

Characterisation of catalysts and their precursors prepared from supported palladium phosphine complexes

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Abstract

Hydrogenation catalysts prepared from the silica-supported binuclear palladium complexes $[\text{Pd}_2\text{X}_4(\text{PR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$ or I , and $\text{R} = \text{Me}, \text{Et}$ and, for $\text{X} = \text{Br}$ only, Pr^i and Bu) and mononuclear complexes $[\text{PdX}_2(\text{PR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$ or I , and $\text{R} = \text{Me}, \text{Et}$) have been examined throughout their life cycle (induction period, selectively active catalyst and deactivation) by XPS, solid state ^{31}P NMR spectroscopy and transmission electron microscopy, and their performance and activities compared to a simple Pd/SiO_2 catalyst. The binuclear chloro complexes partially react with the silica surface producing some $\text{Pd}(0)$ species. The others retain their integrity until contacted by the substrate and hydrogen. The selective solution hydrogenation of cinnamaldehyde to hydrocinnamaldehyde appears to take place at oxidised palladium sites, most likely dipalladium(I) monophosphine species. The formation of phenylpropanol by some of the catalysts, on the other hand, occurs at $\text{Pd}(0)$ sites. The induction period before the catalysts become active results from an autocatalytic process during which the $\text{Pd}(\text{II})$ precursors are converted to the active, $\text{Pd}(\text{I})$ or $\text{Pd}(0)$ species. The catalysts are finally deactivated by a combination of continued conversion of the active species to a new, phosphorus-poisoned $\text{Pd}(0)$ material and the restructuring of a hydrocarbonaceous overlayer. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Both $\text{Pd}(\text{II})$ and $\text{Pd}(0)$ complexes are known to be highly selective in the homogeneous hydrogenation of a range of substrates. Thus, for example, bis-phosphine complexes $[\text{PdCl}_2(\text{PR}_3)_2]$ have been found to be very effective catalysts for the selective reduction of polyenes to monoenes [1], and the zerovalent complex $[(\text{DIAN})\text{Pd}(\text{alkene})]$ (DIAN is N,N' -diaryl-diiminoacene) catalyses the hydrogenation of cinnamaldehyde with 90% selectivity to hydrocinnam-

aldehyde [2]. The hydrogenation mechanisms involve both palladium hydride and palladium-substrate intermediates [3].

Although these homogeneous catalysts are highly selective, they suffer the usual drawbacks of homogeneous catalysts, most importantly the problems of separation after reaction. Initial attempts to “heterogenise” these homogeneous processes involved the use of polymeric support. For example, it has been found that catalysts derived from the interaction of PdCl_2 with phosphinated polymer are more active than unsupported $[\text{PdCl}_2(\text{PPh}_3)_2]$ in the hydrogenation of alkenes and alkynes [4]. This higher activity has been attributed to there being fewer than two phosphine ligands per palladium, thus reducing the stability

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of Pd(II) and enabling small, highly active Pd(0) particles to be formed within the support [5]. Similarly, highly active “atomically dispersed” supported palladium catalysts have been prepared by hydrogen reduction of Pd(II) allyl derivatives anchored to inorganic supports [6].

Another strategy to obtain heterogeneous behaviour from homogeneous catalysts is to chemically bond a metal complex to, for example, a silica or alumina support [7]. This can be achieved either by the direct interaction of the metal complex with the support or by attaching appropriate organofunctional groups to the carrier before introducing the metal salt. Thus, phosphinated silica has been impregnated with PdCl₂ and used to catalyse the hydrogenation of cyclohexene [8], and supported rhodium complexes of formula [RhX{silica-(CH₂)₄(C₆H₄)(PPh₂)}₂] (X = Cl, Br or I) have been prepared by impregnation of the support with the ligand prior to the metal and used in the selective hydrogenation of alkenes [9].

One major disadvantage with supported molecular complexes is that leaching often occurs into the solvent phase. Whilst some control of this can be effected by varying the solvent phase, an alternative approach has been to either intercalate complexes into the layers of pillared clays [10] or encapsulate complexes in zeolites [11]. Thus, for example, encapsulation of [Pd(salen)] in zeolites X and Y greatly enhanced selectivity in the catalytic hydrogenation of alkenes and prevented leaching of the palladium complex into solution.

A serious drawback with these heterogenised catalysts is that they are difficult to characterise, and, consequently, mechanistic interpretation is limited. The catalytically active species are not readily identified since partial or complete breakdown of the complexes may occur under reaction conditions [12]. Previously [13] we reported a study of the hydrogenation of cinnamaldehyde using catalysts prepared from silica-supported binuclear palladium complexes [Pd₂X₄(PR₃)₂] (X = Cl, Br or I and R = Me, Et, Pr^{*i*} or Bu). This paper describes new work on the characterisation of these supported binuclear palladium complexes, the extension of the programme to mononuclear compounds (silica-supported [PdX₂(PR₃)₂], where X = Cl, Br or I and R = Me or Et), and the catalysts originating from these supported complexes at all stages of their preparation and use.

2. Experimental

2.1. Preparation of the catalyst precursors

The palladium complexes were prepared by standard methods as described previously [13]. Gasil 35 M silica supplied by Crosfield was used as the support (surface area of 320 m² g⁻¹, pore volume of 1.2 ml g⁻¹ and mean particle size 4.0 μm). Precursors with a 5% w/w Pd loading were prepared by impregnation of ethanol or ethanol/chloroform solutions of the complexes onto pre-dried silica [13]. The stoichiometry of these vacuum dried yellow or orange precursors was confirmed by microanalyses (Table 1).

2.2. Catalyst activation and hydrogenation

Catalysts derived from the supported palladium complexes were used in the liquid phase hydrogenation of cinnamaldehyde in decalin. The reaction was carried out at either 95 or 135°C as described previously [13]. Under a helium atmosphere, 0.5 g of the catalyst precursor and 25 ml of decalin were treated with 0.25 ml of cinnamaldehyde, and the temperature was raised to the required reaction temperature. Hydrogen gas was then bubbled through the liquid at 1 atm pressure at a rate of 70 ml min⁻¹. The catalysts rapidly turned black. Aliquots of the reaction mixture were removed at intervals, filtered, and analysed by GC [13]. Continuous agitation by magnetic stirring was maintained throughout the catalytic run. Although there will be some mass transfer limitations with this arrangement (liquid–solid), the over-riding limit is more likely to be due to gas–liquid mass transfer due to the limited solubility of H₂ in the solvent. Since the reactor was being used only to compare catalysts and not to carry out a rigorous kinetic study, this limitation should not be critical. The relative reaction rates were determined from plots of cinnamaldehyde concentration against time.

