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Self-replication of tris(cyanoethyl)phosphine catalysed by platinum group metal complexes

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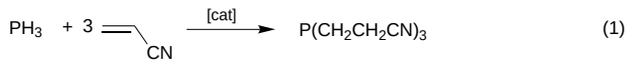
The platinum(0) complex [Pt(tcep)$_3$], tcep = P(CH$_2$CH$_2$CN)$_3$, catalyses the formation of tcep from PH$_3$ and CH$_2$=CHCN. The complexes [M(tcep)$_3$] (M = Pt, Pd or Ni) and [MCl(tcep)$_3$] (M = Rh or Ir) are compared for their catalysis of the reaction of PH(CH$_2$CH$_2$CN)$_2$ with CH$_2$=CHCN to give tcep and it is shown that the platinum(0) complex is the most efficient. The platinum(0) catalysis has been studied in detail, monitoring the kinetics by ^{31}P-{^{1}H} NMR spectroscopy. It is revealed that the kinetics are a complex function of the concentration of product tcep. Qualitatively, the rates also depend on [CH$_2$=CHCN] and [catalyst]. Both ^{31}P-{^{1}H} and ^{195}Pt-{^{1}H} NMR spectroscopy suggests that addition of CH$_2$=CHCN to [Pt(tcep)$_3$] gives the complex [Pt(tcep)$_2$(η^2-CH$_2$=CHCN)] which undergoes phosphine exchange on the NMR time-scale. The binuclear complex [Pt$_2$H$_2$(tcep)$_2${μ-P(CH$_2$CH$_2$CN)$_2$}$_2$], formed upon addition of PH(CH$_2$CH$_2$CN)$_2$ to *trans*-[PtHCl(tcep)$_2$] in the presence of base, is shown to be a catalyst precursor for the reaction of PH(CH$_2$CH$_2$CN)$_2$ with CH$_2$=CHCN. Two parallel mechanisms involving mononuclear and binuclear intermediates are discussed to rationalise these observations.

Hydrophosphination of an alkene, the addition of a P–H bond of R$_n$PH$_{3-n}$ (n = 0–2) to a C=C bond, is a useful route to tertiary phosphines.[1] Alkene hydrophosphinations can be acid- or base-catalysed,[2] and they can also be promoted by radical initiators.[3] Metal–phosphine complexes have been used as templates for the construction of polydentate phosphines *via* stoichiometric P–H additions to alkenes[4] but previous to our work,[5] there were no reports of metal–phosphine catalysed hydrophosphinations. Tertiary phosphine complexes of late transition metals are excellent catalysts for E–H (*e.g.* E = H, BR$_2$ or SiR$_3$) additions to C=C bonds[6] and we were intrigued by the possibility that PR$_3$ complexes may catalyse the formation of PR$_3$ from R$_n$PH$_{3-n}$; such a reaction constitutes a self-replication process at a metal centre.

Tris(cyanoethyl)phosphine (tcep) is commercially important and its co-ordination chemistry has been well studied.[7] It can be conveniently made[8] by the base-catalysed reaction of CH$_2$=CHCN with [P(CH$_2$OH)$_4$]Cl. In 1961, it was reported[9] in a patent that the addition of PH$_3$ to acrylonitrile was catalysed by PtCl$_4$, and other transition-metal compounds, though it was not claimed that the catalysts were homogeneous. In this paper we report an investigation of the hydrophosphination of acrylonitrile catalysed by late-transition-metal complexes of tris(cyanoethyl)phosphine (tcep). Some of these results were previously described in a preliminary communication.[5] Recently Glueck and co-workers[10] have reported platinum(0)-catalysed P^{III}–H additions to acrylonitrile and Han and Tanaka[11] have reported palladium(0)-catalysed P^{V}–H additions to acetylenes.

Results and Discussion

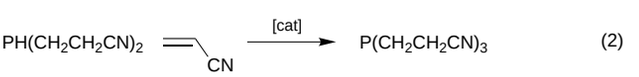
We began our search for metal-complex catalysts for the hydrophosphination of acrylonitrile with the platinum(0) complex, Pt(tcep)$_3$] **1** because we had previously shown that platinum(0) complexes were efficient catalysts for the hydrophosphination of formaldehyde.[12] When PH$_3$ is passed through an acetonitrile solution of acrylonitrile, no reaction was observed after 6 h and only PH$_3$ was observed to be present by ^{31}P-{^{1}H} NMR spectroscopy. Under similar conditions but in the presence of **1** (mol ratio of **1** to acrylonitrile, *ca.* 1:1500) after 6 h, the phosphines PH$_n$(CH$_2$CH$_2$CN)$_{3-n}$ (n = 0–3) were observed in roughly equal amounts; thus we established that **1** catalyses the reaction shown in equation (1). These observations encouraged us to



(1)

investigate the hydrophosphination of acrylonitrile in detail. The PH$_3$ reaction shown in equation (1) would have presented difficulties for study because of the dangers inherent in handling PH$_3$ and furthermore, since it involves three consecutive hydrophosphinations, the kinetics would be very complicated to interpret.

