, the Pt—CH_3 resonances being almost unobservable. On cooling to —30°C, the spectrum of the chloro complex sharpens and at least two sets of Pt—CH_3 resonances are observed, each having $^2J(PtCH_3)$ values of ca. 83 Hz and $^3J(PPtCH_3)$ values of ca. 6 Hz. The P-t-Bu and

TABLE 1

SPECTROSCOPIC DATA FOR PLATINUM(II) HYDROXO COMPLEXES

Complex	ν(OH) [a]	^{1}H NMR (δ) [b–d]	δP[^1J(PtP)] [e]
Pt(OH)Ph(Pcy$_3$)$_2$	3680,3600	1.1, 1.7, 2.1 (br m, C_6H_{11})	20.1 (2900)
Pt(OH)Ph(P-t-Bu$_2$Me)$_2$	3660	−1.07(br s, OH) [f], 0.42[t, PMe, "J(PH)" 6, ^3J(PtH) 38], 1.36[t, P-t-Bu, "J(PH)" 13]	22.0 (3022)
Pt(OH)Ph(P-t-BuMe$_2$)$_2$	3670	0.98[t, PMe, "J(PH)" 6.5, ^3J(PtH) 30], 1.18[t, P-t-Bu, "J(PH)" 14]	8.7 (2911)
Pt(OH)Ph(PEt$_3$)$_2$	3670	1.05[qn, PCH$_2$C*H*$_3$, "J(PH)" 15], ca. 1.5(m, PC*H*$_2$CH$_3$)	15.2 (2900)
Pt(OH)Ph(PMePh$_2$)$_2$	3620	1.44[t, PMe, "J(PH)" 7, ^3J(PtH) 35.5]	7.7 (3101)
Pt(OH)Ph(PMe$_2$Ph)$_2$ [g]	3672,3610	*cis*-isomer: 0.97[d, "J(PH)" 9.5, ^3J(PtH) ca. 18], 1.41[d, "J(PH)" 9.5, ^3J(PtH) ca. 18] (both PMe)	−23.1 (3445) [h], −7.4 (1718) [i] [^2J(PP) 15]
		trans-isomer: 1.24[t, PMe, "J(PH)" 7.5, ^3J(PtH) 32]	−3.8 (2942)
Pt(OH)Me(P-t-Bu$_2$Me)$_2$	3675	1.33 [j]	ca. 24.0 (3049) [k]
Pt(OH)Me(P-i-Pr$_3$)$_2$	3675	0.44[t, PtMe, ^3J(PH) 5, ^2J(PtH) 73], 1.30[qn, PCHC*H*$_3$, "J(PH)" 14], 2.68[m, PC*H*CH$_3$, J(HH) 7]	34.1 (2961)
Pt(OH)Me(dppp)	3600	0.17[dd, PtMe, ^3J(PH) 3.8, 7.2, ^2J(PtH) 58.4]	4.9 (1672) [l], −0.5 (3468) [h]

[a] In CH_2Cl_2; all bands (cm^{-1}) were weak. [b] In C_6D_6 at 28°C except where indicated otherwise, δ in ppm, coupling constants (J) in Hz. Aromatic resonances were multiplets in the range δ 6.8–8.0. [c] Abbreviations: br, broad; s, singlet; d, doublet; dd, doublet of doublets; m, multiplet; qn, quintet; t, triplet. [d] "J(PH)" = ^2J(PH) + ^4J(PH) for P–CH$_3$ or ^3J(PH) + ^5J(PH) for P–C–C*H*$_3$. [e] In C_6H_6 at 32°C except where indicated otherwise; δP in ppm downfield (taken as positive) of external 85% H_3PO_4. [f] δ 0.13(br s) (CD_2Cl_2). [g] *Cis-trans*-mixture. [h] P *trans* to OH. [i] P *trans* to Ph. [j] Broad overlapping multiplets due to P-t-Bu, PMe; peak(s) due to PtMe could not be clearly identified (see text). [k] Central peak and satellites poorly resolved (see text). [l] P *trans* to Me.

TABLE 2

SPECTROSCOPIC DATA FOR PtClRL$_2$ (R = Ph, Me; L = P-t-Bu$_2$Me, P-t-BuMe$_2$, P-i-Pr$_3$) [a]

Complex	ν(PtCl) [b]	^{1}H NMR (δ)	δP [^1J(PtP)] (solvent)
PtClPh(P-t-Bu$_2$Me)$_2$	280	1.45[t, P-t-Bu, "JPH)" 13.5], 0.45[t, PMe, "J(PH)" 6, ^3J(PtH) 39] [c]	22.1 (2925) ($CHCl_3$)
PtClPh(P-t-BuMe$_2$)$_2$	270	1.19[t, P-t-Bu, "J(PH)" 13.5], 1.06[t, PMe, "J(PH)" 13.5, ^3J(PtH) 31] [c]	not measured
PtClMe(P-t-Bu$_2$Me)$_2$	263	0.85[t, PtMe, ^3J(PH 5.7, ^2J(PtH) 82.5] 1.67[t, P-t-Bu, "J(PH)" 12] [d]	25.1 (2969) 22.7 (2930) } (CH_2Cl_2)
PtClMe(P-i-Pr$_3$)$_2$	272	0.36[t, PtMe, ^3J(PH) 5.5, ^2J(PtH) 82], 1.30[qn, PC*H*Me$_2$, "J(PH)" 14], 2.75[m, PC*H*Me$_2$, J(HH) 7] [e]	32.6 (2864) (CH_2Cl_2)

[a] Abbreviations and meaning of "J(PH)" as in Table 1. Spectra were run at 28°C except as indicated otherwise. [b] IR data (cm^{-1}) refer to Nujol mulls (CsI plates). [c] In $CDCl_3$. [d] In toluene-d_8 at 100°C, using dioxan as lock; PMe signals could not be located. At −30°C there were two sets of PtMe triplets at δ 0.92, 0.69 [^3J(PH) 5.8, ^2J(PtH) 83 Hz]. At 27°C the P-t-Bu resonance was a broad unsymmetrical triplet at δ 1.6. [e] In CD_2Cl_2.

PMe ^1H resonances also sharpen to give multiple patterns indicative of the presence of at least two species. On warming to 27°C and then to 60°C, the signals first broaden and then sharpen. At 90°C one time-averaged triplet Pt—CH_3 resonance is observed [^2J(PtCH$_3$) 83 Hz], the chemical shift being between those of the two signals observed at —30°C; even at 100°C, however, the signal is somewhat broader than is usual for the Pt—CH_3 resonances in the other complexes. The $^{31}P\{^1H\}$ NMR spectrum of PtClMe(P-t-Bu$_2$Me)$_2$ at 32°C also shows the presence of two species each containing mutually *trans*-phosphine ligands. These observations are consistent with the presence of conformers resulting from restricted rotation about either Pt—P or P—C bonds caused by the bulky t-butyl substituents. Similar conformers exist for the complexes *trans*-MX$_2$(PH-t-Bu$_2$)$_2$ (M = Pd, X = Br, I; M = Pt, X = Cl, Br, I) [10], *trans*-PdCl$_2${P-t-Bu$_2$(*o*-MeC$_6$H$_4$)}$_2$ [11] and *trans*-MCl(CO)P-t-Bu$_2$R)$_2$ (M = Rh, Ir; R = Me, Et, n-Pr) [12]. The ^1H NMR spectrum of the hydroxo complex Pt(OH)Me(P-t-Bu$_2$Me)$_2$ sharpens on cooling to —50°C but chemical shifts and coupling constants could not be determined. Surprisingly, the ^1H NMR spectra of *trans*-PtXPh(P-t-Bu$_2$Me)$_2$ (X = Cl, OH) exhibit well-resolved t-butyl and methyl resonances at room temperature, consistent with the presence of only one conformer. Presumably the most stable conformation is that with the plane of the phenyl ring normal to the coordination plane.

