

A diphosphino-functionalised MCM-41-anchored platinum complex: an efficient and reusable catalyst for the hydrosilylation of olefins

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A diphosphino-functionalised MCM-41 anchored platinum complex (MCM-41-2P-Pt) was conveniently synthesised from commercially available and cheap γ -aminopropyltriethoxysilane via immobilisation on MCM-41, followed by reaction with diphenylphosphinomethanol and potassium chloroplatinite. It was found that the title complex is a highly efficient catalyst for the hydrosilylation of olefins with triethoxysilane and can be recovered and recycled by a simple filtration of the reaction solution and used for at least 10 consecutive reactions without any decrease in activity.

Keywords: supported catalyst, diphosphino-functionalised MCM-41, platinum complex, hydrosilylation, heterogeneous catalysis

The hydrosilylation of alkenes is one of the most important Si–C bond formation reactions in organosilicon chemistry and a variety of silicon monomers containing functional groups have been synthesised by this reaction.¹ Many metal complexes are known to be catalysts for the reaction,^{2,3} but the discovery by Speier *et al.*,⁴ Louis *et al.*⁵ and Maciejewski *et al.*⁶ that hexachloroplatinic acid is a highly efficient catalyst, even under ambient conditions, has led to Pt complexes becoming the catalysts of choice for these reactions. Generally, hydrosilylation is performed in the liquid phase using a homogeneous catalyst. However, separation of the catalyst from the reaction mixture is troublesome. From the standpoint of green chemistry, the development of more environmentally benign conditions for the reaction, for example, the use of a heterogeneous platinum catalyst would be desirable. Polymer-supported transition metal complex catalysts are used more and more widely because they can combine the advantages of easy catalyst recovery, characteristic for a heterogeneous catalyst, with the high activity and selectivity of soluble complexes.^{7–9} In the preparation of supported catalysts a wide variety of support materials have been used including cross-linked polymers,^{10–12} silica,^{13–18} glass fibre¹⁹ and dendrimers.^{20–23} The support material and surface modifier frequently plays a crucial role in the performance of the resulting supported catalyst. Basically, the support has to be thermally and chemically stable during the reaction process and has to provide accessibility and a good dispersion of the active sites.

Study of new types of supported platinum complexes catalysts which might be suitable for hydrosilylation of olefins with triethoxysilane has theoretical and practical significance. Development of the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilisation of homogeneous catalysts.²⁴ MCM-41 has a regular pore diameter of *ca.* 5 nm and a specific surface area > 700 m² g⁻¹.²⁵ Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach the surface of the channel.^{26–28} Shyu *et al.* reported the immobilisation of Rh(PPh₃)₃Cl on phosphinated MCM-41 for catalytic hydrogenation of olefins and found that the turnover frequency (TOF) of this MCM-41-supported phosphine rhodium complex is three times higher than that of Rh(PPh₃)₃Cl in the hydrogenation of cyclohexene.²⁹ However, to the best of our knowledge, no hydrosilylation reactions of olefins with triethoxysilane catalysed by a MCM-41-supported phosphine platinum complex have been reported until now. It is generally believed that high surface area of a heterogeneous catalyst results in high catalytic activity. Considering the fact that MCM-41 support has an extremely high surface area and the

catalytic platinum species is anchored on the inner surface of the mesopore of the MCM-41 support, we expect that an MCM-41-supported phosphine platinum catalyst will exhibit high activity and good reusability. In this paper, we wish to report the synthesis of the diphosphino-functionalised MCM-41-anchored platinum complex (MCM-41-2P-Pt) and its catalytic properties in the hydrosilylation of olefins with triethoxysilane.

Over the past decade the *N,N*-bis(diphenylphosphinomethyl) amino-functionality has been used for the preparation of dendrimer-supported and supramolecular homogeneous catalysts.^{30–32} Alper and coworkers first reported the synthesis of a polymeric ligand containing the *N,N*-bis(diphenylphosphinomethyl)amino-functionality by using the Mannich reaction.³³ Just recently insoluble versions of this chelating phosphine ligand have been applied in Rh-catalysed hydroformylation,³⁴ Rh-catalysed hydrogenation,³⁵ Pd-catalysed Stille coupling,³⁶ and Pd-catalysed carbonylative cross-coupling of aryl iodides with organoboron or organotin compounds.^{37,38} The novel diphosphino-functionalised MCM-41-anchored platinum complex (MCM-41-2P-Pt) was conveniently synthesised from commercially available and cheap γ -aminopropyl-triethoxysilane via immobilisation on MCM-41, followed by reaction with diphenylphosphinomethanol, which resulted from adduct formation between diphenylphosphine and paraformaldehyde, and potassium chloroplatinite (Scheme 1).

