Journal of Organometallic Chemistry, 322 (1987) 393–404
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CATALYTIC OLEFIN HYDROGENATION BY PLATINUM(II)/TIN(II) SYSTEMS SUPPORTED ON PHOSPHINATED POLYSTYRENES: A SOLID-STATE PHOSPHORUS-31 NMR STUDY

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(Received July 28th, 1986)

Summary

Polymer-supported platinum(II) phosphine complexes have been prepared by the reaction of phosphinated polystyrenes with $[PtCl_2(NCPh)_2]$ and by the direct terpolymerization of styrene, divinylbenzenes, and *cis*-$[PtCl_2L_2]$ (L = *p*-styryldiphenylphosphine). The polymer-supported complexes have been fully characterized by solid-state phosphorus-31 NMR spectroscopy employing cross-polarization, magic angle spinning, and high power proton decoupling techniques and by elemental analysis. Samples of these polymer-supported complexes containing 10, 15, and 30% cross-linking have been employed in the tin(II) chloride co-catalyzed hydrogenation of styrene, using either methylene chloride or acetone as the reaction medium. Following catalysis, the polymer-supported complexes were examined by soild-state phosphorus-31 NMR spectroscopy to determine structural changes. Comparisons with spectroscopic data obtained for analogous homogeneous systems allow insight into the catalytic chemistry.

Introduction

Platinum(II) halide complexes are generally ineffective homogeneous catalysts for the hydrogenation [1] and hydroformylation [2] of olefins unless a tin(II) halide, or related co-catalyst is employed. The pre-catalytic chemistry of Pt^{II}/Sn^{II} reaction systems can be exceedingly complex and is heavily dependent upon the nature of the ligands that are present, the solvent system employed, and the reaction tempera-

0022-328X/87/$03.50

ture. In the case of $[PtCl_2L_2]/SnCl_2$ (L = tertiary phosphine) catalyst precursors, high resolution solution NMR spectroscopy has been of considerable value in investigations of the reaction chemistry [3–5]. The presence of upto seven different nuclei with a spin of one-half (i.e. ^{195}Pt, ^{119}Sn, ^{117}Sn, ^{115}Sn, ^{31}P, ^{13}C, and ^{1}H) allows structural changes to probed effectively.

Pregosin and co-workers have reported [3,4] extensive NMR studies which show that halocarbon solutions of $[PtCl_2(PR_3)_2]$ complexes react with tin(II) chloride via consecutive insertion into the Pt–Cl bonds to form a bis(trichlorostannyl) complex capable of reacting with molecular hydrogen to form the hydride, *trans*-$[PtH(SnCl_3)(PR_3)_2]$. Reactions of such hydrides with unsaturated organic molecules to yield insertion products have been reported [2,4]. In acetone solution, other workers have shown that the chemistry of these systems is complicated by equilibria involving the elimination of $SnCl_2$ from the Pt–$SnCl_3$ bonds [5] while related mixed ligand systems of the type $[PtCl_2LL']$ (where L = tertiary phosphine, L′ = modest donor ligand such as amine, thioether, etc.) undergo a completely different chemistry, involving extensive ligand rearrangement processes [6].

In the case of polymer-supported systems, meaningful application of high resolution solution NMR methods [7] is generally not possible. Cross-linked systems, in particular, resist investigations by high resolution NMR techniques. In this report we describe the application of solid-state phosphorus-31 NMR spectroscopy [8] to the structural characterization of Pt^{II}/Sn^{II} catalyst systems immobilized on phosphinated polystyrenes.

The catalytic chemistry of polymer-supported platinum and palladium phosphine complexes in the tin(II) chloride co-catalyzed hydrogenation of olefins has been studied by Bailar [9] who noted selectivity for polyene to monoene hydrogenation. Higher activity was found for the palladium(II) systems but both were found to be recyclable, with only minor losses in activity, upon addition of fresh tin(II) chloride. After catalysis, infrared spectroscopy and elemental analysis indicated the formation of new immobilized species, but the data were not consistent with those of known products from analogous solution phase chemistry. Other related reports of similar catalytic chemistry have also appeared [1,2].

Experimental

Solid-state CP/MAS ^{31}P NMR spectra were obtained at 36.442 MHz on a Bruker CXP-100 NMR spectrometer operating at 2.114 T. The double tuned, single coil probe was constructed in house. Spectra were accumulated with a 1 s recycle time and a 1 ms single cross polarization contact. Proton decoupling and spin locking fields of approximately 10^{-3} T (10 G) were employed. The magic angle spinning apparatus was for room temperature operation only and was of the general type described by Andrew [10]. Rotors were machined from Delrin (polyformaldehyde) with a sample chamber of approximately 8 mm inside diameter and 10 mm depth. The rotors were typically packed with 300 mg of the samples described here and were spun at a frequency of 3 KHz using compressed air.