Properties

The hydroxo complexes are strong bases. The initial pH's of solutions of Pt(OH)Ph(P-t-Bu$_2$Me)$_2$ (2.99×10^{-3} *M*) and of Pt(OH)Ph(P-t-BuMe$_2$)$_2$ (4.05×10^{-3} *M*) in 9 : 1 methanol-water are 11.93 and 11.82 respectively, but these values fall over a period of hours owing to reaction with methanol giving stable hydrido-aryls PtH(Ph)L$_2$ [13]. Apparent pH's in 2 : 3 v/v aqueous tetrahydrofuran of 14.0, 12.9 and 8.2 have been reported for Pt(PEt$_3$)$_3$, Pt(P-i-Pr$_3$)$_3$ and *trans*-Pt(OH)Ph(PPh$_3$)$_2$, respectively [7].

The complex Pt(OH)Ph(PEt$_3$)$_2$ reacts with nitromethane and *p*-cresol to give, as expected, stable *C*-bonded *σ*-nitromethyl and *O*-bonded *p*-cresolato complexes PtXPh(PEt$_3$)$_2$ (X = CH_2NO_2, *p*-MeC$_6$H$_4$O) respectively. Reaction with acetone over 24 h gives the *σ*-acetonyl complex Pt(CH_2COMe)Ph(PEt$_3$)$_2$ as a thermally unstable oil which was identified spectroscopically (Table 3). The methyl ^1H NMR signals of the coordinated triethylphosphine moieties in these complexes appear as virtually coupled quintets showing that the PEt$_3$ ligands are mutually *trans*. Reaction of Pt(OH)PhL$_2$ (L = PEt$_3$, P-t-Bu$_2$Me) with methyl cyanoacetate, NCCH_2CO_2Me, gives the *N*-bonded methoxycarbonylketeniminato complexes *trans*-Pt(N=C=CHCO_2Me)PhL$_2$ in preference to the alternative *C*-bonded cyano(methoxycarbonyl)methyl structure containing Pt—CH(CN)(CO_2Me). The formulation is based on $^1H\{^{31}P\}$ NMR spectra which, in the case of the PEt$_3$ complex, contain a singlet methine proton resonance with ^{195}Pt satellites at δ 2.97 [*J*(PtH) 6.5 Hz] (Table 3). A much larger value of *J*(PtH) would be expected for the *C*-bonded structure, since for complexes containing Pt—CH_2COMe, Pt—CH_2NO_2 or Pt—CH(COMe)$_2$ *J*(PtH) is of the order of 50—100 Hz [1—3]. The IR spectra of the complexes show characteristic strong bands at ca. 2170 cm^{-1} [*ν*(CN), broad] and at ca. 1640 cm^{-1} [*ν*(C=O)]. In contrast, reaction of Pt(OH)Me(dppp) with methyl

TABLE 3

SPECTROSCOPIC DATA FOR MISCELLANEOUS COMPLEXES $PtXRL_2$

Complex	IR (cm^{-1}) [a]	^1H NMR [b]		
		δ	J(PH)	J(PtH)
cis-$Pt(CH_2NO_2)Me(PPh_3)_2$ [c]	1490s, 1350s [ν(NO_2)]	0.46(t, PtMe)	6.5, 6.5	61
		4.59(dd, $PtCH_2$)	7.5, 9.5	93
cis-$Pt(CH_2COMe)Me(PPh_3)_2 \cdot CH_2Cl_2$	1650s [ν(C=O)]	0.50(dd, PtMe),	6.5, 8.0	64
		2.43(t, $PtCH_2$),	10, 10	98
		1.88(s, COMe)		13
trans-$Pt(CH_2NO_2)Ph(PMe_2Ph)_2$	1483s, 1348s [ν(NO_2)]	4.55(t, $PtCH_2$),	7	63
		1.57(t, PMe)	7	
trans-$Pt(CH_2NO_2)Ph(PPh_3)_2$	1497s, 1357s [ν(NO_2)]	4.04(t, $PtCH_2$) [d]	5.5	59
trans-$Pt(CH_2COMe)Ph(PPh_3)_2$	1641s [ν(C=O)]	2.28(s, $PtCH_2$) [e]	9.5	101
		1.00(s, COMe) [e]		7
trans-$Pt(CH_2NO_2)Ph(PEt_3)_2$	1485s, 1348s [ν(NO_2)]	4.71(t, $PtCH_2$),	6.5	63
		1.05(qn, PCH_2CH_3),	16	
		1.7(m, PCH_2CH_3)		
$Pt(CH_2COMe)Ph(PEt_3)_2$ [f]	1625s (br) [ν(C=O)] [g]	2.12(t, $PtCH_2$),	6.5	68
		2.02(s, COMe)		7
		1.04, 1.12(qn, PCH_2CH_3)		
		1.6(m, PCH_2CH_3) [e]		
trans-$Pt(OC_6H_4Me\text{-}p)Ph(PEt_3)_2 \cdot p\text{-}MeC_6H_4OH$	1608m [ν(C=C), Ar]	2.25, 2.20(s, $CH_3C_6H_4$),		
	1282s [ν(C—O)]	6.9(m, Ar) [e]		
trans-$Pt(NCCHCO_2Me)Ph(PEt_3)_2$	2172s (br) [ν(CN)]	2.97(br s, =CH—),		ca. 6.5
	1638s [ν(C=O)] [g]	3.60(s, OMe)		
trans-$Pt(NCCHCO_2Me)Ph(P\text{-}t\text{-}BuMe_2)_2$	1653, 1630s (sh) [ν(C=O)]	3.52(s, OMe),		
		1.19(t, t-Bu),	14	
		1.09(t, PMe)	6	31
$Pt[CH(CN)(CO_2Me)]Me(dppp)$ [h]	2210s sp [ν(CN)], 1698s [ν(C=O)], 1235s [ν(C—O)]	0.32(t, PtMe),	6.8, 6.8	61
		ca. 3.0 [i],		
		3.47(s, OMe) [d]		