A number of reactions were carried out in which the reaction was stopped before completion in order to obtain catalyst samples for analysis at various stages of reaction. Typically, catalyst samples were obtained (a) after an induction period in which the catalyst precursor had changed colour from yellow/orange to black but analysis had shown that it was not yet active, (b) when the catalyst was at optimum activity (des-

Table 1
Microanalytical results

Catalyst/precursor	C (% , calculated)	H (% , calculated)	X (% , calculated)	P (% , calculated)
[PdCl ₂ (PMe ₃) ₂]/SiO ₂	3.70 (3.38)	1.36 (0.85)	3.31 (3.33)	
[PdCl ₂ (PMe ₃) ₂]/SiO ₂ after 48 h at 135°C	7.75	1.13		
[Pd ₂ Cl ₄ (PMe ₃) ₂]/SiO ₂	1.72 (1.69)	0.81 (0.42)	3.77 (3.33)	2.11 (1.46)
[Pd ₂ Cl ₄ (PMe ₃) ₂]/SiO ₂ after 0.25 h at 95°C	2.67	1.14	2.80	
[Pd ₂ Cl ₄ (PMe ₃) ₂]/SiO ₂ after 1.5 h at 95°C	5.81	1.16	0.95	
[Pd ₂ Cl ₄ (PMe ₃) ₂]/SiO ₂ after 48 h at 95°C	5.73	1.04	1.24	0.81
[PdCl ₂ (PEt ₃) ₂]/SiO ₂	6.81 (6.77)	1.76 (1.41)	3.01 (3.34)	
[PdCl ₂ (PEt ₃) ₂]/SiO ₂ after 48 h at 135°C	6.84	1.19	0.54	
[Pd ₂ Cl ₄ (PEt ₃) ₂]/SiO ₂	3.78 (3.38)	1.31 (0.71)	4.22 (3.33)	
[Pd ₂ Cl ₄ (PEt ₃) ₂]/SiO ₂ after 48 h at 95°C	7.90	1.27	1.27	
[PdBr ₂ (PMe ₃) ₂]/SiO ₂	3.80 (3.38)	1.37 (0.85)	7.80 (7.50)	
[PdBr ₂ (PMe ₃) ₂]/SiO ₂ after 48 h at 135°C	5.95	0.99	6.33	
[Pd ₂ Br ₄ (PMe ₃) ₂]/SiO ₂	1.84 (1.69)	0.90 (0.42)	9.40 (7.50)	2.39 (1.45)
[Pd ₂ Br ₄ (PMe ₃) ₂]/SiO ₂ (mechanical mix)	1.94	1.15	5.50	
[Pd ₂ Br ₄ (PMe ₃) ₂]/SiO ₂ (induction period)			4.39	
[Pd ₂ Br ₄ (PMe ₃) ₂]/SiO ₂ after 2 h at 95°C	3.88	0.83		
[Pd ₂ Br ₄ (PMe ₃) ₂]/SiO ₂ after 48 h at 95°C	6.52	1.71	4.78	0.79
[PdI ₂ (PMe ₃) ₂]/SiO ₂	3.30 (3.38)	0.24 (0.85)	11.8 (11.93)	
[PdI ₂ (PMe ₃) ₂]/SiO ₂ after 48 h at 135°C	6.56	1.39	7.74	
[Pd ₂ I ₄ (PMe ₃) ₂]/SiO ₂	1.66 (1.69)	1.04 (0.42)	8.15 (11.93)	
[Pd ₂ I ₄ (PMe ₃) ₂]/SiO ₂ after 48 h at 135°C	8.94	1.93	7.20	
[Pd ₂ I ₄ (PEt ₃) ₂]/SiO ₂	4.49 (3.38)	1.30 (0.70)	11.8 (11.93)	
[Pd ₂ I ₄ (PEt ₃) ₂]/SiO ₂ after 48 h at 135°C	8.84	1.41	8.24	

ignated the active catalyst), and (c) after the reaction was either complete or the catalyst had lost its activity (designated the used catalyst). Catalytic runs were also carried out for a standard 5% Pd/SiO₂ catalyst, prepared as described previously [13], in order to correlate the activities and selectivities of this catalyst with any changes in properties during reaction, and to compare these with the behaviour of the catalysts derived from the supported molecular complexes. All the catalysts extracted from reaction were filtered, washed with diethyl ether to remove decalin, and pumped on a vacuum line prior to analysis.

2.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectra were obtained for a selection of the catalysts and precursors using Al K α ($h\nu = 1486.6$ eV) monochromated radiation with a SCIENTA ESCA 300 spectrometer linked to a computer for data acquisition and analysis. All these experiments were carried out using the EPSRC

Research Unit for Surfaces and Interfaces (RUSTI) facility at Daresbury.

The analysis chamber was evacuated to $<1 \times 10^{-8}$ Torr before running the spectra. The samples were loaded using double-sided Scotch Tape. A low-energy electron flood gun was used and residual charging effects were corrected to C 1s with a binding energy of 285 eV using adventitious carbon. Spectra were recorded at room temperature. Data analysis involved background subtraction by either a Shirley or linear type integral profile and a curve fitting procedure by a least squares method. The spectra were analysed qualitatively in terms of their relative peak area intensities and the chemical shifts of the 3d_{5/2} transitions of Pd and Br, and the 2p_{3/2} transitions of Cl and P (from mononuclear compounds only). Spectra were collected with a pass energy of 150 eV. Experimental errors were estimated to be ± 0.2 eV for the photoelectron peak binding energy positions. (It is emphasised that the objective of this study is to identify trends rather than absolute values.)

2.4. Solid state ^{31}P magic angle spinning (MAS) NMR

^{31}P MAS NMR spectra were recorded using either the EPSRC solid state NMR service at UMIST, or on a Varian Unity Plus 300 spectrometer operating at 121 MHz, at the Chemistry Department, University of Missouri at St. Louis, USA. Peaks were referenced to an external standard of 80% H_3PO_4 (UMIST) or K_2HPO_4 (St. Louis). In each case, both cross-polarisation (CPMAS) and single pulse (SPMAS) experiments were carried out.

