XVIII, 87157-26-4; XIX, 87157-12-8; XX, 87157-13-9; XXI, 87157-14-0; XXII, 87157-15-1; XXIII, 87157-16-2; XXIV, 87157-17-3; XXV, 87157-18-4; XXVI, 87205-51-4; XXVII, 87157-19-5; XXVIII, 68981-71-5; XXIX, 87157-03-7; XXX, 87157-21-9; XXXI, 61994-85-2; XXXII, 87157-22-0; XXXIII, 87157-23-1; XXXIV, 55075-35-9; XXXV, 55075-34-8; XXXVI, 87157-24-2; XXXVII, 87157-25-3; $Mn(NO_3)_2{\cdot}6H_2O$, 17141-63-8; $Co(NO_3)_2{\cdot}6H_2O$, 10026-22-9; $Ni(NO_3)_2{\cdot}8H_2O$, 18534-07-1; $Th(NO_3)_4{\cdot}3H_2O$, 87174-21-8; $UO_2(H_2O)_4{}^{2+}{\cdot}2NO_3{}^-$, 87206-06-2; $Mn(H_2O)_6{}^{2+}{\cdot}2NO_3{}^-$, 42029-67-4; $Co(H_2O)_6{}^{2+}{\cdot}2NO_3{}^-$, 23730-86-1; $Ni(H_2O)_6{}^{2+}{\cdot}2NO_3{}^-$, 10171-09-2; $Th(H_2O)_3(NO_3)_4$, 61525-13-1; 18-crown-6, 17455-13-9; 18-crown-6 potassium acetate, 53585-81-2.

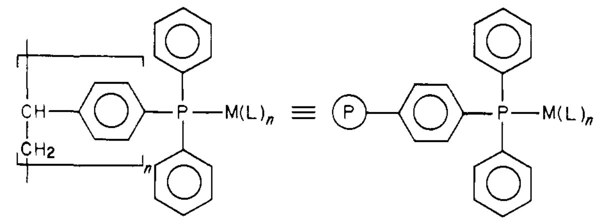
Polymer-Immobilized Complexes of Platinum(II): Their Precursors and Preparation Studied by High-Resolution Solid-State ^{31}P NMR Using Magic-Angle Spinning Techniques

C. A. Fyfe,* H. C. Clark, J. A. Davies, P. J. Hayes, and R. E. Wasylishen[1]

Contribution from The Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada. *Received April 9, 1982*

Abstract: Solid-state ^{31}P NMR employing high-power proton decoupling, cross-polarization, and magic-angle spinning has been used to characterize various polymer-immobilized phosphine ligands and their platinum complexes. The reduction of polymer (polystyrene cross-linked with divinylbenzene) bound phosphine oxide, to tertiary phosphine, was monitored by these solid-state ^{31}P NMR techniques. The immobilization of a platinum complex, through reaction with the immobilized tertiary phosphine ligands, and the success of an alternate preparation of such a system were also monitored by this NMR method. To demonstrate the versatility of the NMR technique, platinum complexes were coordinated to 4-poly(vinyl)pyridine, through the pyridine nitrogen, and the outcome of this process was elucidated from the solid-state ^{31}P spectra of triphenylphosphine ligands that were coordinated to the platinum but were not part of the polymer support.

In recent years there has been a great deal of research on polymer-immobilized transition-metal catalysts. In many cases these catalysts involve a cross-linked (with 2–20% divinylbenzene), insoluble polystyrene backbone linked to a previously homogeneous transition-metal catalyst through a phosphorus ligand on the polymer (**1**).



1, M = metal centre; L = ligand

These "heterogenized" catalysts offer the advantages of insoluble heterogeneous catalysts, such as ease of separation, but still retain the high selectivity of homogeneous catalysts. The fixed position of the catalyst on the polymer may also impart greater site isolation and, in some cases, this can drastically increase the activity of the catalyst. Extensive study has been done on the preparation of these systems, and their activity, selectivity, and other properties have been well documented. A number of general reviews that delineate the state of the art in these areas have been published,[2-8] but as yet little success has been achieved in determining either their general structure or the structure at the active site. Such techniques as elemental analysis, microprobe analysis,[9] Fourier transform infrared spectroscopy (FTIR),[10] X-ray photoelectron spectroscopy (ESCA),[11] ESR,[12,13] and photoacoustic spectroscopy[14] have been employed with varying degrees of success. In principle, ^{31}P NMR spectroscopy is an attractive technique with which to investigate these species. The high abundance of ^{31}P (100%, $I = {}^1/_2$) and the generation of metal–^{31}P couplings (for $I = {}^1/_2$ metals, such as ^{103}Rh and ^{195}Pt) make this method highly sensitive and extremely elucidative for studies of homogeneous solutions of transition-metal complexes. The application of this technique, however, to polymer-immobilized systems has met with only limited success. Recent high-resolution solution ^{31}P NMR, on solvent-swollen polymers, by Grubbs et al.[15] reports that a signal observed for an uncoordinated immobilized phosphorus group subsequently disappeared upon coordination to a rhodium complex (with no new peaks appearing). Other related work has been reported by Naaktgeboren et al.[16,17] A general explanation[18] of

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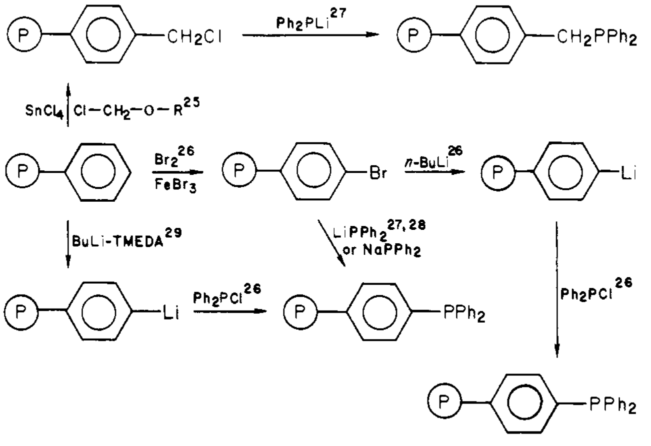
Scheme I



the phenomenon may be that the coordination of the metal center restricts the motion of the phosphorus so severely as to prevent its detection in a ^{31}P NMR high-resolution solution spectrum by a number of possible line-broadening mechanisms, and this lack of motion precludes the use of high-resolution techniques in this area in general. Naaktgeboren's group went on to examine linear polystyrene polymers (via high-resolution solution ^{31}P NMR of these solvent-swollen polymers) containing regularly occurring phosphorus monomers but were only able to observe 5% of the phosphorus after coordination.[17] The properties of the observable, and probably more mobile, ligands cannot, however, be assumed to be truly representative of the bulk of the polymer, which in this case was not cross-linked and thus not a totally insoluble polymer support.

To date very little research has been done on these systems by solid-state ^{31}P NMR spectroscopy employing cross-polarization[19] with magic-angle spinning[20] (CP/MAS). Selected ^{31}P spectra of homogeneous transition-metal complexes appear in two recent communications.[21,22] We have recently reported an extensive study of tertiary phosphines, transition-metal phosphine complexes, and their analogues immobilized on glass and silica surfaces using solid-state CP/MAS ^{31}P NMR.[23] A number of tertiary phosphine ligands, phosphine oxides, and tertiary phosphine complexes of transition metals were examined by using both solid-state CP/MAS ^{31}P NMR and high-resolution solution ^{31}P NMR. The number of spectra obtained during this study[23] confirmed that, between the two techniques, the chemical shifts and coupling constants were directly comparable for each given compound and that solid-state CP/MAS ^{31}P NMR may, in general, be used for purposes of structural elucidation of immobilized catalysts.

