Synthesis of the first polymer-supported tripodal triphosphine ligand and its application in the heterogeneous hydrogenolysis of benzo[*b*]thiophene by rhodium catalysis

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A *p*-styrenyl substituent attached to the ligand framework allows the tripodal triphosphine moiety $-C(CH_2PPh_2)_3$ to be introduced as a pendant group in polystyrene matrices *via* free-radical copolymerisation; in conjunction with rhodium(I), the polytriphos material forms an effective heterogeneous catalyst for the hydrogenolysis of benzo[*b*]thiophene to 2-ethylthiophenol and ethylbenzene.

The immobilisation of metal complexes on solid supports to obtain single-site heterogeneous catalysts is a research topic of much current interest. Several heterogenisation techniques are available which span from hydrogen-bonding to covalent grafting, to physical and ionic immobilisation.[1,2] Similarly, many different types of materials (metal oxides, dendrimers, polyolefins, heteropoly acids, gels, *etc.*) may be employed as the support, which may be either inert or chemically interacting with metal, substrate and/or product. Irrespective of the grafting mode and of the type of support, a major drawback of any heterogenised catalyst is represented by metal leaching into the mobile phase. In order to reduce, and ultimately inhibit, undesired loss of metal during the catalysis, the structure of the tethered complex must be thermally and chemically robust. In general, tertiary phosphines meet these requisites and beyond, as they behave as strong ligands towards most transition metals and can also be finely tuned so as to determine the steric and electronic properties of the metal centre. Polydentate phosphines show superior control properties over monophosphines and those having tripodal structure, such as $MeC(CH_2PPh_2)_3$ (triphos), are almost insuperable with regard to the stability of the metal complexes.[3]

Here, we describe the synthesis of the first tripodal triphosphine anchored to a cross-linked styrene/divinylbenzene polymer and of its complex with the 'Rh(cod)+' moiety (cod = cycloocta-1,5-diene). It is also shown here that the supported rhodium complex is a powerful catalyst for the hydrogenolysis of benzo[*b*]thiophene to 2-ethylthiophenol and ethylbenzene, which represents the first evidence of a successful single-site catalyst in the heterogeneous hydrodesulfurisation (HDS) of a thiophenic substrate.[4,5]

The synthetic route to the triphosphine-containing styrene monomer is illustrated in Scheme 1. The strategy is to prepare a triphos ligand bearing a single reactive hydroxy functionality for attachment of the styrene group. Nucleophilic attack by diphenylphosphide at the heterocycle of 3,3-bis(diphenylphosphinomethyl)oxacyclobutane,[6] followed by reaction with 4-vinylbenzyl chloride is an excellent method to accomplish the high-yield synthesis of the desired *p*-styrenyl-functionalised triphos ligand 2,2,2-tris(diphenylphosphinomethyl)ethyl 4-vinylbenzyl ether (TVBE).† Copolymerisation of TVBE with divinylbenzene alone (DVB) or with styrene–DVB in THF/MeOH using AIBN as the radical initiator generates cross-linked triphosphine polymers (polytriphos) as off-white solids insoluble in organic solvents. Besides elemental analysis (C, H, P), the presence of triphosphine units is shown by CP MAS ^{31}P NMR spectroscopy.‡ The spectrum of a polytriphos sample obtained by copolymerisation of TVBE with DVB (1:1) is given in Fig. 1a. Note that the chemical shift ($\delta -25.6$) is similar

to that of monomeric TVBE as well as silica-supported triphos.[2] A soluble polystyrene-bound diphosphine ligand with the 1,3-bis(diphenylphosphino)propane moiety has been described previously.[7]

Advantages of the present technique over heterogenisation procedures involving the reaction of functionalised phosphines with functionalised cross-linked styrene–DVB resins[8] are: (1) the ease of synthesis since only the phosphine needs to be chemically modified; (2) the effective control on the phosphine loading (and hence of the metal loading) by simply varying the phosphine:DVB:styrene ratio; (3) the absence of residual functional groups on the resins.