All ^{31}P NMR chemical shifts are relative to external 85% phosphoric acid with more positive values of the chemical shift representing deshielding. The errors in chemical shifts and coupling constants are estimated to be ± 2.0 ppm and $\pm$ 50 Hz respectively.

Gas chromatographic analyses of solutions from catalytic experiments were performed using an Aerograph Autoprep Model A-700 chromatograph equipped with an 8 ft ×0.25 in column of 20% carbowax 20M on HP 80/100 mesh Chromosorb W. Elemental analyses were performed by Huffman Laboratories, Wheatridge, Colorado.

Preparations of phosphinated polystyrenes by suspension polymerization and treatment of the resulting co-polymers with trichlorosilane have been reported previously [11,12]. Reactions of these polymers with $[PtCl_2(NCPh)_2]$ have been described [11,12]. The synthesis and terpolymerization of $[PtCl_2L_2]$ (L = *p*-styryldiphenylphosphine) to yield immobilized complexes have been reported [11,12].

Preparations of phosphinated polystyrenes by solution polymerization were performed as follows: *p*-Styryldiphenylphosphine (0.6539 g, 2.27 mmol) and the appropriate quantities of styrene and divinylbenzenes were placed in a 3-necked flask containing AIBN (0.0546 g, 0.333 mmol) under a nitrogen atmosphere. Degassed benzene (25 ml) was added and the solution refluxed for 14 h after which time a gelatinous mass had formed. The solvent was removed in vacuo and the solid mass transferred to a Soxhlet thimble under nitrogen and Soxhlet extracted over night with toluene. The polymer remaining in the Soxhlet thimble was dried in vacuo.

Catalytic studies were performed using freshly distilled styrene (Aldrich, 99%) methylene chloride (Fisher, spectra-analyzed), acetone (Fisher), and anhydrous tin(II) chloride (Fisher, technical). Reactions were performed in a high pressure stainless steel autoclave constructed in house and fitted with a glass liner. In a typical experiment, the autoclave, containing a magnetic stirring bar, was charged with the platinum catalyst (typically about 7.35×10^{-5} moles of platinum), tin(II) chloride (Pt/Sn = 1/10), degassed styrene (20 ml) and degassed solvent (20 ml of acetone or 5 ml of methylene chloride) under a nitrogen atmosphere. The autoclave was then sealed, flushed with hydrogen by repeated pressurization and release, and then pressurized to 250 psi. The autoclave was then placed in an oil bath which was heated to 80°C (temperature variations during an experiment were approximately ±3°C), followed by final pressurization to 300 psi. The vessel was stirred at this temperature for 3 h and then plunged into an ice bath to quench the reaction. The autoclave was then opened and the solution filtered. The polymer samples were analyzed spectroscopically and the solutions were analyzed chromatographically. Although the oil bath temperature was maintained at 80°C during these experiments, this is probably higher than the reaction temperature inside the autoclave. Thus heating a loosely closed autoclave containing a thermometer immersed in toluene in an oil bath at 80°C gave an internal temperature of 65°C.

The catalytic activity of platinum metal was examined by utilizing the above reaction conditions with 0.0226 g (1.16×10^{-4} mol) of platinum metal (Aldrich) as the catalyst. No production of ethylbenzene was found.

Results and discussion

Throughout this study we have employed immobilized complexes synthesized by two different routes. The first synthetic method involved the reaction of $[PtCl_2(NCPh)_2]$ with phosphinated polystyrenes. We have previously shown [11,12] that commercial phosphinated polystyrenes and phosphinated polystyrenes prepared by suspension polymerization in water are typically contaminated by the presence of variable, and often large, amounts of phosphine oxide residues which may be reduced to generate immobilized tertiary phosphine moieties using trichlorosilane [11–13]. The complete removal of residual trichlorosilane and its reaction products is problematic and treatment of a phosphinated polystyrene with $[PtCl_2(NCPh)_2]$, after reduction of phosphine oxide utilizing trichlorosilane and Soxhlet extraction, leads to darkening of the polymeric product [11,12], presumably through reduction of platinum(II) to platinum metal. Although we were able to partially characterize the immobilized complexes formed during this reaction [11,12], the presence of metallic decomposition products led us to look for better routes to prepare samples for use in catalytic studies.