It was reasoned that the reaction shown in equation (2)



(2)

would be convenient for detailed study since the secondary phosphine PH(CH$_2$CH$_2$CN)$_2$ (dcep) is an easily handled, commercially available liquid and the reaction involves only one hydrophosphination step. The conversion was readily monitored by ^{31}P-{^{1}H} NMR spectroscopy (see Fig. 1 for a typical run); to obtain quantitative information about the course of the hydrophosphination, the ^{31}P-{^{1}H} NMR spectra were measured with 2 s pulse delay and inverse-gated decoupling so that the relative intensities of signals for the secondary and tertiary phosphines corresponded to their relative proportions. Under the reaction conditions we used (see Experimental section), in the absence of metal complex, it took 8 d for the P–H addition to go to completion. Under the same conditions, but in the presence of 0.04 equivalent of **1** (see Experimental section) the reaction was 50% complete after 2 h and no secondary phosphine could be detected after 6 h.

The complexes **2–5** were screened for hydrophosphination catalytic activity and compared with **1**. The synthesis of each of these complexes has been previously reported[7] with the exception of [Ni(tcep)$_3$] **3**. Complex **3** was generated *in situ* from [Ni(cod)$_2$] (cod = cycloocta-1,5-diene) and 3 equivalents of tcep as evidenced by the ^{31}P-{^{1}H} NMR spectrum at −44 °C in MeCN which showed a sharp signal at δ +16.7. Though solutions of **3** were apparently stable, an attempt to isolate the complex by evaporation of the MeCN led to formation of a nickel

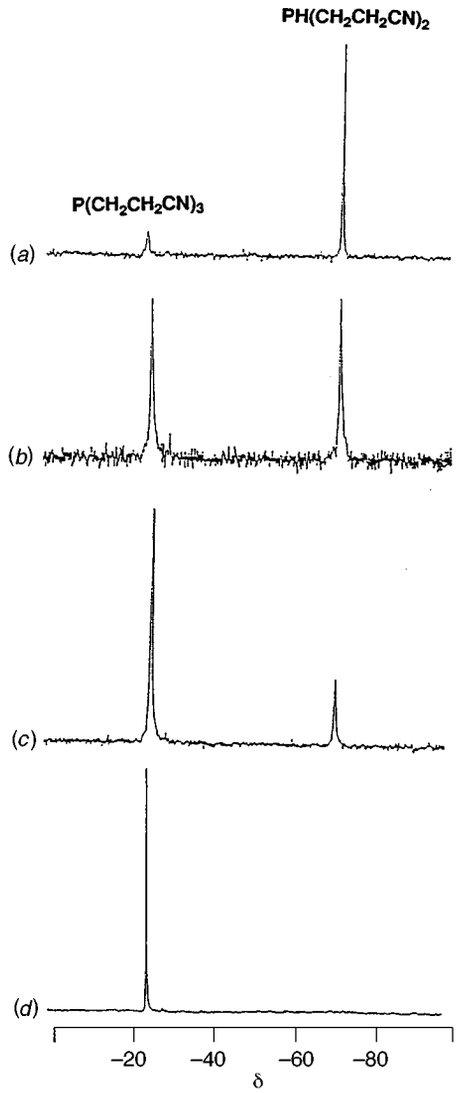
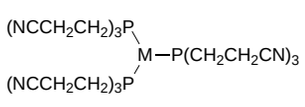


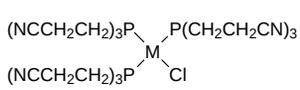
Fig. 1 Variation of $^{31}P-\{^{1}H\}$ NMR spectra with time upon addition of dcep to CH_2=CHCN in the presence of [Pt(tcep)$_3$] under the standard conditions (see Experimental section) after (*a*) 10, (*b*) 120, (*c*) 240 and (*d*) 720 min



1 M = Pt

2 M = Pd

3 M = Ni



4 M = Rh

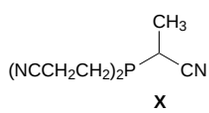
5 M = Ir

mirror. Addition of a fourth equivalent of tcep gave two broad signals in the ratio of 3:1 at δ +16.9 and −25.9 (the latter assigned to free tcep) which had coalesced at +28 °C to a very broad singlet centred at *ca.* δ +5, consistent with rapid exchange of co-ordinated and non-co-ordinated tcep on the NMR time-scale. Thus it appears that nickel(0) forms a co-ordinatively unsaturated tcep complex **3** analogous to the palladium(0) and platinum(0) complexes (**1** and **2**). Exchange of tcep is observed for each of the species **1–3** and from the broadening of the $^{31}P-\{^{1}H\}$ NMR signals, it is clear that the rate of the exchange is greatest for nickel and slowest for platinum.