[a] In Nujol mulls, except where indicated otherwise. Abbreviations: *s*, strong, *br*, broad, *sh*, shoulder, *sp*, sharp. [b] In $CDCl_3$ except where indicated otherwise. Abbreviations and use of J(PH) as in Table 1. [c] $^{31}P\{^1H\}$NMR (δ_P, $CHCl_3$) 27.5(d, P *trans* to Me, J(PP) 12, J(PtP) 1921], 26.1(d, P *trans* to CH_2NO_2, J(PtP) 2666]. [d] In CD_2CL_2; δ 4.37 (C_6D_6). [e] In CD_2Cl_2. [f] PEt_3 resonances suggest presence of isomeric mixture. [g] Liquid film. [h] $^{31}P\{^1H\}$NMR (δ_P, CD_2Cl_2) 3.05(d, P *trans* to Me, J(PP) 22, J(PtP) 1696] 4.0[d, P *trans* to CH(CN)(CO_2Me), J(PtP) 2856]. [i] Partly obscured by dppp resonances.

cyanoacetate gives the *C*-bonded complex Pt[CH(CN)(CO_2Me)]Me(dppp), which shows a strong, sharp ν(CN) band at 2210 cm^{-1} and a ν(C=O) band at 1698 cm^{-1} in its IR spectrum. It has been shown [14] that *C*-bonded dicyanomethide complexes containing the unit M—$CH(CN)_2$ show a strong, sharp ν(CN) band at ca. 2200 cm^{-1}, whereas *N*-bonded dicyanoketeniminato complexes containing the unit M—N=C=CH(CN) shows a broad, intense ν(CN) band in the range 2120—2150 cm^{-1}. Thus the IR ν(CN) data support the respective formulations of Pt(N=C=CHCO_2Me)PhL_2 and Pt[CH(CN)(CO_2Me)]-Me(dppp). Unfortunately, the methine proton resonance could not be observed in the ^{1}H NMR spectrum of Pt[CH(CN)(CO_2Me)]Me(dppp), probably because it is masked by the dppp methylene resonances. However, the near equality of the *cis*- and *trans*-($PPtCH_3$) coupling constants (6.8 Hz) suggests the presence of a *C*-bonded ligand, since in the series PtXMe(dppe) these values are usually about 3 Hz and 7 Hz when X is an *N*-donor and each about 7 Hz when X is a *C*-donor [3]. Also in agreement with our assignment are the ^1J(PtP) values derived from the $^{31}P\{^1H\}$ spectrum, viz. 1699 Hz (*P* trans to Me) and 2856 Hz [*P* trans to CH(CN)(CO_2Me)]. The latter value is close to that for *C*-bonded acac in the complex Pt[CH($COMe)_2$]Me(dppe) (2948 Hz) [3] and is far smaller than the value expected for *N*-donors (ca. 4000 Hz).

Complexes of the type *cis*-$PtClX(PEt_3)_2$ (X = CH_2NO_2, CH_2COMe) can be made by reaction of *cis*-$PtCl_2(PEt_3)_2$ with nitromethane or acetone in the presence of silver oxide [15]. We have used this method to obtain the complexes *cis*-$PtXMe(PPh_3)_2$ (X = CH_2NO_2, CH_2COMe) and *trans*-Pt(CH_2NO_2)PhL_2 (L = PMe_2Ph, PEt_3) from *trans*-$PtIMe(PPh_3)_2$ and *trans*-$PtClPhL_2$, respectively, but the yields are generally poorer than those obtained starting from the hydroxo complexes.

Catalytic hydration of nitriles.

In common with previously reported members of the series [1,2,7,8], the new hydroxo- and *N*-carboxamido-platinum(II) complexes [16] catalyse the addition of water to simple nitriles at 80° C to give carboxamides. Results for acetonitrile as substrate are given in Table 4. Irrespective of the nature of the initial catalyst, the platinum-containing residue obtained after reaction for 20 h and removal of solvents and acetamide always consisted of the corresponding *N*-acetamido complex Pt(NHCOMe)RL_2 (R = Me, Ph) (identified by IR and ^{1}H NMR spectroscopy [16]), together with traces of colourless, insoluble polymeric material. In several cases (Table 4) the residue was re-used with a fresh charge of acetonitrile and water; this showed catalytic activity to decrease with prolonged heating. Comparison of the turnover rates of acetamide production (Table 4, entries 3 and 7) shows that Pt(OH)$Ph(PEt_3)_2$ and Pt(NHCOMe)-$Ph(PEt_3)_2$ have identical catalytic activity, within experimental error, and the same is true for the complexes Pt(NHCOMe)$Me(PEt_3)_2$ and Pt(NHCOCH=CH_2)-$Me(PEt_3)_2$ (entries 10 and 11). The turnover rate for Pt(NHCOMe)$Ph(PPh_3)_2$ (102 mol of acetamide/mol of catalyst in 20 h) is somewhat larger than that reported for Pt(OH)$Ph(PPh_3)_2$ (77 mol/mol in 20 h) [7] under conditions apparently similar to ours. Assuming that both hydroxo and *N*-acetamido complexes are involved in the catalytic cycle and can be discussed interchangeably, the order of catalytic activity with varying phosphine ligand L in the series

TABLE 4

CATALYTIC HYDRATION OF ACETONITRILE [a]

Catalyst (mmol)			MeCN (mmol)	H_2O (mmol)	$MeCONH_2$ [b]
1(i)	$Pt(NHCOMe)Ph(PMe_2Ph)_2$ [c]	(0.05)	80	80	102
(ii)	$Pt(NHCOMe)Ph(PMe_2Ph)_2$	(0.05)	40 [d]	55	26
2	$Pt(NHCOMe)Ph(PPh_3)_2$	(0.05)	80	80	102 [e]
3	$Pt(NHCOMe)Ph(PEt_3)_2$	(0.05)	80	80	169
4(i)	$Pt(OH)Ph(Pcy_3)_2$	(0.024)	40	40	trace
(ii)	$Pt(OH)Ph(Pcy_3)_2$	(0.024)	40 [f]	40	49 [g]
5	$Pt(OH)Ph(P\text{-}t\text{-}Bu_2Me)_2$	(0.05)	80	80	22
6	$Pt(OH)Ph(P\text{-}t\text{-}BuMe_2)_2$	(0.05)	80	80	129
7	$Pt(OH)Ph(PEt_3)_2$	(0.05)	80	80	173
8	$Pt(NHCOPh)Ph(PMe_2Ph)_2$	(0.05)	40 [d]	55	28
9	$Pt(NHCOMe)Me(PPh_3)_2$	(0.05)	80	80	86
10	$Pt(NHCOMe)Me(PEt_3)_2$	(0.05)	80	80	144
11	$Pt(NHCOCH{=}CH_2)Me(PEt_3)_2$	(0.0175)	28	28	150 [h]
12	$Pt(OH)Me(P\text{-}t\text{-}Bu_2Me)_2$	(0.025)	40	40	63

[a] Heated at 80 ± 3°C for 20 h, except where stated. [b] Mol per mol catalyst. [c] Heated for 19 h. [d] Plus benzene (23 mmol). [e] When experiment was repeated with a fresh charge of acetonitrile/water under identical conditions using recovered catalyst, only 22 mol acetamide per mol catalyst was obtained. [f] Plus benzene (28 mmol). [g] When experiment was repeated over 68 h with a fresh charge of acetonitrile/water/benzene, only 37 mol acetamide per mol catalyst was obtained. [h] When experiment was repeated over two successive 20 h periods with fresh charges of acetonitrile/water and recovered catalyst, only 60 mol and 17 mol respectively of acetamide per mol of catalyst were obtained.

