Platinum(0)-catalysed Hydrophosphination of Acrylonitrile

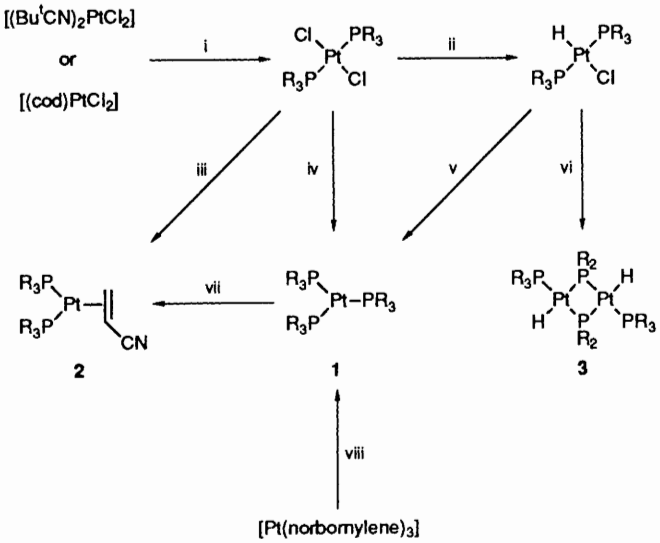
Paul G. Pringle* and Martin B. Smith

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

The tris(cyanoethyl)phosphine complex $[Pt\{P(CH_2CH_2CN)_3\}_3]$ catalyses the addition of PH_3 or $PH(CH_2CH_2CN)_2$ to CH_2=CHCN to give $P(CH_2CH_2CN)_3$.

Metal-phosphines catalyse many HX additions to alkenes including hydrogenation,[1,2] hydroformylation,[3] hydrosilylation[4] and more recently, hydroamination.[5] We now report the first example of a hydrophosphination of an alkene catalysed by a metal complex.

Tris(cyanoethyl)phosphine is an air-stable, white solid which finds use in the photographic industry[6] and has been extensively investigated as a ligand.[7] We have recently shown[8] the PH_3 addition to H_2C=O to give $P(CH_2OH)_3$ is catalysed by a platinum(0) complex of $P(CH_2OH)_3$ and we therefore reasoned that platinum(0) complexes of $P(CH_2CH_2CN)_3$ may catalyse the addition of PH_3 to CH_2=CHCN. Platinum(0) complexes of $P(CH_2CH_2CN)_3$ have not been reported so the routes shown in Scheme 1 have been developed for the synthesis of $[Pt\{P(CH_2CH_2CN)_3\}_3]$ **1**. The three-coordination of the platinum(0) in complex **1** is deduced from its $^{195}Pt\{^1H\}$ NMR spectrum, which is a 1:3:3:1 quartet, and has been confirmed by elemental analysis, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.† The $^{31}P\{^1H\}$ NMR spectrum of a $(CD_3)_2SO$ of complex **1** containing an excess of $P(CH_2CH_2CN)_3$ (10 equiv.) showed slightly broadened singlets for the two components, indicating that complex **1** has surprisingly little tendency to form the four-coordinate