In the present work, high-resolution solution ^{31}P NMR and solid-state CP/MAS ^{31}P NMR have been used to explore further the area of immobilized catalysts, concentrating on complexes supported on organic polymers functionalized with tertiary phosphine and pyridine moieties. Throughout this work we have examined complexes of platinum(II) as model systems. The presence of ^{195}Pt (33.8% abundance, $I = {}^1/_2$) gives rise to metal–phosphorus couplings, known from high-resolution solution ^{31}P NMR to be sensitive to the geometry of the complexes and environment of the ^{31}P nucleus. Complexes of platinum(II), as opposed to those of rhodium(I), were studied initially as, despite the higher catalytic activity of many rhodium(I) complexes, the magnitude of $^1J(^{103}\mathrm{Rh},^{31}\mathrm{P})$ is small compared with $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$. Preliminary results from this work have been reported.[24]

Scheme II

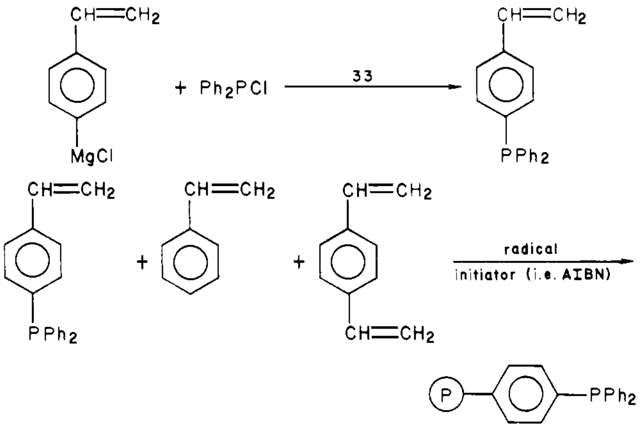


Table I. Summary of Solid-State CP/MAS ^{31}P NMR and High-Resolution Solution ^{31}P NMR Chemical Shift Data (with Respect to External 85% Phosphoric Acid) for Functionalized Polymers and Reference Compounds

	CP/MAS ^{31}P NMR		solution ^{31}P NMR	
sample	δ/ ppm	$\nu_{1/2}$/ Hz	δ/ ppm	$\nu_{1/2}$/ Hz
(*p*-vinylphenyl)diphenylphosphine	−7.0	100	−5.8	20[a]
(*p*-vinylphenyl)diphenylphosphine oxide	23.6	320		
commercial polymer-bound (polystyrene cross-linked with 2% divinylbenzene) triphenylphosphine	26.3, −6.2	292, 330		
commerical polymer-bound (polystyrene cross-linked with 20% divinylbenzene) triphenylphosphine	27.3, −4.3	365, 340		
polymer of composition 90% styrene, 2% divinylbenzene, 8% (*p*-vinylphenyl)diphenylphosphine	25.8, −5.1	360, 290		

[a] Solution spectrum in $CDCl_3$.

Results and Discussion

A. Preparation and Characterization of Functionalized Polymers. In previous studies, as mentioned earlier, the preparation of immobilized catalyst systems has been examined in depth. Research in this field has concentrated on synthesizing functionalized polymers by attaching phosphine ligands to polymer matrices. Once prepared, these polymers can be reacted with metal complexes to yield the immobilized catalysts.

In general, two methods have been used to prepare such functionalized polymers. The first, and most commonly used, procedure involves performing a chemical reaction of polystyrene–divinylbenzene beads to introduce the phosphorus group. Scheme I, outlines the major routes used to achieve this. Great care must be taken to employ reactions that ensure the absence of unwanted surface-bonded species[30] and a uniform ligand distribution.[29] Problems may also arise from surface and texture changes of the polymer during the chemical reactions.[7]

The second method of preparing the functionalized polymer has been to synthesize a functionalized monomer[31] and then co-

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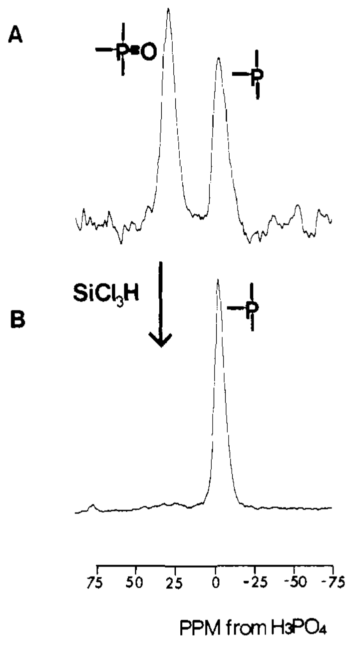

Figure 1. (A) Solid-state CP/MAS ^{31}P NMR spectrum of a sample of polymer-bound (polystyrene cross-linked with 2% divinylbenzene) triphenylphosphine; 2870 scans and 50-Hz line broadening. (B) Solid-state CP-MAS ^{31}P NMR spectrum of polymer-bound triphenylphosphine after trichlorosilane treatment and Soxhlet extraction; 2250 scans and 30-Hz line broadening.

polymerize[32] it with styrene and divinylbenzene as outlined in Scheme II.

Functionalized polymer samples, prepared by both methods, were analyzed by solid-state CP/MAS ^{31}P NMR. High-resolution solution ^{31}P NMR spectra of these polymers, as solvent-swollen solids, were also run for comparison (see Table I for summary of results). The solid-state CP/MAS ^{31}P NMR spectrum of (*p*-vinylphenyl)diphenylphosphine itself consisted of a single resonance at −7.0 ppm (relative to phosphoric acid). The solid-state CP/MAS ^{31}P NMR spectra of commercial samples of polymer-immobilized triphenylphosphine (prepared via one of the routes in Scheme I) showed two resonances (see Figure 1a for example of spectrum). The resonance peaks at −4.3 and −6.2 ppm, in the 20% and 2% cross-linked samples, respectively, could be identified as the immobilized tertiary phosphine but in both cases another resonance appeared at approximately 25 ppm. Because the presence of phosphine oxide was suspected, the solid-state CP/MAS ^{31}P NMR spectrum of (*p*-vinylphenyl)diphenylphosphine oxide was obtained for comparison; a resonance peak at 23.5 ppm confirmed that a large percentage of the phosphorus in these samples was present as phosphine oxide.

Samples of functionalized polymer prepared by Scheme II were also analyzed spectroscopically (see Table I). It was found that when benzoyl peroxide was employed as the radical initiator, the suspension copolymerization was sometimes unsuccessful and solid-state CP/MAS ^{31}P NMR spectra showed a large proportion of phosphine oxide. This suggested that the benzoyl peroxide may be enhancing the oxidation of the phosphine rather than initiating the polymerization and so azobis(isobutyronitrile) (AIBN) was substituted as the initiator. The resulting polymers had lower phosphine oxide levels than both the polymers prepared by using benzoyl peroxide as initiator and the commercial samples studied.

