may detect cannot be discounted so easily, but it needs further definition. We are left with the possibilities that aggregation from monomer to micelle (i) alters the polarity of microenvironment of the ester groups, perhaps rendering them more susceptible to attack by phospholipases, and (ii) produces an interface with surface characteristics such as surface charge, counterion binding, etc., which alter enzyme catalysis. While the outcome of this study does not explain interfacial activation, it at least allows us to eliminate major conformational changes and ordering of the lecithin molecules as the culprits. It also provides background for further detailed studies with the enzymes.

Acknowledgment. We would like to thank Dr. George Benedek and Mr. Paul Missel for preliminary quasielastic light-scattering data for the size/concentration dependence of dihexanoyl-PC. The NMR experiments were performed at the NMR facility for Biomolecular Research located at the Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology (N.I.H. Grant RR00995 and N.S.F. Contract C-670), and at the Southern New England High-Field NMR facility located at Yale University. M.F.R. gratefully acknowledges support from N.S.F. PCM 7912622 and Whitaker Health Science Fund, M.I.T. R.A.B. is supported by a Whitaker Health Sciences Predoctoral Fellowship.

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Studies of Phosphorus(III) Ligands and Their Complexes of Ni(II), Pd(II), and Pt(II) Immobilized on Insoluble Supports by High-Resolution Solid-State ^{31}P NMR Using Magic-Angle Spinning Techniques

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Abstract: High-power proton decoupling, cross-polarization, and magic-angle spinning techniques have been employed to obtain high-resolution ^{31}P NMR spectra of solid tertiary phosphines, tertiary phosphine oxides, and tertiary phosphine complexes of nickel(II), palladium(II), and platinum(II). Solid-state effects can result in nonequivalence of ^{31}P shieldings in simple *cis*-$[PtCl_2(PR_3)_2]$ complexes. The magnitudes of the scalar couplings, $^1J(^{195}Pt,^{31}P)$, in platinum(II) complexes are comparable with those obtained by high-resolution solution ^{31}P NMR measurements, allowing the geometry of such complexes to be determined in the solid state. The ligand $Ph_2PCH_2CH_2Si\{OEt\}_3$ and its Ni(II), Pd(II), and Pt(II) complexes have been immobilized on silica gel and high-surface-area glass beads and the immobilized species studied by solid-state ^{31}P NMR. The results show that the geometry of surface-immobilized complexes may be determined and the surface reactions may be monitored. The merits of some preparative routes to supported transition-metal catalysts have been studied and some common representations of surface reactions and surface-immobilized species shown to be misleading.

The immobilization of transition-metal complexes on insoluble supports has been extensively studied in recent years as a method of combining the most desirable characteristics of homogeneous and heterogeneous catalysts.[2,3] Systematic research efforts in this field have been severely restricted because of the lack of suitable analytical techniques for the study and structural characterization of surface-immobilized species. The most widely utilized technique has been infrared spectroscopy,[4-6] which provides structural information in the case of immobilized species with characteristic infrared absorptions (e.g., ν(CO) in metal carbonyls, ν(M-H) in metal hydrides). Less commonly, electron-spin resonance,[7,8] ESCA,[9,10] photoacoustic spectroscopy,[11] and electron-probe microanalysis[12] have been utilized in attempts to obtain structural information about supported transition-metal complexes. A great many surface-immobilized complexes contain phosphorus(III) donor ligands,[2,3] but the solid-phase nature of the supported species has prevented any study by high-resolution ^{31}P NMR, the technique of choice when studying many homogeneous systems in solution.[13]

In recent years, the development of high-power decoupling,[14] cross-polarization,[15] and magic-angle spinning[16] techniques has allowed "high-resolution" NMR studies of dilute nuclei to be performed on solid samples. These techniques have allowed extensive study by ^{13}C NMR, and more recently ^{29}Si NMR, to be performed in many diverse areas of solid-state chemistry, including the study of surface-attached species.[17-21] The application of these techniques to the observation of the ^{31}P nucleus ($I = {}^1/_2$, abundance = 100%) in the solid state has recently been described in studies of the phosphate-containing phases of bones[22] and of solid