X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the modified materials MCM-41-2P, MCM-41-2P-Pt are displayed in Fig. 1. Small angle X-ray powder diffraction of the parent MCM-41 gave peaks corresponding to hexagonally ordered mesoporous phases. For MCM-41-2P and MCM-41-2P-Pt, the (100) reflection of the parent MCM-41 with decreased intensity remained after functionalisation, while the (110) and (200) reflections became weak and diffuse, which could be due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results indicated that the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation.

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterise this polymeric platinum complex. The P:Pt mole ratio of the MCM-41-2P-Pt was determined to be 4.37. The XPS data for MCM-41-2P-Pt, MCM-41-2P, K₂PtCl₄ and Pt foil are listed in Table 1. It can be seen that the binding energies of N_{1s}, Si_{2p} and O_{1s} of MCM-41-2P-Pt are similar to those of MCM-41-2P. However, the difference of P_{2p} binding energies between MCM-41-2P-Pt and MCM-41-2P is 0.5 eV and the difference of Cl_{2p} binding energies between MCM-41-2P-Pt and K₂PtCl₄ is 1.6 eV. The binding energy of Pt_{4f_{7/2}} in MCM-41-2P-Pt is 0.8 eV less than

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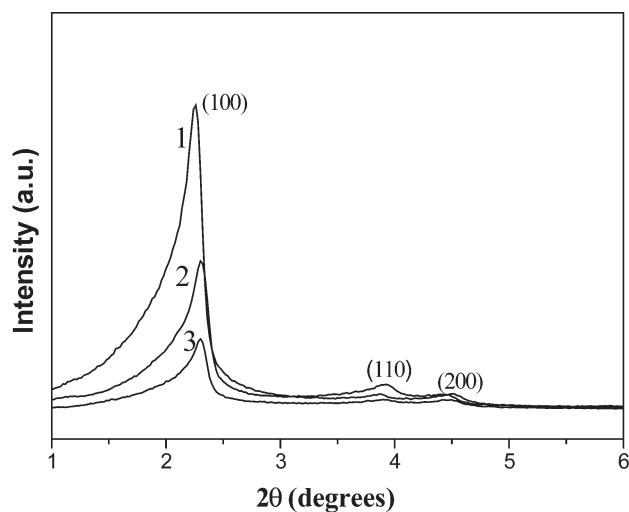
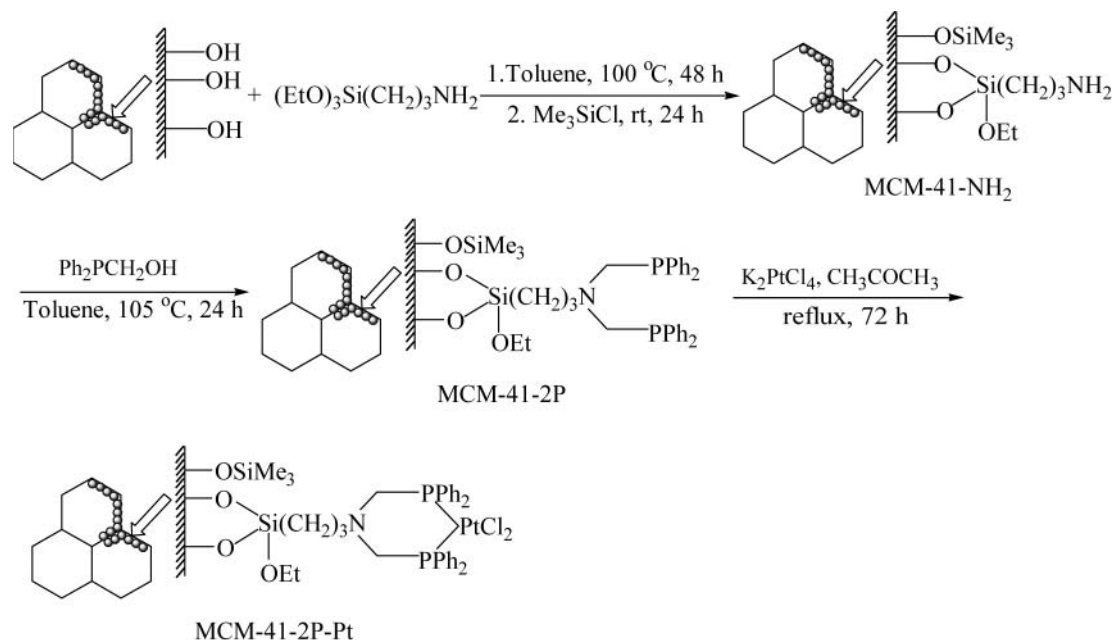