B. Conversion of Polymer-Immobilized Phosphine Oxide to Tertiary Phosphine. In order to optimize the efficiency of the reaction between the functionalized polymer and metal complex, it was necessary to convert the immobilized phosphine oxide to tertiary phosphine. Considerable research has been done on the reduction of tertiary phosphine oxides.[34,35] Typically, silane reagents, especially trichlorosilane, are reacted with the oxide to accomplish the reduction via eq 1.

$$R_3P{=}O + 2SiHCl_3 \rightarrow R_3P \rightarrow SiCl_4 + H_2 + (Cl_2SiO) \qquad (1)$$

These reductions are well-known for free phosphine oxides but have only recently been reported[23] for glass-immobilized phosphine oxides. No report has previously been made of the reduction of polymer-bound phosphine oxides by this method. Samples of functionalized polymer that were largely in the phosphine oxide form, according to the solid-state CP/MAS ^{31}P NMR spectrum, were treated with trichlorosilane in benzene. In all cases a dramatic decrease in the size of the phosphine oxide resonance in the solid-state CP/MAS ^{31}P NMR spectrum was observed after silane treatment, and in the most instances the reduction was virtually quantitative (see Figure 1 for comparison of spectra). This appears to be a direct, practical method for ensuring that all phosphorus is present as the tertiary phosphine and should be incorporated into preparative schemes for the synthesis of immobilized transition-metal catalysts.

C. Preparation of Polymer-Supported Platinum Complexes by Reaction of a Platinum Complex with Immobilized Phosphorus Ligands. The final step in the preparation of polymer-immobilized catalysts, as previously outlined, is the reaction between a free metal complex and polymer-immobilized phosphorus ligand. Polymer-supported catalysts of the general type considered here, derived from the reaction of $[PtCl_2(NCPh)_2]$ with immobilized tertiary phosphines, have previously been studied as catalysts for the hydrogenation of unsaturates.[36,37] Solid-state CP/MAS ^{31}P NMR spectra were used to observe the conversion of functionalized polymer to immobilized complex.

Samples of functionalized polymer, before and after treatment with trichlorosilane, were reacted with $[PtCl_2(NCPh)_2]$ to determine the effect of phosphine oxide on the reaction. The untreated samples, when reacted with the metal complex, showed only a broad resonance due to phosphine oxide in the solid-state CP/MAS ^{31}P NMR spectrum. The treated samples, on the other hand, displayed a pattern of resonances similar to those found in the high-resolution ^{31}P NMR of the analogous free metal complex. The reaction thus appears to be inhibited by the presence of phosphine oxide, and silane treatment, prior to the reaction, seemed essential for success.

The reaction of $[PtCl_2(NCPh)_2]$ with a treated, functionalized polymer was examined in detail by solid-state CP/MAS ^{31}P NMR spectroscopy. Initial reaction of the polymer with the complex yielded a solid whose spectrum confirmed the success of the immobilization (see Figure 2A for spectrum and Table II for summary of results), but a slight blackening of the product seemed to indicate a partial decomposition of the complex (probably due to interaction with remaining silane). By comparison of the spectrum with that of the supported phosphine before reaction, the resonance at −5.4 ppm (marked with an arrow in Figure 2) was identified as uncomplexed, immobilized tertiary phosphine. Comparison with the high-resolution solution ^{31}P NMR spectrum of *trans*-$[PtCl_2(PPh_3)_2]$ (19.8 ppm, $^1J(^{195}Pt,^{31}P)$ = 2637 Hz) and the solid-state CP/MAS ^{31}P NMR spectrum of *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ (15.5 and 11.8 ppm, $^1J(^{195}Pt,^{31}P)$ = 3516 and 3570 Hz; see Figure 4A and Table III) demonstrates that the resonances at 20.9 and 11.8 ppm arise from the immobilized complex. The appearance of more than one peak in this region with more than one pair of associated ^{195}Pt–^{31}P satellites indicates that a mixture of cis and trans isomers is present. Clearly the spectrum shown in Figure 2A shows that a complex mixture of surface-bound products is formed. The resulting spectrum cannot be interpreted without ambiguity, and species other than *cis*- and

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Table II. Summary of Solid-State CP/MAS ^{31}P NMR and High-Resolution Solution ^{31}P NMR Chemical Shift Data (with Respect to External 85% Phosphoric Acid) for Trichlorosilane-Treated Polymers, Treated Polymers Reacted with a Platinum Complex and Reference Compounds

	CP/MAS ^{31}P NMR			solution ^{31}P NMR		
sample	δ	$\nu_{1/2}$/ Hz	^1J-(^{195}Pt-^{31}P)/ Hz	δ	$\nu_{1/2}$/ Hz	^1J-(^{195}Pt-^{31}P)/ Hz
cis-$[PtCl_2(PPh_3)_2]$[a]	12.9		3877	14.3		3673
	8.6		3623			
trans-$[PtCl_2(PPh_3)_2]$[b]	20.9		2695	19.8		2637
	19.8		2559			
polymer of composition 90% styrene, 2% divinylbenzene, and 8% (*p*-vinylphenyl)diphenylphosphine treated with trichlorosilane[c]	−4.8	255		−6.9	20	
polymer of composition 90% styrene, 2% divinylbenzene, and 8% (*p*-vinylphenyl)diphenylphosphine treated with trichlorosilane and then initially reacted with $[PtCl_2(NCPh)_2]$	20.9	470	2550[d]			
	12.4		3550			
	−5.4	330				
polymer of composition 90% styrene, 2% divinylbenzene, and 8% (*p*-vinylphenyl)diphenylphosphine treated with trichlorosilane, initially reacted with $[PtCl_2(NCPh)_2]$ and then reacted a second time with $[PtCl_2(NCPh)_2]$	21.4	560	2590[d]			
	11.8		3550	~19.8[e]	600	

[a] Solution spectrum in $CDCl_3$, ref 22 for both solid and solution. [b] Solution spectrum in $CDCl_3$, ref 22 for solid and ref 50 for solution spectrum. [c] Solution spectrum in C_6D_6. [d] Estimated values. [e] Solution spectrum in C_6D_6.

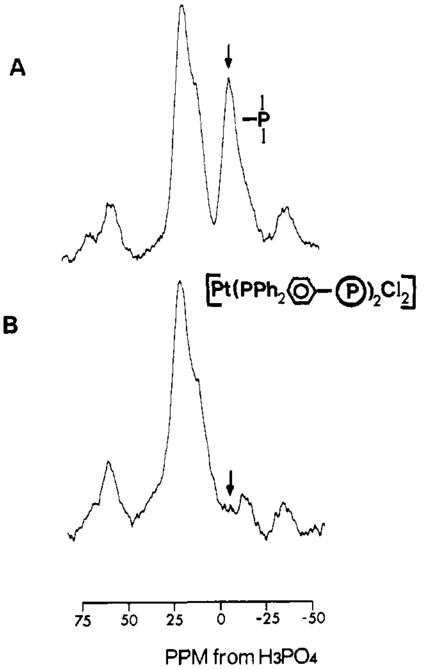

Figure 2. (A) Solid-state CP/MAS ^{31}P NMR spectrum of a copolymer of 90% styrene, 2% divinylbenzene, and 8% $CH_2{=}CHC_6H_4PPh_2$ partially reacted with $[PtCl_2(NCPh)_2]$ and Soxhlet extracted; 102 848 scans and 20-Hz line broadening. (B) Solid-state CP/MAS ^{31}P NMR spectrum of the copolymer completely reacted with $[PtCl_2(NCPh)_2]$ and Soxhlet extracted; 59 794 scans and 30-Hz line broadening.