$Pt(NHCOMe)PhL_2$ under identical conditions is L = PEt_3 > P-t-$BuMe_2$ > PPh_3 ~ PMe_2Ph > P-t-Bu_2Me >> Pcy_3. For the more limited series $Pt(NHCOMe)MeL_2$ a similar order of catalytic activity is evident, viz. L = PEt_3 > PPh_3 > P-t-Bu_2Me. The poor activity of the tricyclohexylphosphine complex is probably a consequence of its insolubility in acetonitrile/water, since addition of benzene as co-solvent markedly improves the yield of acetamide. However, in the case of $Pt(NHCOMe)Ph(PMe_2Ph)_2$ addition of benzene has the opposite effect. Comparison of the turnover rates for $Pt(NHCOMe)PhL_2$ and $Pt(NHCOMe)MeL_2$ for a given L (L = PPh_3, entries 2 and 9; L = PEt_3, entries 3 and 10) indicates the phenyl complexes to be somewhat more efficient than the methyl complexes.

Even the most active compounds examined in our work, $Pt(OH)Ph(PEt_3)_2$ or $Pt(NHCOMe)Ph(PEt_3)_2$, fail to approach the platinum(0) complexes $Pt(Pcy_3)_2$ and $Pt(P\text{-}i\text{-}Pr_3)_3$ [7] in catalytic efficiency for the hydration of acetonitrile, although the *N*-carboxamido complexes have the advantage of being less air-sensitive and more easily handled than the platinum(0) complexes. They are also not very efficient for the catalysis of hydration of higher alkane nitriles and benzonitrile, probably owing in part to the limited miscibility of the higher nitriles with water.

Hydration of acrylonitrile catalysed by the platinum(II) complexes gives a mixture of acrylamide, β-cyanoethanol and β,β-dicyanoethyl ether (Table 5). The second product arises by addition of water to the double bond of acrylonitrile and the third product arises from the base-catalysed addition of β-cyanoethanol to acrylonitrile. This behaviour has been reported previously using the complexes, *trans*-$Pt(OH)R(PPh_3)_2$ (R = Ph, $CH{=}CCl_2$, $CCl{=}CCl_2$), PtL_n (n = 2,

TABLE 5

CATALYTIC HYDRATION OF ACRYLONITRILE [a]

Catalyst (mmol)			CH_2=CHCN (mmol)	H_2O (mmol)	CH_2=CHCONH$_2$ [b]	HOCH$_2$CH$_2$CN [b]	(NCCH$_2$CH$_2$)$_2$O [b]	C≡C/C≡N [c]
1	Pt(NHCOMe)Ph(PMe$_2$Ph)$_2$	(0.05)	80	80	21.5	5.5	9	0.67
2	Pt(NHCOMe)Ph(PPh$_3$)$_2$	(0.05)	80	80	52	8	20	0.54
3	Pt(NHCOMe)Ph(PEt$_3$)$_2$	(0.034)	55	55	44	5	13	0.41
4(i)	Pt(OH)Ph(Pcy$_3$)$_2$	(0.024)	40	40	27 [d]	80 [d]	32 [e]	ca. 4
(ii)	Pt(OH)Ph(Pcy$_3$)$_2$	(0.024)	40 [f]	40	11	5	10 [g]	1.4
5	Pt(OH)Ph(P-t-Bu$_2$Me)$_2$	(0.05)	80	80	17.5	17	42 [h]	3.4
6(i)	Pt(NHCOMe)Me(PPh$_3$)$_2$	(0.05)	80	80	26	16	40 [h]	2.15
(ii)	Pt(NHCOMe)Me(PPh$_3$)$_2$	(0.05)	80 [i]	80	30	64.5	40 [j]	3.5
7	Pt(NHCOMe)Me(PEt$_3$)$_2$	(0.054)	86	86	41	38	45	2.0
8	Pt(NHCOCH=CH$_2$)Me(PEt$_3$)$_2$	(0.05)	80	80	59	23	36	1.0
9	Pt(OH)Me(dppe) · C$_6$H$_6$	(0.05)	80	80	17.7	0.3	3.6	0.22
10	Pt(OH)(C$_6$H$_9$)(dppe)	(0.05)	80	80	10.4	*trace*	2.2	0.21
11(i)	Pt(C$_6$H$_8$)(dppe)	(0.05)	80	80	13.6	trace	2.8	0.21
(ii)	Pt(C$_6$H$_8$)(dppe)	(0.05)	80 [k]	80	15	0.5	2.5	0.2
(iii)	Pt(C$_6$H$_8$)(dppe)	(0.05)	63 [i]	80	21.2	26.6	22.8	2.3

[a] Heated at 80 ± 3°C for 20 h, except where stated. [b] Mol per mol catalyst. [c] Ratio (mmol HOCH$_2$CH$_2$CN + mmol (NCCH$_2$CH$_2$)$_2$O)/mmol CH_2=CHCONH$_2$. [d] Estimated values (peaks not resolved on GLC). [e] Plus CH_2=CH(CN)CH$_2$CH$_2$CN (15 mol/mol catalyst). [f] Plus benzene (28 mmol). [g] Plus CH_2=CH(CN)CH$_2$CH$_2$CN (48 mol/mol catalyst). [h] Plus CH_2=CH(CN)CH$_2$CH$_2$CN (trace). [i] Acrylonitrile freshly distilled under nitrogen. [j] Plus CH_2=CH(CN)CH$_2$CH$_2$CN (2 mol/mol catalyst). [k] Heated at 115°C for 20 h.

L = Pcy_3, P-t-Bu_2Ph; n = 3, L = P-i-Pr_3, PEt_3) [7] and the cyclohexyne complex $Pt(C_6H_8)$(dppe) [8] as catalysts. The last of these was reported [8] to show a strong preference for catalysing addition of water to the C=C bond, but we have been unable to reproduce this result in the present work. We find that, if the acrylonitrile is carefully distilled and degassed before reaction, the proportion of β-cyanoethanol in the product increases dramatically, using either $Pt(C_6H_8)$(dppe) or Pt(NHCOMe)$Me(PPh_3)_2$ as catalyst. We do not therefore place too much emphasis on the ratios of C=C hydration to C≡N hydration quoted in Table 5, since these ratios may be sensitive to the presence of low concentrations of unknown impurities in the acrylonitrile. With this proviso, the results in Table 5 indicate that, using Pt(NHCOMe)RL_2 (L = PEt_3, PPh_3) as catalysts, hydration at the C=C bond is favoured in the order R = Me > Ph. There are no consistent trends discernible with varying phosphine ligand; in the series Pt(NHCOMe)MeL_2, the total turnover for hydration at both C=C and C≡N is in the order L = PEt_3 > PPh_3, as found also for acetonitrile, whereas in the series Pt(NHCOMe)PhL_2 the corresponding order is PPh_3 ~ P-t-Bu_2Me > PEt_3. However, hydration at the C=C double bond appears to be favoured by the presence of the bulky ligands P-t-Bu_2Me and Pcy_3.