2.5. Transmission electron microscopy

Selected samples were examined using a JEOL 1200 EX transmission electron microscope. They were prepared by dispersing them in either water or isopropyl alcohol and mounting them on carbon-coated copper grids.

3. Results

We previously described the catalysis of the liquid phase hydrogenation of cinnamaldehyde by silica-supported binuclear complexes $[\text{Pd}_2\text{X}_4(\text{PR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$ or I , and $\text{R} = \text{Me}, \text{Et}$ and, for $\text{X} = \text{Br}$ only, Pr^i and Bu) [13]. Catalysts formed from the bromide complexes selectively produce *only* hydrocinnamaldehyde, and at a single type of catalytic site. The iodide complexes behave similarly, but very slowly. The binuclear chloro complexes, however, behave differently and produce a catalyst with two site types, one of which is similar to the bromides and leads to hydrocinnamaldehyde, and a second which catalyses the conversion of cinnamaldehyde to phenylpropanol at a single visit to the catalyst. These contrast with a “standard” Pd/SiO_2 catalyst, which catalyses the hydrogenation of cinnamaldehyde sequentially to hydrocinnamaldehyde and then phenylpropanol.

We have now investigated catalysts made from the mononuclear complexes $[\text{PdX}_2(\text{PR}_3)_2]$, and subjected all of the catalysts to a variety of analytical techniques in order to better elucidate the mechanisms of the processes. Catalysts formed from the supported mononuclear compound $[\text{PdCl}_2(\text{PR}_3)_2]/\text{SiO}_2$ ($\text{R} = \text{Me}$ or Et), were active for the hydrogenation of cinnamaldehyde.

Like the binuclear complexes, the catalysts turned black on introduction of hydrogen, and also exhibited an induction period, active phase, and deactivation after about 48 h on line. The hydrogenation reactions proceeded rapidly. At 135°C $[\text{PdCl}_2(\text{PMe}_3)_2]$ reacted with a rate constant of $4.1 \times 10^{-2} \text{ mol l}^{-1} \text{ h}^{-1}$ (5% Pd loading) compared with $1.3 \times 10^{-2} \text{ mol l}^{-1} \text{ h}^{-1}$ for its dinuclear equivalent. The results obtained using these catalysts proved not to be reproducible, however, sometimes giving 100% selectivity to hydrocinnamaldehyde formation and on other occasions also producing some phenylpropanol. Preparation of fresh batches of these chloride catalysts led to similar variations in use.

In contrast to the chloro complexes described above, catalysts prepared from $[\text{PdBBr}_2(\text{PMe}_3)_2]$ and $[\text{PdI}_2(\text{PMe}_3)_2]$ on silica were very slow in use. For example, the catalyst from the bromo complex produced only 3% conversion in the hydrogenation of cinnamaldehyde at 95°C after 48 h, and 6% after 48 h at 135°C . They were, however, reproducibly selective to hydrocinnamaldehyde formation.

Finally, we note that, as ascertained previously [13], the supported metal complexes were not active in the homogeneous phase under these conditions.

3.1. Microanalyses

Carbon, hydrogen and halogen microanalyses of the supported palladium complexes and the catalysts formed by their partial decomposition are presented in Table 1. The theoretical values are for a 5% w/w palladium loading, the basis for preparing the catalysts. Microanalysis suggested that all the complexes retained their integrity on the silica, though in each case, the analytical values for hydrogen were about 0.5% higher than calculated. These discrepancies were assigned to the presence of surface silanol groups on the silica, since porous silica is known to be hydroxylated to the extent of $\sim 5 \times 10^{18} \text{ OH m}^{-2}$ after drying at 100°C [14].

The $[\text{Pd}_2\text{Cl}_4(\text{PMe}_3)_2]/\text{SiO}_2$ catalysts were analysed after the hydrogenation of cinnamaldehyde had proceeded for 0.25, 1.5 and 48 h at 95°C , corresponding to the induction period, the active catalyst and the deactivated or used catalyst, respectively. Carbon deposition occurs during the reaction, reaching a maximum after 1.5 h on line. This implies that formation

of a hydrocarbonaceous overlayer (which builds up as the reaction proceeds) accompanies the activation of the catalyst. The formation of such overlayers in the hydrogenation of alkenes and alkynes over supported *metal* catalysts is well established [15]. Carbon lay-down was accompanied by loss of chloride, with the active catalyst (after 1.5 h on line) retaining only about 25% of the original chloride. No further halogen loss was detected as the catalyst underwent deactivation. Microanalyses do not, of course, reveal whether the retained Cl in the active and used catalysts is still associated with the palladium or is attached elsewhere. Similar results were observed for the $[\text{Pd}_2\text{Cl}_4(\text{PEt}_3)_2]/\text{SiO}_2$ catalysts, which retained about 30% of the original chloride whilst the carbon increased from 3.8 to 7.9% after 48 h reaction in cinnamaldehyde/decalin at 95°C.

Phosphorus analyses on the precursor $[\text{Pd}_2\text{Cl}_4(\text{PMe}_3)_2]/\text{SiO}_2$ and the catalyst that had been on line for 48 h showed that this catalyst lost about 60% of its phosphorus during reaction, implying that the active catalyst retains less than one phosphorus per pair of palladium atoms. Since phosphorus loss is accompanied by substantial chloride loss, it is reasonable to conclude that some reduction of Pd(II) occurs during cinnamaldehyde hydrogenation using our chloro-bridged dipalladium materials. Support for phosphorus loss from the chloro-bridged dipalladium compounds during reaction was provided by the GC analysis of the reaction products [13], which indicated the presence of small amounts of PR_3 -derived species in the solvent layer. Carbon build-up was also observed during the course of the reactions of the monopalladium complex $[\text{PdCl}_2(\text{PMe}_3)_2]$.

Microanalyses for $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ and catalysts prepared from it are also listed in Table 1. Results were recorded for the precursor, the active catalyst after cinnamaldehyde hydrogenation for 2 h at 95°C, and for the catalyst after use in cinnamaldehyde hydrogenation for 48 h at 95°C, by when it had undergone substantial deactivation. Substantial carbon lay-down was observed, carbon increasing from 1.8% in the precursor to 6.5% after 48 h reaction. The bromide loss from the supported bromo-bridged dipalladium compound was much less than the chloride loss in the chloro-bridged analogue, however, with the catalyst retaining 50% of the bromide after 48 h on line. The catalysts from $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ also

lost almost 70% of the phosphorus during reaction. This is comparable to the phosphorus loss observed for the chloro-bridged compounds, implying the loss of more than one phosphorus per two Pd atoms by the time the catalyst is deactivated.