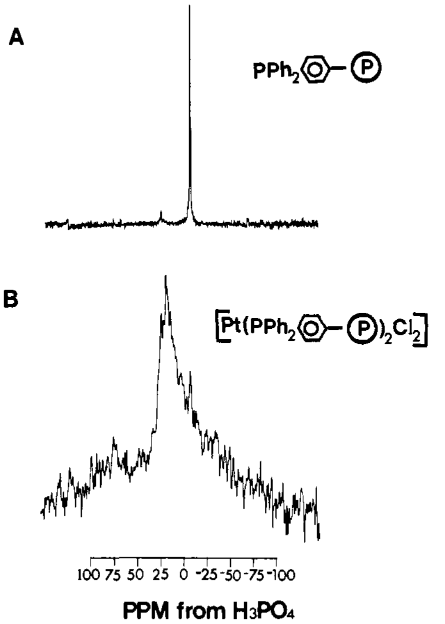

Figure 3. (A) High-resolution solution ^{31}P NMR spectrum of a copolymer of 90% styrene, 8% $CH_2{=}CHC_6H_4PPh_2$, and 2% divinylbenzene after trichlorosilane treatment; 10 232 scans and 2.0-Hz line broadening. (B) High-resolution solution ^{31}P NMR spectrum of copolymer in (a) after complete reaction with $[PtCl_2(NCPh)_2]$; 110,048 scans and 20-Hz line broadening.

trans-$[PtCl_2(PR_3)_2]$ and free PR_3 units may well be present. Well-defined products have been prepared and characterized unambiguously by other routes (vide infra), demonstrating that this particular pathway is not a synthetically clean reaction sequence.

The partially reacted, functionalized polymer was treated again with $[PtCl_2(NCPh)_2]$ and the solid-state CP/MAS ^{31}P NMR spectrum of the resulting solid was compared to the solid-state CP/MAS ^{31}P NMR spectrum of the polymer after the initial treatment (see Figure 2 for comparison). The spectra of the two polymers were very similar except that in the case of the re-treated polymer the resonance at −5.4 ppm, due to uncoordinated phosphine (marked by an arrow in Figure 2B), was no longer visible, indicating that reacting the polymer under more vigorous conditions caused all available phosphine sites to be coordinated.

Elemental analyses, to determine the percentage of phosphorus by weight (and percentage of platinum in cases where platinum was present), were performed on the polymer-supported ligand before and after reaction with the metal complex. Prior to reaction 1.3% P was found in the sample (expected 2.0% P; 8% (*p*-vinylphenyl)diphenylphosphine, by molar ratio, polymerized with styrene and DVB) while after reaction there was 0.9% P and 6.94% Pt (if 0.9% P is present, the expected percent Pt is 2.7%). This discrepancy in the P/Pt ratio can be explained in terms of some decomposition of the complex by silane and the substantial inaccuracies previously encountered by others when analyzing polymer-bound metal catalysts[38].

High-resolution solution ^{31}P NMR spectra (of solvent swollen solids) were run on the trichlorosilane treated, functionalized

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Table III. Summary of Solid-State CP/MAS ^{31}P NMR and High-Resolution Solution ^{31}P NMR Chemical Shift Data (with Respect to External 85% Phosphoric Acid) for *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ Derived Copolymers and Reference Compounds

	CP/MAS ^{31}P NMR			solution ^{31}P NMR		
sample	δ	$\nu_{1/2}$/Hz	^1J-(^{195}Pt-^{31}P)/Hz	δ	$\nu_{1/2}$/Hz	^1J-(^{195}Pt-^{31}P)/Hz
cis-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]^a$	11.8, 15.6	120 120	3516, 3750	13.6	15	3672
polymer of composition 94% styrene, 2% divinylbenzene, and 4% *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]^b$	16.6	365	3691	13.7, 14.6, 19.5	65 60	3652 3660 2651
polymer of composition 77% styrene, 15% divinylbenzene, and 8% (*p*-vinylphenyl)diphenylphosphine after trichlorosilane treatment^c	−6.2	310		−7.2	550	
polymer of composition 81% styrene, 15% divinylbenzene, and 4% *cis*-$[PtCl_2(PPh_2(PPh_2C_6H_4CH{=}CH_2)_2]$	15.6	370	3691	~14.6^d	900	
polymer of composition 62% styrene, 30% divinylbenzene, and 8% (*p*-vinylphenyl)diphenylphosphine after trichlorosilane treatment^c	−5.9	260		−6.4	988	
polymer of composition 66% styrene, 30% divinylbenzene, and 4% *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$	15.5	370	3691	~15.5^d	1100	

[a] Solution spectrum in $CdCl_3$. [b] Solution spectrum in $C_6D_6/CDCl_3$. [c] Solution spectrum in C_6D_6. [d] An excessively broad resonance prevented the accurate measurement of the chemical shift and the $^1J(^{195}Pt$-$^{31}P)$.

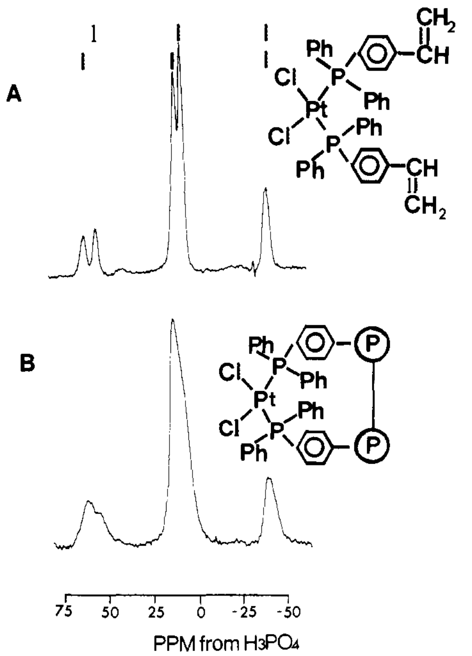
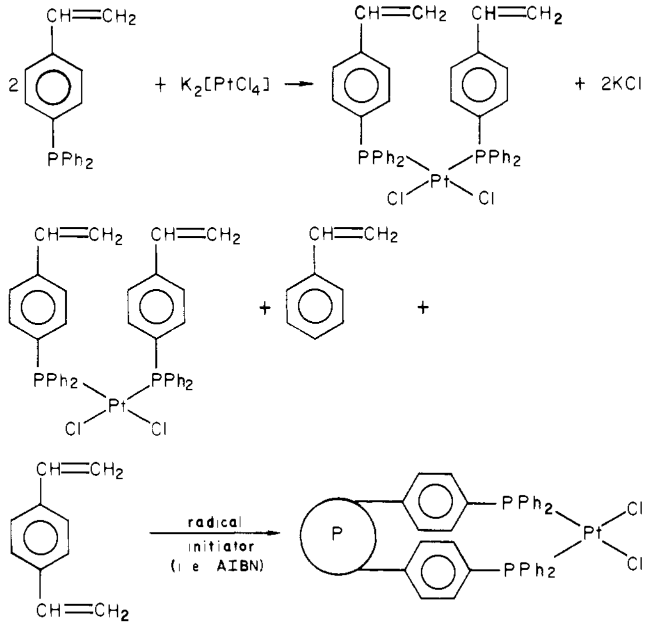