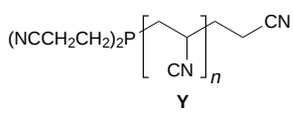
Table 1 Kinetic data

Entry	Catalyst	Conditions/solvent[a]	*t*(50%)/min
1	None	Standard	6400
2	**1**		120
3	**2**		240
4	**3**		1290
5	**4**		*b*
6	**5**		250
7	**1**	MeCN	120
8	**1**	Me_2CO	80
9	**1**	Me_2SO	70
10	**1**		120
11	**1**	2 × [**1**]	65
12	**1**	1/30 [CH_2=CHCN]	4250

[a] See experimental for the standard conditions used in these reactions and how the *t*(50%) values were obtained. [b] The reaction did not reach 50% completion even after several days.



X



Y

Comparison of the catalysts

The hydrophosphination shown in equation (2) was followed by $^{31}P-\{^{1}H\}$ NMR spectroscopy in the presence of complexes **1–5** and *t*(50%), the average time for the reaction to be 50% complete, was measured in order to compare the relative efficiency. It can be seen from entries 2–6 in Table 1 that the order of activity of the complexes was: [Pt(tcep)$_3$] > [Pd(tcep)$_3$] ≈ [IrCl(tcep)$_3$] > [Ni(tcep)$_3$]. In the presence of the rhodium complex **4**, catalysis was observed in the early stages but the reaction failed to reach the 50% point even after several days. In the runs with **4**, a pale yellow precipitate formed during the reaction which was insoluble in all common solvents and was most likely a phosphido-bridged rhodium species which is not only inactive catalytically but apparently slows the hydrophosphination reaction. The reaction in the absence of metal complex is likely to be a radical process and the rhodium–phosphido species may be acting as a radical scavenger and thereby inhibiting the reaction.

Effect of solvent

The solvent has a small effect on the rate of the reaction (entries 7–9, Table 1): under similar conditions the rate increases in the order MeCN < Me_2CO ≈ Me_2SO. More significantly the solvent influences the course of the reaction. In MeCN, the product is mainly tcep [δ(P) −24.0] but a small amount (<5%) of a second product with similar δ(P) of −24.6, is observed. Two possibilities were considered for the structure of the minor species: (*i*) the branched species **X** derived from Markovnikov addition of the P–H to acrylonitrile; (*ii*) the telomeric species **Y** which would be the product of multiple insertions of acrylonitrile into the P–H bond. The proportion of the second product is greater (*ca.* 20%) in Me_2CO and is the main product (*ca.* 60%) in Me_2SO. Therefore we investigated the products of hydrophosphination in these solvents by ^{13}C distortionless enhancements by polarisation transfer (DEPT) NMR spectroscopy. In both solvents, the spectra obtained were complex with several signals in the alkyl region (δ 10–45) and CN region (δ 115–135) in addition to the tcep signals. For **X** we would expect one new CH signal and one new CH_3 signal but significantly, there were at least five CH/CH_3 signals in the range δ 25–30 which is more consistent with the formation of **Y**. This assignment is further supported by the observation that the proportion of this product in MeCN increased when the initial concentration of CH_2=CHCN was increased.