Hydration of crotonitrile in the presence of Pt(NHCOMe)PhL_2 (L = PMe_2Ph, PPh_3), Pt(OH)Me(dppe) or $Pt(C_6H_8)$(dppe) gives low yields of crotonamide together with traces of other unidentified compounds (Table 6). Contrary to a previous report [8], the olefin hydration product, $CH_3CH(OH)CH_2CN$, could not be detected, even when the nitrile had been freshly distilled and degassed. Platinum(0) complexes such as Pt(P-t-$Bu_2Ph)_2$, Pt(P-i-$Pr_3)_3$ and $Pt(PEt_3)_3$ are also much less effective in catalysing hydration of crotonitrile than that of acetonitrile, although they are more efficient than the platinum(II) complexes and they also catalyse formation of $CH_3CH(OH)CH_2CN$ [7].

The complexes Pt(NHCOMe)PhL_2 (L = PPh_3, PEt_3) catalyse cyanoethylation of ethanol to 2-ethoxypropionitrile, $EtOCH_2CH_2CN$, the yields being, respectively, 840 and 1200 mol/mol catalyst after 20 h under reflux, but an attempt to catalyse hydration of methyl acrylate with Pt(NHCOMe)$Me(PPh_3)_2$ gave no apparent reaction.

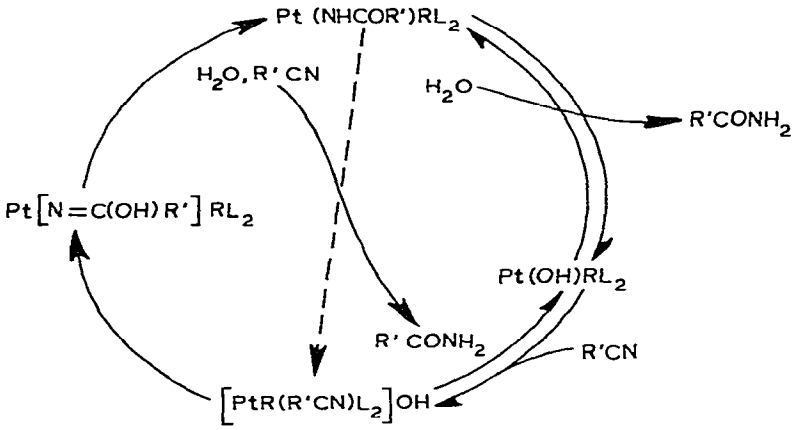
TABLE 6

CATALYTIC HYDRATION OF MISCELLANEOUS NITRILES [a]

Catalyst (mmol)		Nitrile (mmol)		H_2O (mmol)	Amide [b]
Pt(NHCOMe)Ph(PMe_2Ph)$_2$	(0.05)	MeCH=CHCN	(80)	80	16
Pt(NHCOMe)Ph(PPh_3)$_2$	(0.05)	MeCH=CHCN	(80)	80	12
$Pt(C_6H_8)$(dppe)	(0.05)	MeCH=CHCN	(80)	80	3.5[c]
	(0.05)	MeCH=CHCN [d]	(80)	80	3[e]
Pt(OH)Me(dppe) · C_6H_6	(0.05)	MeCH=CHCN	(80)	80	7[f]
Pt(NHCOMe)Ph(PPh_3)$_2$	(0.04)	PhCN	(29)	29	0.5
Pt(NHCOMe)Ph(PPh_3)$_2$	(0.05)	t-BuCN	(80)	80	3

[a] All reactions at 80 ± 3°C, for 20 h. [b] Mol/mol catalyst. [c] Plus unknown compound A, ca. 6 mg. [d] Freshly distilled under nitrogen. [e] Plus compound A, ca. 4 mg, and $CH_3CH(OH)CH_2CN$, trace. [f] Plus compound A, ca. 11 mg.

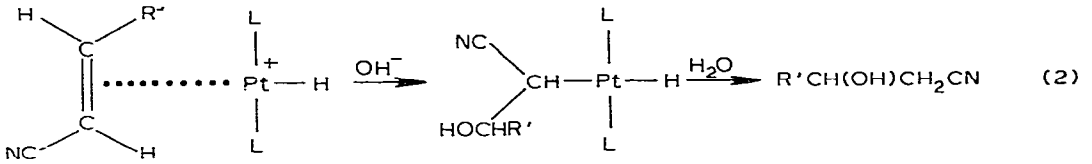
SCHEME 1. PROPOSED CATALYTIC CYCLE FOR NITRILE HYDRATION



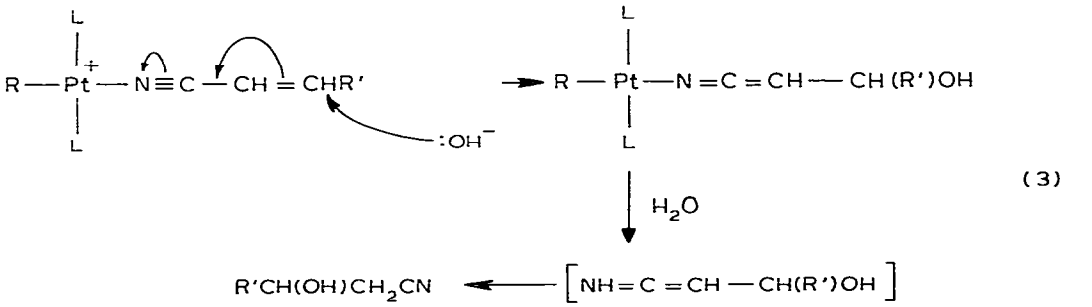
Mechanism of nitrile hydration

As discussed elsewhere [7,8], the key step of the catalysis is probably attack of OH^- on a cationic platinum(II)-nitrile complex to form an imino-enol complex $Pt[N{=}C(OH)R']RL_2$, which rapidly tautomerizes to an *N*-bonded carboxamido-complex $Pt(NHCOR')RL_2$. A possible catalytic cycle is shown in Scheme 1. The *N*-carboxamido complex could react directly either with water to give a discrete hydroxo complex, or with nitrile to give an ion-paired species $[PtR(R'CN)L_2]OH$. At this point, *N*-amido- and hydroxo-catalyst precursors become equivalent. The extent of dissociation of the ion-pair can be expected to depend on the *trans*-influence (or electron-donating ability) of R and on the basicity and size of the tertiary phosphine L. Electron-donating ligands should favour dissociation of OH^- in the hydroxo complexes and should weaken the Pt—NHCOR' bond in the carboxamido complexes, thus facilitating hydrolysis and formation of amide. Smaller ligands such as PEt_3 may offer less steric hindrance to the approach of ligands or nucleophiles such as water or nitrile. These factors provide a reasonable explanation for the trends observed in the hydration of acetonitrile.