Figure 4. (A) Solid-state CP/MAS ^{31}P NMR spectrum of *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$; 1774 scans and no line broadening. (B) Solid-state CP/MAS ^{31}P NMR spectrum of a copolymer of 65% styrene, 31% divinylbeznene, and 4% *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ after Soxhlet extraction; 36 196 scans and 10-Hz line broadening.

polymer prior to reaction and after vigorous reaction with $[PtCl_2(NCPh)_2]$. The spectrum of the polymer before reaction showed a single, relatively sharp resonance at −6.9 ppm ($\nu_{1/2}$ = 20 Hz; see Table II for summary of results and Figure 3A for spectrum), comparing favorably with the chemical shift, in the solid-state CP/MAS ^{31}P NMR spectrum, of −4.8 ppm. The high-resolution solution ^{31}P NMR spectrum of the polymer after vigorous reaction showed only a broad featureless resonance ($\nu_{1/2}$ = 600 Hz). Small resonances, of negligible area, appear on top of this large broad resonance (see Figure 3B) and most likely represent a small proportion (less than 5% of all phosphorus atoms) of very mobile phosphorus nuclei. This inability to observe any large, relatively sharp resonances due to the immobilized phosphine, upon complexation,[15,18] has been discussed earlier.

D. An Alternate Route to Immobilized Catalysts: Copolymerization of a Functionalized Metal Complex with Styrene and Divinylbenzene To Yield Polymer-Immobilized Catalyst. The success in preparing a functionalized polymer by copolymerizing a functionalized monomer with styrene and divinylbenzene prompted further investigations in this area. The polymer-immobilized catalyst could, in principle, be prepared by copolymerizing a metal complex containing (*p*-vinylphenyl)diphenylphosphine ligands, with styrene and divinylbenzene, rather than preparing a functionalized polymer and then reacting it with a metal complex. Extensive research has already been done using this type of strategy to prepare organometallic vinyl polymers by using vinyl-substituted organometallic monomers.[39-43] Some limited work has been reported on the use of this method in the preparation of the type of phosphine-supported catalyst systems

Scheme III



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discussed in this paper.[44,45] Scheme III illustrates how this approach might be employed.

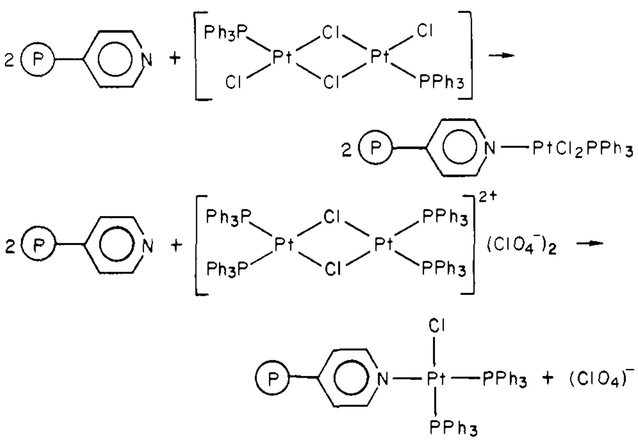
The complex to be copolyermized, *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$, was prepared by reacting (*p*-vinylphenyl)diphenylphosphine with $K_2[PtCl_4]$. The high-resolution solution ^{31}P NMR of this complex consisted of a single, relatively sharp resonance ($\nu_{1/2}$ = 15 Hz) at a chemical shift of 13.6 ppm with an associated pair of ^{195}Pt–^{31}P satellites ($^1J(^{195}Pt,^{31}P)$ = 3762). This spectrum correlated well with the spectrum of *cis*-$[PtCl_2(PPh_3)_2]$ (δ = 15.5, $^1J(^{195}Pt,^{31}P)$ = 3679) (see Table III for summary of results), thus confirming the cis geometry. The solid-state CP/MAS ^{31}P NMR spectrum of the complex showed central resonances due to two types of phosphorus nuclei with chemical shifts of 11.8 and 15.6 ppm and couplings, $^1J(^{195}Pt,^{31}P)$, of 3516 and 3750 Hz (see Figure 4A). The freezing in of a fixed conformation (the equivalence in solution results from rotation about the P–Pt bond) that minimizes the steric effects of the bulky ligands could explain the existence of two inequivalent phosphorus nuclei. This hypothesis is confirmed by a recent X-ray crystal structure of *cis*-$[PtCl_2(PPh_3)_2]$.[46]

The copolymerization of this complex was not possible via the suspension copolymerization reaction used before, as *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ was not soluble in styrene and thus a solution polymerization in chloroform was employed. Problems in precipitating the polymer from solution necessitated preparing more heavily cross-linked samples (15% and 30% divinylbenzene) to confirm the successful incorporation of the complex. For the sake of comparison, functionalized polymers with similar levels of cross-linking were prepared, treated with trichlorosilane, and Soxhlet extracted. The solid-state CP/MAS ^{31}P NMR spectra of the 2%, 15%, and 30% divinylbenzene cross-linked polymers, prepared from copolymerizing the complex, definitely confirmed phosphorus nuclei coordinated to a platinum center (see Figure 4B for spectrum). The central resonance at a chemical shift of 15.5 ppm, for the 2% cross-linked sample, and a coupling, $^1J(^{195}Pt,^{31}P)$, of 3691 Hz confirms that the complex remained in the cis geometry. A shoulder on the central resonance and the appearance of an extra pair of ^{195}Pt–^{31}Pt satellites imply that the two cis phosphorus ligands are still not completely equivalent (see Figure 4 for comparison of spectra of complex and resulting copolymer). This is possible if the steric effect of the two bulky cis ligands still causes a nonequivalence even though now part of a polymer. Rigorous Soxhlet extraction of 15% and 30% cross-linked samples was done and the spectra, before and after extraction, remained the same, thus confirming the successful incorporation of the complex.

Elemental analyses yielded values for the immobilized ligands of 1.3% P (2% DVB), 1.3% P (15% DVB), and 1.5% P (30% DVB) compared with the expected results for all three samples of 2.0% P. The results for the polymers prepared by direct incorporation of metal complex were less reliable: 2.50% P, 8.81% Pt (2% DVB, which could not be Soxhlet extracted due to its soluble nature, for 2.50% P present one would expect 7.9% Pt); 2.4% P, 3.24% Pt (15% DVB; for 2.4% P present one would expect 7.6% Pt); and 1.45% P, 2.58% Pt (30% DVB; for 1.45% P present then one would expect 4.6% Pt). These values can be compared with the expected result of 1.80% P present, expected from stochiometric reaction of 4% *cis*-$[PtCl_2(p\text{-}CH_2{=}CH(C_6H_4PPh_2)_2]$, by molar ratio, copolymerized with styrene and DVB. The inaccuracy of these results may be due to preferential incorporation of the complex into the polymer and/or the limitations of the analytical techniques.