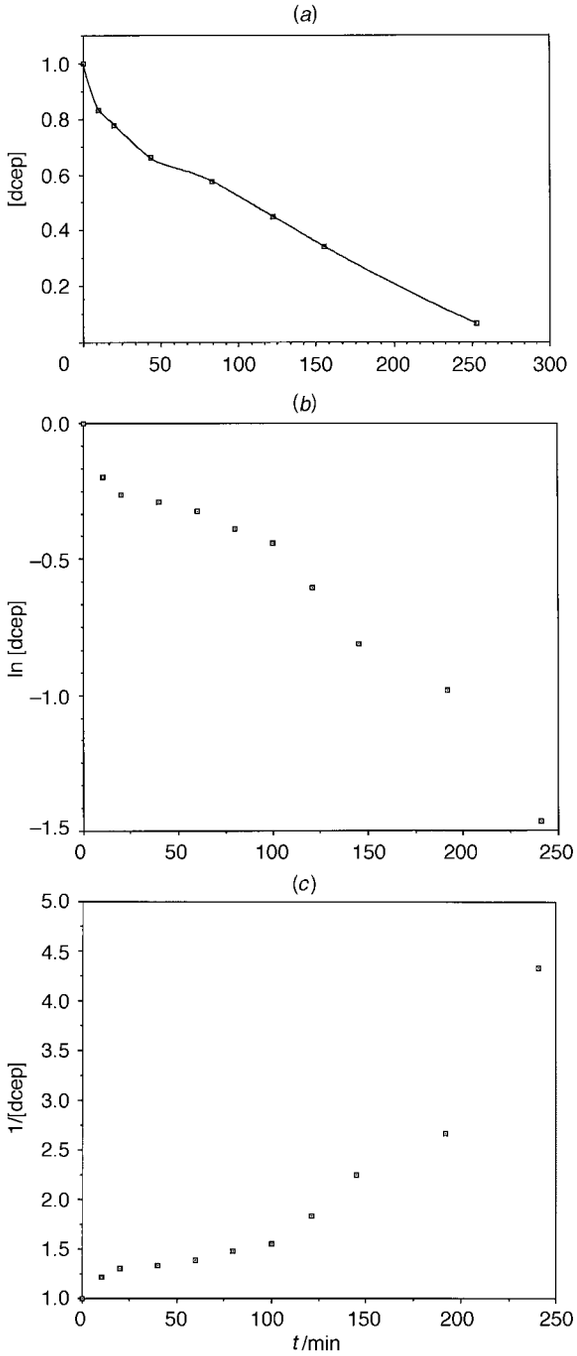


Fig. 2 (*a*) Plot of [dcep] [mole fraction of $PH(CH_2CH_2CN)_2$], determined from the integrals of spectra such as those in Fig. 1, against time, *t*. (*b*) A plot of ln[dcep] against time, *t*, illustrating that the kinetics are not first order and (*c*) a plot of 1/[dcep] against time, *t*, illustrating that the kinetics are not second order

Kinetic investigation of the platinum(0)-catalysed reaction

A more detailed investigation of the hydrophosphination reaction was carried out using the most effective of the catalysts, $[Pt(tcep)_3]$. We initially made the assumption that the rate equation would be of the form given in equation (3). Assuming

$$\text{rate} = k\,[PHR_2]^{\alpha}[CH_2{=}CHCN]^{\beta}[\text{Pt catalyst}]^{\gamma} \qquad (3)$$

the [Pt catalyst] term remains constant throughout (and there is no catalyst degradation) and a large excess of CH_2=CHCN (15 mol equivalents were used) is present, equation (3) reduces to expression (4).

$$\text{rate} = k'\,[PHR_2]^{\alpha} \qquad (4)$$

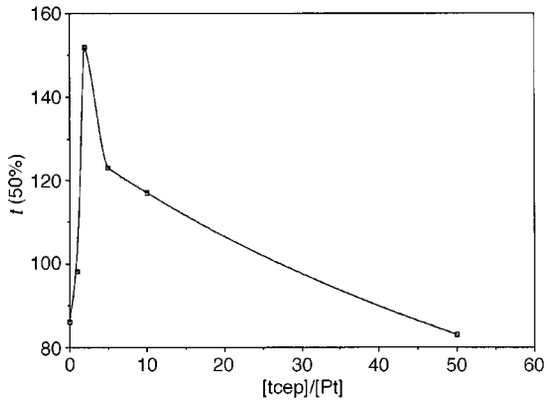


Fig. 3 The variation of time, $t(50\%)$, to equal proportions of dcep and tcep against initial concentration of tcep, [tcep]

The course of the hydrophosphination was monitored as a function of time by integration of the $^{31}P\text{-}\{^1H\}$ NMR spectra as described in the Experimental section. A plot of a typical run of this type is shown in Fig. 2(*a*) and from the attempts to fit these data to first order [Fig. 2(*b*)] or second order [Fig. 2(*c*)] behaviour, it is clear that the kinetics are not simple since the data do not fit with any single value of α. It was suspected that the kinetics may be complicated by the presence of increasing amounts of product tcep as the reaction ensues. To test this, the time taken for conversion of half the $PH(CH_2CH_2CN)_2$ to $P(CH_2CH_2CN)_3$ was measured as a function of initial [tcep] (0–50 equivalents relative to Pt catalyst) and the unusual curve plotted in Fig. 3 was observed. At low initial concentrations of tcep, increasing [tcep] reduces the rate of reaction while at high initial concentrations of tcep, increasing [tcep] increases the rate of reaction. This behaviour can be explained if the rate law has the form shown in equation (5). At high [tcep] the k_1 term

$$\text{rate} = k_1\,[\text{tcep}]^{\delta} + k_2/[\text{tcep}]^{\varepsilon} \qquad (5)$$