We have found that solution polymerization in benzene is a suitable method for the synthesis of terpolymers prepared from styrene, *p*-styryldiphenylphosphine (8 mol%) and divinylbenzenes (> 10 mol%). Only with > 10 mol% divinylbenzenes were polymers formed with high enough molecular weights to spontaneously precipitate from benzene solution. Using this method, 10, 15, and 30% cross-linked terpolymers containing 8 mol% *p*-styryldiphenylphosphine were prepared. The solid-state CP/MAS ^{31}P spectra of these samples each showed a single resonance in the range −3.8 to −4.8 ppm (cf. triphenylphosphine [13], Table 1), attributable to the immobilized tertiary phosphine groups. The spectrum of the 10% cross-linked

TABLE 1

SOLID-STATE CP/MAS ^{31}P NMR DATA OF PHOSPHINATED POLYSTYRENES, POLYMER-SUPPORTED PLATINUM COMPLEXES AND RELATED MODEL COMPOUNDS

Sample [a]	δ (ppm)	$\nu_{1/2}$ (Hz)	$^1J(^{195}Pt, ^{31}P)$ (Hz)
Co-polymer of 10% DVB, 8% *p*-styryldiphenylphosphine and 82% styrene	−3.8	320	–
	26.8		–
Co-polymer of 15% DVB, 8% *p*-styryldiphenylphosphine and 77% styrene	−4.8	298	–
Co-polymer of 30% DVB, 8% *p*-styryldiphenylphosphine and 62% styrene	−3.8	287	–
Co-polymer of 10% DVB, 8% *p*-styryldiphenylphosphine and 82% styrene after reaction with $[PtCl_2(NCPh)_2]$ in acetone	19.0	485	2600 [b]
	12.1		3433
	−4.6	340	
Co-polymer of 15% DVB, 8% *p*-styryldiphenylphosphine and 77% styrene after reaction with $[PtCl_2(NCPh)_2]$ in benzene	20.4	386	– [c]
	11.7		–
	−5.4	427	
PPh_3	−7.2	78	–
$OPPh_3$	29.2	145	–
cis-$[PtCl_2(PPh_3)_2]$	12.9	120 [b]	3877
	8.6	120	3623
trans-$[PtCl_2(PPh_3)_2]$	20.9	120	2695
	19.0	120	2559

[a] DVB = divinylbenzenes. [b] Approximate values due to signal overlap. [c] Unable to measure due to signal overlap.

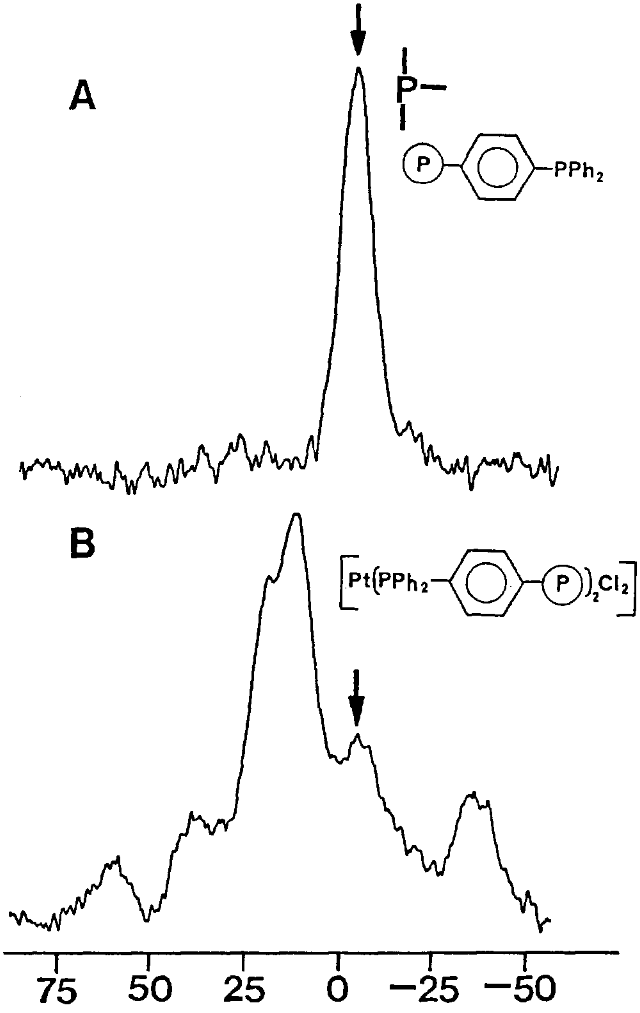

Fig. 1. Solid-state CP/MAS ^{31}P NMR spectra of: (a) Co-polymer of 10% divinylbenzenes, 8% *p*-styryldiphenylphosphine and 82% styrene after Soxhlet extraction. 1244 scans and 10 Hz line broadening. (b) Above sample after reaction with [$PtCl_2(NCPh)_2$]. 40,342 scans and 35 Hz line broadening.

sample (Fig. 1a) also showed a minor resonance of negligible area at 26.8 ppm due to a small amount of oxide impurity (cf. triphenylphosphine oxide [13], Table 1), presumably the result of adventitious air in the reaction system. Data on these samples are collected in Table 1.