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calcium phosphates.[23] The present work describes the application and evaluation of ^{31}P NMR as a technique to study surface-immobilized transition-metal complexes containing phosphorus(III) donors. In order to evaluate the potential of ^{31}P NMR using cross polarization and magic-angle spinning, CP/MAS ^{31}P NMR, in this field, a number of tertiary phosphine ligands, phosphine oxides, and tertiary phosphine complexes of nickel(II), palladium(II), and platinum(II) have been studied. The technique has also been used to detect and to characterize surface-immobilized analogues of these complexes and to examine the efficiency of the various accepted routes to the preparation of these species. Some mention of the study of transition-metal phosphine complexes by CP/MAS ^{31}P NMR has been made[24,25] and the spectra of four such complexes described in a recent communication.[26] Preliminary results of our studies on surface-immobilized species have been reported.[27]

Experimental Section

NMR Spectra. ^{31}P cross-polarization spectra were obtained 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. Proton-decoupling fields of approximately 10^{-3} T (10 G) were used. Spectra were typically accumulated with a 1-s recycle time and a 1-ms single-CP contact. The magic-angle spinning assembly was for room-temperature operation only and of the general type described by Andrew.[16] Rotors were machined from Delrin (polyformaldehyde) with a sample chamber of approximately 8 mm i.d. and depth of approximately 10 mm. Such holders typically were packed with 200–300 mg of the samples described in this paper and were routinely spun at 3 kHz.

High-resolution solution ^{31}P NMR spectra were obtained using a Bruker WP-60 spectrometer operating in the Fourier transform mode at 24.3 MHz with proton decoupling.

All ^{31}P chemical shifts (solid state and solution) are reported with respect to external 85% H_3PO_4. More positive shifts represent deshielding. The errors in δ and $^1J(^{195}Pt,^{31}P)$ values (solid-state measurements) are estimated to be ±2.0 ppm and ±50 Hz, respectively. Errors in reported line widths and chemical shielding anisotropies are estimated to be ±10%.

Tertiary Phosphines and Metal Complexes. Tertiary phosphine ligands were obtained from Strem Chemicals. Samples of Ph_3PO and $(C_{14}H_{29})_3PO$ were gifts from Dr. R. C. Shrivastava and Dr. S. Franks.

The complexes *cis*-$[PtCl_2(PR_3)_2]$ (PR_3 = PEt_3, $PMePh_2$) were prepared by reaction of $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) with the ligands as previously described.[28] The complex *trans*-$[PtCl_2(PPr_3)_2]$ was prepared by reaction of $K[PtCl_3(C_2H_4)]$ with the ligand using the method described for PPh_3.[29] The complexes *cis*-$[PtCl_2(CO)PR_3]$ were prepared by the reported method.[28] $[Pd(CN)_2(Ph_2PCH_2CH_2PPh_2)]$ was prepared as previously described.[30] $[Pd(PPh_3)_4]$ was obtained from Strem Chemicals. The complexes $[NiCl_2(PR_3)_2]$ (R_3P = PPh_2Me, PCy_3) were prepared by the reaction of $NiCl_2{\cdot}6H_2O$ with the ligand in ethanol solution.[31]

$[PtCl_2(PPh_3)_2]$ was obtained by the reaction of $[PtCl_2(NCPh)_2]$ (10 mmol) with PPh_3 (20 mmol) in CH_2Cl_2 solution (50 mL). Reduction of solvent in vacuo led to the precipitation of a mixture of cis and trans isomers, identified by their solution ^{31}P NMR spectra.

Complexes of the ligand $Ph_2PCH_2CH_2Si(OEt)_3$ were all prepared in an inert atmosphere using standard vacuum line techniques. Reaction of $[PtCl_2(NCPh)_2]$ (10 mmol) with the ligand (20 mmol) in dry benzene (30 mL) led to the formation of $[PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$. The cis isomer was obtained by reducing the volume of the solution to ca. 20 mL and allowing the white crystalline product to precipitate. The complete removal of the solvent in vacuo led to the isolation of a yellow oil which crystallized upon treatment with hexane. This product was shown to be a mixture of cis and trans isomers by solution ^{31}P NMR spectroscopy.

