Chemoselective platinum(0)-catalysed hydrophosphination of ethyl acrylate

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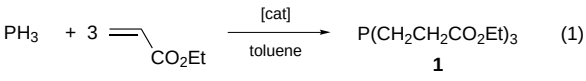
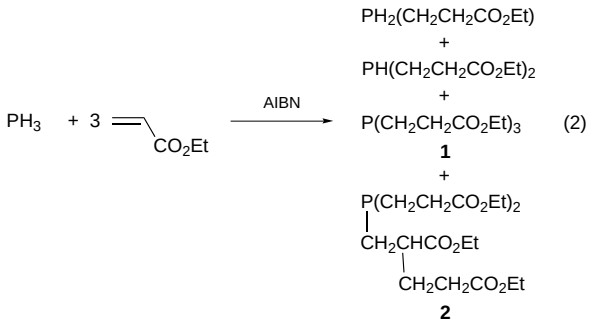
Platinum(0) complexes of $P(CH_2CH_2CO_2Et)_3$ are efficient and selective catalysts for the addition of PH_3 to CH_2=$CHCO_2Et$.

Homogeneous catalysis of the addition of Si–H,[1] B–H[2] or P–H[3–5] to C=C bonds by transition-metal complexes is a field of academic interest and industrial potential. We are interested in the additions of P^{III}–H to C=C bonds catalysed by metal–phosphine complexes and have shown that platinum(0) complexes of tris(cyanoethyl)phosphine catalyse the hydrophosphination of acrylonitrile.[3] We report here that the synthesis of the triester phosphine **1** by the addition of PH_3 to CH_2=$CHCO_2Et$ [eqn. (1)] is catalysed by platinum(0) com-



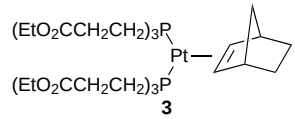
plexes of **1** and the efficiency and selectivity of this catalysis is superior to the alternative radical-initiated process. Phosphine **1** is of interest as a flame retardant intermediate[6] and as a phosphine ligand amenable to further functionalisation.[7]

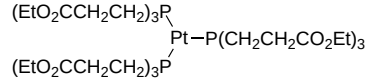
Rauhut *et al.*[8] reported that at 70 °C and *ca*. 25 atm of PH_3, hydrophosphination of ethyl acrylate [eqn. (2)] is promoted by

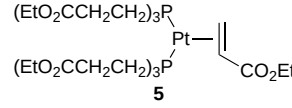


AIBN to give a mixture of primary, secondary and tertiary phosphines in the ratio of *ca*. 1 : 1 : 1. The conversion based on ethyl acrylate was 83% and the tertiary phosphine component was a *ca*. 1 : 1 mixture of phosphine **1** and the telomer **2**. Thus the overall selectivity of this radical reaction to the desired phosphine **1** is *ca*. 15%. We investigated the efficacy of platinum(0) complexes as catalysts for the hydrophosphination of ethyl acrylate in the hope that they would be more selective than the radical initiated process.

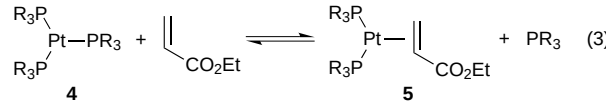
Treatment of [Pt(norbornene)$_3$] with 2 or 3 equiv. of **1** in toluene gave platinum(0) complexes assigned structures **3** and **4** on the basis of the characteristic ^{31}P NMR data and the multiplicity of the ^{195}Pt NMR signals.† Addition of further ligand **1** to solutions of **4** led to broad ^{31}P NMR signals for both **1** and **4** showing that ligand exchange takes place on the NMR timescale at ambient temperatures but there was no evidence for a stable [Pt$(PR_3)_4$] species. Addition of 1 equiv. of ethyl acrylate to a solution of **3** in toluene gave a species assigned structure **5** on the basis of the AB pattern observed in the ^{31}P NMR







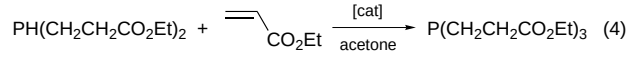
spectrum and the doublet of doublets in the ^{195}Pt NMR spectrum. Interestingly the same species **5** is obtained upon addition of 1 equiv. of ethyl acrylate to **4** but in this case the ^{31}P NMR signals are broad for both **5** and displaced **1** indicating that phosphine exchange is taking place; addition of 5 equiv. of phosphine **1** to solutions of **5** broadened the signals further but there was no evidence for reformation of **4**. It was therefore inferred that the equilibrium shown in eqn. (3) lies to the right



and K was estimated to be > 100. This suggests that complex **5** will be the predominant form of the platinum(0) during the course of the catalysis described below particularly in the initial stages when the ethyl acrylate is in abundance. Complexes **3**–**5** are very reactive and attempts to isolate them in pure form were unsuccessful; thus they have been generated *in situ* for the catalysis.