Carbon lay-down also occurred with $[\text{PdBr}_2(\text{PMe}_3)_2]/\text{SiO}_2$, but only about half that observed for the bromo-bridged dipalladium compounds, a variation also shown by the chloro analogues. An amount of 80% of the bromide was retained. Finally, microanalysis on the $[\text{Pd}_2\text{I}_4(\text{PMe}_3)_2]/\text{SiO}_2$ catalysts revealed that 90% of its iodide was retained under reaction conditions and that there was substantial carbon lay-down on the surface.

It is apparent that despite the relatively mild reaction conditions, carbon lay-down accompanies the induction period and the active catalysis stage, and remains at the deactivation stage. This applies to each of the materials derived from the phosphine–palladium complexes, whether or not the particular catalyst is selective. Mass balance calculations indicate that in each case about 10% of the substrate or products are accounted for in this way. Moreover, since carbon lay-down is apparent at each stage of the catalysts' life, it does not appear that either activation or deactivation are dependent on it. Many previous studies on other types of heterogeneous catalyst have indicated that hydrocarbonaceous overlayers form an intimate part of the active catalyst [15]. The operation of our standard Pd/SiO₂ catalysts is also accompanied by carbon lay-down, but these neither require an induction period nor become deactivated upon use.

Loss of halide, presumably into solution, must accompany Pd(II) reduction. Cl compounds are most easily reduced, followed by Br then I. The same general trend is accompanied by loss of phosphorus. Thus, most of the palladium–chloro complexes end up as Pd(0) species, whilst the others could be either mostly Pd(I) or 50% Pd(II) plus 50% Pd(0).

3.2. Surface analysis

Surface analysis by XPS was carried out on PdO/SiO₂, $[\text{Pd}_2\text{Cl}_4(\text{PMe}_3)_2]/\text{SiO}_2$, $[\text{Pd}_2\text{Cl}_4(\text{PEt}_3)_2]/\text{SiO}_2$, $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$, $[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$ and the catalysts prepared from these precursors at various stages of reaction in the hydrogenation of cinnamaldehyde. The photo-emission energies and

Table 2
XPS results^a

Catalyst/precursor	Pd 3d _{5/2}	Cl 2p _{3/2}	Br 3d _{5/2}
[Pd ₂ Cl ₄ (PMe ₃) ₂]/SiO ₂	337.6 (85); 335.7 (15)	198.2	
[Pd ₂ Cl ₄ (PMe ₃) ₂]/SiO ₂ after 2 h at 135°C	337.6 (65); 335.6 (35)	198.8	
[Pd ₂ Cl ₄ (PMe ₃) ₂]/SiO ₂ after 48 h at 135°C	335.1	Not observable	
[Pd ₂ Cl ₄ (PEt ₃) ₂]/SiO ₂	337.7 (70); 336.0 (30)	198.8	
[Pd ₂ Br ₄ (PMe ₃) ₂]/SiO ₂	337.7		69.5
[Pd ₂ Br ₄ (PMe ₃) ₂]/SiO ₂ (mechanical mix)	337.7		69.1
[Pd ₂ Br ₄ (PMe ₃) ₂]/SiO ₂ after 2 h at 95°C	337.0		69.5
[Pd ₂ Br ₄ (PMe ₃) ₂]/SiO ₂ after 48 h at 95°C	337.8 (65); 336.1 (35)		69.6
[PdCl ₂ (PEt ₃) ₂]/SiO ₂ ^b	338.0	198.4	
[PdCl ₂ (PEt ₃) ₂]/SiO ₂ (induction period)	337.8 (90); 335.6 (10)	Not observable	
[PdCl ₂ (PEt ₃) ₂]/SiO ₂ (active catalyst)	337.6 (75); 335.3 (25)	Not observable	
[PdCl ₂ (PEt ₃) ₂]/SiO ₂ after 48 h at 135°C	337.7 (40); 335.5 (60)	Not observable	
PdO/SiO ₂	337.3		
Pd/SiO ₂	335.5		
Pd/SiO ₂ after reaction for 24 h at 95°C	335.7		

^a Values denote E_B in eV and values in parentheses denote peak ratios.

^b Phosphorus 2p_{3/2} is 131.1 eV.

relative intensities for Pd 3d_{5/2}, Cl 2p_{3/2} and Br 3d_{5/2} are presented in Table 2. Binding energies for the Pd 3d_{5/2} signals are particularly helpful.

Most straight-forward are the “standard” Pd/SiO₂ catalysts. The precursor, PdO/SiO₂, generated by calcination at 200°C of palladium nitrate impregnated onto silica, showed a binding energy of 337.3 eV, typical of Pd(II) [16–18]. The value is slightly higher than reported for unsupported PdO [19], perhaps attributable to the influence of the support. On reduction in H₂ at 200°C, a peak with binding energy 335.5 eV for the 5% Pd/SiO₂ catalyst is produced, typical of Pd(0). There was little further change in the active catalyst which had been used in the hydrogenation of cinnamaldehyde for 24 h at 135°C. The Pd 3d_{5/2} signal intensity was lower in the active catalyst, however, a factor ascribed to the presence of the hydrocarbonaceous overlayer masking the surface. Pd(0) has been reported to have a Pd 3d_{5/2} binding energy of 335.3 eV [20], but this has been found to shift to 336.4 eV for 5% Pd/carbon [20].