Fig. 1 XRD profiles of the parent MCM-41 (1), MCM-41-2P (2), and MCM-41-2P-Pt (3).

that in K_2PtCl_4 , but 1.1 eV larger than that in Pt foil. These results show that a coordination bond between P and Pt is formed.

In order to evaluate the catalytic activity of the novel diphosphino-functionalised MCM-41-anchored platinum complex catalyst (MCM-41-2P-Pt), the hydrosilylation reaction of olefins with triethoxysilane was studied. At first, the

Table 1 XPS data for MCM-41-2P-Pt, MCM-41-2P, K_2PtCl_4 and Pt foil (in eV)^a

Sample	Pt _{4f7/2}	P _{2p}	N _{1s}	Si _{2p}	O _{1s}	Cl _{2p}
MCM-41-2P-Pt	72.3	131.7	399.2	103.2	533.1	197.5
MCM-41-2P		132.2	399.1	103.2	533.0	
K_2PtCl_4	73.1					199.1
Pt foil	71.2					

^a The binding energies are referenced to C_{1s}(284.6 eV), and the energy differences were determined with an accuracy of ± 0.2 eV.

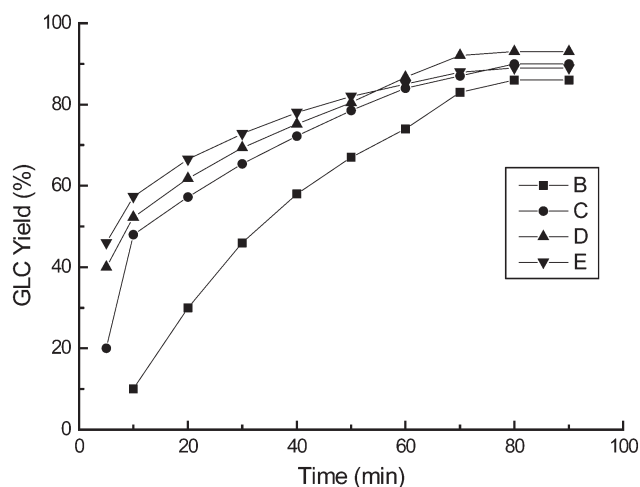


Fig. 2 Effect of reaction temperature on the yield of decyltriethoxysilane.

Conditions: dec-1-ene 5.0 mmol, $HSi(OEt)_3$ 5.0 mmol, catalyst 5.0×10^{-4} mmol Pt. B, 100 °C; C, 110 °C; D, 120 °C; E, 130 °C.

catalytic activity of this supported platinum complex at different temperatures was investigated using the hydrosilylation of dec-1-ene with triethoxysilane as the model reaction. The results are presented in Fig. 2. The experimental results show that no remarkable induction period was observed, and the reaction rate became faster with the increase in the reaction temperature. When the hydrosilylation reaction was carried out at 120 °C, decyltriethoxysilane was obtained in 93% yield after 90 min. So, for the temperatures evaluated [100, 110, 120, 130 °C], 120 °C gave the best result.