Table I. CP/MAS ^{31}P NMR Data of Solid Tertiary Phosphines and Phosphine Oxides with Comparative High-Resolution Solution ^{31}P NMR Data

	CP/MAS ^{31}P NMR			solution ^{31}P NMR
compound	δ	$\nu_{1/2}$, Hz	$\Delta\sigma$,[d] ppm	δ
PPh_3	−7.2	78	50	−5.4 to −8.0[a]
$P\{p\text{-}CH_3C_6H_4\}_3$	−10.2	75	35	−8.0[a]
$P\{p\text{-}FC_6H_4\}_3$	−10.7	80		−8.8 to −9.4[a]
$P\{p\text{-}MeOC_6H_4\}_3$	−13.7	83		−9.8 to −10.2[a]
$P\{c\text{-}C_6H_{11}\}_3$	7.5	78		7 to 11.3[a]
$PMePh_2$[b]				−28.0 to −28.1[a]
$Ph_2PCH_2PPh_2$	−23.3	127		−23.6[a]
$Ph_2PCH_2CH_2PPh_2$	−12.6	146		−13.2[a]
$Ph_2PCH_2CH_2AsPh_2$	−11.5	98		−12.6[c]
$Ph_2PCH_2CH_2Si(OEt)_3$[b]				−10.25
$OPPh_3$	29.2	145	200	23 to 27[a]
$OP(C_{14}H_{29})_3$	51.5	107	190	48.55[c]

[a] Ranges of values for various solvents from ref 39. [b] Liquid at room temperature. [c] Solution spectrum in $CDCl_3$. [d] Approximately axially symmetric.

Reaction of an acetone solution of $K[PtCl_3(C_2H_4)]$ (10 mmol) with a benzene solution of the ligand (20 mmol) produced *trans*-$[PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ which was isolated by reducing the volume of the solution and precipitating the yellow solid by the addition of hexane. *trans*-$[PdCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ was prepared by reaction of $[PdCl_2(NCPh)_2]$ with the ligand in benzene solution. The product was identified by its solution ^{31}P NMR spectrum and solid-state infrared spectrum ($\nu_{M\text{-}Cl}$ = 348 cm^{-1}, Nujol mull).

trans-$[NiCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ was prepared by reaction of $NiCl_2{\cdot}6H_2O$ with the ligand in ethanol solution. The product was identified by its low-temperature solution ^{31}P NMR spectrum and solid-state infrared spectrum ($\nu_{M\text{-}Cl}$ = 351 cm^{-1}, Nujol mull).

Supported Ligands and Metal Complexes. Condensation reactions of $Ph_2PCH_2CH_2Si\{OEt\}_3$, or its metal complexes, with activated high-surface-area glass beads and silica gel were performed in benzene (room temperature) or toluene (low or high temperature) solutions, under a nitrogen atmosphere. In a typical experiment, dry, surface-activated, silica gel or glass beads (0.5 g) were slurried in the solvent and an excess of the metal complex (0.2 g) or ligand (0.2 g) added. After being stirred at room temperature for 4 h and 273 K for 6 h or refluxed for 2 h, the slurry was filtered, washed with the appropriate solvent, and dried in vacuo. Samples were then transferred to a drying pistol and heated to 373 K in vacuo for 12 h. All samples, except those of nickel(II), were Soxhlet extracted with either benzene or toluene for 12 h and then dried in vacuo at room temperature for 6 h.

Reduction of supported phosphorus(V) species was accomplished by stirring a sample of the supported ligand (0.5 g) in $HSiCl_3$ (10 mL) for 4 h and then removing the highly volatile silane in vacuo at room temperature.

Reaction of the supported ligand with $[PtCl_2(NCPh)_2]$ was achieved by stirring the supported ligand (0.5 g) in benzene (25 mL) and adding a dilute solution of $[PtCl_2(NCPh)_2]$ (0.2 g in 100 mL) dropwise over several hours. The product was removed by filtration, treated, extracted, and dried as described above. A similar reaction was performed by mixing the supported ligand (0.5 g) with solid $[PtCl_2(NCPh)_2]$ (0.2 g) and then adding benzene, followed by the standard isolation procedure described above. The nature of the products of these reactions is discussed below.