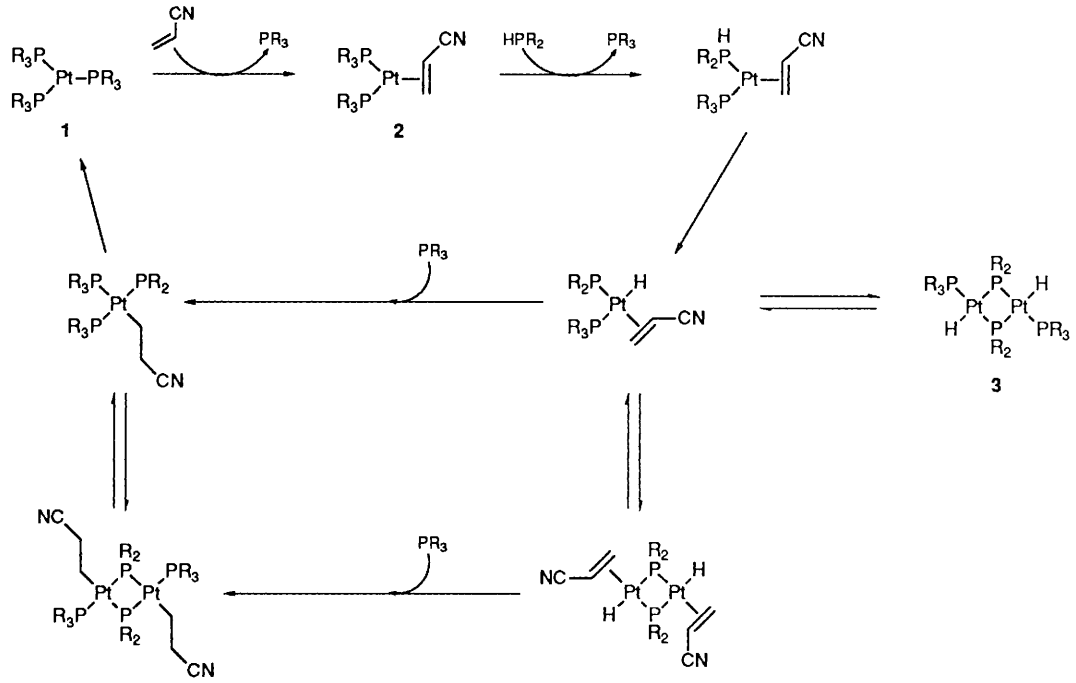


Scheme 1 *Reagents and conditions* (R = CH_2CH_2CN): i, 2 equiv. PR_3 in CH_2Cl_2; ii, $NaBH_4$ in MeCN; iii, CH_2=CHCN in MeCN followed by $NaBH_4$; iv, 1 equiv. of PR_3 in MeCN followed by $NaBH_4$; v, 1 equiv. of PR_3 and Et_3N in Me_2SO; vi, 1 equiv. of $PH(CH_2CH_2CN)_2$ and Et_3N in MeCN; vii, 1 equiv. of CH_2=CHCN in Me_2SO; viii, 3 equiv. of PR_3 in acetone–toluene (cod = cycloocta-1,5-diene)

† *Selected NMR spectroscopic data:* all spectra were recorded in $(CD_3)_2SO$ (^{31}P and ^{195}Pt chemical shifts are to high frequency of 85% H_3PO_4 and Ξ 21.4 MHz respectively). **1**: δ(P) 39.9, ^1J(PtP) 4217 Hz; δ(Pt) + 15.8 (quartet).

2: δ(P_A) 18.9, $^1J(PtP_A)$ 3801 Hz, δ(P_B) 15.6, $^1J(PtP_B)$ 3327 Hz, J(PP) 44 Hz; δ(Pt) −550 (dd).

3: δ(PR_3) 28.2 (m), ^1J(PtP) 2366 Hz, δ(μ-PR_2) −160.9 (m), ^1J(PtP) 1874 Hz, J(PP) 288 Hz; δ(H) −4.80 (m), ^1J(PtH) 948 Hz, $J(P_{trans}H)$ 146 Hz.



Scheme 2 Suggested mechanism for the hydrophosphination of CH_2=CHCN

complex $[Pt\{P(CH_2CH_2CN)_3\}_4]$ and further, that phosphine exchange at **1**, though occurring, is not rapid on the NMR timescale.