The effect of the amount of the MCM-41-2P-Pt complex on the hydrosilylation reaction was also investigated using 5.0 mmol of dec-1-ene as substrate at 120 °C and the results are shown in Fig. 3. It was found that the reaction rate increased with the increase of the amount of the catalyst, for the amounts evaluated [1.0×10^{-4} , 5.0×10^{-4} , 2.0×10^{-3} mmol Pt], 5.0×10^{-4} mmol Pt gave the best result and decyltriethoxysilane was

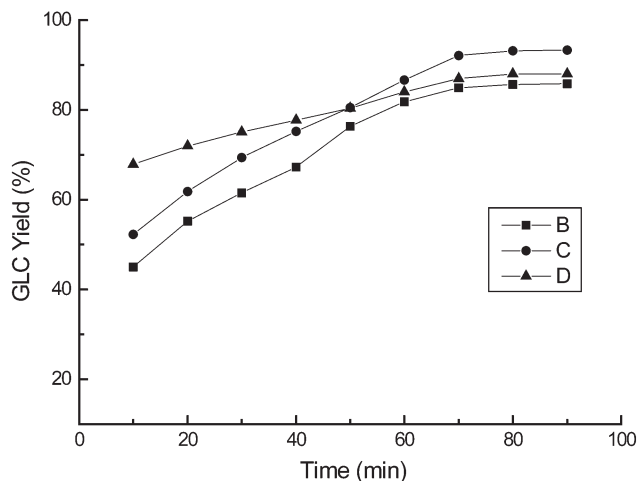


Fig. 3 Effect of the amount of the catalyst on the yield of decyltriethoxysilane.

Conditions: dec-1-ene 5.0 mmol, HSi(OEt)₃ 5.0 mmol, reaction temperature 120 °C

B, 1.0 × 10⁻⁴ mmol Pt; C, 5.0 × 10⁻⁴ mmol Pt; D, 2.0 × 10⁻³ mmol Pt.

obtained in 93% yield. When 2.0 × 10⁻³ mmol of MCM-41-2P-Pt was used, the reaction rate was the greatest, but the final yield of decyltriethoxysilane was only 84% and tetraethoxysilane was formed in 5% yield.

Hydrosilylation reactions of a variety of olefins with triethoxysilane were studied at 120 °C using 0.01 mol% of MCM-41-2P-Pt as catalyst (Scheme 2), and the typical results are listed in Table 2. As shown in Table 2, in the presence of a catalytic amount of MCM-41-2P-Pt catalyst, hydrosilylation reactions of dec-1-ene, dodec-1-ene and ω-chloroundec-1-ene with HSi(OEt)₃ proceeded smoothly and the corresponding hydrosilylation products were obtained in 91–94% yields. Speier's catalyst (H₂PtCl₆) was not as effective as this when HSi(OEt)₃ was used and it was reported that the yield of decyltriethoxysilane was only 40%.³⁹ Under our conditions, hydrosilylation reactions of allyl phenyl ether, allylbenzene and allyl glycidyl ether with HSi(OEt)₃ also proceeded smoothly to give the corresponding addition products in good yields. Hydrosilylation of styrene with HSi(OEt)₃ afforded α-adduct in 16% yield in addition to the β-adduct as a major product.

A further objective of our studies was to determine whether the catalysis was due to the MCM-41-2P-Pt complex or to a homogeneous platinum complex that came off the support during the reaction and then returned to the support at the end. To test this, we focused on the hydrosilylation reaction of dec-1-ene with triethoxysilane. We filtered off the MCM-41-2P-Pt complex after 20 min of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (120 °C) in order to avoid possible recoordination or precipitation of soluble platinum upon cooling. We found that, after this hot filtration, no further reaction was observed. This suggests that the platinum catalyst remained on the support at elevated temperatures during the reaction. The heterogeneous hydrosilylation catalysed by MCM-41-2P-Pt may proceed through a catalytic cycle analogous to that proposed for homogeneous platinum catalysts (Scheme 3).⁴⁰

Table 2 Catalytic activity of MCM-41-2P-Pt for the hydrosilylation reaction of olefins with triethoxysilane