The reaction of the 10% cross-linked phosphinated polymer with [$PtCl_2(NCPh)_2$], using acetone as the reaction medium, led to formation of a bright yellow product, with no visible sign of darkening due to the formation of metallic platinum, which we had previously observed [11,12] with trichlorosilane treated samples. The solid-state CP/MAS ^{31}P NMR spectrum of this product (Fig. 1b) shows the presence of small amounts of unreacted phosphine (−4.6 ppm) and resonances due to *cis* and *trans* immobilized complexes. The chemical shifts and coupling constants assigned for these isomers agree well with the corresponding data of the *cis* and *trans* isomers of $[PtCl_2(PPh_3)_2]$ [13] (see Table 1). The presence of the *trans* isomer is presumably responsible for the yellow color of the polymeric product. The appearance of more than one central resonance in this spectrum and the corresponding overlap of satellites suggests that a complex array of immobilized species may be present in addition to the *cis* and *trans* isomers and residual tertiary phosphine. The 15% cross-linked phosphinated polymer behaves similarly (see Table 1). The spectra obtained for these samples are remarkably similar to those obtained for the darkened product of the analogous reaction using phosphinated supports treated with trichlorosilane [11,12], showing that the decomposition does not significantly affect the nature of the phosphorus containing products.

The second group of supported catalysts that we have employed in this study was prepared by the terpolymerization of *cis*-$[PtCl_2L_2]$ (where L = *p*-styryldiphenylphosphine), styrene, and divinylbenzenes using a solution co-polymerization method with chloroform as the reaction medium. We have previously described the syntheses and solid-state CP/MAS ^{31}P NMR spectra of 2, 15 and 30% cross-linked terpolymers prepared using this method [11,12]. We found that these samples were characterized by the presence of immobilized *cis*-$[PtCl_2L_2]$ species and contained from zero to trace amounts of phosphine oxide. In the case of the 2% cross-linked sample we were able to confirm that the preparative method leads to a minor amount of isomerization and that a small quantity of immobilized *trans*-$[PtCl_2L_2]$ species is produced [11,12]. This may also be the case for the 15 and 30% cross-linked terpolymers but remains unconfirmed due to limitations caused by the higher levels of cross-linking.

Elemental analyses of these samples gave rise to conflicting results. Thus, the 2% cross-linked sample yielded values of 2.5% phosphorus and 8.81% platinum (for 2.5% phosphorus the calculated platinum content is 7.9%). The 15% cross-linked sample gave rise to values of 2.4% P and 3.24 Pt (for 2.4% P the calculated Pt content is 7.6%) while the 30% cross-linked sample yielded values of 1.45% P and 2.58% Pt (for 1.45% P the calculated Pt content is 4.6%). The values found for percentage phosphorus in these samples should be compared with a calculated value of 1.80%, based on the stoichiometric ratios of reactants used in the terpolymerization reactions. While it is possible that the differences between the phosphorus contents of these samples and the calculated value is due to some type of preferential polymerization, this does not explain the lack of consistency between the phosphorus and platinum values for these samples. The solid-state CP/MAS ^{31}P NMR spectra of these samples [11,12] indicate that virtually all of the detected phosphorus is present as immobilized $[PtCl_2L_2]$ species and yet the molar P/Pt ratio differs considerably from 2/1. These errors could be intrinsic to the thermal method employed in analysis, but other workers [14] have found that misleading results can be obtained since thermally stable species, such as polynuclear phosphides, may form during analysis. In the present studies, the lack of truly reliable analytical data is very important since it necessitates making assumptions about the molar ratios of reactants used in catalytic reactions and hence leads to uncertainties in the derived turnover numbers.