XPS studies were also carried out for the catalyst precursor [Pd₂Br₄(PMe₃)₂]/SiO₂, the active catalyst formed from it (used in the hydrogenation of cinnamaldehyde for 2 h at 95°C), and the used catalyst that had undergone considerable deactivation after 48 h. The 3d_{5/2} transition for palladium in the precursor gave only one peak with a binding energy of

337.7 eV, typical of Pd(II) [16–18]. Analysis of a dry mix prepared by grinding together the same amount of complex (sufficient to give 5% loading) with silica also yielded only one peak at 337.7 eV, indicating that the integrity of the complex was retained when supported on silica, that all the palladium was present as Pd (II), and that no beam damage was suffered by the complex. Surface analysis of the active catalyst formed from [Pd₂Br₄(PMe₃)₂]/SiO₂ after hydrogenation of cinnamaldehyde for 2 h at 95°C indicated that there was only one 3d_{5/2} peak for palladium at 337.0 eV, and with an intensity of 25% of that observed for the precursor. This might be assigned to a palladium species in oxidation state (I) or (II), covered with a hydrocarbonaceous overlayer. Although it has been reported that binding energies for palladium increase with increase in oxidation state, the transition from an oxidation state of (II) to (I) does not always give an identifiable step change, as pointed out in [17]. It is therefore not possible by this technique alone to distinguish between these oxidation levels. The observed bromine loss from this catalyst is compatible with reduction to Pd(I), however. The strong indication, therefore is that the selective cinnamaldehyde to hydrocinnamaldehyde hydrogenation takes place at Pd(I) sites.

The deactivated catalyst had two Pd 3d_{5/2} peaks, at 337.8 and 336.1 eV, typical of Pd(II) (or Pd(I))

and Pd(0), respectively. The nature and identities of these species represents a problem. Clearly the Pd(0) is different to that of the simple Pd/SiO₂ described before as it is inactive. It is possibly in the form of palladium metal crystallites poisoned by the presence of phosphine compounds [21]. The other signal could be a Pd(II) compound (resulting from a redox disproportionation of the Pd(I) precursor), or another Pd(I) compound. Whichever the identity, the material is clearly different from the catalyst precursor or active stage, since it is inactive itself.

The [Pd₂Cl₄(PMe₃)₂]/SiO₂ system is yet more complicated. This catalyst showed evidence for the operation of two active site types, one specific to hydrocinnamaldehyde formation, the other producing phenylpropanol at one visit to the catalyst [13]. Analysis of the precursor [Pd₂Cl₄(PMe₃)₂]/SiO₂ showed that the 3d_{5/2} transition for palladium was comprised of two peaks at 337.6 and 335.7 eV in the ratio 85:15. This indicated that palladium was present predominantly as Pd(II), but some of the palladium had a binding energy that is normally associated with the presence of Pd(0) [16–18]. The Pd(0) must result either from X-ray beam damage or from the interaction of the compound with the silica support. Since there appears to be no precedent for beam damage to [PdCl₂(PEt₃)₂] (vide infra) or to other reported Pd complexes, we favour the latter explanation. There are precedents for OH groups leading to reduction of Pd(II) chlorides to Pd(0) compounds. [PdCl₂(PMe₃)₂] is reduced to palladium metal by aqueous alkali [22]. [PdCl₂(PPh₃)₂] behaves likewise at 60–80, Ph₃PO being produced also. Reactions proceed via nucleophilic attack at the metal atom. Indeed water alone is able to lead to reduction of Pd(II) halide complexes, at least under some circumstances. Thus, the reaction of sodium triphenylphosphine trisulfonate (tppts) with PdCl₂ produces first [PdCl(tppts)₃]⁺, which is reduced in the presence of water to [Pd(tppts)₃] [23]. It therefore seems quite feasible that the surface silanol groups could be responsible for the reaction.

The precursor [Pd₂Cl₄(PEt₃)₂]/SiO₂ similarly revealed two peaks, one corresponding to Pd(II) (337.2 eV) and one to Pd(0) (335.6 eV), in ratio 70:30. Such minor variations in the Pd(II) binding energies are to be expected with different ligands [16–18], though it is of interest to note that the two Pd(0) signals are identical within experimental error. It is

also interesting to note that the Pd 3d_{5/2} binding energy for [Pd₂Br₄(PMe₃)₂]/SiO₂ was identical to that observed for Pd 3d_{5/2} in the chloro-bridged dipalladium analogue. Identical binding energies have also been found for [Pd(PPh₃)₂Cl₂] and [Pd(PPh₃)₂Br₂] [16]. Kumar et al. interpreted these results as being due to a balance of σ and π effects in the electron density at palladium resulting from the halogen and the phosphine [16].

The active catalyst formed from [Pd₂Cl₄(PMe₃)₂]/SiO₂ after 2 h reaction of cinnamaldehyde in decalin at 135°C also consists of Pd(II) (or Pd(I)) and Pd(0), with the amount of Pd(0) raised to 35%. The final, inactive state consists of only Pd(0). The overall signals diminish in intensity due, presumably, to hydrocarbonaceous overlayer coverage. It seems likely that the Pd(II) or Pd(I) in the active catalyst is the chloride analogue of the bromo species which selectively reduces cinnamaldehyde to hydrocinnamaldehyde in that catalyst. The greater Cl loss (compared to Br loss in the bromo analogue) is due to formation of a substantial amount of a Pd(0) species. This Pd(0) species, some of which may be derived from that formed by the initial reaction with silica and some from hydrogen reduction of the Pd(II), most probably contains the species responsible for the one-visit formation of phenylpropanol from cinnamaldehyde. The final Pd(0) compound (335.1 eV) can be neither of these, however, since this material is catalytically inactive. It presumably corresponds to the phosphine-poisoned Pd(0) of the bromide system.

Analysis of the mononuclear precursor [PdCl₂(PEt₃)₂]/SiO₂ showed that the 3d_{5/2} transition for palladium consisted of only one peak at 338.0 eV, close in value to binding energies reported by Kumar et al. [16] and Nefedov et al. [17] for [PdCl₂(PPh₃)₂] (337.9 and 338.2 eV, respectively). No Pd(0) was discerned in the precursor, and the amount formed throughout is less than from the binuclear complexes. In a number of cases it has been reported that bis-phosphine palladium complexes are more resistant to reductive eliminations leading to Pd(0) species than monophosphine compounds [24]. The final, inactive catalyst contains both Pd(II) (or Pd(I)) and Pd(0), somewhat similar to that from the bromo complex [Pd₂Br₄(PMe₃)₂].

