

Synthesis of Polymer-supported Transition Metal Catalysts via Phosphido Linkages: Heterogeneous Catalysts for the Hydrogenation of Aromatic Compounds under Mild Conditions

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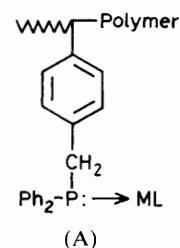
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A new method of anchoring transition metal species [Rh(COD) (COD = cyclo-octa-1,5-diene), Pt(COD)Cl etc.] to polymers via phosphido type linkages and their use as arene hydrogenation catalysts is described.

'Heterogenized' homogeneous transition metal catalysts are of current interest since they offer the advantages of both homogeneous and heterogeneous catalysts (e.g. ease of separation of products plus mild conditions and selectivity).¹ So far all interactions involving transition metal complexes linked to polymer supports via phosphorus were of the type (A) in which the polymer-bound phosphorus group (polymer-PR₂) behaves like a typical trialkyl or triaryl phosphine and donates an electron pair to the metal. [One example is RhCl(PPh₂)₂ anchored to polystyrene.] One disadvantage of this type of linkage is that the expensive metal complex can be easily leached from the polymer and lost. These types of catalysts have never been economically viable mainly for this reason.²

This communication reports a new method of anchoring transition metal complexes to heterogeneous support materials³ and the use of these materials as heterogeneous catalysts for the hydrogenation of unsaturated compounds under mild conditions including the stereospecific catalysis of arene (benzene) hydrogenation at 1 atm and 25 °C. We describe a general method for the anchoring of a transition metal complex to a polymer via a phosphido type of linkage. The reaction sequence is outlined in Scheme 1.

In a typical reaction *t*-butylphosphine (Bu^tPH₂) in tetrahydrofuran (THF) is cooled to -100 °C and treated with one equiv. of BuⁿLi in hexane. The mixture is stirred while room temperature is attained. During this time Bu^tPHLi precipitates and then redissolves as the temperature rises (above ca. -30 °C). The mixture is then recooled (-100 °C) and added to a suspension of Merrifield's Peptide Resin (2% cross-linked divinylbenzene (DVB) polystyrene containing 1 mequiv. Cl per gram of resin)⁴ at -100 °C. Stirring is continued at room temperature for 24 h until loss of yellow colour in the solution. The beads are decanted from the supernatant and washed with THF until the washings are free of chloride ion. They are then resuspended in THF (100 ml) and a second equivalent of BuⁿLi in hexane is added at -100 °C. After warming to room temperature the suspension is recooled (-100 °C) and a



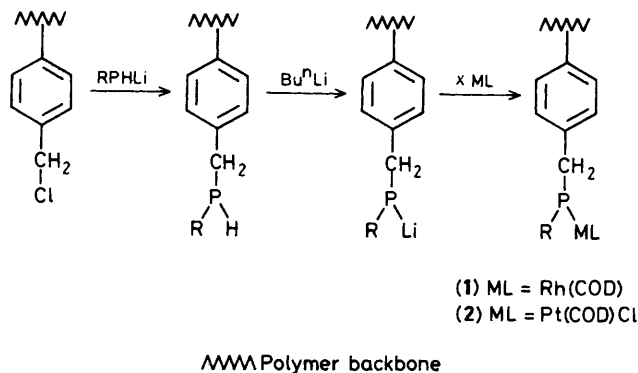
solution of [Rh(COD)Cl]₂ (COD = cyclo-octa-1,5-diene) in THF is added. The mixture is allowed to warm to room temperature and stirred for a further 48 h. The deep red beads are then collected, washed with THF and dried under vacuum.

Microanalytical data for this material indicate that Rh(COD) units are attached to a very high proportion of the sites originally available as Cl.[†] Although the actual coordination of geometry of the metals in these systems is not known at present in precise detail, it seems reasonable to assume that based on both the method of preparation and the available physical data[†] the metal complex is attached to the polymer via a phosphido type of linkage.⁵

We have been able to anchor a variety of other transition metal groups to this and other polymers by similar methods. With 2% DVB-styrene copolymer, halide-containing transition metal starting complexes give materials of the following colours: [Rh(CO)₂Cl]₂, black; [Rh(COD)Cl]₂, red; [Ir(COD)Cl]₂, red; Co(CO)₄I, black; Pt(COD)Cl₂, yellow; Ni(PMe₃)₂Cl₂, brown. The physical properties of these materials are typical of the material based on Rh(COD) which is indefinitely air stable. Both the materials based on Rh(COD) (**1**) and on Pt(COD)Cl (**2**) catalyse arene (benzene, toluene) hydrogenation under very mild conditions [25 °C, 1 atm for (**1**), 45 °C, 2 atm for (**2**)]. The hydrogenation of alkenes is considerably faster.[‡] For (**1**), when suspended in benzene under a hydrogen atmosphere (1 atm, 25 °C), there is an induction period during which there is virtually no uptake