When PH_3 is bubbled through a warmed solution of ethyl acrylate, no reaction is apparent after 3 h but under similar conditions‡ in the presence of 0.002 equiv. of platinum(0), the reaction proceeded smoothly and after 8 h essentially all of the ethyl acrylate had been consumed. According to ^{31}P NMR spectroscopy, a *ca*. 10 : 1 mixture of the tertiary phosphines **1** and **2** was the product and therefore the selectivity of the platinum(0) process for **1** is > 90%. The addition of PH_3 to ethyl acrylate involves three consecutive hydrophosphinations and the preference for tertiary phosphine in the product implies that the rate of the P–H additions increases in the order PH_3 < RPH_2 < R_2PH. From the proportion of **1** obtained in the product, the average selectivity of each step is apparently *ca*. 97%.

The final step in the hydrophosphination [eqn. (4)] has been



monitored by ^{31}P NMR spectroscopy in the presence and absence of platinum(0) complex **3**. Under the conditions used,§

the P–H addition [eqn. (4)] proceeded 30% after 24 h in the absence of platinum(0) while in the presence of **3** (0.1 equiv.) the hydrophosphination had proceeded 50% after 15 min and was complete in less than 90 min with the desired phosphine **1** constituting >95% of the product according to ^{31}P NMR spectroscopy.

Platinum(0) complexes are catalysts for the hydrophosphination of CH_2=CHZ (Z = CN or CO_2Et).[3,4] Both of these Z substituents withdraw electron density from the C=C bond by virtue of their electronegativity (−I) and resonance (−R) effects. Since no catalysis was detected when PH_3 was passed through a toluene solution of CH_2=$CHCF_3$ in the presence of [Pt{$P(CH_2CH_2CF_3)_3$}$_2$(norbornene)], it is the resonance (or Michael) activation of the alkene that appears to be critical.

While the coordination chemistry of the commercially available $P(CH_2CH_2CN)_3$ has been well studied,[9] to our knowledge, the reported metal complex chemistry of **1** is restricted to one iridium cluster.[7] A study of the precious metal chemistry of **1** is in progress.

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Footnotes and References

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† *NMR data* for compounds **1**–**5**: Phosphine **1**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.27 [t, ^3J(HH) 7.2 Hz, 3 H], 1.75 [t, ^3J(HH) 8.3, ^2J(HP) 8.3 Hz, 2 H], 2.45 [dt, ^3J(HH) 8.3, ^3J(HP) 8.1 Hz, 2 H], 4.15 [q, ^3J(HH) 7.2 Hz, 2 H]; ^{13}C NMR ($C_6D_5CD_3$, 100 MHz, assigned with the aid of DEPT) δ 14.2 (s, CH_3), 21.9 [d, ^1J(CP) 14.7 Hz, CH_2], 30.7 [d, ^2J(CP) 16.5 Hz, CH_2], 60.2 (s, CH_2), 172.5 [d, ^3J(CP) 11.0 Hz, C=O]; ^{31}P{^{1}H} NMR ($C_6D_5CD_3$, 162 MHz) δ −25.9. Phosphine **2** characterised in solution by subtracting the peaks for **1** from the spectra of mixtures of **1** and **2**: ^{13}C NMR ($C_6D_5CD_3$, 100 MHz, assigned with the aid of DEPT) δ 14.3 (s, CH_3), 22.3 [d, ^1J(CP) 14.7 Hz, CH_2], 22.4 [d, ^1J(CP) 14.7 Hz, CH_2] 27.8 (s, CH_2), 30.7 [d, ^1J(CP) 16.5 Hz, CH_2], 31.9 (s, CH_2), 44.6 [d, ^2J(CP) 14.7 Hz, CH], 60.6 (s, CH_2), 60.4 (s, CH_2), 60.3 (s, CH_2), 172.1 (s, C=O), 172.5 [d, ^3J(CP) 11.0 Hz, C=O], 174.5 [d, ^3J(CP) 3.0 Hz, C=O]; ^{31}P{^{1}H} NMR ($C_6D_5CD_3$, 162 MHz) δ −30.1. Complex **3**: ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz) δ −19.7 [^1J(PtP) 3390 Hz]; ^{195}Pt{^{1}H} NMR [C_6D_6, 85.6 MHz, δ relative to Ξ(Pt) 21.4 MHz] δ −574.6 [t, ^1J(PtP) 3390 Hz]. Complex **4**: ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz) δ −40.5 [^1J(PtP) 4202 Hz]; ^{195}Pt{^{1}H} NMR (C_6D_6, 85.6 MHz) δ −0.6 [q, ^1J(PtP) 4202 Hz]. Complex **5**: ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz) δ 15.9 [d, ^2J(PP) 46, ^1J(PtP) 3410 Hz], 17.4 [d, ^2J(PP) 46, ^1J(PtP) 3854 Hz]; ^{195}Pt{^{1}H} NMR (C_6D_6, 64.2 MHz) δ −604.0 [dd, ^1J(PtP) 3405, 3865 Hz].