The Cl 2p_{3/2} and Br 3d_{5/2} signals tended to be broad and no resolution of bridge and terminal groups could be seen even in the catalyst precursors, although

Table 3
 $^{31}\text{P}\{^1\text{H}\}$ MAS NMR results^a

Catalyst/precursor	Chemical shift (ppm)
$[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]$	20.4 (b)
$[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$	14.7 (s) + trace at ~20
$[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ (mechanical mix)	15.2 (b) + sh at ~20
$[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ after 30 min at 95°C	52.8 (s)
$[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ after 2 h at 95°C	53.1 (s)
$[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ after 48 h at 95°C	31.2 + sh, 53.6 (s) (1:5)
$[\text{Pd}_2\text{Br}_4(\text{PEt}_3)_2]/\text{SiO}_2$	54.5 (s)
$[\text{PdBr}_2(\text{PMe}_3)_2]/\text{SiO}_2$	-16.7 (s), 0.4 (b), 4.7 (b),
$[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$	14.4, 34.0 (~3:1)
$[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$ after 15 min at 135°C	14.4, 33.7, 59.5 (~1:2:trace)
$[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$ after 2 h at 135°C	14.0, 32.7, 36.2, 59.0 (trace:1:4:trace)
$[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$ after 48 h at 135°C	36.3, 57.7 (~3:1)

^a s: sharp; b: broad; sh: shoulder.

different binding energies for bridge and terminal bromides (albeit in different compounds) have been claimed before [16]. The Cl values are typical of those found in group 10 transition metal chlorides [19,20]. The signals diminished rapidly as the catalysts were used, and Cl $2p_{3/2}$ was often not detectable. No doubt this can be ascribed to overlayer coverage and halide loss, especially in the case of chlorides. Signals for phosphorus $2p_{3/2}$ were weak and could only be observed in the precursor $[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$. The transition was observed at 131.3 eV, corresponding closely to that reported for $[\text{PdCl}_2(\text{PPh}_3)_2]$ [17].

3.3. NMR analysis

Selected catalysts and precursors were analysed by ^{31}P MAS NMR in order to see if their surface properties were also representative of the state of the complexes in the bulk, and to provide a further handle on the nature of the active sites in the catalysts derived from the supported complexes. The ^{31}P chemical shifts for $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$, $[\text{PdBr}_2(\text{PMe}_3)_2]/\text{SiO}_2$ and $[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$ and catalysts prepared from these supported complexes are presented in Table 3. The ^{31}P MAS NMR for $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ prepared by wet impregnation gave one sharp signal at 14.7 ppm which was shifted upfield by 5.7 ppm relative to that of the unsupported complex. A finely-ground dry mix of the complex and silica gave a similar result, although the signal was broadened, possibly due to particle size variations. All of these values are close to the solution ^{31}P NMR

parameters (which consist of a singlet at 12.3 ppm), and can be taken as the typical range of $\delta\text{-}^{31}\text{P}$ for PMe_3 coordinated to Pd(II).

The ^{31}P MAS NMR for $[\text{Pd}_2\text{Br}_4(\text{PEt}_3)_2]/\text{SiO}_2$ prepared by wet impregnation also gave only one signal with a shift of 54.5 ppm. Such chemical shift variations with different phosphines are quite usual. The value again compares favourably with that obtained for the solution ^{31}P NMR of the complex (a single peak at 47.8 ppm). These results show that the phosphorus remains in only one chemical environment and that these complexes remained intact when supported on silica.

The ^{31}P MAS NMR for the catalyst prepared from $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$, after 0.5 h reaction in the hydrogenation of cinnamaldehyde at 95°C, i.e. shortly after the induction period, also consisted of a single peak, shifted considerably downfield to 52.8 ppm. No change in the peak was observed after the reaction had run for 2 h. This indicated that after the initial activation process there was essentially no further change in the chemical identity of the associated phosphorus species whilst the catalyst remained active, and only one type of phosphorus was present. This is consistent with the XPS results for this catalyst which showed that there was only one type of active phosphorus- and bromide-containing supported palladium complex in the active catalyst. This corresponds to a possible Pd(I) species of stoichiometry Pd_2P , indicated by the XPS and microanalytical results. The phosphorus lost from the dipalladium compounds must be eliminated into solution, possibly as $[\text{PR}_3\text{H}]^+$, and not retained

on the support since only one phosphorus signal was observed. (Confirmation of this was obtained by the detection of PR_3 -derived species by GC analysis of the reaction products.)

^{31}P MAS NMR analysis of the catalyst after the hydrogenation of cinnamaldehyde for 48 h, i.e. when the catalyst had undergone considerable deactivation, gave two peaks, at 53.6 and 31.2 ppm in the ratio 7:3. The first resonance can be assigned to the same palladium species that was observed in the active catalyst. The new signal at 31.2 ppm might be assigned to the $\text{Pd}(0)$ -phosphine species attributed to the inactive $\text{Pd}(0)$ species observed by XPS in the same catalyst. Since it appears that most of the material present in the active catalyst still remains, deactivation is not, in fact, due to the loss of this palladium species. This leaves either a change in the nature of the hydrocarbonaceous overlayer, or poisoning by the $\text{Pd}(0)$ species that is undoubtedly formed, as responsible for the deactivation in this catalyst (and presumably all the others).

Solid state ^{31}P MAS NMR indicated the presence of three phosphorus-containing species in $[\text{PdBr}_2(\text{PMe}_3)_2]/\text{SiO}_2$. The largest signal at -16.7 ppm corresponded with the ^{31}P singlet observed for the *trans*-complex in solution. The signal at 0.4 ppm may be due to the *cis*-isomer, which has a solution ^{31}P singlet peak at -1.7 ppm. The third peak was observed at 4.7 ppm and appeared to be yet another phosphorus-containing material resulting from the impregnation process.

Solid state ^{31}P MAS NMR spectroscopy indicated that there were two types of phosphorus in $[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$. These peaks observed at 14 and 34 ppm could be due to the presence of both the *trans*- and *cis*-complexes on the surface. Its solution spectrum gave a singlet at 17.8 ppm for the *trans*-complex, and the *cis*-complex has been reported at 34.1 ppm [25]. Analysis after an induction period of 0.25 h indicated that the signals at 14 and 34 ppm had diminished and a new peak was observed at 59 ppm. The peak at 59 ppm has a similar chemical shift to that observed for the catalyst formed from $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ after induction and in the active and used catalysts, and has been attributed to the formation of a phosphine- and bromide-containing palladium complex that is the active site for the hydrogenation of cinnamaldehyde to hydrocinnamaldehyde. Since microanalysis and XPS studies have shown that the catalyst formed from $[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$ is also a phosphine- and

chloride-containing palladium complex that is active in the hydrogenation of cinnamaldehyde to hydrocinnamaldehyde, it is likely that the peak at 59 ppm can be attributed to the formation of a similar active species. Phenylpropanol is sometimes detected using this catalyst, and $\text{Pd}(0)$ sites are normally required for this, but the inability to generate this reproducibly indicates that these sites are probably randomly generated and few in number. The retention of signals at 14 and 34 ppm after the induction period may indicate that some of the impregnated complex is retained in the bulk of the catalyst. A further signal at 36 ppm was detected in the active catalyst formed from $[\text{PdCl}_2(\text{PEt}_3)_2]/\text{SiO}_2$ after cinnamaldehyde hydrogenation for 2 h, and after 48 h reaction when the catalyst had undergone substantial deactivation only two signals were seen in the ^{31}P MAS NMR at 36 and 58 ppm. A similar low field signal was observed in the catalyst formed from $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ after use, and XPS studies have shown that this inactive palladium species is $\text{Pd}(0)$.