A cycle similar to that shown in Scheme 1 presumably operates in the formation of α,β-unsaturated amides from acrylonitrile and crotonitrile, but the situation is complicated in the case of acrylonitrile by a competing and apparently irreproducible hydration of the olefinic double bond. Otsuka et al. [7] have suggested that olefin hydration of acrylonitrile and crotonitrile catalysed by platinum(0) complexes proceeds by attack of OH^- on a hydrido cation containing η^2-(C=C)-coordinated nitrile (equation 2). In support, they note the marked reduction in olefin hydration of crotonitrile relative to acrylonitrile using $Pt(P\text{-}i\text{-}Pr_3)_3$ or $Pt(P\text{-}t\text{-}Bu_2Ph)_2$ in place of $Pt(PEt_3)_3$, which they ascribe to steric restraint on η^2-(C=C) coordination. The observation [16] that the salt $[PtH(CH_2{=}CHCN)(PEt_3)_2]BF_4$ contains *N*-bonded acrylonitrile does not conclusively rule out this mechanism, since a small concentration of an unobserved η^2-(C=C)-cation could be the reactive intermediate. However, the finding that the presence of bulky, basic phosphines such as $P\text{-}t\text{-}Bu_2Me$ or Pcy_3 in the alkyl- or aryl-platinum(II) catalysts favours olefin hydration is not compatible with a



(L = PEt_3, P-i-Pr_3, P-t-Bu_2Ph; R′ = H, Me)



η^2-(C=C)-bonded intermediate. Thus, in our case, olefin hydration is more likely to involve conjugate Michael addition of OH^- to the remote β-carbon atom of the *N*-bonded unsaturated nitrile (equation 3), a process which may be favoured relative to attack at the nitrile carbon atom if bulky ligands are present in the coordination sphere. Such a mechanism also accounts for the failure of methyl acrylate to undergo olefin hydration, since in this case presumably neither the olefin nor the carbonyl oxygen atom bind strongly to platinum(II).

Although β,β-dicyanoethyl ether may be formed by conjugate attack on coordinated acrylonitrile by $HOCH_2CH_2CN$ or $^-OCH_2CH_2CN$, cyanoethylations of this type are known to be catalysed by bases such as NaOH [17], so the metal complex in this case may only be acting as a source of OH^-.

Experimental

Instrumentation and general techniques have been described [16]. Hydroxo complexes were prepared under dry nitrogen using conventional Schlenk and syringe techniques, although most were air-stable once isolated. Compounds which were obviously hygroscopic were handled in a polythene glove-bag under nitrogen. Elemental analyses and melting-points are given in Table 7; spectroscopic data are in Tables 1—3.

The following compounds were prepared by literature methods: PtClMe(COD) [18], PtClPh(COD) [19], $PtIMe(PPh_3)_2$ [20], PtClMe(dppp) [21] Pt(OH)Ph-$(PPh_3)_2$ [2], Pt(OH)Me(dppe).C_6H_6 [3], $Pt(C_6H_8)$(dppe) [1], $Pt(OH)(C_6H_9)$(dppe) [1] and $Pt(NHCOR')RL_2$ (R = Ph, R′ = Me, L = PMe_2Ph, PPh_3, PEt_3; R = R′ = Ph, L = PMe_2Ph; R = Me, R′ = Me, L = PPh_3, PEt_3; R = Me, R′ = $CH{=}CH_2$, L = PEt_3) [1,16]. The known complexes *trans*-$PtClRL_2$ (R = Ph, L = PPh_3, $PMePh_2$, PMe_2-Ph, PEt_3, Pcy_3; R = Me, L = PEt_3) were prepared by displacement of 1,5-COD

TABLE 7

ANALYSES AND MELTING POINTS FOR NEW COMPLEXES

Complex	Analysis found (calcd.) (%)							
	Melting point (°C)	C		H		P		
$PtClPh(P\text{-}t\text{-}Bu_2Me)_2$	212—215	45.9	(45.9)	7.8	(7.5)	5.6	(5.6)	[a]
$PtClPh(P\text{-}t\text{-}BuMe_2)_2$	190—193	39.4	(39.7)	6.4	(6.5)	6.9	(6.5)	[a]
$PtClMe(P\text{-}t\text{-}Bu_2Me)_2$	205—210	40.7	(40.3)	8.05	(8.0)	6.4	(6.3)	[a]
$PtClMe(P\text{-}i\text{-}Pr_3)_2$	225—228	40.3	(40.3)	8.1	(8.0)	6.3	(6.3)	[a]
$Pt(OH)Ph(Pcy_3)_2$	200—204	59.3	(59.3)	8.6	(8.5)	7.0	(7.3)	
$Pt(OH)Ph(P\text{-}t\text{-}Bu_2Me)_2$	147—157	47.3	(47.5)	7.9	(7.9)	10.2	(10.2)	[b]
$Pt(OH)Ph(P\text{-}t\text{-}BuMe_2)_2$	130—135	40.7	(41.1)	6.9	(6.9)	11.5	(11.8)	
$Pt(OH)Ph(PEt_3)_2$	ca. 32	40.85	(41.1)	7.1	(6.9)			
$Pt(OH)Ph(PMePh_2)_2$	122—123	55.55	(55.7)	4.8	(4.7)	8.7	(9.0)	
$Pt(OH)Me(P\text{-}t\text{-}Bu_2Me)_2$	104—110	41.4	(41.7)	8.5	(8.5)	11.15	(11.3)	
$Pt(OH)Me(P\text{-}i\text{-}Pr_3)_2$	150 dec.	41.6	(41.7)	8.6	(8.5)	11.3	(11.3)	[c]
$Pt(CH_2COMe)Ph(PPh_3)_2$	170—175	63.7	(63.3)	5.1	(4.7)	7.6	(7.3)	
$Pt(CH_2COMe)Me(PPh_3)_2 \cdot CH_2Cl_2$	150—158 dec.	56.4	(56.2)	4.5	(4.6)	7.1	(7.1)	[d]
$Pt(CH_2NO_2)Ph(PMe_2Ph)_2$	95—100	45.2	(45.4)	5.0	(4.8)	9.9	(10.2)	[e]
$Pt(CH_2NO_2)Ph(PEt_3)_2$	88— 93	40.1	(40.1)	6.7	(6.6)	10.8	(10.9)	[f]
$Pt(CH_2NO_2)Me(PPh_3)_2 \cdot 0.8\ CHCl_3$	187—191	52.9	(52.35)	4.1	(4.05)	9.6	(9.6)	[g] [a]
$Pt(OC_6H_4Me\text{-}p)Ph(PEt_3)_2 \cdot p\text{-}MeC_6H_4OH$	120—126	53.15	(53.1)	7.1	(7.0)	8.6	(8.6)	
$Pt(NCCHCO_2Me)Ph(PEt_3)_2$	ca. —20	43.8	(43.6)	6.6	(6.5)			
$Pt(NCCHCO_2Me)Ph(P\text{-}t\text{-}BuMe_2)_2$	162—165 [h]	43.75	(43.6)	6.4	(6.5)	2.3	(2.3)	[i]
Pt[CH(CN)CO_2Me]Me(dppp)	238—242 dec.	53.0	(53.3)	4.6	(4.6)	1.8	(1.9)	[i]

[a] Cl analysis. [b] Mol wt (osmometry, toluene, 37°C): found, 613; calcd, 610. [c] Mol wt (osmometry, CH_2Cl_2 25°C): found, 537; calcd, 548. [d] Cl(%): found, 7.4; calcd, 8.1. [e] N(%): found, 2.0; calcd, 2.3. [f] N(%): found, 2.2; calcd, 2.5. [g] N(%): found, 1.5; calcd, 1.6. [h] Partial melting at 135—145°C, then resolidifaction. [i] N analysis.

from PtClR(COD) using 2 molar equivalents of L in dichloromethane, following a recently described procedure [19]. The following new compounds were also prepared by this method in ca. 80% yield (recrystallization solvent in parenthesis): $PtClPh(P\text{-}t\text{-}Bu_2Me)_2$ (methanol/water), $PtClPh(P\text{-}t\text{-}BuMe_2)_2$ (methanol/water) and $PtClMe(P\text{-}i\text{-}Pr_3)_2$ (chloroform/ether).

