Syntheses of Interlamellar Montmorillonitebipyridinepalladium(II) Catalysts: the First Examples of Chelation in Smectite Clay

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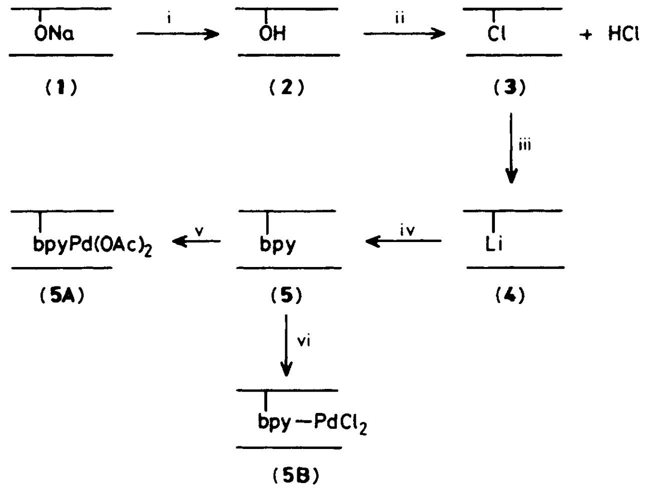
Palladium(II) salts anchored *via* a bipyridine group in the interlamellar region of montmorillonite have been synthesised, characterised, and found to hydrogenate alkynes and alkenes more effectively than analogous polymer-anchored bipyridinepalladium(II) complexes.

Recent interest in anchored catalysts has been focused on the development of new classes, such as polymers with a phosphido linkage,[1] or with a σ-bond,[2] or soluble and recoverable ethylene oligomer ligated complexes,[3] devised to combat the problem of metal leaching from the support. We have reported the synthesis and characterisation of a series of montmorillonitephosphinepalladium(II) complexes, and have shown that the montmorillonitediphenylphosphinepalladium(II) complex hydrogenates styrene and hex-1-ene with constant activity over several runs.[4—7] This constant activity is ascribed to the presence of interlamellar oxygens between the silicate sheets of montmorillonite that act as polydentate centres for binding the metal during deco-ordination and reco-ordination with the phosphine ligands. We have now used bipyridine as a chelating ligand; the potential advantages of this system include greatly decreased metal complex lability, distortion-free binding of the bidentate ligand to a metal, and variable catalyst selectivity, besides the availability of additional binding sites. We report briefly the syntheses and characterisation of montmorillonitebipyridine (**5**) and its complexes with palladium(II) acetate (**5A**) and chloride (**5B**), and the superior activity of the complex (**5A**) over poly(styryl)bipyridinepalladium(II).[8,9]

The preparation of bipyridyl-ligated montmorillonite and its complexes is outlined in Scheme 1. The product (**5**) showed all the bipyridine bands[8] in its i.r. spectrum. Bands at 1560 and 1545 cm^{-1} in the spectrum of the complex (**5A**) and at 350 cm^{-1} in that of the catalyst (**5B**) were observed, indicating the presence of acetate and chloride ligands; furthermore, both complexes showed a new weak and broad band at 1700 cm^{-1}.



Scheme 1. *Reagents and conditions:* i, HCl; ii, $SOCl_2$, C_6H_6, reflux, 24 h; iii, Bu^nLi (−80 to −100 °C); iv, bipyridine, tetrahydrofuran, reflux, 4 h; v, $Pd(OAc)_2$, C_6H_6; vi, $PdCl_2(PhCH_2CN)_2$, C_6H_6.

Table 1. Comparison between activities of clay-bound (**5A**) and polymer-bound catalysts (initial H_2 uptake in ml min^{-1}).[a]

Substrate	Clay-bound	Polymer-bound
Styrene	17	4.3
Hex-1-ene	3	2.5
Phenylacetylene	18	14.19
Diphenylacetylene	8	3.87

[a] Reaction conditions: [catalyst] 6.9×10^{-2} mM; [substrate] 10 mM; temp. 25 °C; $p(H_2)$ 1 atm; solvent tetrahydrofuran.

ESCA data indicated that the palladium is present in the divalent state before and after hydrogenation, with well resolved spin doublets with Pd $3d_{5/2}$ binding energies (E_b) of 338.8 for (**5A**), 339.4 for (**5B**) (corrected to Si 2*s* $E_b = 153.4 \pm 0.2$ eV). *X*-Ray powder diffraction (thin film) showed a basal region expansion (d_{001}) of 14.07 Å for (**5**) and 15.0 and 14.54 Å for (**5A**) and (**5B**), respectively, from 9.4 Å for dehydrated (**1**).

Although both (**5A**) and (**5B**) catalyse the hydrogenation of alkynes and alkenes under mild conditions, we were particularly interested in (**5A**), as an analogue for comparison with poly(styryl)bipyridinepalladium(II) acetate.[8,9] Table 1 shows the superior activity of (**5A**) in the hydrogenation of alkynes and alkenes under identical conditions; the enhanced activity may be attributed to the change in electronic environment around palladium in the complex. Furthermore, the activity of the catalyst (**5A**) in hydrogenation of styrene was maintained for eight recycles, with constant palladium content.

The catalyst (**5A**) also showed a higher rate ratio for hydrogenation of styrene relative to hex-1-ene than the montmorillonitephosphinepalladium(II) catalysts reported earlier.

The activity of the catalyst (**5A**) in various solvents decreased in the order tetrahydrofuran > ethyl alcohol > acetone. No hydrogenation of styrene was observed in benzene, which does not induce sufficient swelling of montmorillonite layers[10] for a substrate to approach the palladium complex.

Analogous Cu, Rh, and Ru montmorillonitebipyridine complexes are being studied.

In conclusion, the use of montmorillonite as a support for a palladium(II) hydrogenation catalyst is a practical alternative to the use of polymers and inorganic oxides; its advantages include easy recovery, effective reuse, and possible manoeuverability of interlayer spacing for the design of tailor-made catalysts.

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