Results and Discussion

Tertiary Phosphine Ligands and Transition-Metal Complexes. Tertiary phosphine ligands containing both one (monodentate) and two (bidentate) phosphorus(III) nuclei have been examined. The solid-state spectroscopic data are presented in Table I with comparative solution NMR data obtained by conventional high-resolution measurements. The CP/MAS ^{31}P NMR spectra yield values of the isotropic chemical shift, δ, comparable to those found in solution. The technique is thus shown to be sensitive enough to differentiate between different chemical environments of the

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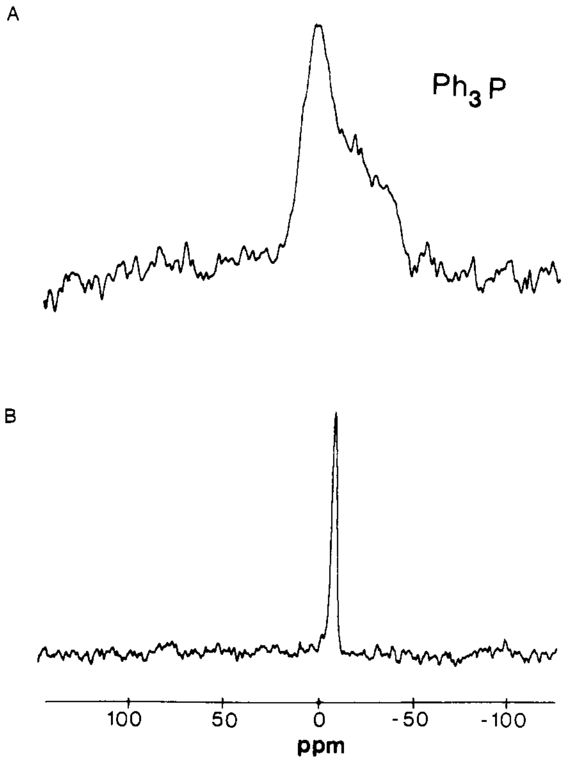

Figure 1. (A) Solid-state ^{31}P NMR spectrum of a stationary sample of PPh_3. (B) CP/MAS ^{31}P NMR spectrum of PPh_3.

phosphorus(III) nuclei. The line widths, $\nu_{1/2}$, are appreciably higher than those obtained by solution measurements being typically 75–150 Hz. In the case of $P\{p\text{-}FC_6H_4\}_3$, the line width is not substantially larger than for PPh_3, indicating that any unresolved scalar couplings to ^{19}F must be small, and that dipolar interactions with ^{19}F are negligible and/or are effectively eliminated by magic-angle spinning. A comparison of the solid-state spectrum of a stationary sample of PPh_3 with one obtained by CP/MAS ^{31}P NMR, Figure 1, shows that the chemical shift anisotropy, $\Delta\sigma$ = 50 ppm, necessitates the use of CP/MAS techniques to obtain "high-resolution" ^{31}P NMR spectra of such samples. The value of $\Delta\sigma$ = 50 ppm for PPh_3 is substantially larger than the value of 23 ppm obtained by ^{31}P NMR analyses of data obtained for samples oriented in liquid crystals.[32] Measurement of the ^{31}P NMR spectra of the phosphorus(V) compounds, $OP(C_{14}H_{24})_3$, and $OPPh_3$ using CP/MAS techniques yields values of the isotropic chemical shifts comparable to those obtained by solution measurements, Table I. Solid-state spectra of $OPPh_3$ as a stationary sample and with slow and fast sample spinning at the magic angle are shown in Figure 2. The value of the chemical shift anisotropy, $\Delta\sigma$ = 200 ppm, for $OPPh_3$ differs considerably from the value of 280 ppm derived from liquid-crystal studies. Clearly, the phosphorus(V) nucleus exhibits considerable deshielding relative to phosphorus(III) and also displays a much larger anisotropy. These two factors taken together thus allow differentiation of phosphorus(III) and phosphorus(V) species in the solid state, an observation of considerable importance in the study of surface-immobilized species (vide infra).

