Immobilised Phosphines incorporating the Chiral Biopolymers Chitosan and Chitin

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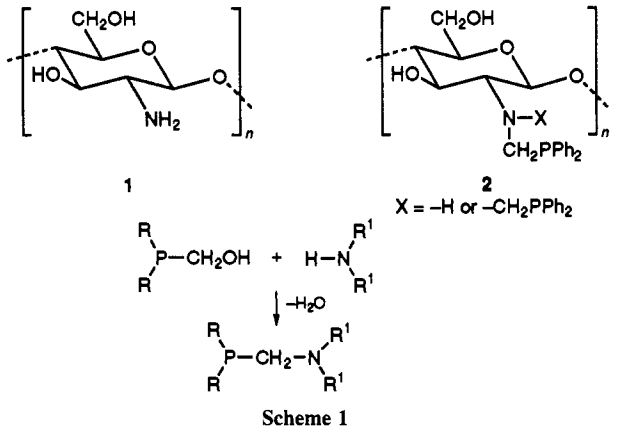
Reaction of chitosan with hydroxymethyl phosphines R_2PCH_2OH proceeds readily *via* a Mannich-type condensation reaction with the polymer NH_2 groups to give a new type of chiral, immobilised phosphine.

Chitosan, poly β-(1→4)-D-glucosamine **1**, is a polymeric amino sugar, readily obtained in large quantities by *N*-deacetylation of chitin, a byproduct of the seafood industry. The potential applications of chitosan, however, are only just beginning to be realised.[1-3] We reasoned that there may be considerable potential for using chitosan as a novel support for the immobilisation of phosphines which, to the best of our knowledge, appears to have escaped any previous attention. Phosphines and phosphinites immobilised on the related biopolymer cellulose have been known for some time.[4] Phosphines themselves have been the subject of long-standing interest; chiral phosphines have been synthesised in order to facilitate enantioselective syntheses using metal–phosphine complexes;[5] immobilised phosphines are of much interest for the development of new improved 'heterogenised homogeneous catalysts',[6] and certain phosphines also exhibit anticancer activity.[7]

Reaction of a methanolic suspension of finely ground crab chitosan (Sigma) with an excess of Ph_2PCH_2OH [generated from $Ph_2P(CH_2OH)_2{}^+Cl^-$[8] and 1.0 equiv. of KOH] proceeded readily at room temp. *via* a Mannich-type condensation reaction[9] of the polymer amine groups (Scheme 1) giving the immobilised phosphine **2** as a white powder after filtration, washing and drying *in vacuo*. The immobilised phosphine was identified by a 54% mass increase, and characterised by IR spectroscopy, EDAX scanning electron microscopy and elemental analysis, which showed the material to contain 5.1% m/m P. The P–N mole ratio of 0.48 is significantly lower than the theoretical value of 2.0 and indicates that incomplete reaction of chitosan NH_2 groups has occurred. It is highly likely that some chitosan–NH_2 groups are inaccessible to Ph_2PCH_2OH (due to the insoluble nature of chitosan). Furthermore, the degree of deacetylation of the starting commercial chitosan was 72%, and the residual NHC(O)Me groups were considered to be unreactive towards Ph_2PCH_2OH. In order to verify this, the reaction of powdered Sigma crab chitin, the *N*-acetylated analogue of chitosan, with Ph_2PCH_2OH was investigated. The resulting material, after thorough washing and drying, was found to contain a small amount of phosphorus (0.38%), consistent with the small number of NH_2 groups present in chitin (commercial Sigma crab chitin is *ca.* 95% acetylated, *i.e.* 5% reactive NH_2 groups theoretically available). Additional evidence for covalent phosphine binding, as opposed to surface adsorption, comes from the observation that no phosphorus whatsoever is immobilised on treatment of either chitosan or chitin with excess phosphine oxide $Ph_2P(O)CH_2OH$ under identical reaction conditions, as evidenced by microanalytical data. Such hydroxymethylphosphine oxides typically require much more extreme reaction conditions for condensation to occur with amines. Studies indicate that chitosan from other bio-sources (*e.g.* squid pens) behaves in the same manner as crab chitin.