The samples described above were used in the catalytic hydrogenation of styrene, employing a tin(II) chloride co-catalyst. Details of the techniques employed are given in the Experimental section. Initial studies were performed using methylene chloride as the reaction medium with a Pt^{II}/Sn^{II} ratio of 1/10 and an external autoclave temperature of 80°C. At 300 psi of hydrogen, the 15 and 30% cross-linked samples prepared by direct incorporation of *cis*-$[PtCl_2L_2]$ (L = *p*-styryldiphenylphosphine) gave turnover numbers of 32.5 and 17.3 moles of ethylbenzene produced per mole of platinum per hour, respectively. Turnover numbers are based on the platinum content of the samples found by elemental analysis (vide supra).

The solid-state CP/MAS ^{31}P NMR spectra of the polymer samples isolated after catalysis were virtually identical to those of the samples before reaction. This is not a surprising observation since tin(II) chloride is of very limited solubility in methylene chloride and so the reaction with the insoluble polymer is inhibited in this reaction medium. No color change was observed during the initial addition of tin(II) chloride to the supported complex when methylene chloride was employed as the reaction medium (vide infra). Homogeneous reactions [3,4] in this solvent rely on the solubility of the Pt^{II} complex to drive the equilibrium insertion of tin(II) chloride into the Pt–Cl bond and this driving force is absent in the heterogenized system. The low activities which we observe may be due to catalysis by the immobilized $[PtCl_2L_2]$ complex or by an undetectably small amount of a platinum-tin complex. The results do indicate, however, a decrease in activity with the higher level of cross-linking. Since the low solubility of tin(II) chloride in methylene chloride is detrimental to catalysis, further experiments were performed using acetone as the reaction medium, since this solvent has been successfully employed for related catalytic studies [2,6] and is a good solvent for tin(II) chloride.

Using acetone as the reaction medium, the hydrogenation of styrene employing a *cis*-$[PtCl_2(PPh_3)_2]/SnCl_2$ (Pt/Sn = 1/10) catalyst precursor was performed at 80°C and 300 psi of hydrogen pressure. Two separate experiments gave rise to turnover numbers of 120.1 and 109.2 (mean = 114.7) moles of ethylbenzene produced per mole of platinum per hour for this homogeneous system. Samples of 10 and 15% cross-linked polymers prepared by the reaction of $[PtCl_2(NCPh)_2]$ with phosphinated polystyrenes were employed as supported catalysts for this reaction. Virtually identical turnover numbers (86.9 and 86.2) were obtained for these catalysts with a Pt/Sn ratio of 1/10. These samples, although active, were severely discolored during catalysis. Prior to hydrogenation, the supported complex was bright orange after treatment with tin(II) chloride. After catalysis, the sample was almost completely black. The solid-state CP/MAS ^{31}P NMR spectra of the discolored samples after catalysis showed significant changes from the spectra obtained prior to reaction. Figure 2 compares the spectra of the 10% cross-linked sample before and after catalysis.

The spectrum shown in Fig. 2b is complex and consists of at least three central resonances at 43.2, 28.7 and 20.1 ppm (see Table 2). The resonance at 28.7 ppm showed an observable coupling to platinum-195 with $^1J(^{195}Pt, ^{31}P)$ 3018 Hz. None of the resonances allow couplings to the isotopes of tin to be established with certainty. The low natural abundances and the complex nature of the spectrum prohibit this useful information from being obtained. The data for this sample do not compare favorably with those obtained by solution measurements on homogeneous platinum-tin complexes containing triphenylphosphine as a ligand (comparative solution data are collected in Table 2). The spectrum of the 15% cross-linked sample after catalysis was similar to that observed for the 10% cross-linked sample except that a resonance at −6.7 ppm, due to uncomplexed phosphine, which was present in the sample prior to catalysis was also present after the reaction. In summary the