High-resolution solution (solvent swollen solids) ^{31}P NMR spectra were run of 2%, 15%, and 30% cross-linked samples of the copolymerized complex, and these were compared to spectra of similarly cross-linked samples of trichlorosilane treated, functionalized polymers. Two general trends were observed in these two series of spectra: For the three functionalized polymers there was a broadening of the single resonance, due to the immobilized phosphine ligand, indicating that as the degree of cross-linking increases, the mobility of the phosphorus nuclei decreases. A second trend was apparent when comparing the spectra of similarly cross-linked samples of the functionalized polymer with those of the copolymerized complexes. For samples of identical degrees of cross-linking, the resonances were much broader in the spectra of the copolymerized complexes than in the spectra of the corresponding functionalized polymers, in agreement with the earlier conclusion[18] that when the immobilized phosphine is coordinated, its mobility is greatly restricted.

Scheme IV



Upon closer examination of these series of high-resolution solution ^{31}P NMR spectra, it is seen that only those with the 2% levels of cross-linking have narrow enough resonances to be useful in structural analysis. The spectrum of the copolymerized complex, 2% cross-linked, showed that the majority of the complex was in the cis geometry (13.7 and 14.6 ppm, $^1J(^{195}Pt,^{31}P)$ = 3652 and 3660 Hz, $\nu_{1/2}$ = 65 Hz) but there was also a small proportion of the trans isomer (19.5 ppm, $^1J(^{195}Pt,^{31}P)$ = 2651 Hz, $\nu_{1/2}$ = 60 Hz) and a minute quantity of phosphine oxide. The complex existed only in the cis geometry prior to polymerization, and therefore the presence of some of the *trans* isomer afterwards indicates that some isomerization occurred during the process. This is not an unlikely result, as during the polymerization, radicals are generated at an elevated temperature. This isomerization to the trans isomer was not detected in the solid-state CP/MAS ^{31}P NMR spectrum as the central resonance due to the cis complex was broad enough to obscure any small resonance due to formation of the trans isomer.

Advantages may be gained by direct incorporation. The distribution of metal catalyst can be carefully controlled and the possibility of creating phosphine oxide is minimized since all phosphorus is already four-coordinate. The chance of liberting the metal from the polymer, due to phosphine exchange during catalysis, is also reduced since two phosphorus nuclei are coordinated to each metal center.

E. Detection of Species on Other Polymers via a Phosphine Ligand. In order to demonstrate the versatility of the CP/MAS solid-state ^{31}P NMR technique in examining polymer-immobilized catalysts, a system that does not employ a phosphorus ligand as a link between polymer and complex was studied. 4-Poly(vinyl)pyridine beads (cross-linked) were reacted with both neutral and cationic halide-bridged dimeric platinum complexes such that the nitrogen of the pyridine was directly coordinated to the platinum center (see Scheme IV). The structures of the resulting immobilized complexes were monitored by observing the solid-state CP/MAS ^{31}P NMR spectra of the phosphine ligands coordinated to the metal. These were compared to ^{31}P NMR spectra of the analogous complexes in which the coordinated pyridine is not part of a polymer (see Table IV for summary of results and Figures 5 and 6 for comparison of spectra).

Examination of Figures 5 and 6 shows that the CP/MAS solid-state ^{31}P spectra of the 4-poly(vinyl)pyridine complexes are almost identical with those of the free pyridine complexes. All

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[44] Imperial Chemical Industries, French Patent 2030134.

[45] Imperial Chemical Industries, French Patent 2013481.

[46] Anderson, G. K.; Clark, H. C.; Davies, J. A. Ferguson, G.; Parvez, M., *J. Crystallogr. Spectrosc. Res.*, in press.

Table IV. Summary of Solid-State CP/MAS ^{31}P NMR and High-Resolution Solution ^{31}P NMR Chemical Shift Data (with Respect to External 85% Phosphoric Acid) for 4-Poly(vinyl)pyridine Beads Reacted with Platinum Complexes and for Reference Compounds

	CP/MAS ^{31}P NMR			solution ^{31}P NMR		
sample	δ	$\nu_{1/2}$/Hz	$^1J(^{195}Pt-^{31}P)$/Hz	δ	$\nu_{1/2}$/Hz	$^1J(^{195}Pt-^{31}P)$/Hz
trans-[PtCl$_2$(PPh$_3$)(pyr)]^a	5.6	270	3516	2.3	15	3584
mixture of *cis*- and *trans*-[PtCl$_2$(PPh$_3$)(pyr)]	4.6, 6.2	330	3594 3828	2.4, 7.0	15 10	3584, 3896
[PtCl$_2$(PPh$_3$)(pyrⓅ)]	4.6, 6.3	420	3600^b 3800			
cis-[PtCl(PPh$_3$)$_2$(pyr)]$^+$(ClO$_4$)$^-$ ^{a}	15.6, 6.4	260 295	3809, 3184	14.8, 3.7	15 15	3682, 3222
[PtCl(PPh$_3$)$_2$(pyrⓅ)]$^+$(ClO$_4$)$^-$	16.1, 5.4	265 350	3828 3144	14.3^c 3.7	42 35	3842 3215

^{a} Solution spectrum in CDCl$_3$. ^{b} Estimated values due to overlap of peaks. ^{c} $^2J(^{31}P-^{31}P) = 17$ Hz.

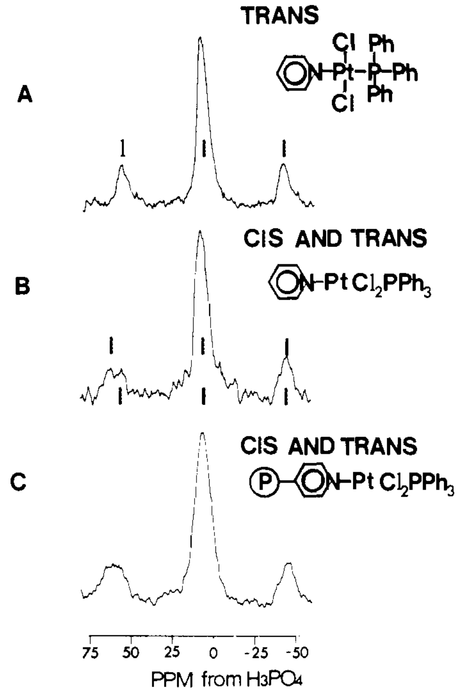

Figure 5. (A) Solid-state CP/MAS ^{31}P NMR spectrum of *trans*-[PtCl$_2$(PPh$_3$)(pyr)]; 8472 scans and 20-Hz line broadening. (B) Solid-state CP/MAS ^{31}P NMR spectrum of a mixture of *cis*- and *trans*-[PtCl$_2$(PPh$_3$)(pyr)]; 9050 scans and 30-Hz line broadening. (C) Solid-state CP/MAS ^{31}P NMR spectrum of a mixture of *cis*- and *trans*-[PtCl$_2$(PPh$_3$)(pyrⓅ)] after Soxhlet extraction; 17518 scans and 30-Hz line broadening.