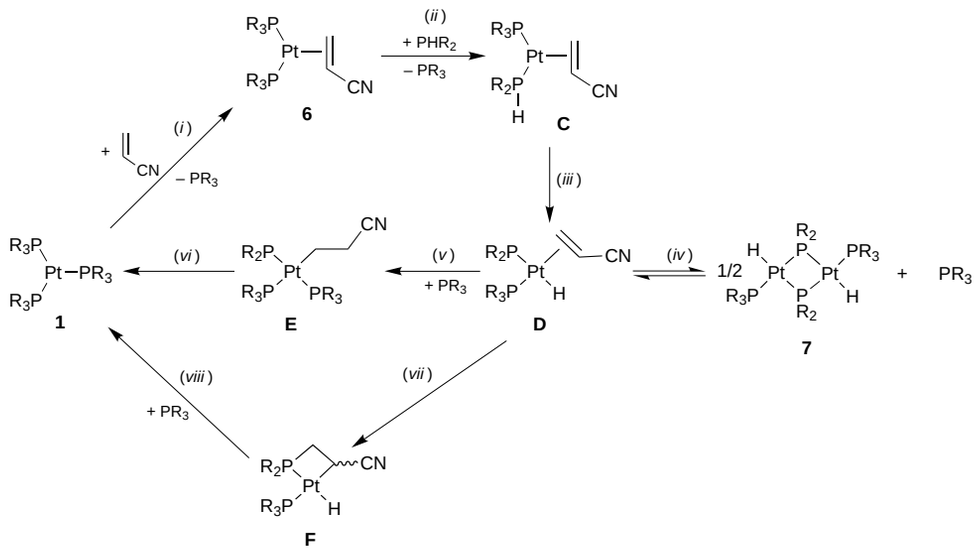
would dominate and at low [tcep] the k_2 term would dominate. This expression is consistent with parallel mechanistic pathways operating (see below).

The complexity of the kinetics of product formation [*e.g.* Fig. 2(*a*)] is a reflection of the complexity of the dependence of this rate on [tcep] concentration (Fig. 3); indeed since the ratio of [tcep] to [Pt catalyst] rises from 0 to 50:1 during a typical run, the entire curve of Fig. 3 is traversed in each experiment. It is likely that for similar reasons, the kinetics will also be a complex function of the secondary phosphine (dcep) concentration. The conclusion is that this reaction defies simple kinetic analysis! However we have attempted to determine the sensitivity of the rate on [Pt catalyst] and [CH_2=CHCN] by measuring the effect on $t(50\%)$ of varying their initial concentration while keeping the other conditions constant. Doubling [Pt catalyst] halved $t(50\%)$ while reducing [CH_2=CHCN] by a factor of 30 increased the $t(50\%)$ by a factor of 30 (entries 10–12, Table 1). It is tempting to draw quantitative significance from these numbers but in view of the above discussion of the complexity of the reaction we will resist this and put these simple numerical relationships down to a coincidence of many factors and conclude that [CH_2=CHCN] and, not surprisingly, [Pt catalyst] are factors in the rate equation.

Some properties of platinum–tcep systems

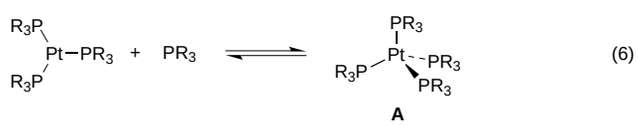
Insight into likely elementary steps in the hydrophosphination catalysis [equation (2)] has been obtained from our study of the properties of $[Pt(tcep)_3]$ and related systems.

The co-ordinatively unsaturated **1** does not form a new species in the presence of a large excess of tcep but the $^{31}P\text{-}\{^1H\}$



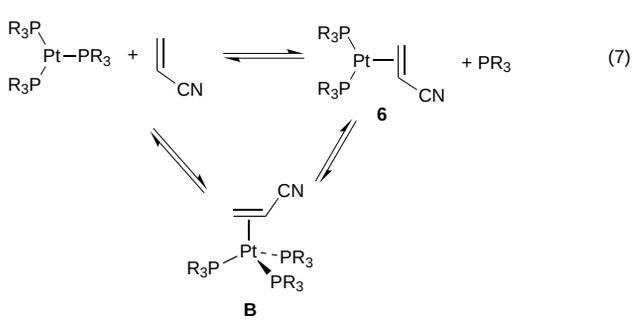
Scheme 1 Mononuclear mechanism proposed for the hydrophosphination at high [tcep] (R = CH_2CH_2CN)

NMR signals are broadened indicating that tcep exchange takes place on the NMR time-scale.[7] This exchange very likely proceeds *via* the 18-electron intermediate **A** shown in equation (6).