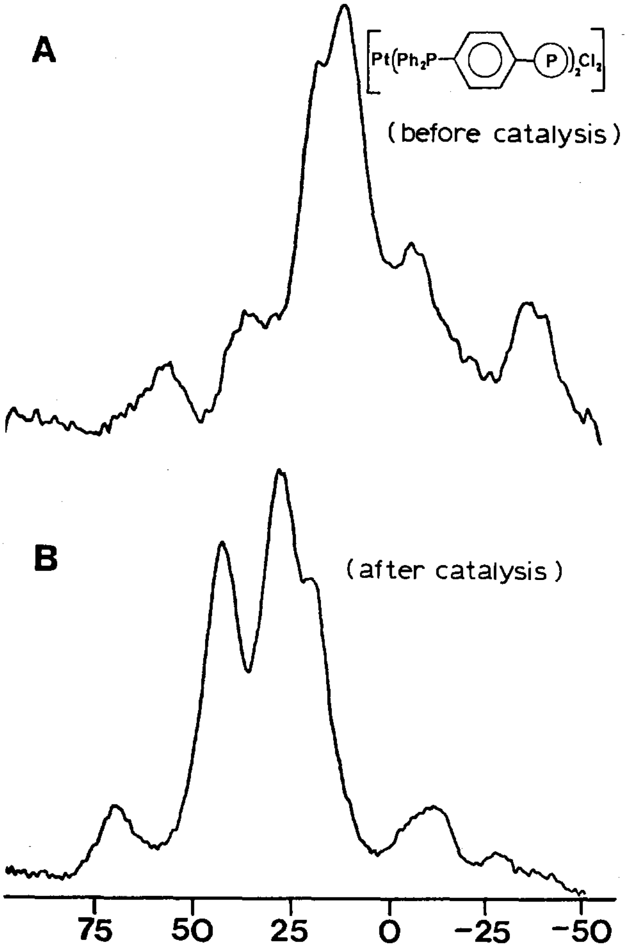

Fig. 2. Solid-state CP/MAS ^{31}P NMR spectra of: (a) Co-polymer of 10% divinylbenzenes, 8% *p*-styryldiphenylphosphine and 82% styrene after Soxhlet extraction, reaction with $[PtCl_2(NCPh)_2]$. 40,342 scans and 35 Hz line broadening. (b) Above sample after use in catalysis and Soxhlet extraction. 56,212 scans and 10 Hz line broadening.

polymer-supported catalysts prepared by the reaction of $[PtCl_2(NCPh)_2]$ with phosphinated polystyrenes contain a complex array of supported species prior to catalysis which exhibit reactivity with tin(II) chloride to produce new complexes which undergo partial decomposition during the catalytic hydrogenation of styrene. None of the resulting supported complexes could be identified by comparison with data of homogeneous analogs. Under the conditions employed in this study, bulk platinum metal does not catalyze the hydrogenation of styrene (see Experimental), although activity due to the formation of colloids and/or small metallic clusters has not been excluded. Clearly, these polymer-supported complexes are susceptible to reduction, observed by instability in both reactions with trichlorosilane (or its reaction products) [11,12] and during olefin hydrogenation. This instability may indicate the presence of solvated or coordinatively unsaturated species.

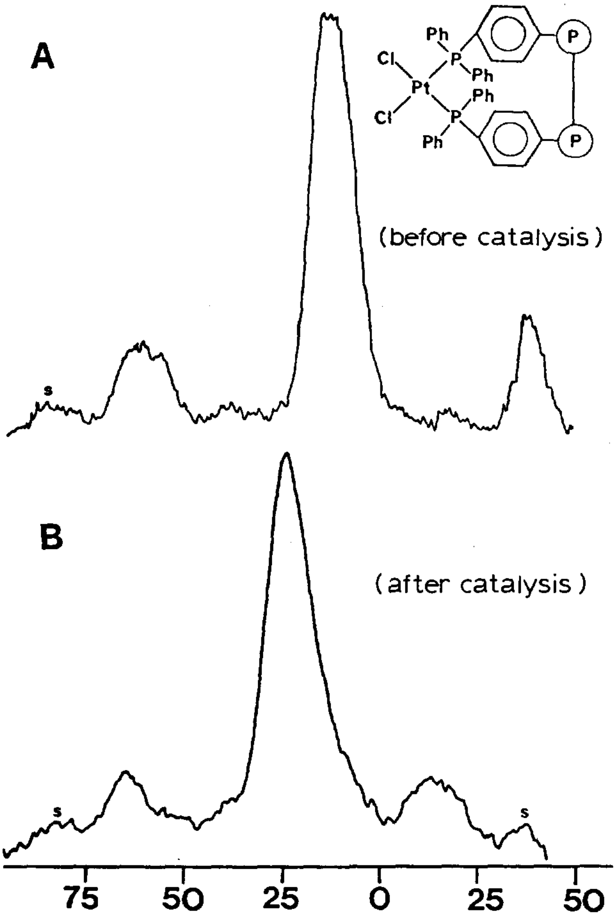

Fig. 3. Solid-state CP/MAS ^{31}P NMR spectra of: (a) Co-polymer of 15% divinylbenzenes, 4% *cis*-[$PtCl_2L_2$] (L = *p*-styryldiphenylphosphine) and 81% styrene after Soxhlet extraction. 4,640 scans and 10 Hz line broadening. (b) Above sample after use in catalysis and Soxhlet extraction. 17,238 scans and 30 Hz line broadening.