Scheme 1

The immobilised phosphine **2** swells sufficiently in a D_2O–ethanol mixture to permit a ^{31}P $\{^1H\}$ NMR spectrum to be recorded. A single somewhat broad peak ($w_{\frac{1}{2}}$ 1700 Hz) centred at δ *ca.* −28 is highly diagnostic of aminomethyl phosphine species of the type $Ph_2PCH_2N(R)R^1$,[8,10] and rules out the possibility of adsorbed Ph_2PCH_2OH (^{31}P δ −11).

Preliminary reactions of chitosan with other hydroxymethyl phosphines indicate that this represents a new general method for immobilisation of phosphines on chitosan and chitin. In a similar fashion to the synthesis of **2**, reaction of chitosan with an excess of $MeP(CH_2OH)_2$ yields an analogous immobilised phosphine (3.1% m/m P), although in this case we have been unable to record a ^{31}P $\{^1H\}$ NMR spectrum. It is likely that a certain degree of cross-linking has occurred in this case with the difunctional phosphine.

Treatment of an ethanolic suspension of **2** with oxygen gas yielded the immobilised phosphine oxide, which shows a P=O stretching frequency at 1123 cm^{-1}. Preliminary studies indicate that reaction of **2** with an excess of $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) in dichloromethane, a bright yellow supported palladium complex containing 13.2% m/m Pd is formed. No palladium is incorporated onto chitosan itself upon treatment with $[PdCl_2(cod)]$ under analogous conditions, although chitosan has previously been demonstrated to form metal–amine complexes.[11]

The Mannich-type condensation of hydroxymethyl phosphines onto the biopolymers chitosan and chitin represents a new method for the preparation of chiral immobilised phosphines. Such readily-prepared materials can be envisaged to have a range of potential applications and studies on these materials are in progress.

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References

1 *Chitin in Nature and Technology*, ed. R. A. A. Muzzarelli, C. Jeuniaux and G. W. Gooday, Plenum, New York, 1986.
2 P. A. Sanford and A. Steinnes, in *Water-soluble Polymers, ACS Symp. Ser. 467*, ed. S. W. Shalaby, C. L. McCormick and G. B. Butler, ACS, Washington DC, 1991, ch. 28, pp. 430–45.
3 B. Krajewska, M. Leszko and W. Zaborska, *J. Chem. Tech. Biotechnol.*, 1990, **48**, 337; T. Hayashi and Y. Ikada, *J. Appl. Polym. Sci.*, 1991, **42**, 85.
4 See for example Y. Kawabata, M. Tanaka and I. Ogata, *Chem. Lett.*, 1976, **11**, 1213.
5 H. B. Kagan and M. Sasaki, in *The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, Wiley, Chichester, 1990, ch. 3.

6 N. R. Champness, W. Levason, R. D. Oldroyd and D. J. Gulliver, *J. Organomet. Chem.*, 1994, **465**, 275; *Tailored Metal Catalysts*, ed. Y. Iwasawa, Reidel, Dordrecht, Holland, 1986; *Supported Metal Complexes*, ed. F. R. Hartley, Reidel, Dordrecht, Holland, 1985.
7 P. J. Sadler, *Adv. Inorg. Chem.*, 1991, **36**, 1; S. J. Berners-Price and P. J. Sadler, *Chem. Brit.*, 1987, 541.
8 J. Fawcett, P. A. T. Hoye, R. D. W. Kemmitt, D. J. Law and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1993, 2563.
9 H. Coates and P. A. T. Hoye, *Br. Pat.*, 842 593, 1960; *Chem. Abstr.*, 1962, **56**, 1482; A. W. Frank, D. J. Daigle and S. L. Vail, *Textile Res. J.*, 1982, 678; 738.
10 L. Maier, in *Organic Phosphorus Compounds*, ed. G. M. Kosolopoff and L. Maier, Wiley-Interscience, New York, 1972, vol. 1, ch. 1.
11 K. Ogawa, K. Oka and T. Yui, *Chem. Mater.*, 1993, **5**, 726, and references cited therein.