3.4. Transmission electron microscopy

TEM studies of catalysts prepared from $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$, $[\text{Pd}_2\text{Cl}_4(\text{PMe}_3)_2]/\text{SiO}_2$ and Pd/SiO_2 and used in the hydrogenation of cinnamaldehyde were carried out in order to detect any correlation between their observed catalytic behaviour and any changes in palladium particle size. Analysis of $[\text{Pd}_2\text{Br}_4(\text{PMe}_3)_2]/\text{SiO}_2$ showed that the palladium was distributed uniformly across the surface of the silica. Particle sizes ranged from 2.9 to 8.1 nm and the mean particle size was estimated as 4.7 ± 0.2 nm based on the measurement of 100 particles. After cinnamaldehyde hydrogenation for 3 h the particles had aggregated into clusters which were generally in the size range 10–39 nm, though some larger clusters with particle sizes of up to 170 ± 9 nm were also present. The mean particle size was estimated as 20.5 ± 1.0 nm based on the measurement of 25 particles.

Analysis of the catalyst formed from $[\text{Pd}_2\text{Cl}_4(\text{PMe}_3)_2]/\text{SiO}_2$ after it had been used in the hydrogenation of cinnamaldehyde for 2 h (i.e. the active catalyst), showed that it was comprised of particles ranging from 6.1 to 41.5 nm in size, and the mean particle size was estimated to be 22.5 ± 1.1 nm based on the measurement of 100 particles. A few

isolated clusters of up to 133 ± 6.7 nm were also observed.

The standard Pd/SiO₂ catalyst and active Pd/SiO₂ catalyst after 23 h on line were also analysed by TEM. The Pd/SiO₂ catalyst was found to contain both large and small particles. The particle size distribution was narrower in the active catalyst but there was some evidence of clustering.

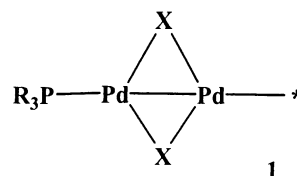
4. Discussion

The dipalladium compounds [Pd₂X₄(PR₃)₂]/SiO₂ (where X = Cl or Br and R = Me or Et) and mononuclear [PdCl₂(PR₃)₂]/SiO₂ are precursors to active catalysts for the hydrogenation of cinnamaldehyde but behave quite differently to the standard Pd/SiO₂ catalyst which is also an active catalyst for this reaction. The bromide complexes retain their integrity when supported on silica, although the chloride complexes are more labile. The dinuclear chlorides partially react with hydroxide groups on the support to produce some Pd(0) species. This is consistent with our observed failure to remove all of the complex into solution by deliberate solvent leaching at the catalyst precursor stage.

At the start of the catalysis procedure, all of the supported palladium complexes turn black, undergo an induction period of inactivity, have an active phase of up to about 48 h under the conditions used and are finally deactivated. These changes are accompanied by lay-down of a hydrocarbonaceous overlayer. The bromide compounds produce active sites selective to the hydrogenation of cinnamaldehyde to hydrocinnamaldehyde. The dinuclear chloride complexes form two active site types, one equivalent to the bromo compounds and selective to hydrocinnamaldehyde production and the other which converts cinnamaldehyde to phenylpropanol at one visit. The mononuclear chloride complexes are rather ambiguous in their behaviour, and the iodo complexes are very unreactive. It has been noted previously that surface deposits of iodide have a strong inhibitory role in palladium-catalysed hydrogenations [18].

We suggested previously that the activation and subsequent deactivation of the catalysts was controlled by the development of the hydrocarbonaceous overlayer [13] but noting its growth from induction and

persistence through the active and de-active stages we now believe that other factors must contribute. The partial loss of halide and phosphine by the active stage is indicative of reduction of the Pd(II) precursor. The XPS data suggest that the species present at the active phase responsible for the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde contains either Pd(II) or Pd(I), and with microanalytical data we conclude that it must be a Pd(I) compound. ³¹P NMR measurements indicate a single, diamagnetic species so a Pd–Pd bonded compound like that below is indicated.



There are many precedents for such Pd–Pd bonded species [26,27] and in particular compounds with halides spanning the Pd–Pd links are known [28,29]. The resolution of the XPS experiments do not allow us to differentiate between unsymmetrical species of the type drawn and those in which the Pd atoms are identical. It is also quite feasible that the remaining phosphine of the Pd₂P core unit does not retain its integrity, allowing for the possibility of PR₂ bridging units. Cleavage of aryl or alkyl groups from tertiary phosphines under mild, catalytic hydrogenation conditions has been observed [24].

Reductions of Pd(II) compounds under hydrogenation conditions are, of course, very common and we note that some compounds, for example [Pd₂(OAc)₄(PPh₃)₂] with one phosphine per palladium, are reduced by an autocatalytic route involving binuclear Pd–Pd bonded species related to compound **1**. These processes display an induction period [24]. We therefore suggest that the catalytic induction period observed in our reactions is caused by an autocatalytic reduction of the Pd(II) precursor to active Pd(I) catalysts of the type above.

By the inactive stage, each catalyst has produced a significant amount of Pd(0) species. It is clearly different to the active Pd(0) catalyst in the standard Pd/SiO₂ catalysts, and is probably poisoned by phosphine or a reaction product from it. The NMR and XPS data do, however, indicate that some of the

Pd(I) species of the active catalysts also survives at this stage, and must itself be inactive after this time lapse. The hydrocarbonaceous overlayer is also still present, but does not seem to grow significantly from the active to de-activated stages. We cannot rule out, therefore, the possibility that the deactivation is assisted by a restructuring of the overlayer, despite the relatively mild conditions of our reactions. Such activity changes associated with overlayer restructuring are well documented [15]. The TEM evidence of changing particle size is indicative of a restructuring process.