When PH_3 was bubbled through an acetonitrile solution of acrylonitrile for 6 h, no reaction was observed by $^{31}P\{^1H\}$ NMR spectroscopy but, under similar conditions, addition of $[Pt\{P(CH_2CH_2CN)_3\}_3]$ led to the formation of the phosphines $PH_n(CH_2CH_2CN)_{3-n}$ (n = 0–2). There are three parallel reactions taking place in the conversion of PH_3 to $P(CH_2CHCN)_3$ (eqn. 1–3) making further analysis of this system very complex. We have therefore concentrated on the final step: the conversion of $PH(CH_2CH_2CN)_2$ to $P(CH_2CH_2CN)_3$ (eqn. 3). After 8 h, there is no observed reaction between $PH(CH_2CH_2CN)_2$ and CH_2=CHCN but under similar conditions,‡ upon addition of the platinum complex **1**, this reaction proceeds smoothly to completion within 1 h.

$$PH_3 + CH_2{=}CHCN \rightarrow PH_2(CH_2CH_2CN) \quad (1)$$

$$PH_2(CH_2CH_2CN) + CH_2{=}CHCN \rightarrow PH(CH_2CH_2CN)_2 \quad (2)$$

$$PH(CH_2CH_2CN)_2 + CH_2{=}CHCN \rightarrow P(CH_2CH_2CN)_3 \quad (3)$$

A mechanism for the hydrophosphination reaction is suggested in Scheme 2. The first step in the mechanism is supported by the observation that treatment of $[Pt\{P(CH_2CH_2CN)_3\}_3]$ with CH_2=CHCN gives $[Pt(\eta^2\text{-}CH_2{=}CHCN)\{P(CH_2CH_2CN)_3\}_2]$ **2** quantitatively (see Scheme 1). Upon addition of 3 equivalents of $P(CH_2CH_2CN)_3$ to **2** the AB pattern of its $^{31}P\{^1H\}$ NMR spectrum is broadened but essentially no displacement of the alkene is observed indicating that the equilibrium between **1** and **2** lies greatly in favour of **2**; this may account for the observation that whereas normally metal-phosphine catalysed additions to alkenes are suppressed by the addition of phosphine ligand, the hydrophosphination reaction reported here is not slowed upon addition of even 50 equivalents of $P(CH_2CH_2CN)_3$. Subsequent steps in the mechanism have much in common with the mechanism proposed for catalytic hydrosilylation[4] by platinum-phosphines. Binuclear μ-phosphido complexes are possible intermediates since we have found that the binuclear complex **3**, which can be made independently (see Scheme 1), is also a catalyst precursor for the hydrophosphination of CH_2=CHCN (eqn. 3). Clearly further study of the mechanism is required and an investigation of the generality of the hydrophosphination reaction is presently underway.

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‡ *Reaction conditions:* A mixture of $PH(CH_2CH_2CN)_2$ (0.48 g, 3.42 mmol), CH_2 = CHCN (2.25 cm^3, 3.42 mmol) and complex **1** (0.10 g, 0.13 mmol) in MeCN (10 cm^3) was stirred at +20 °C.

References

1 B. R. James, *Homogeneous Hydrogenation*, Wiley, New York, 1973.
2 *Homogeneous Catalysis by Metal Phosphine Complexes*, ed. L. H. Pignolet, Plenum Press, New York, 1983.
3 B. Cornils in *New Syntheses with Carbon Monoxide*, ed. J. Falbe, Springer-Verlag, Berlin, 1980.
4 M. Green, J. L. Spencer, F. G. A. Stone and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 1977, 1519.
5 A. L. Casalnuovo, J. C. Calabrese and D. Milstein, *J. Am. Chem. Soc.*, 1988, **110**, 6738.
6 BP 1 430 998 (1976) to Ciba Geigy (*Chem. Abstr.*, 1976, **85**, 114 752).
7 M. S. Holt and J. H. Nelson, *Inorg. Chem.*, 1986, **25**, 1316 and references therein.
8 K. N. Harrison, P. A. T. Hoye, A. G. Orpen, P. G. Pringle and M. B. Smith, *J. Chem. Soc., Chem. Commun.*, 1989, 1096.