Olefin	Product ^a	Time /min	Yield /b/%
CH ₃ (CH ₂) ₇ CH=CH ₂	CH ₃ (CH ₂) ₉ Si(OEt) ₃	90	93
CH ₃ (CH ₂) ₉ CH=CH ₂	CH ₃ (CH ₂) ₁₁ Si(OEt) ₃	100	91
C ₆ H ₅ OCH ₂ CH=CH ₂	C ₆ H ₅ O(CH ₂) ₃ Si(OEt) ₃	120	80
C ₆ H ₅ CH ₂ CH=CH ₂	C ₆ H ₅ (CH ₂) ₃ Si(OEt) ₃	140	71
Cl(CH ₂) ₉ CH=CH ₂	Cl(CH ₂) ₁₁ Si(OEt) ₃	110	94
C ₆ H ₅ CH=CH ₂	C ₆ H ₅ (CH ₂) ₂ Si(OEt) ₃	130	66
		100	78

^a The structure of product was further identified by ¹H NMR.

^b The yield was by calibrated GLC and no increase in yield was observed with increasing the reaction time.

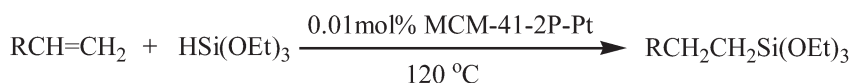
Conditions: olefin, 5.0 mmol; triethoxysilane, 5.0 mmol; MCM-41-2P-Pt, 5.0 × 10⁻⁴ mmol; temperature, 120 °C.

The reduction of MCM-41-2P-Pt with HSi(OEt)₃, followed by coordination with olefins provides the key intermediate (1). Oxidative addition of HSi(OEt)₃ to the intermediate (1) gives the MCM-41-bound platinum(III) complex (2), which is followed by insertion of the double bond to the Pt–H bond giving the MCM-41-bound platinum(III) complex (3). The reductive elimination of the addition products from the MCM-41-bound platinum(III) complex (3) regenerates the intermediate (1).

This heterogeneous platinum catalyst can be easily recovered by simple filtration. We also investigated the possibility to reuse of this platinum catalyst by using the hydrosilylation of dec-1-ene with triethoxysilane. In general, the continuous recycle of resin-supported platinum catalysts is difficult owing to leaching of the platinum species from the polymer supports, which often reduces their activity within a five-recycle run. However, when the reaction of dec-1-ene with triethoxysilane was performed even with 0.01 mol% of MCM-41-2P-Pt, the catalyst could be recycled 10 times without any loss of activity. The results are summarised in Table 3. The reaction promoted by the tenth recycled catalyst gave decyltriethoxysilane in 91% yield (entry 2). The average yield of decyltriethoxysilane in consecutive reactions promoted by the 1st through the 10th recycled catalyst was 92% (entry 3). The high stability and excellent reusable property of MCM-41-2P-Pt should result from the chelating action of the bidentate phosphine ligand on platinum and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view.

Experimental

All hydrosilylation products were characterised by comparison of their spectra and physical data with authentic samples. IR spectra were obtained using a Perkin-Elmer 683 instrument. ¹H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in CDCl₃ as solvent. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyser. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a KRATOS XSAM 800 electron energy spectrometer. X-ray powder diffraction patterns were obtained on a Damx-rA (Rigaku). The mesoporous material MCM-41 was prepared according to the literature procedure.⁴¹ Acetone, triethoxysilane and olefins were distilled before use and other reagents were used as received without further purification.