[†] The commercially available (ref. 4) chlorinated polymer contained 1 mequiv. Cl per gram. However, this figure is not likely to be very accurate and so calculations on the exact amount of coverage are not possible. Assuming exactly 1 mequiv. g⁻¹ of Cl⁻ is present then 1.00 g of polymer contains 0.0355 g Cl and 0.9645 g polymer backbone (hydrocarbon). If all Cl units are replaced by Bu^tPRh(COD) (*M* = 299) groups, then the new weight of the polymer = [0.9645 g + 0.299 g] = 1.2635 g, which should contain 1 mequiv. Rh, 1 mequiv. P, and 1 mequiv. [(Bu^t) + (COD)] (*M* = 165) (hydrocarbon). This would give calculated microanalytical figures of: (C + H), 89.39; P, 2.45; Rh, 8.15. Found: C, 76.82; H, 7.98; (C + H), 84.8; P, 2.26; Rh, 9.87%. As noted above discrepancies are not surprising in view of the uncertainty in the Cl⁻ loading of the polymer. ³¹P-¹H N.m.r. spectroscopy on solid beads at room temperature (32.384 MHz) δ 42.0 p.p.m. (relative to 85% aqueous H₃PO₄ at δ 0.0 p.p.m., Δω_{1/2} 1000 Hz). The i.r. spectrum of the beads showed only polystyrene absorption except for a weak band at 850 cm⁻¹.

[‡] Catalysis of benzene hydrogenation using (**1**) was studied at constant pressure (1 atm) as a function of temperature and also at higher pressures (2–3 atm). In a typical experiment (**1**) (0.006 g) was suspended in benzene (5.0 ml) at 25 °C and the uptake of H₂ at one atm was measured as a function of time. After the induction period (ca. 20 min) a linear uptake is observed of 20.0 ml H₂/(g of catalyst)⁻¹ min⁻¹; turnover = 16 [mol C₆H₆ (mol Rh)⁻¹ h⁻¹]. Similar rates were observed with toluene hydrogenation (giving methylcyclohexane). The rate of hex-1-ene hydrogenation is considerably faster. Thus 5 ml hex-1-ene can be completely hydrogenated at ca. 3.4 atm in ca. 1 h. The reaction products were analysed on a Perkin-Elmer Sigma 2B gas chromatograph using a 5% DNBP-BEN-34 stationary phase on 80–100 mesh CHROM-wNAW support at 80 °C. We assume that the induction period involves the hydrogenation of co-ordinated COD since we detect cyclo-octane in the reaction medium. Species (**2**) (0.2 g) hydrogenated benzene (5 ml) to cyclohexane at 45 °C, 3 atm H₂, in ca. 12 h.



Scheme 1

of H₂. During this time the beads darken.‡ Also, interestingly, the hydrogenation of benzene is completely stereospecific; thus with D₂, 100% *cis*-[²H₆]cyclohexane is produced.⁶ This potentially useful catalytic transformation was only recently achieved by Muetterties and coworkers using homogeneous cobalt-based catalysts.⁷ The turnover numbers in our system [for (1)] (*ca.* 16 turnovers per h) are somewhat slower than those observed in the homogeneous one (*ca.* 1 turnover per min).⁷ Species (1) is also catalytically active for benzene hydrogenation in the presence of aqueous acid (1 M HCl) or base (1 M NaOH) and is thermally quite robust. It retains its catalytic activity after heating to *ca.* 100 °C (5 h). In the case of (1), in order to determine whether or not Rh metal (possibly in the form of crystallites) is responsible for the catalytic behaviour we examined samples by ESCA (*X*-ray photoelectron spectroscopy) and by *X*-ray diffraction analysis. ESCA data indicate that the Rh is present in an oxidized form both before and after hydrogenation§ and preliminary studies *via X*-ray diffraction analysis have failed to reveal significant deposits of Rh metal in the samples. ESCA data for the Pt(COD)Cl-based material clearly indicate that Pt is present in an oxidized (Pt²⁺) form.§ In addition, based on the properties of homogeneous rhodium phosphido complexes it seems unlikely that reduction to Rh metal occurs in the presence of H₂ under the reaction conditions employed.⁸ Both ESCA and *X*-ray diffraction analysis are surface techniques,

§ ESCA Spectra were obtained on a VG Scientific Escalab Mark II spectrometer. Spectra were taken in a constant pass energy mode with a Mg(K_α) *X*-ray anode. Samples were either pressed into indium foil which in turn was pressed onto nickel sample pedestals or were mounted in silver paint. The polymer support was 2% DVB-styrene copolymer (1 mequiv. per g). For (1) and Rh(CO)₂ species the position of the Rh peak was adjusted for electrostatic charging by using the carbon line as a reference (284.6 eV). Doublet splittings are given in parentheses. Species (1) before hydrogenation reaction: Rh(3d_{5/2}) binding energy = 309.1(4.6) eV. After hydrogenation reaction: Rh(3d_{3/2}) binding energy = 309.0(4.2) eV. Rh(CO)₂ species after hydrogenation reaction: Rh(3d_{5/2}) binding energy = 310.3(4.3) eV. Binding energies for Rh⁰ generally fall below 307.5 eV, for Rh¹⁺ they fall in the range 307.8 to 309.0 eV and for Rh³⁺ 309.0 to 310.5 eV (ref. 9). For (2) the Pt(4f_{7/2}) peak was observed at 74.9(3.2) eV; after adjusting for charging *via* the C line the effective binding energy was 72.6 eV. This is consistent with Pt²⁺ (ref. 9).

however, and we are planning further studies to probe the nature of the material inside the beads (cross polarisation magic angle spinning n.m.r., EXAFS, and Fourier transform i.r.).† These observations suggest that these types of catalysts may have unusual and useful reactivities.

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