Preparation of hydroxo-complexes

(1) $Pt(OH)Ph(Pcy_3)_2$. A solution of $PtClPh(Pcy_3)_2$ (0.26 g, 0.3 mmol) in acetone (10 ml) was treated with $AgBF_4$ (0.058 g, 0.3 mmol) dissolved in acetone (2 ml) and the mixture was stirred at room temperature for 2 h. Silver chloride was filtered off, the filtrate was evaporated to dryness, and the colourless solid residue was washed with ether and dried briefly in vacuo. It was then dissolved in the minimum volume of acetone and treated with a solution of KOH (0.017 g, 0.3 mmol) in water (1 ml). A fine white precipitate of the hydroxo complex formed after 5 min. After being stirred for 30 min, the suspension was evaporated to dryness in vacuo. The residue was extracted with benzene (ca. 50 ml) and, after filtration through Celite, the extract was concentrated to yield very fine, colourless needles of $Pt(OH)Ph(Pcy_3)_2$ (0.214 g, 84%).

(2) $Pt(OH)Ph(P\text{-}t\text{-}Bu_2Me)_2$. This was prepared as in (1) from PtClPh(P-t-

$Bu_2Me)_2$ (0.523 g, 0.83 mmol), $AgBF_4$ (0.163 g, 0.83 mmol) and KOH (0.047 g, 0.84 mmol). In this case the product did not precipitate on addition of KOH. After removal of acetone and water in vacuo, the hydroxo-complex was extracted with n-hexane (20 ml). Filtration and evaporation to dryness gave white crystals (0.46 g, 91%), from which an analytically pure sample was obtained by recrystallization from n-pentane/isopentane at —78°C.

Similarly prepared were Pt(OH)Ph(P-t-$BuMe_2)_2$ (60%) and Pt(OH)Me(P-t-$Bu_2Me)_2$ (74%). Owing to their solubility, these complexes were recovered in only poor yields from attempted recrystallization at —78°C.

(3) Pt(OH)Me(P-i-$Pr_3)_2$. This was prepared as in (1) from PtClMe(P-i-$Pr_3)_2$ (0.189 g, 0.33 mmol), $AgBF_4$ (0.065 g, 0.33 mmol) and KOH (0.022 g, 0.4 mmol). Acetone and water were removed in vacuo and the residue was extracted with benzene (2 × 5 ml). Filtration and evaporation to dryness yielded colourless crystals (0.153 g, 84%), which were washed with n-pentane and dried.

(4) Pt(OH)Ph(PMe$Ph_2)_2$. This was prepared as in (3). Addition of n-hexane to the benzene extract precipitated brown oily material. The pale yellow supernatant liquid was evaporated to dryness and the residue was recrystallized from benzene/n-hexane to give the colourless crystalline product in 20% yield.

The complex Pt(OH)Ph($PMe_2Ph)_2$ was prepared similarly but could not be purified. Successive precipitations of coloured impurities by addition of n-hexane to the concentrated benzene extract finally gave a pale brown oil, which gave a colourless sticky solid from ether/n-pentane at —50° C. This was shown by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Table 1) to contain *cis-* and *trans*-Pt(OH)Ph($PMe_2Ph)_2$ (ca. 20% yield), in addition to other unidentified species.

(5) Pt(OH)Ph(PEt$_3)_2$. A solution of PtClPh($PEt_3)_2$ (0.816 g, 1.5 mmol) in acetone was treated with $AgBF_4$ (0.292 g, 1.5 mmol). Silver chloride was filtered off and the solvent was evaporated to give [PtPh($OCMe_2$)($PEt_3)_2$]BF_4 as a colourless oil. This was dissolved in the minimum volume of ether and stirred vigorously for 0.5 h with a solution of KOH (0.096 g, 1.7 mmol) in water (5 ml). The ether layer was separated, dried (Na_2SO_4) and evaporated to yield a colourless, viscous oil which was recrystallized from isopentane at —78°C. After decantation of the mother liquor, the product (0.6 g, 76%) was dried in vacuo, the temperature meanwhile being allowed to reach that of the surroundings. So prepared, the complex remained solid under nitrogen at room temperature, but liquefied rapidly in moist air.

(6) Pt(OH)Me(dppp). The method followed that used for Pt(OH)Me(dppe) [3]. A solution of PtClMe(dppp) (0.314 g, 0.43 mmol) in acetone was treated with the stoichiometric amount of $AgBF_4$ and stirred for 30 min. After removal of AgCl by filtration, the solution was evaporated under reduced pressure without warming to give a colourless oil containing [PtMe($OCMe_2$)(dppe)]BF_4. The coordinated acetone was removed by twice dissolving in methanol and then evaporating to dryness. A slight excess of methanolic NaOH was added, methanol was removed in vacuo, and the residue was extracted with dichloromethane. The product was obtained in ca. 50% yield by addition of n-hexane to the filtered extract.

Reactions with weak acids. The hydroxo complex (ca. 0.1 mmol) was

stirred at room temperature with the acid as solvent (in the case of nitromethane and acetone).or with a slight excess of the acid in benzene or dichloromethane. After evaporation of the solvent, the residue was recrystallized. Variations in reaction solvents, reaction times and recrystallization solvents are listed below. Yields for PEt_3 complexes after recrystallization were usually only 30—40% because of the small scale and the solubilities of the products. [$Pt(CH_2NO_2)Ph(PEt_3)_2$]: 5 h, hexane; *trans*-[$Pt(CH_2COMe)Ph(PEt_3)_2$]; 24 h, product decomposed on attempted recrystallization; *trans*-[$Pt(OC_6H_4Me\text{-}p)Ph(PEt_3)_2$] · *p*-$MeC_6H_4OH$: in dichloromethane, 3 h, ether; *trans*-[$Pt(N{=}C{=}CHCO_2Me)Ph(PEt_3)_2$]: in benzene, 3 h, ether/n-pentane (—78° C); *trans*-[$Pt(N{=}C{=}CHCO_2Me)Ph(P\text{-}t\text{-}BuMe_2)_2$]; in benzene, 2 h, 100%; *cis*-[Pt{CH(CN)COOMe}Me(dppp)]: in CH_2Cl_2, 4 h, dichloromethane/hexane, 65%; *trans*-[$Pt(CH_2COMe)Ph(PPh_3)_2$]: in acetone/benzene (2 : 1), 72 h, benzene/n-hexane.