Supported complexes of the general formula [Rh(cod)(poly-triphos)]PF$_6$ have been prepared by stirring CH$_2$Cl$_2$ solutions of [RhCl(cod)]$_2$ and NBu$_4$PF$_6$ in the presence of polytriphos at room temperature for 24 h. The filtered yellow solids are washed with CH$_2$Cl$_2$ at reflux temperature using a Soxhlet
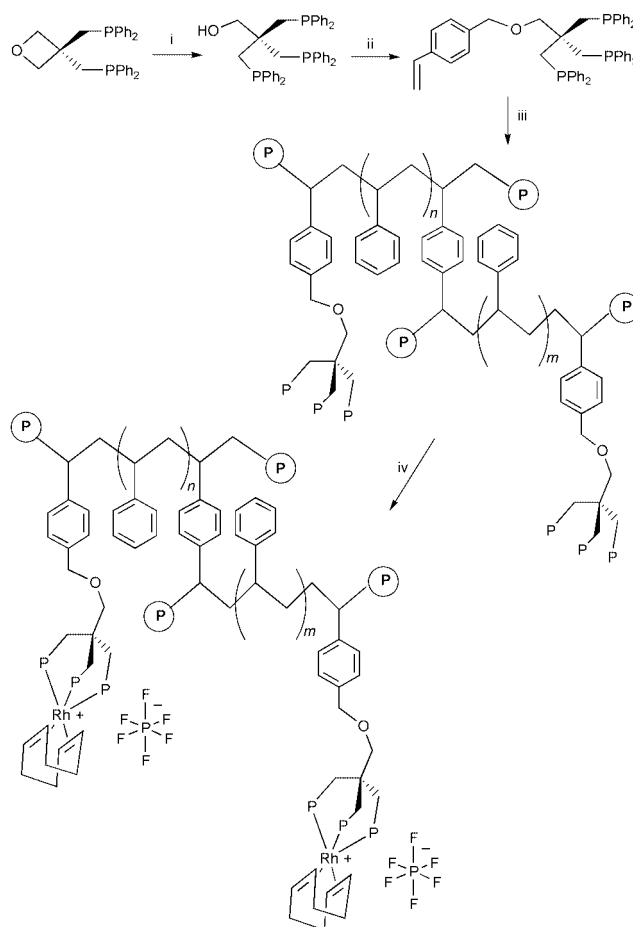
Scheme 1 *Reagents and conditions*: i, HPPh$_2$, BuLi, THF (65%); ii, NaH, 4-vinylbenzyl chloride, DMF (90%); iii, styrene–divinylbenzene, AIBN, THF/MeOH (1:2, v/v), 85 °C; iv, [RhCl(cod)]$_2$, NBu$_4$PF$_6$, CH$_2$Cl$_2$ (98%).

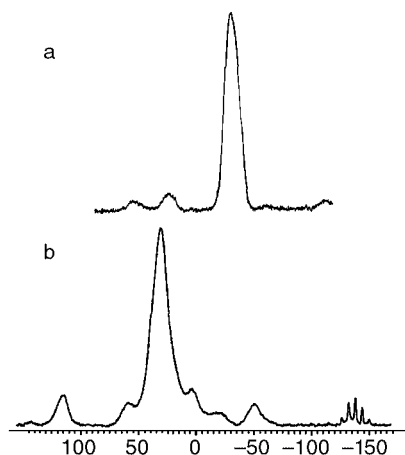**Fig. 1** CP MAS ^{31}P NMR (121.50 MHz) spectra of polytriphos (a) and [Rh(cod)(polytriphos)]PF$_6$ (b).

Notes and references

† *Selected NMR data* for 2,2,2-tris(diphenylphosphinomethyl)ethyl 4-vinylbenzyl ether (TVBE): ^{1}H NMR (CDCl$_3$) δ_H 2.57 (d, 6H, C*H*$_2$P, ^3J 2.91 Hz), 3.16 (s, 2H, OC*H*$_2$C(CH$_3$)$_3$), 3.71 (s, 2H, OCH$_2$Ph), 5.24 (dd, H$_{cis}$, CH$_2$=CH, J_{cis} 10.90 Hz, J_{gem} 0.97 Hz), 5.74 (dd, H$_{trans}$, CH$_2$=CH, J_{trans} 17.53 Hz, J_{gem} = 0.97 Hz), 6.71 (dd, 1H C*H*=CH$_2$), 6.91–7.31 (m, 34H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$) δ_C 38.87 (m, CH$_2$P), 43.58 (q, CH$_2$*C*(CH$_2$PPh$_2$), J(CP) 12.4 Hz), 72.50 (s, O*C*H$_2$Ph), 77.19 (m, O*C*H$_2$C(CH$_3$)$_3$), 114.03 (s, *C*H$_2$=CH), 123.48-137.42 (m, Ph), 133.92 (s, *C*H=CH$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$) δ_P −26.1 (s). Satisfactory elemental analyses were obtained for all compounds.