4-poly(vinyl)pyridine complexes were Soxhlet extracted after reaction so the similarity between their spectra and those of the free pyridine analogues indicates that the immobilization of the complexes on the polymer was successful. The comparison of spectra in Figure 5 illustrates that there is a mixture of cis and trans isomers of the type [PtCl$_2$(pyr)PPh$_3$] present in the neutral 4-poly(vinyl)pyridine complex. The central resonances overlap to produce the broadened peak observed. The solid-state CP/MAS ^{31}P NMR spectra of the free and polymeric cationic pyridine complexes in Figure 6 show two resonances due to two different phosphorus nuclei. This nonequivalence of the two phosphine ligands is due to the fact that each phosphorus is trans to a different ligand. One phosphorus is trans to a chloride while the other is trans to pyridine. The trans influence of each ligand results in values of $^1J(^{195}Pt,^{31}P)$ of 3144 Hz for phosphorus trans to pyridine and 3828 Hz for phosphorus trans to the chloride.

Elemental analyses for these two complexes showed the correct P/Pt ratios by weight expected for the molar ratios predicted. For the cationic pyridine (immobilized) complex 0.42% P and 1.23% Pt were found (if 0.42% P is present, then one would expect 1.32% Pt) and for the neutral pyridine (immobilized) complex 0.27% P and 1.71% Pt were found (if 0.27% P is present, then 1.70% Pt is expected).

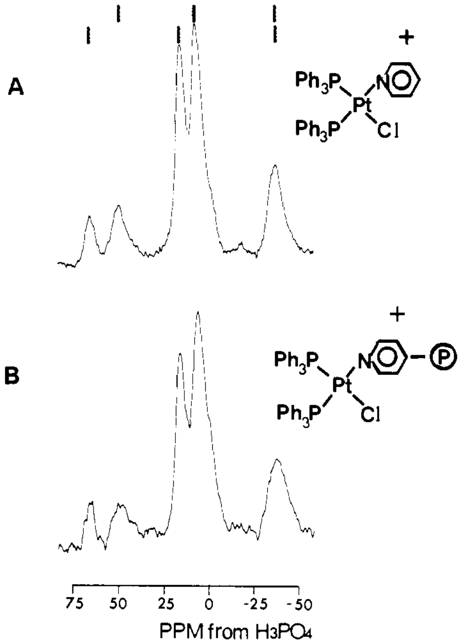

Figure 6. (A) Solid-state CP/MAS ^{31}P NMR spectrum of *cis*-[PtCl(PPh$_3$)$_2$(pyr)]$^+$(ClO$_4$)$^-$ after Soxhlet extraction; 2720 scans and 15-Hz line broadening. (B) Solid-state CP/MAS ^{31}P NMR spectrum of *cis*-[PtCl(PPh$_3$)$_2$(pyrⓅ)]$^+$(ClO$_4$)$^-$ after Soxhlet extraction; 17142 scans and 25-Hz line broadening.

Conclusions

This study has demonstrated the utility of solid-state CP/MAS ^{31}P NMR in elucidating the structure and geometry of polymer-immobilized transition-metal complexes. It offers a distinct advantage over high-resolution solution ^{31}P NMR, of the solvent swollen polymers, in its ability to observe all phosphorus nuclei in the coordinated state. The technique can be used to monitor chemical reactions, such as the conversion of phosphine oxide to tertiary phosphine, and has been extremely useful in determining the validity of an alternate method for preparing polymer-immobilized transition-metal complexes.

Experimental Section

NMR Spectra. All solid-state ^{31}P CP/MAS spectra were run at 36.442 MHz on a Bruker CXP-100 spectrometer operating at 2.114 T. The double-tuned single-coil probe was constructed in this department. Spectra were accumulated with a 1-s recycle time and a 1-ms single CP contact. Proton decoupling and spin-locking fields of approximately 10^{-3} T (10 G) were used. The magic-angle spinning assembly was for room temperature operation only and was of the general type described by Andrew.[20] Rotors were machined from Delrin (polyformaldehyde) with a sample chamber of approximately 8-mm inside diameter and depth of approximately 10 mm. These spinners were usually packed with about 300 mg of the samples described in this paper and were spun at 3 kHz by using compressed air as the driving gas.

High-resolution solution ^{31}P NMR spectra were run on a Bruker WP-60 spectrometer at 24.3 MHz with proton decoupling.

All ^{31}P chemical shifts (solid-state and solution) were referenced to external 85% H_3PO_4. The errors in δ and $^1J(^{195}Pr,^{31}P)$ values for solid-state spectra were estimated to be ±2.0 ppm and ±50 Hz, respectively. All $\nu_{1/2}$ values were reported at a line broadening of 0 Hz. More positive values of the chemical shift represent deshielding.

Physical Determination. All melting points were determined on a Fisher-Johns melting point apparatus and were uncorrected. Elemental analyses were performed by Guelph Chemical Labs (Guelph, Ontario, Canada) and Huffman Laboratories (Wheatridge, CO). The % P was determined colorometrically with ammonium vanadate/ammonium molybdate reagent after digestion of the sample in mixed acids. The % Pt was determined by ashing the sample, dissolving the residue in aqua regia, and fuming off excess acid. The partially dried sample was dissolved in hydrochloric acid and the % Pt determined colorometrically with stannous chloride reagent. Polystyrene-immobilized triphenylphosphine was obtained from Strem Chemicals, Inc.

Preparation of (*p*-Vinylphenyl)diphenylphosphine. (*p*-Vinylphenyl)diphenylphosphine was prepared by the reaction of (*p*-vinylphenyl)magnesium chloride with chlorodiphenylphosphine by using 0–10 °C inverse addition by the reported method.[31] The Grignard reagent, (*p*-vinylphenyl)magnesium chloride, was synthesized by the reported method[33] with the variation that it was refluxed for 2 h to ensure complete reaction (56% yield of product; mp 75.5–77.0 °C, 77–78 °C lit.[37]).

Preparation of Functionalized Polymer by Suspension Copolymerization. A copolymer of composition 90% styrene, 2% divinylbenzene, and 8% (*p*-vinylphenyl)diphenylphosphine was synthesized by a variation of a previously described method.[47] All styrene used was vacuum distilled prior to use to ensure absence of inhibitor. The divinylbenzene used was found to be 80% pure, by ^1H NMR, and was washed with 1 M NaOH and water prior to use. Distilled water (10 mL) was introduced into a 25-mL round-bottomed flask that had been fitted with a magnetic stirring bar and a reflux condenser. The water was heated to 80 °C and 0.4503 g of gelatin was added and dissolved with stirring. The solution was allowed to cool to 40 °C while 0.2715 g (9.40×10^{-4} mol) of (*p*-vinylphenyl)diphenylphosphine was dissolved in a solution of 1.0920 g (1.05×10^{-2} mol) of styrene and 0.0473 g (2.33×10^{-4} mol) of divinylbenzene. The flask was flushed with nitrogen gas and the styrene solution was added with 0.0403 g (2.45×10^{-4} mol) of recrystallized azobis(isobutyronitrile) (AIBN). Vigorous stirring was effected and after 5 min the temperature was raised to 80 °C and the flask contents were left to react for 24 h. The small white beads produced were filtered and dried in vacuo to yield approximately 1.1 g of polymer.

