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Attachment of Polyphosphine Ligands to a Controlled-pore Glass Support for Hybrid Catalysis

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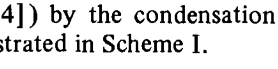
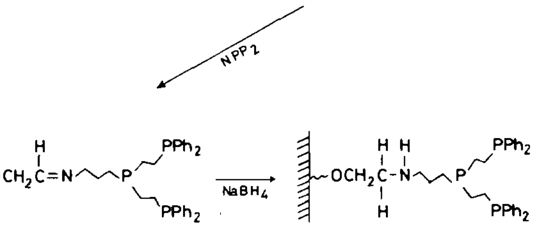
Recently, considerable interest has arisen in the area of polymer supported catalysis. The advantages and disadvantages of such hybrid catalysts compared to their homogeneous and heterogeneous analogs have been documented [1]. Recent developments in synthetic methods for organosphosphines now permit one to 'tailor-make' a wide range of polyphosphine and mixed-donor ligands [2, 3]. Herein, we report: (1) attachment of the first examples of polyphosphine ligands onto a solid, controlled-pore glass (C.P.G.) support; (2) characterization of a $CoCl_2$ complex of an attached triphosphine ligand; and (3) hydrogenation experiments at 25 °C and 1 atm H_2 pressure with this immobilized cobalt complex.

The polyphosphine ligands were designed to have a long, flexible tail in order for the attached chelating polyphosphine portion to extend several angstroms from the solid support into the solution. The ligand $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2NH_2$ was prepared by a radical-chain condensation reaction [3] between allylamine and  $Ph_2PCH_2CH_2CH_2P\langle^{Ph}_{H}$, and the ligand $H_2NCH_2CH_2CH_2P(CH_2CH_2PPh_2)_2$ was prepared by photolyzing cyanoethylphosphine, $N{\equiv}CCH_2CH_2PH_2$, with two equivalents of vinyldiphenylphosphine, $CH_2{=}CH{-}PPh_2$, and then reducing the cyano group with $LiAlH_4$. The resultant NP_2 and NPP_2 ligands were attached to oxidized, 555 Å-pore glycophase derivativized glass beads (manufactured by Corning Glass Co [4]) by the condensation and reduction reactions illustrated in Scheme I.



Confirmation that the NP_2 and NPP_2 ligands were attached to the glass support was obtained by ESCA, which clearly showed nitrogen 1s and phosphorus 2s, 2p peaks, in addition to those present for the aldehyde derivative on the glass [5]. Also, a Fourier-transform $^{31}P\{^1H\}$ nmr spectrum of a slurry of the supported NP_2 ligand in benzene was obtained, and a broad resonance was observed at −23 ppm. Even though the ligand is bonded to the solid, the long alkyl chain apparently permits enough solubility of the phosphorus groups in the solvent to give a broad phosphorus resonance. In order to obtain a better phosphorus spectrum, the glass support was dissolved in sodium methoxide; sharp resonances were then obtained at −18.2 and −27.2 ppm, which correspond to the $Ph_2P{-}$ and $-P(Ph){-}$groups, respectively, in the authentic $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2NH_2$ compound.

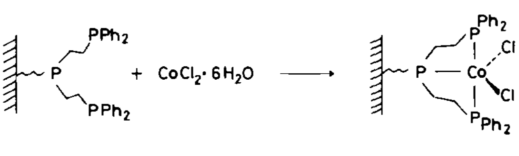
Several studies of attached monodentate phosphine groups (mainly $-PPh_2$) on polymer supports have appeared [1]; in contrast, very few examples of supported polydentate phosphine-containing ligands have been reported [6, 7]. Biologists and biochemists have utilized controlled-pore glass for some time to immobilize enzymes [8], and such material appeared attractive to us for supported phosphine catalysts. Controlled-pore glass supports have several advantages over gel or crosslinked solid supports; some of these are listed in Table I.

TABLE I. Advantage of Controlled-pore Glass Supports [4].

No swelling in changing environments
Convenently handled
Stable in solvents and acid
Thermally stable
High mechanical strength
High flow rate possible
Usable in high pressure applications.

To demonstrate that attachment of polyphosphine ligands to glass supports for use in hybrid catalysis is viable and potentially very valuable, we describe below some results with the $CoCl_2$ complex of $H_2NCH_2CH_2CH_2P(CH_2CH_2PPh_2)_2$.

A cobalt chloride solution was stirred with the supported NPP_2 ligand; the color of the glass changed from white to blue-green, consistent with the reaction depicted by eqn. 1.



(1)

Analysis of the amount of cobalt taken up during the reaction was monitored spectrophotometrically at 655 nm, and 0.211 mmol of cobalt was absorbed from the solution per gram of glass beads. The presence of $CoCl_2$ was also confirmed by ESCA. Although the cobalt 2s and 2p peaks were masked by the Auger peaks of oxygen (775 and 785 *eV*), an unmasked cobalt Auger peak was observed at 485 *eV*; the chlorine peak at 200 *eV* was also observed.

After the quantity of supported $CoCl_2(NPP_2)$ was determined, catalytic hydrogenation experiments were performed in a modified Schlenk flask that was alternately rotated 270° to achieve uniform agitation. A typical catalysis experiment used 1-octene (500:1, olefin:Co ratio), 50-ml of total volume (benzene as solvent), 400 mg of supported cobalt complex, and 1 ml of OMH-1 (29% in toluene) [9]. After addition of OMH-1, the color of the solid material changed from blue-green to red and hydrogen was consumed fairly rapidly (66.2% as rapid as the maximum rate of Wilkinson's homogeneous $RhCl(PPh_3)_3$) at ambient conditions. If the oscillating agitation is stopped, the rate of H_2 consumption decreases rapidly; however, the rate of H_2 consumption returns to normal upon re-agitating. Gas chromatographic analysis of the hydrogenation product after 15 hours at room temperature showed only n-octane.

Additional metals are being tested for catalysis efficiency, using the glass supported NPP_2 and NP_2 ligands.

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9 OMH-1 is the commercial trade name for $Na^{+}AlH_2Et_2^{-}$.