(6)

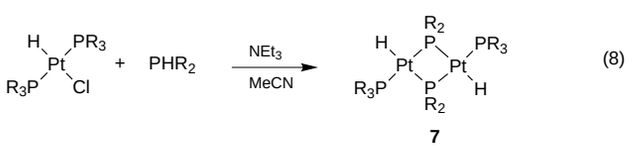
Addition of 1 equivalent of acrylonitrile to **1** in Me_2SO [equation (7)] gave a new platinum-containing species quantit-



(7)

atively, characterised as **6** in solution from the AB pattern of its ^{31}P-{^1H} NMR spectrum and the doublet of doublets in the ^{195}Pt-{^1H} NMR spectrum. The same complex is formed by reduction of *trans*-[$PtCl_2$(tcep)$_2$] with $NaBH_4$ in the presence of acrylonitrile (see Experimental section). While the NMR signals for **6** are sharp in the absence of tcep, the addition of 10 equivalents of tcep to solutions of **6** resulted in broad signals ($w_{\frac{1}{2}}$ = 25 Hz) but no evidence for the re-formation of **1**. We can conclude that while phosphine exchange in **6** takes place on the NMR time-scale, presumably *via* **B**, the equilibrium shown in equation (7) lies to the right with $K \gg 10$.

The diplatinum complex **7** [equation (8)] was made in high



(8)

yield by treatment of *trans*-[PtHCl(tcep)$_2$] with $PH(CH_2CH_2CN)_2$ and has been fully characterised (see Experimental section). The ^{31}P-{^1H} NMR signal at δ −160.9 is characteristic of μ-PR_2 ligands[13] and the ^1H NMR signal at δ −4.84 is characteristic of the presence of a Pt–H bond. The small ^1J(PtH) of 948 Hz and low frequency ν(PtH) of 1967 cm^{-1} reflect the high *trans* influence of the μ-PR_2 ligands. Significantly, we have found that binuclear **7** also catalyses the hydrophosphination of acrylonitrile [equation (2)].

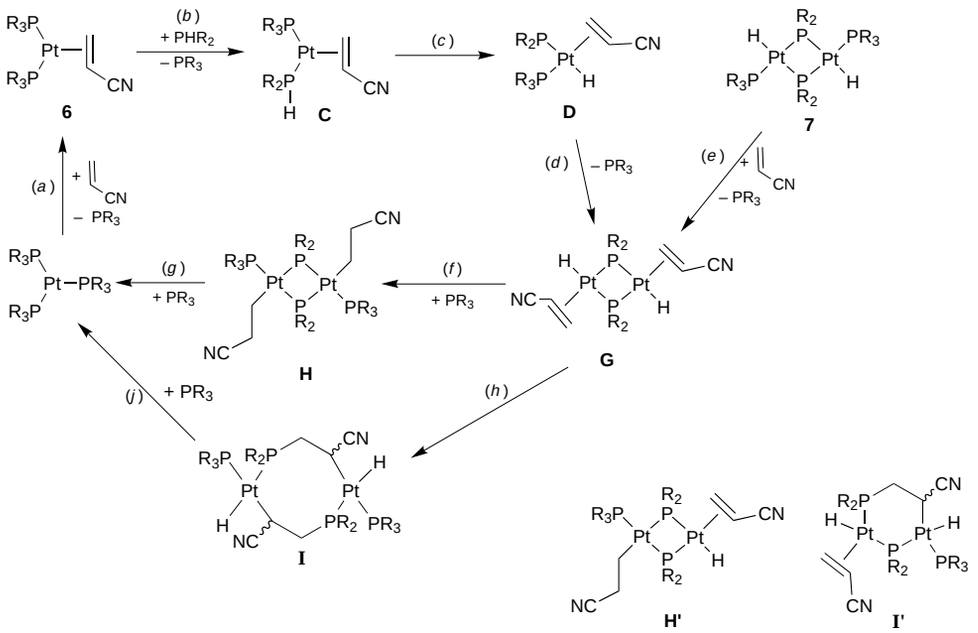
Mechanistic hypothesis

The conclusions that can be drawn from our kinetic measurements are complicated by our observation that the product tcep strongly influences the rate in a way that suggests that more than one pathway is operating. The mechanisms shown in Schemes 1 and 2 form the basis of the discussion below.

In Scheme 1, the simplest sequence of reactions is presented. We have shown [equation (7)] that displacement of tcep from **1** by acrylonitrile to give **6** [step (*i*)] occurs readily and since acrylonitrile was in large excess, **6** is likely to be the main Pt species present. Exchange of tcep in **6** occurs on the NMR time-scale and therefore displacement of tcep by $PH(CH_2CH_2CN)_2$ [step (*ii*)] to give **C** is reasonable. Oxidative addition of the P–H bond to platinum(0), which is known with other low-valent metals,[14] is proposed [step (*iii*)] to give mononuclear intermediate **D** (and its geometric isomers). The displacement of acrylonitrile from **D** [step (*iv*)] would give the μ-PR_2 complex **7**.