Reactions of $PtXRL_2$ (X = halide; L = tertiary phosphine) complexes with weak acids in the presence of Ag_2O

(1) A solution of $PtIMe(PPh_3)_2$ (0.258 g, 0.3 mmol) in dichloromethane (3 ml) containing nitromethane (3 ml) was stirred vigorously with freshly prepared silver oxide (0.043 g, 0.19 mmol) for 72 h in the dark. The suspension was filtered through Celite and the filtrate was evaporated to give a yellow oil which slowly crystallized in vacuo. Two recrystallizations from dichloromethane/n-hexane gave pale cream crystals of *cis*-[$Pt(CH_2NO_2)Me(PPh_3)_2$] (0.1 g, ca. 40%).

(2) Similarly prepared from $PtIMe(PPh_3)_2$ (0.18 g, 0.21 mmol), silver oxide (0.03 g, 0.13 mmol) and acetone (5 ml) in dichloromethane (3 ml) was *cis*-[$Pt(CH_2COMe)Me(PPh_3)_2$], which formed shiny pale yellow crystals from chloroform/n-hexane (0.064 g, 35%).

(3) A mixture of $PtClPh(PMe_2Ph)_2$ (0.106 g, 0.18 mmol), silver oxide (0.022 g, 0.095 mmol) and nitromethane (4 ml) was stirred for 24 h. After removal of solvent, the product was extracted with benzene/n-hexane (1 : 1), leaving undissolved orange oil. Concentration of the extract gave an almost colourless oil, which afforded pale yellow crystals of *trans*-[$Pt(CH_2NO_2)Ph(PMe_2Ph)_2$] (0.055 g, 50%) from ether/n-hexane.

(4) Similarly prepared from $PtClPh(PEt_3)_2$ (0.136 g, 0.25 mmol), silver oxide (0.035 g, 0.15 mmol) and nitromethane (4 ml) was *trans*-[$Pt(CH_2NO_2)Ph(PEt_3)_2$] (0.032 g, 23%), which crystallized from n-hexane.

Catalytic hydration of nitriles

(1) Acetonitrile. The complex was heated and stirred under nitrogen with a mixture of acetonitrile and water. Standard conditions used in most experiments were complex (0.05 mmol), acetonitrile (4.2 ml), water (1.44 ml), 80 ± 3°C, 20 h. After cooling, solvents were removed on a rotary evaporator, the white residue was dried briefly at ca. 1 mm, and acetamide was sublimed at ca. 60°C/1 mm. Yields were calculated as mol of acetamide/mol of catalyst (Table 4). The residue after sublimation was weighed and examined by NMR or IR spectroscopy to assess the extent of decomposition of the starting complex. In some experiments, this residue was re-used with more acetonitrile/water. In some cases, where the complex was insoluble in acetonitrile/water, benzene was used as co-solvent.

(2) Acrylonitrile. The procedure was as described above, except for the use of acrylonitrile (5.3 ml on most occasions). After cooling, the solvents were pumped off, leaving an oily yellow residue, which was taken up in a few ml of methanol, filtered if necessary to remove polymeric material, and examined by GLC (20% BDS on Chromosorb W, 150°C until the CH_2=$CHCONH_2$ and $HOCH_2CH_2CN$ peaks emerged then programmed heating to 245°C at which temperature the $(NCCH_2CH_2)_2O$ peak emerged). Quantitative estimation of yields and peak identification were achieved by comparison with standard mixtures of authentic samples using a Hewlett-Packard 3380A Integrator. The methanol was then evaporated at room temperature until constant weight was achieved; the weight of starting complex was subtracted from the weight of residue and the turnover was calculated (Table 5). In some experiments the acrylonitrile was freshly distilled under nitrogen into the nitrogen-filled reaction flask.

(3) Crotonitrile. These experiments were carried out similarly using crotonitrile (6.54 ml of *cis/trans*-mixture). Solvents were evaporated to leave an orange/brown residue from which crotonamide was isolated by sublimation at ca. 80°C/0.3 mm. Alternatively, the reaction product was examined by GLC as in (2) (20% BDS column, 120°C for 2 min, then programmed to 190°C at 20°C/min). This showed the presence or otherwise of residual CH_3CH=$CHCN$, and other products, notably $CH_3CH(OH)CH_2CN$ (Table 6). Products were identified by comparison with authentic samples.

(4) Other nitriles. As in (1), benzamide was obtained from benzonitrile and t-$BuCONH_2$ from t-BuCN (Table 6).

Cyanoethylation of ethanol

The complex was stirred at 80°C for 20 h with acrylonitrile (5.1 ml) and absolute ethanol (4.9 ml). Solvents were evaporated and the yellow residue was distilled using water pump vacuum over the range 57—63°C. The distillate was shown by NMR and IR spectra to be pure $EtOCH_2CH_2CN$.

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References

1 M.A. Bennett, G.B. Robertson, P.O. Whimp and T. Yoshida, J. Amer. Chem. Soc., 95 (1973) 3028; M.A. Bennett and T. Yoshida, J. Amer. Chem. Soc., 100 (1978) 1750.
2 T. Yoshida, T. Okano and S. Otsuka, J. Chem. Soc., Dalton Trans., (1976) 993.
3 T.G. Appleton and M.A. Bennett, Inorg. Chem., 17 (1978) 738.
4 M.E. Fakley and A. Pidcock, J. Chem. Soc., Dalton Trans., (1977) 1444.
5 R. Ros, R.A. Michelin, R. Bataillard and R. Roulet, J. Organometal. Chem., 161 (1978) 75.
6 R.A. Michelin, M. Napoli and R. Ros, J. Organometal. Chem., 175 (1979) 239.
7 T. Yoshida, T. Matsuda, T. Okano, T. Kitani and S. Otsuka, J. Amer. Chem. Soc., 101 (1979) 2027.
8 M.A. Bennett and T. Yoshida, J. Amer. Chem. Soc., 95 (1973) 3030.
9 R. Ros, J. Renaud and R. Roulet, J. Organometal. Chem., 104 (1976) 271.
10 A. Bright, B.E. Mann, C. Masters, B.L. Shaw, R.M. Slade and R.E. Stainbank, J. Chem. Soc., A, (1971) 1826.
11 A.J. Cheney and B.L. Shaw, J. Chem. Soc. Dalton Trans., (1972) 860.
12 B.E. Mann, C. Masters, B.L. Shaw and R.E. Stainbank, J. Chem. Soc., Chem. Commun., (1971) 1103.

13 D.P. Arnold and M.A. Bennett, unpublished work.
14 W.H. Baddley and P. Choudhury, J. Organometal. Chem., 60 (1973) C74.
15 M.A. Cairns, K.R. Dixon and M.A.R. Smith, J. Organometal. Chem., 135 (1977) C33.
16 D.P. Arnold and M.A. Bennett, J. Organometal. Chem., (1980) in press.
17 W.A. Bruson, Organic Reactions, 5 (1949) 79.
18 H.C. Clark and L.E. Manzer, J. Organometal. Chem., 59 (1973) 411.
19 C. Eaborn, K.J. Odell and A. Pidcock, J. Chem. Soc., Dalton Trans., (1978) 357.
20 J. Chatt and B.L. Shaw, J. Chem. Soc., (1959) 705.
21 T.G. Appleton, M.A. Bennett and I.B. Tomkins, J. Chem. Soc., Dalton Trans., (1976) 439.