The behaviour of the mononuclear complexes is puzzling. We suspect that the non-reproducible nature of the catalysts from the chlorides $[\text{PdCl}_2\text{L}_2]$ is due to the tendency of these compounds to reversibly lose traces of PR_3 in solution, leading to isomerisations and a redistribution of phosphine, and the presence in solution of palladium compounds with one, two and three phosphines attached. The NMR data support such an intricacy. Thus, the impregnating solutions could contain any of *cis*- or *trans*- $[\text{PdCl}_2(\text{PR}_3)_2]$, $[\text{PdCl}(\text{PR}_3)_3]^+$, or $[\text{PdCl}_3(\text{PR}_3)_3]^-$, though fewer were detected by NMR at least in the more selective catalysts. The composition of catalysts prepared by impregnating these solutions on silica would be impossible to control, and this, coupled to the ease of reduction of chloropalladium compounds, can lead to very variable catalyst composition. The mononuclear chloro complexes are not converted to any Pd(0) material simply on contact with surface hydroxides. This is compatible with the reported higher stability of complexes with two phosphines per palladium.

The mononuclear bromide complexes are less labile, and less prone to H_2 reductions. It is entirely feasible that any small loss of PR_3 would lead to a catalyst analogous to those from the binuclear bromo compounds, hence their low activity but high selectivity in operation.

Unlike the catalysts derived from the molecular phosphine complexes, Pd/SiO₂ catalysts retains their reactivity even after extensive use, and despite the formation of a hydrocarbonaceous overlayer. This could signify a different role for the overlayer with these catalysts. These reactions proceeded sequentially and without any induction period by hydrogenation of cinnamaldehyde to hydrocinnamaldehyde and its

subsequent hydrogenation to phenylpropanol. The rate of reaction was also much faster on the Pd/SiO₂ catalyst than on any of the catalysts prepared from the supported complexes.

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References

- [1] J.C. Bailar, *Plat. Met. Rev.* 15 (1971) 2.
- [2] R. van Asselt, C.J. Elsevier, *J. Mol. Catal.* 65 (1991) L13.
- [3] J.A. Davies, F.R. Hartley, S.G. Murray, *J. Mol. Catal.* 10 (1981) 171.
- [4] K. Kaneda, M. Terasawa, T. Iminaka, S. Teranishi, *Chem. Lett.* (1975) 1005.
- [5] C. Andersson, R. Larsson, *J. Am. Oil Chem. Soc.* 58 (1981) 675.
- [6] G. Carturan, G. Strukul, *J. Catal.* 57 (1979) 516.
- [7] M.S. Scurrell, *Catalysis, Chem. Soc. Spectrosc. Per. Rep.* 2 (1978).
- [8] K. Kochloeff, W. Liebelt, H. Knozinger, *J. Chem. Soc., Chem. Commun.* (1977) 510.
- [9] K.G. Allun, R.D. Hancock, I.V. Howell, T.E. Lester, S. McKenzie, R.C. Pitkethly, P.J. Robinson, *J. Organomet. Chem.* 107 (1976) 393.
- [10] K.R. Kumar, B.M. Chaudary, Z. Jamil, G. Thygarajan, *J. Chem. Soc., Chem. Commun.* (1986) 130.
- [11] S. Kowalak, R.C. Weiss, K.J. Bulkus, *J. Chem. Soc., Chem. Commun.* (1991) 57.
- [12] F.R. Hartley, *Supported Metal Complexes*, Riedel, Holland, 1985.
- [13] G.R. Cairns, R.J. Cross, D. Stirling, *J. Catal.* 166 (1997) 89.
- [14] R.K. Iler, *The Chemistry of Silica: Solubility, Polymerisation, Colloidal and Surface Properties and Biochemistry*, 2nd Edition, Wiley, New York, 1969.
- [15] G. Webb, *Catal. Today* 7 (1990) 139 and references therein.
- [16] G. Kumar, J.R. Blackburn, R.G. Albridge, W.E. Moddeman, M.M. Jones, *Inorg. Chem.* 11 (1972) 296.
- [17] V.I. Nefedov, Ya.V. Salyn, I.I. Moiseev, A.P. Sadovskii, A.S. Berenbljum, A.G. Knizhnik, S.L. Mund, *Inorg. Chim. Acta* 35 (1979) L343.
- [18] J. Kiviahio, T. Hanaoka, Y. Kubota, Y. Sugi, *J. Mol. Catal.* (A) 101 (1995) 25.
- [19] D. Briggs, M.P. Seah, *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, Wiley, Chichester, 1983.

- [20] B.M. Choudary, K.R. Kumar, Z. Jamil, G. Thyagarajan, J. Chem. Soc., Chem. Commun. (1985) 931.
- [21] D.W. Goodman, J.E. Houston, *Science* 236 (1987) 403.
- [22] V.V. Grushin, H. Alper, *Organometallics* 12 (1993) 1890.
- [23] G. Papadogianakis, J.A. Peters, L. Maat, R.A. Sheldon, J. Chem. Soc., Chem. Commun. (1995) 1105.
- [24] A.S. Berenblyum, A.G. Knizhnik, S.L. Mund, I.I. Moiseev, *J. Organomet. Chem.* 234 (1982) 219.
- [25] N.W. Alcock, T.J. Kemp, F.L. Wimmer, *J. Chem. Soc., Dalton Trans.* (1981) 635.
- [26] G. Wilkinson, R.D. Gillard, J.A. McLverty (Eds.), *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon Press, Oxford, 1987.
- [27] E.W. Abel, F.G.A. Stone, G. Wilkinson, R.J. Puddephatt (Eds.), *Comprehensive Organometallic Chemistry II*, Vol. 9, Pergamon Press, Oxford, 1995.
- [28] A. Kuhn, Ch. Burschka, H. Werner, *Organometallics* 1 (1982) 496.
- [29] V. Dura-Vila, D.M.P. Mingos, R. Vilar, A.J. White, D.J. Williams, *J. Chem. Soc., Chem. Commun.* (2000) 1525.