The completion of the catalytic cycle from **D** could be achieved by β-hydrogen migration to the co-ordinated acrylonitrile [step (*v*)] to give **E** followed by reductive P–C elimination [step (*vi*)]; though literature precedent for neither of these reactions is available for Pt compounds, insertion of acrylonitrile into other M–H[15] bonds and P–C reductive elimination[16] have been reported. Alternatively a Michael-type attack by the PR_2 on the co-ordinated acrylonitrile [step (*vii*)] would yield the metallacycle **F** which upon reductive formation of the C–H bond [step (*viii*)] would regenerate **1**; a similar metallacycle is proposed in the mechanism for iridium(I)-catalysed hydroamination.[17] Insertion of another CH_2=CHCN into the Pt–C bond in **F** would relieve the strain and may explain the formation of telomeric species **Y** under certain conditions (see above).

The terminal phosphido–platinum(II) complexes proposed in the mechanism in Scheme 1 should be stable with respect to μ-PR_2 complexes only at high [tcep]. We suggest that in low [tcep] regimes, the mechanism shown in Scheme 2 is more likely. In this mechanism steps (*a*)–(*c*) are the same as steps (*i*)–(*iii*) in Scheme 1 but then **D** dissociates a tcep [step (*d*)] to give the binuclear species **G** which could also be formed from **7** [step (*e*)]. From **G** the cycle can be completed by β-hydrogen



Scheme 2 Binuclear mechanism proposed for the hydrophosphination at low [tcep] (R = CH_2CH_2CN)

migration [step (*f*)] to give **H** (or more likely **H'**) followed by reductive P–C elimination [step (*g*)] which are directly analogous to steps (*v*) and (*vi*) in Scheme 1. Intramolecular Michael addition in the binuclear **G** [step (*h*)] may give the species **I** (or more likely **I'**) from which reductive formation of the C–H bond [step (*j*)] would regenerate **1**.

If we propose that at high [tcep] a mononuclear pathway (Scheme 1), while at low [tcep] a binuclear pathway (Scheme 2), operates then we can rationalise the complicated dependence of the rate on [tcep].

Conclusion

It has been demonstrated that the formation of $P(CH_2CH_2CN)_3$ from $PH(CH_2CH_2CN)_2$ and CH_2=CHCN is catalysed by tcep complexes of d^{10} and d^8 metals and platinum(0) is the most efficient. The mechanism of this self-replication probably involves parallel mononuclear and binuclear processes. The application of metal-complex-catalysed hydrophosphinations to the synthesis of other phosphines is in progress.

Experimental

The general methods used were as described in recent papers from this laboratory.[7] The phosphine tcep and its complexes **1**, **2**, **4** and **5** were made by routes previously reported.[7] The compounds $PH(CH_2CH_2CN)_2$ and $[Ni(cod)_2]$ were purchased from Strem.

in situ Preparation of $[Ni(tcep)_3]$ 3

In a glovebox under nitrogen solid $[Ni(cod)_2]$ (10 mg, 0.036 mmol) and tcep (21 mg, 0.109 mmol) were put in a 5 mm NMR tube and dry CD_3CN (0.4 cm^3) was added. The ^{31}P-{^1H} NMR spectrum of the resulting amber solution showed at −44 °C a sharp peak at δ +16.7.

Preparation of $[Pt(tcep)_2(\eta^2\text{-}CH_2{=}CHCN)]$ 6

To a solution of *trans*-$[PtCl_2(tcep)_2]$[7] (100 mg, 0.153 mmol) in MeCN (10 cm^3) was added CH_2=CHCN (0.50 cm^3, 0.760 mmol, 50 equivalents) followed by $NaBH_4$ (30 mg, 0.793 mmol, 5.18 equivalents) and the mixture was stirred. After 1 h, the solvent was evaporated to dryness and the residue washed with water (2 × 10 cm^3). Yield 70 mg of crude product. Satisfactory elemental analyses were not obtained (possibly because of the presence of small amounts of polyacrylonitrile) but the phosphorus-containing product was identified as **6** from the NMR data which are very similar to those reported[18] for $[Pt(PR'_3)_2(\eta^2\text{-}CH_2{=}CHCN)]$. ^{31}P-{^1H} NMR [36.2 MHz, $(CD_3)_2SO$]: δ 18.1 [d, *J*(PP) 44, ^1J(PtP) 3784], 16.4 [d, *J*(PP) 44, ^1J(PtP) 3345 Hz]. ^{195}Pt-{^1H} NMR [19.2 MHz, $(CD_3)_2SO$]: −550 (d,d). The same species **6** was identified in the following experiment carried out in a 5 mm NMR tube. To a solution of $[Pt(tcep)_3]$ (30 mg, 0.039 mmol) in $(CD_3)_2SO$ (0.4 cm^3) was added CH_2=CHCN (0.015 cm^3, 0.228 mmol, 5.85 equivalents) to give a pale yellow solution, the ^{31}P-{^1H} NMR spectrum of which showed the presence of **6** and tcep only.