The polymer-supported complexes prepared by the direct incorporation of *cis*-[$PtCl_2L_2$] (L = *p*-styryldiphenylphosphine) were employed in the hydrogenation of styrene in acetone. For a 15% cross-linked sample, with 10 equivalents of tin(II) chloride, the turnover numbers obtained for two experiments at 80° C and 300 psi of hydrogen were 137.3 and 122.6 (mean = 130.0) moles of ethylbenzene per mole of platinum per hour. Under the same conditions, a 30% cross-linked sample gave turnover numbers of 149.6 and 139.4 (mean = 144.5). These values are based upon the percentage of platinum found in the samples by elemental analysis and thus must be viewed as qualitative measures of activity. If, as we suspect, the elemental analysis underestimates the platinum content of the samples, then these turnover numbers will be artificially elevated. The samples have a catalytic activity of the same order of magnitude as their homogeneous analog (turnover number = 114.7, vide supra), but comparisons between these rates are not meaningful with the inherent inaccuracies involved.

TABLE 2

SOLID-STATE CP/MAS ^{31}P NMR DATA OF POLYMER-SUPPORTED PLATINUM COMPLEXES AFTER USE IN CATALYTIC OLEFIN HYDROGENATION AND HIGH RESOLUTION ^{31}P NMR DATA OF RELATED MODEL COMPOUNDS

Sample	δ (ppm)	$^{1}J(^{195}\text{Pt}, ^{31}\text{P})$ (Hz)
Co-polymer of 10% DVB, 8% *p*-styryldiphenylphosphine and 82% styrene after reaction with $[PtCl_2(NCPh)_2]$ and use in catalysis	28.7	3018
	20.1	–[a]
	43.2	–
Co-polymer of 15% DVB, 8% *p*-styryldiphenylphosphine and 77% styrene after reaction with $[PtCl_2(NCPh)_2]$ and use in catalysis	25.7	–[a]
	18.2	–[a]
	40.7	–
	−6.7	–
Co-polymer of 15% DVB, 4% *cis*-$[PtCl_2L_2]$ (L = *p*-styryldiphenylphosphine) and 81% styrene after use in catalysis	24.9	2871
Co-polymer of 30% DVB, 4% *cis*-$[PtCl_2L_2]$ (L = *p*-styryldiphenylphosphine) and 66% styrene after use in catalysis	25.7	2617
	18.0	–[a]
trans-$[PtH(SnCl_3)(PPh_3)_2]$ [b]	28.5	2650
cis-$[PtCl(SnCl_3)(PPh_3)_2]$ [c]	27.9	3083
	10.5	3637

[a] Unable to measure due to signal overlap. [b] High resolution data obtained at −60 °C in $CDCl_3/CH_2Cl_2$ solution. See ref. 15. [c] High resolution data obtained at −50 °C in CH_2Cl_2 solution. See ref. 3.

The 15% cross-linked sample was converted from yellow to bright orange during catalysis while the 30% cross-linked sample was changed from yellow to yellow-orange. The literature [3–5] describes the colors of the closely related homogeneous analogs, *trans*-$[PtCl(SnCl_3)(PPh_3)_2]$ and *trans*-$[Pt(SnCl_3)_2(PPh_3)_2]$, as being yellow and orange respectively. With neither polymer sample was any discoloration or formation of metallic decomposition products visually detected.

The solid-state CP/MAS ^{31}P NMR spectra of the 15% cross-linked sample before and after catalysis are shown in Fig. 3. The spectrum after catalysis shows a single central resonance at 24.9 ppm with a coupling, $^{1}J(^{195}\text{Pt}, ^{31}\text{P})$, of 2871 Hz. These data for the immobilized complex are in reasonable agreement with the high resolution ^{31}P NMR data of *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ [15] (see Table 2 for summary of data for supported complexes and comparative literature high resolution ^{31}P NMR data).

The spectrum of the 30% cross-linked sample after catalysis was very similar, with a central resonance at 25.7 ppm with a coupling constant of 2617 Hz, but displayed an additional resonance at 18.0 ppm for which coupling to platinum-195 could not be unambiguously established due to peak overlap. No couplings to the isotopes of tin were identified in the spectra of the 15 and 30% crosslinked samples which eliminates a sensitive structural probe and hinders identification.

Both the 15 and 30% cross-linked samples could be recycled upon addition of fresh tin(II) chloride (Pt/Sn = 1/10) with no significant loss of activity. In all cases, the polymers become deeper orange after reuse, but the solid-state CP/MAS ^{31}P NMR spectra were identical to those described above, obtained after a single cycle.