For our initial studies of transition-metal complexes we examined a variety of platinum(II) compounds. The choice of platinum (^{195}Pt, $I = {}^1/_2$, abundance = 33.4%) as the metal center produces complexes exhibiting scalar coupling between ^{195}Pt and ^{31}P in their high-resolution solution ^{31}P NMR spectra. Platinum complexes were chosen in preference to complexes of rhodium (^{103}Rh, $I = {}^1/_2$, abundance = 100%) as the value of $^1J(^{195}Pt,^{31}P)$ is typically an order of magnitude larger than $^1J(^{103}Rh,^{31}P)$.[13] Further, the magnitude of $^1J(^{195}Pt,^{31}P)$ is known to be very sensitive to the nature of the trans ligand in square-planar platinum(II) complexes[13] and thus provides a useful probe for geometry of possible isomeric species. Calculations based on the known magnetic moments and internuclear distances indicate that ^{31}P–^{31}P dipolar couplings in typical *cis*-(bisphosphine)platinum(II) complexes are less than 0.5 kHz; also, ^{195}Pt–^{31}P dipolar couplings are of a similar magnitude and hence spinning the solid samples at 3 kHz at the magic angle is expected to effectively eliminate both these dipolar interactions. In the case of stationary solid samples, however, these interactions are expected to contribute to the observed line widths. In complexes of the type $[PtCl_2(PR_3)_2]$, solution measurements show that values of $^1J(^{195}Pt,^{31}P)$ are typically ca. 3500 Hz for cis complexes and ca. 2500 Hz for trans complexes.[13] Solid-state measurements on the complexes *cis*-$[PtCl_2(PEt_3)_2]$ and *trans*-$[PtCl_2(PPr_3)_2]$ yield values of $^1J(^{195}Pt,^{31}P)$ of 3467 and 2422 Hz, respectively, clearly showing that the two geometries may be differentiated in the solid state from the magnitude of this coupling. The spectra of these complexes are shown in Figure 3. Interestingly, the complex *cis*-$[PtCl_2(PMePh_2)_2]$ exhibits two central components in its CP/MAS ^{31}P NMR spectrum, Figure 4B, each with coupling to ^{195}Pt. The values of $^1J(^{195}Pt,^{31}P)$ of 3466 and 3759 Hz for the two components, with isotropic shifts of −2.1 and −1.6 ppm, respectively, clearly show that the complex has not crystallized as a mixture of cis and trans isomers, but that both components are due to the cis complex. The observed inequivalence in the values of δ and $^1J(^{195}Pt,^{31}P)$ may be due to asymmetry, induced by the solid state, rendering the two phosphorus nuclei within each molecule inequivalent. Alternatively, there may be two nonequivalent sites within the crystal lattice, resulting in different resonances for each type of site. In the absence of X-ray crystallographic data it is not possible to differentiate these two cases as, in complexes of the type *cis*-$[PtCl_2(PR_3)(PR'_3)]$, scalar coupling between two inequivalent cis phosphorus nuclei which could, if observed, distinguish between these two possibilities is known to be very small (ca. 10 Hz typically) and can even be

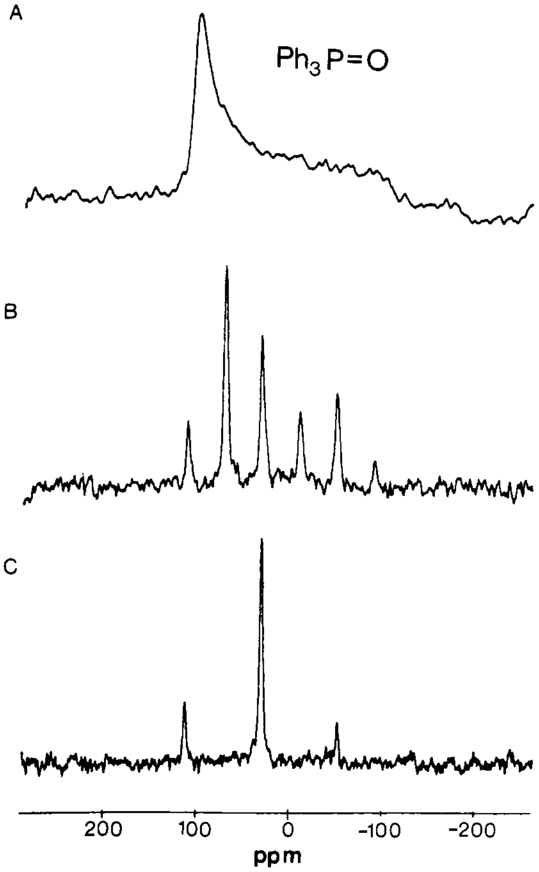

Figure 2. (A) Solid-state ^{31}P NMR spectrum of a stationary sample of $OPPh_3$. (B) Solid-state ^{31}P NMR spectrum of $OPPh_3$ obtained with slow MA spinning (ν = 1.5 kHz). (C) Solid-state ^{31}P NMR spectrum of $OPPh_3$ obtained with fast MA spinning (ν = 3.0 kHz).