‡ Solid-state ^{31}P NMR spectra were recorded at room temperature on a Bruker AMX 300 WB spectrometer equipped with a 4 mm BB-CP MAS probe at a working frequency of 121.50 MHz. The spectra were acquired using the cross-polarisation pulse sequence under magic angle spinning at a spinning rate of 10 kHz. The 90° pulse was 3.3 µs, and the contact pulse was 1 ms. The spectra of the supported triphosphine were collected after 400 scans with a recycle delay of 1 s and a line broadening of 30 Hz, whereas the spectra of the supported rhodium complex were acquired with 700 scans, a recycle delay of 1 s and a line broadening of 50 Hz. H$_3$PO$_4$ (85%) was used as the external standard.

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apparatus and then dried. The rhodium content in the heterogeneous catalysts depends on the polytriphos sample; in particular, a loading of 7.24 wt% has been found for a polymer obtained by copolymerising TVBE and DVB in a 1:1 ratio, while a loading of 0.94 wt% has been found for a polymer obtained by copolymerising TVBE, DVB and styrene in a 0.6:1:36 ratio. The coordination of rhodium(I) to the tethered phosphine is demonstrated by the low-field shift to δ 28.4 of the phosphorus resonance as well as the presence of the PF$_6^-$ sextuplet at δ −143.5 (Fig. 1b).

As an example of the great potential of polytriphos metal complexes in heterogeneous catalysis, [Rh(cod)(polytriphos)]PF$_6$ (0.94 wt%) has been employed to hydrogenate benzo[*b*]thiophene (BT) in tetrahydrofuran (THF) under basic conditions (Scheme 2).[4,5]
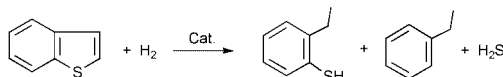
Scheme 2 Hydrogenolysis of BT to 2-ethylthiophenol and ethylbenzene.

Under rather harsh experimental conditions (160 °C, 30 bar H$_2$), the thiophenic substrate is mainly converted to 2-ethylthiophenol (ET) but appreciable formation of the desulfurised product ethylbenzene (EB) also occurs. Interestingly, no trace of 2,3-dihydrobenzo[*b*]thiophene was detected by GC. Table 1 reports catalytic data obtained for runs at 2, 5 and 10 h. In all cases, no rhodium leaching was observed by ICP-AES (<1 ppm), while an effective catalyst recycling with no loss of catalytic activity was accomplished by removing the liquid phase *via* the liquid sampling valve and recharging the autoclave with a solution containing substrate and base (entries 4 and 5).

Under comparable experimental conditions, both the aqueous-biphase catalyst [Rh(cod)(sulphos)] in MeOH/*n*-heptane [sulphos = $^-$O$_3$S(C$_6$H$_4$)CH$_2$C(CH$_2$PPh$_2$)$_3$][5] and the homogeneous catalyst [Rh(DMAD)(triphos)]PF$_6$ in THF (DMAD = dimethyl acetylenedicarboxylate)[9] are slightly less efficient than [Rh(cod)(polytriphos)]PF$_6$ for the hydrogenolysis of BT to ET (TON *ca.* 90 *vs.* 124) and cannot be recycled after catalysis.

The data reported in Table 1 are of great relevance in the field of model studies of heterogeneous HDS as they show that a single metal site belonging to the class of the HDS promoters[10] can open and hydrogenate a thiophenic substrate without the need of any cooperative effect.[4,5] Besides this important result, we have succeeded for the first time in producing a polymer-supported tripodal triphosphine ligand with which we intend to prepare a large variety of metal catalysts and study their performance in heterogeneous processes.