Reduction of Phosphine Oxide to Tertiary Phosphine via Trichlorsilane Treatment. Functionalized polymer (1.0 g) was placed in a 50-mL Erlenmeyer flask equipped with a magnetic stirring bar. Stirring was effected and the flask was flushed with nitrogen. Degassed benzene (15 mL) and $SiCl_3H$ (15 mL) were introduced into the flask, which was then sealed with a rubber septum and placed in a nitrogen-flushed glove bag. The flask was opened to this atmosphere to release any pressure buildup and after 10 min the flask was again sealed. The flask contents were stirred for 6 h and then the solvent and trichlorosilane were removed by filtering under nitrogen. The polymer was dried in vacuo, Soxhlet extracted under nitrogen, with toluene, and redried in vacuo. % P by elemental analysis = 1.3%.

Immobilization of a Metal Complex. (a) Initial Reaction of a Functionalized Polymer with a Free Metal Complex. The treated and extracted functionalized polymer (0.5 g) was placed in a round-bottomed flask with $[PtCl_2(NCPh)_2]$ (0.2 g) and a magnetic stirring bar. The flask was sealed with a rubber septum and then evacuated with stirring. Alternate flushings of nitrogen and evacuations were carried out, and then degassed benzene (50 mL) was added via syringe. The flask contents were stirred for 1 h at room temperature. After filtration, under nitrogen, the product was dried in vacuo, Soxhlet extracted overnight in toluene, under a nitrogen atmosphere, and then redried in vacuo.

(b) Further Reaction of Free Metal Complex with Partially Reacted, Functionalized Polymer. The 0.5-g sample of initially reacted polymer was again reacted with $[PtCl_2(NCPh)_2]$ (0.2 g). Conditions similar to those of the initial reaction were employed except that the reactants were refluxed for 2 h. The product was Soxhlet extracted and dried in vacuo (% P = 0.86, % Pt = 6.94).

Preparation of *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$. *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ was prepared from $K_2[PtCl_4]$ and (*p*-vinylphenyl)diphenylphosphine by the general method previously described[48] with a yield of 78%.

Solution Copolymerization of *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ with Styrene and Divinylbenzene To Produce Polymer-Immobilized Catalyst. A copolymer of composition 94% styrene, 2% divinylbenzene, and 4% *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ was synthesized. Styrene (1.0920 g; 1.05×10^{-2} mol), 0.0473 g (2.33×10^{-4} mol) of divinylbenzene, and chloroform (50 mL) were placed in 100-mL round-bottomed flask, which has been fitted with a stirring bar and a reflux condenser. *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ (0.3948 g; 4.66×10^{-4} mol) and 0.0426 g (2.60×10^{-4} mol) of AIBN were added and the system was flushed with nitrogen prior to attachment of a nitrogen outlet to the top of the condenser. The flask contents were stirred and refluxed for 40 h. At the end of this period a small amount of precipitated polymer was present, but an attempt to precipitate the rest of the polymer with cold methanol failed to yield particles of sufficient size. The contents were therefore reduced to dryness to yield all of the white product. Yield was 1.0549 g after drying in vacuo (% P = 2.50, % Pt = 8.81).

Copolymers of composition 66% styrene, 30% divinylbenzene, 4% *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ and 81% styrene, 15% divinylbenzene, 4% *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$ were synthesized by the method described above. After the 40-h reaction period was up a much larger quantity of solid polymer had spontaneously precipitated. The flask was cooled in a dry ice–acetone bath to ensure complete precipitation, and the product was filtered under nitrogen and then dried in vacuo. It was then Soxhlet extracted with a mixture of chloroform and toluene and redried in vacuo to yield 0.07015 g of final product (15% cross-linked sample: % P = 2.40, % Pt = 3.24; 30% cross-linked sample: % P = 1.45, % Pt = 2.58).

Preparation of *cis*-$[PtCl_2(pyr)(PPh_3)]$ and *trans*-$[PtCl_2(pyr)(PPh_3)]$. (a) Trans Isomer. To a solution of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ (0.2 g) in CH_2Cl_2 (100 mL) was added a solution of pyridine (2 equiv) in CH_2Cl_2 (20 mL) dropwise over 15 min. After stirring for 30 min. the solution was reduced to a small volume in vacuo and the product was precipitated by dropwise addition of diethyl ether. The product was filtered and air-dried to yield 0.1716 g (75%).

(b) Mixture of Cis and Trans Isomers. To a solution of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ (0.2 g) in CH_2Cl_2 (50 mL) was added pyridine (5 mL) and the solution was refluxed for 4 h. The solution was reduced to a small volume in vacuo and the product was precipitated by dropwise addition of hexane. It was filtered and air-dried, yielding 0.1738 g (76%).

Preparation of *cis*-$[PtCl(pyr)(PPh_3)_2]^+[ClO_4]^-$. This complex was prepared from $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][ClO_4]_2$ by cleavage with prydine using the method described for the preparation of $[PtCl(pyr)(Ph_2PCH_2CH_2PPh_2)][ClO_4]$.[49]

Reaction of 4-Poly(vinyl)pyridine with Platinum(II) Complexes. Cross-linked 4-poly(vinyl)pyridine (1.0 g) was refluxed in methanol (100 mL) for 30 min. in order to swell the polymer and then $[Pt_2(\mu\text{-}Cl)_2(Cl)_2(PPh_3)_2]$ (0.2 g) or $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][ClO_4]_2$ (0.2 g) in CH_2Cl_2 (50 mL) was added. After refluxing for 4 h the polymer was filtered off and air-dried. The polymer was Soxhlet extracted in chloroform for 6 h and dried in vacuo. Solid-state CP/MAS ^{31}P NMR spectra were run on the polymer before and after Soxhlet extraction ($[Pt(4\text{-pyrⓅ})Cl(PPh_3)_2]^+ClO_4^-$: % P = 0.42, % Pt = 1.23; $[Pt(4\text{-pyrⓅ})Cl_2(PPh_3)]$: % P = 0.27, % Pt = 1.71).

Acknowledgment. We acknowledge the financial support of the Natural Science and Engineering Research Council of Canada in the form of operating grants (to H.C.C., C.A.F., and R.E.W.) and Johnson Matthey Limited for a very generous loan of platinum metal salts. We also thank Reilly Tar and Chemical Corporation for a gift of 4-poly(vinyl)pyridine and Dr. R. L. Dudley for his assistance. R.E.W. thanks the University of Winnipeg for the granting of a sabbatical leave.

Registry No. $PtCl_2(NCPh)_2$, 14220-64-5; *cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$, 83831-00-9; *trans*-$[PtCl_2(PPh_3)(pyr)]$, 60243-31-4; *cis*-$[PtCl_2(PPh_3)(pyr)]$, 60268-99-7; *cis*-$[PtCl(PPh_3)_2(pyr)](ClO_4)$, 87172-14-3; $Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2$, 78309-42-9; $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][ClO_4]_2$, 53128-59-9; $SiHCl_3$, 10025-78-2; Ph_3P, 603-35-0; (*p*-vinylphenyl)diphenylphosphine, 40538-11-2; (*p*-vinylphenyl)diphenylphosphine oxide, 47182-95-6; (styrene)·(divinylbenzene) (copolymer), 9003-70-7; (styrene)·(divinylbenzene)·((*p*-vinylphenyl)diphenylphosphine) copolymer, 39319-11-4; (styrene)·(divinylbenzene)·(*cis*-$[PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2]$) (copolymer), 87136-03-6; 4-poly(vinyl)pyridine, 25232-41-1.

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