Conclusions

From these studies we conclude that polymer-supported platinum(II) complexes prepared by terpolymerization of *cis*-$[PtCl_2L_2]$ (L = *p*-styryldiphenylphosphine) with styrene and divinylbenzenes offer distinct advantages over complexes prepared from the reactions of preformed phosphinated polystyrenes wtih $[PtCl_2(NCPh)_2]$. Foremost among these is the presence of essentially just the *cis*-isomer of the immobilized $[PtCl_2L_2]$ complex which resists degradation through repeated catalytic cycles. After catalysis, either one or two new platinum(II) complexes are present in the polymer samples, depending upon the degree of cross-linking. Presumably this difference is due to mobility factors which differ as the matrix is altered. The major species formed has been tentatively identified as a polymeric analog of *trans*-$[PtH(SnCl_3)(PPh_3)_2]$. Our inability to observe coupling between phosphorus-31 and the spin one-half isotopes of tin prevents a definitive structural assignment from being made. If our tentative assignment is indeed correct then this indicates considerable geometric mobility for the immobilized species since the vast majority of the complex was initially of a *cis* geometry whereas the hydride has a *trans* structure. Solid-state CP/MAS ^{119}Sn NMR would clearly be a valuable tool in studying these catalytic systems and may prove to be the way to access the required coupling constant data to provide definitive structural assignments.

Since many workers have prepared co- and terpolymers containing tertiary phosphines [16] and investigated their chemistry with transition metals as catalysts, the techniques described here should be of general utility in characterization.

Acknowledgements

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 thank the University of Toledo Office of Research for assistance (to J.A.D.). Thanks are expressed to Johnson Matthey, Inc. and Kigre, Inc. for generous loans of platinum metals.

References

1 R.D. Cramer, E.L. Jenner, R.V. Lindsey and U.G. Stolberg, J. Am. Chem. Soc., 85 (1963) 1691. B.R. James, Homogeneous Hydrogenation, Wiley, New York, 1973. C. Billard, H.C. Clark, and C.S. Wong, J. Organomet. Chem., 190 (1980) C3.

2 H.C. Clark and J.A. Davies, J. Organomet. Chem., 213 (1981) 503. C. Hsu and M. Orchin, J. Am. Chem. Soc., 97 (1975) 3553. I. Schwager and J.F. Knifton, J. Catal., 45 (1976) 256.

3 P.S. Pregosin and S.N. Sze, Helv. Chim. Acta, 61 (1979) 1848.

4 K.A. Ostaja-Starzewski, P.S. Pregosin and H. Ruegger, Inorg. Chim. Acta, 36 (1979) L445.

5 B.R. Koch, G.V. Fazakerley, and E. Dijkstra, Inorg. Chim. Acta, 45 (1980) L51.

6 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem. 22 (1983) 427 and 434. G.K. Anderson, C. Billard, H.C. Clark, J.A. Davies and C.S. Wong, Inorg. Chem., 22 (1983) 439.

7 R.H. Grubbs and S.C.-H. Su, Prepr., Div. Pet. Chem., J. Am. Chem. Soc., 22 (1977) 1193. A.J. Naaktgeboren, R.J.M. Nolte and W.J. Drenth,, J. Am. Chem. Soc., 102 (1980) 3350.

8 C.A. Fyfe, Solid State NMR For Chemists, C.F.C. Press, Guelph, Ontario, Canada, 1983.

9 J.C. Bailar, J. Am. Oil Chem. Soc., 47 (1970) 475. E.N. Frankel, E.A. Emken, H. Itatani and J.C. Bailar, J. Org. Chem., 32 (1967) 1447.
10 E.R. Andrew, Prog. Nucl. Magn. Reson. Spectrosc., 8 (1971) 1.
11 H.C. Clark, J.A. Davies, C.A. Fyfe, P.J. Hayes and R.E. Wasylishen, Organometallics, 2 (1983) 177.
12 C.A. Fyfe, H.C. Clark, J.A. Davies, P.J. Hayes and R.E. Wasylishen, J. Am. Chem. Soc., 105 (1983) 6577.
13 L. Bemi, H.C. Clark, J.A. Davies, C.A. Fyfe and R.E. Wasylishen, J. Am. Chem. Soc., 104 (1982) 438.
14 F.R. Hartley, S.G. Murray and P.N. Nicholson, J. Organomet. Chem., 231 (1982) 369.
15 K.A.O. Starzewski and P.S. Pregosin, Am. Chem. Soc., Adv. Chem. Ser., 196 (1982) 23.
16 F.R. Hartley, Supported Metal Complexes: A New Generation of Catalysts, D. Reidel Publishing Company, New York, 1985.