Preparation of $[Pt_2H_2(tcep)_2\{\mu\text{-}P(CH_2CH_2CN)_2\}]$ 7

To a solution of *trans*-$[PtHCl(tcep)_2]$[7] (233 mg, 0.38 mmol) in MeCN (5 cm^3) was added $PH(CH_2CH_2CN)_2$ (0.066 cm^3, 0.38 mmol) followed by NEt_3 (0.130 cm^3, 0.933 mmol) and the mixture was stirred. After 10 min, the white solid product was filtered off, washed with acetonitrile (5 cm^3) and then diethyl ether (20 cm^3) and dried (150 mg, 75%) [Found (Calc): C, 34.15 (34.10); H, 4.15 (4.00); N, 12.00 (12.45) %]. IR (Nujol mull, cm^{-1}): 2247m (ν_{CN}), 1967m (ν_{PtH}). ^1H NMR [270 MHz, $(CD_3)_2SO$]: 2.77 (m, 10 H, CH_2), 2.50 (m, 10 H, CH_2), −4.84 [d × m, *J*(PH) 146, ^1J(PtH) 948 Hz]. ^{31}P-{^1H} NMR [36.2 MHz, $(CD_3)_2SO$]: 28.1 [m, ^1J(PtP) 2051, *J*(PP) 293], −160.9 [m, ^1J(PtP) 1777 Hz].

Platinum(0)-catalysed reaction of PH_3 with acrylonitrile

CAUTION: Phosphine gas is extremely toxic and should only be handled in a well ventilated fume cupboard; the exit gases were passed through a solution of commercial bleach to oxidise unreacted PH_3.

A 250 cm^3, three-necked flask equipped with a gas inlet and outlet was charged with acetonitrile (100 cm^3). The solution was purged with nitrogen for 30 min and then $[Pt(tcep)_3]$ (77 mg, 0.10 mmol) was added. After purging for a further 10 min, acrylonitrile (10 cm^3, 8.06 g, 152 mmol) was added and then PH_3 was admitted at a slow rate for *ca.* 6 h. The solution was then purged with nitrogen for 20 min and an aliquot (0.4 cm^3) removed for analysis by ^{31}P-{^1H} NMR spectroscopy which showed the presence of four signals in approximately equal intensity corresponding to the species $PH_n(CH_2CH_2CN)_{3-n}$ (n = 0–3).

Platinum(0)-catalysed reaction of $PH(CH_2CH_2CN)_2$ with acrylonitrile

Acrylonitrile (1.62 cm^3, 24.5 mmol, 2.65 mol dm^{-3}) was added to a solution of $[Pt(tcep)_3]$ (72 mg, 0.093 mmol, 0.01 mmol dm^{-3}) in acetonitrile (7.2 cm^3). The phosphine dcep (0.43 cm^3, 2.45 mmol, 0.265 mol dm^{-3}) was then added and the reaction monitored by ^{31}P-$\{^1H\}$ NMR spectroscopy and the time, t(50%), required for the signals for dcep and tcep to be approximately equal was measured (see Table 1). The same conditions (referred to as standard conditions in Table 1) were used to compare the other metal catalysts **2–5**; the reaction with the rhodium complex **4** was carried out in Me_2CO because it is insoluble in MeCN.

Kinetic investigations of the platinum(0) catalysis by ^{31}P-$\{^1H\}$ NMR spectroscopy

In a typical experiment, acrylonitrile (4.86 cm^3, 73.4 mmol, 5.87 mol dm^{-3}) was added to a solution of $[Pt(tcep)_3]$ (81 mg, 0.105 mmol, 8.4 mmol dm^{-3}) in acetonitrile (6.77 cm^3). Secondary phosphine, dcep (0.86 cm^3, 4.90 mmol, 0.392 mol dm^{-3}) was then added and 0.4 cm^3 samples were removed at regular intervals and frozen in liquid nitrogen. The ^{31}P-$\{^1H\}$ NMR spectra were later recorded and the intensity of the signals measured (see Fig. 2 for a typical plot). Similar runs were carried out at different [dcep] (0.392, 0.489 and 0.588 mol dm^{-3}) and $[CH_2{=}CHCN]$ (0.20 mol dm^{-3}). The conditions were different for the runs with different initial [tcep] (0, 8.4, 17.0, 41.8, 84.0 and 420 mmol dm^{-3}) and runs where [catalyst] was varied (3.4, 5.6 and 11.1 mol dm^{-3}): more dcep (0.86 cm^3, 0.394 mol dm^{-3}) and complex **1** (105 mg, 10.1 mmol dm^{-3}) were used and the NMR signal intensities for tcep corrected for the amount of tcep added initially.

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