‡ **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. Toluene (50 cm^3) was carefully deaerated by passing nitrogen through it for 1.5 h and then [Pt(norbornene)$_3$] (0.123 g, 0.257 mmol), the phosphine **1** (1.034 g, 3.093 mmol) and ethyl acrylate (13.1 cm^3, 121 mmol) were added sequentially. PH_3 gas was bubbled through the solution for 8 h maintaining the temperature at 55 °C. The solution was stirred for a further 3 h at 55 °C and the reaction was monitored throughout by ^{31}P NMR spectroscopy.

§ Oxygen was rigorously excluded from the reaction mixture. In an 5 mm NMR tube, to a solution of [Pt(norbornene)$_3$] (5 mg, 0.010 mmol) in $C_6D_5CD_3$ (0.10 cm^3), phosphine **1** (7.0 μl, 0.020 mmol) and then ethyl acrylate (35.0 μl, 0.32 mmol) were added. To this mixture a solution of $PH(CH_2CH_2CO_2Et)_3$ (50 μl, 0.21 mmol) in $C_6D_5CD_3$ (0.30 cm^3) was added in one portion and the reaction monitored by ^{31}P NMR spectroscopy.

1 T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki and N. Miyaura, *Organometallics*, 1996, **15**, 713 and references 8(*a*)–(*p*) within; B. Marciniec and J. Gulinski, *J. Organomet. Chem.*, 1993, **446**, 15 and references therein.

2 K. Burgess, W. A. van der Donk, S. A. Westcott, T. B. Marder, R. T. Baker and J. C. Calabrese, *J. Am. Chem. Soc.*, 1992, **114**, 9350 and references therein; K. Burgess and M. J. Ohlmeyer, *Chem. Rev.*, 1991, **91**, 1179 and references therein.

3 P. G. Pringle and M. B. Smith, *J. Chem. Soc., Chem. Commun.*, 1990, 1701; E. Costa, P. G. Pringle, M. B. Smith and K. Worboys, *J. Chem. Soc., Dalton Trans.*, 1997, 4277.

4 D. K. Wicht, I. V. Kourkine, B. M. Lew, J. M. Nthenge and D. S. Glueck, *J. Am. Chem. Soc.*, 1997, **119**, 5039.

5 L.-B. Han and M. Tanaka, *J. Am. Chem. Soc.*, 1996, **118**, 1571; N. Choi, L.-B. Han and M. Tanaka, *Organometallics*, 1996, **15**, 3259.

6 R. K. Valetdinov, A. N. Zuikova and R. D. Murtazina, *USSR Pat.* 819 115, 1981; *Chem. Abstr.*, 1981, **95**, 62 414.

7 J. Werner, *Z. Naturforsch., Teil B*, 1989, **44**, 79.

8 M. M. Rauhut, H. A. Currier, A. M. Semsel and V. P. Wystrach, *J. Org. Chem.*, 1961, **26**, 5138.

9 A. G. Orpen, P. G. Pringle, M. B. Smith and K. Worboys, *J. Organomet. Chem.*, 1997, in press, and references therein.

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