Scheme 2

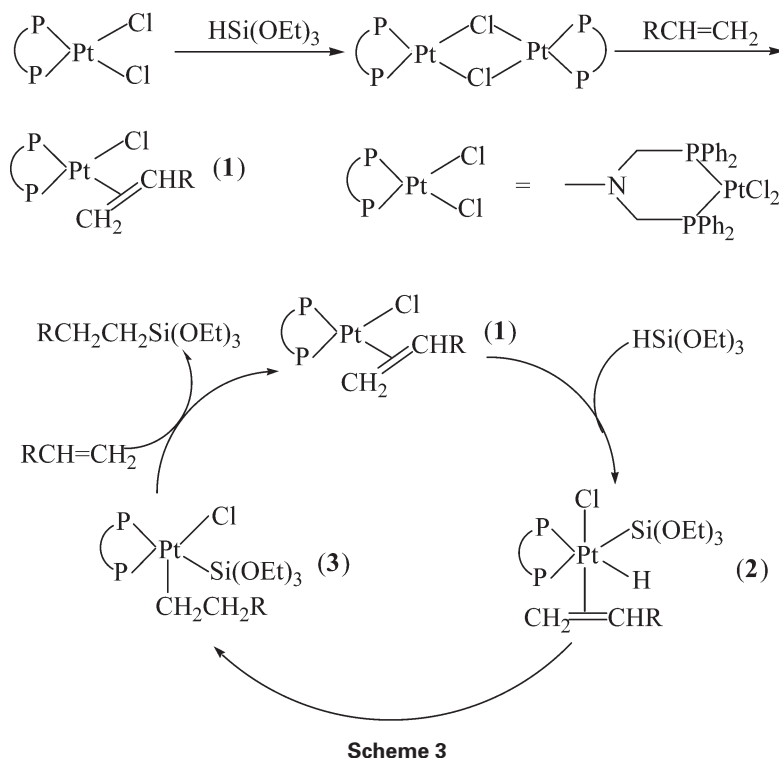


Table 3 Hydrosilylation reaction of dec-1-ene with triethoxysilane catalysed by recycled catalyst

Entry	Catalyst cycle	Yield /%	TON
1	1st	93	9300
2	10th	91	9100
3	1st to 10th consecutive	av 92	total of 92000

Preparation of MCM-41-NH₂

A solution of γ -aminopropyltriethoxysilane (2.20 g, 10 mmol) in dry chloroform (18 mL) was added to a suspension of the mesoporous support MCM-41 (2.80 g) in dry toluene (180 mL). The mixture was stirred for 48 h at 100 °C. Then the solid was filtered and washed by CHCl₃ (2 × 20 mL), and dried in a vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of Me₃SiCl (4.36 g, 40 mmol) in dry toluene (150 mL) at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried in a vacuum at 120 °C for 5 h to obtain 3.54 g of hybrid material MCM-41-NH₂. The nitrogen content was found to be 1.27 mmol g⁻¹ by elemental analysis.

Preparation of MCM-41-2P

A Schlenk flask was charged with paraformaldehyde (0.701 g, 23.3 mmol), dry MeOH (20 mL) and diphenylphosphine (4.340 g, 23.3 mmol). The reaction mixture was heated to 60 °C under Ar until the white suspension formed a colourless solution. After removal of MeOH under reduced pressure the remaining viscous oil was diluted in dry toluene (20 mL). This solution was added to a suspension of MCM-41-NH₂ (3.020 g) in dry toluene (60 mL) and the reaction mixture was heated to 105 °C under Ar for 24 h. In the cooler regions of the flask the water-toluene azeotrope separated indicating the reaction progress. After cooling to room temperature the solid product was collected by filtration under Ar, washed with dry toluene (4 × 30 mL), CH₂Cl₂/THF (1/1) (2 × 30 mL), CH₂Cl₂ (2 × 30 mL) and dried in a vacuum (100 °C) for 5 h to give 4.08 g of the light yellow MCM-41-2P. The nitrogen and phosphine content was found to be 0.76 mmol g⁻¹ and 1.44 mmol g⁻¹, respectively.

Preparation of the MCM-41-2P-Pt complex

To a solution of K₂PtCl₄ (0.151 g) in acetone (40 mL) was added MCM-41-2P (1.117 g). The mixture was heated at reflux under

nitrogen for 72 h. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under nitrogen for 3 h to give 1.124 g of the light yellow polymeric platinum complex (MCM-41-2P-Pt). The phosphine and platinum content was 1.18 mmol g⁻¹ and 0.27 mmol g⁻¹, respectively.

Hydrosilylation of olefins with triethoxysilane

Hydrosilylation was carried out in a 5 mL flat-bottomed flask equipped with a magnetic stirrer and a reflux condenser to the upper of which a drying system was attached. The olefin and the platinum complex were stirred at the reaction temperature for 30 min before triethoxysilane was added. The structure and yield of hydrosilylation products were determined based on a standard sample and a standard curve by GLC at regular intervals. Typical reaction conditions are as follows: olefin 5.0 mmol, triethoxysilane 5.0 mmol, platinum complex 5.0 × 10⁻⁴ mmol Pt. The products were isolated by distillation under reduced pressure and characterized by IR and ¹H NMR.

Decyltriethoxysilane:⁴² Oil. IR (film): ν (cm⁻¹) 2974, 2927, 2855, 1469, 1391, 1295, 1158, 1106, 1083; ¹H NMR (400 MHz, CDCl₃): δ 3.81 (q, $J = 7.2$ Hz, 6H), 1.41–1.38 (m, 2H), 1.31–1.22 (m, 23H), 0.88 (t, $J = 7.2$ Hz, 3H), 0.66–0.64 (m, 2H).

Dodecyltriethoxysilane:⁴² Oil. IR (film): ν (cm⁻¹) 2973, 2926, 2853, 1468, 1390, 1294, 1157, 1105, 1084; ¹H NMR (400 MHz, CDCl₃): δ 3.82 (q, $J = 7.2$ Hz, 6H), 1.40–1.38 (m, 2H), 1.32–1.21 (m, 27H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.67–0.64 (m, 2H).

3-Phenoxypropyltriethoxysilane:⁴³ Oil. IR (film): ν (cm⁻¹) 3056, 2943, 2841, 1595, 1471, 1389, 1245, 1086, 753, 690; ¹H NMR (400 MHz, CDCl₃): δ 7.19–7.13 (m, 2H), 6.91–6.78 (m, 3H), 3.94 (t, $J = 7.6$ Hz, 2H), 3.83 (q, $J = 7.2$ Hz, 6H), 1.83–1.78 (m, 2H), 1.23 (t, $J = 7.2$ Hz, 9H), 0.59–0.57 (m, 2H).

3-Phenylpropyltriethoxysilane:⁴⁴ Oil. IR (film): ν (cm⁻¹) 3058, 2980, 1594, 1576, 1494, 1465, 1390, 1107, 1067, 750, 692; ¹H NMR (400 MHz, CDCl₃): δ 7.35–7.18 (m, 5H), 3.76 (q, $J = 7.2$ Hz, 6H), 2.64–2.61 (m, 2H), 1.75–1.72 (m, 2H), 1.19 (t, $J = 7.2$ Hz, 9H), 0.57–0.54 (m, 2H).

11-Chloroundecyltriethoxysilane:⁴⁴ Oil. IR (film): ν (cm⁻¹) 2977, 2927, 2856, 1441, 1391, 1297, 1167, 1104, 1081, 957, 791; ¹H NMR (400 MHz, CDCl₃): δ 3.83 (q, $J = 7.2$ Hz, 6H), 3.42 (t, $J = 6.8$ Hz, 2H), 1.83–1.76 (m, 2H), 1.42–1.39 (m, 2H), 1.35–1.21 (m, 23H), 0.68–0.64 (m, 2H).

Phenylethyltriethoxysilane:⁴⁵ Oil. IR (film): ν (cm⁻¹) 3057, 2974, 1598, 1575, 1497, 1461, 1392, 1104, 1076, 752, 690; ¹H NMR (400 MHz, CDCl₃): δ 7.27–7.18 (m, 5H), 3.82 (q, $J = 7.2$ Hz, 6H), 2.75–2.73 (m, 2H), 1.22 (t, $J = 7.2$ Hz, 9H), 1.01–0.97 (m, 2H).

3-(2,3-Epoxypropoxy)propyltriethoxysilane.⁴⁴ Oil. IR (film): ν (cm^{-1}) 2944, 2841, 1468, 1264, 1194, 1160, 1088, 910, 821; ¹H NMR (400 MHz, CDCl_3): δ 3.82 (q, $J = 7.2$ Hz, 6H), 3.52–3.49 (m, 2H), 3.42–3.33 (m, 2H), 2.91–2.80 (m, 1H), 2.61–2.49 (m, 2H), 1.55–1.46 (m, 2H), 1.23 (t, $J = 7.2$ Hz, 9H), 0.58–0.56 (m, 2H).

Conclusion

In conclusion, we have described a novel diphosphino-functionalised MCM-41 anchored platinum complex whose preparation is simple and convenient. This platinum complex has not only high activity for the hydrosilylation of olefins with triethoxysilane, but offers practical advantages such as easy handling, separation from the product and reuse.

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