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Table II. CP/MAS ^{31}P NMR Data of Solid $[PtCl_2(PR_3)_2]$ Complexes with Comparative High-Resolution Solution ^{31}P NMR Data

		CP/MAS ^{31}P NMR		solution ^{31}P NMR	
complex	geometry	δ	$^1J(^{195}Pt,^{31}P)$	δ	$^1J(^{195}Pt,^{31}P)$
$[PtCl_2(PEt_3)_2]$[a]	cis	8.9	3467	9.6	3520
$[PtCl_2(P\text{-}i\text{-}Pr_3)_2]$[b]	trans	30.0	24.22	26.9	2413
$[PtCl_2(PMePh_2)_2]$[c]	cis	−2.1	3466	−1.2	3621
		1.6	3759		
$[PtCl_2(PPh_3)_2]$[d]	cis	12.9	3877	14.3	3673
		8.6	3623		
	trans	20.9	2695	19.8	2637
		19.0	2559		
$[PtCl_2(Ph_2P\{CH_2\}_2Si\{OEt\}_3)_2]$	cis[e]	15.3	3740	10.5	3616
		12.9	3711		
		4.8	3418		
	trans	19.0	2616	16.1	2566

[a] Solution spectrum in $CDCl_3$, ref 38. [b] Solution spectrum in $CDCl_3$. [c] Solution spectrum in $CDCl_3$, ref 28. [d] Solution spectrum in $CDCl_3$, ref 29 trans isomer. [e] Solution spectrum in C_6D_6; $\Delta\sigma \simeq 70$ ppm, asymmetric, $\Delta\sigma = \sigma_{33} - \sigma_{11}$.

Table III. CP/MAS ^{31}P NMR Data of Solid *cis*-$[PtCl_2(CO)(PR_3)]$ Complexes with Comparative High-Resolution Solution ^{31}P NMR Data

	CP/MAS ^{31}P NMR			solution ^{31}P NMR	
cis-$[PtCl_2(CO)(PR_3)]$ PR_3	δ	$\nu_{1/2}$, Hz	$^1J(^{195}Pt,^{31}P)$, Hz	δ	$^1J(^{195}Pt,^{31}P)$, Hz
$P\{p\text{-}CH_3C_6H_4\}_3$	12.6	120	2988	7.8	3035[a]
$P\{p\text{-}FC_6H_4\}_3$	6.2	215	3096	6.9	3083[b]
$P\{c\text{-}C_6H_{11}\}_3$	43.4	195	2744	36.5	2852[c]
$P\text{-}n\text{-}Bu_3$	19.6	88	2754	14.1	2788[c]

[a] In $MeCN\text{-}d_3$ solution at room temperature. [b] In $CDCl_3/CH_2Cl_2$ solution at room temperature, ref 28. [c] In $CDCl_3$ solution at room temperature, ref 28.

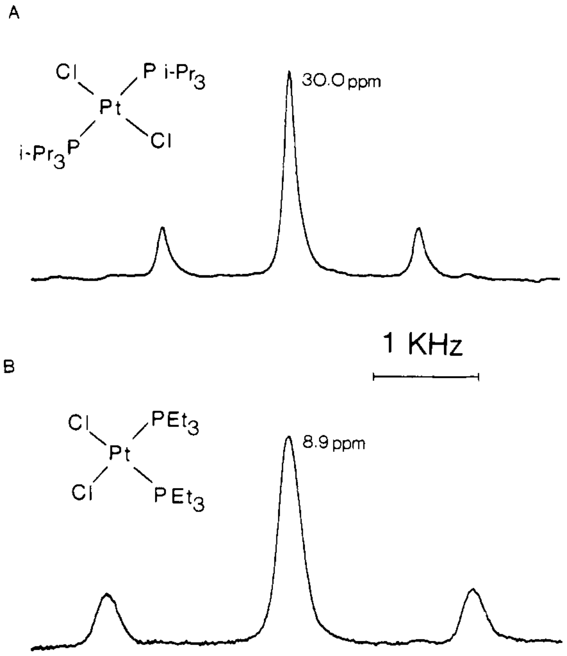

Figure 3. (A) CP/MAS ^{31}P NMR spectrum of *trans*-$[PtCl_2(P\text{-}i\text{-}Pr_3)_2]$. (B) CP/MAS ^{31}P NMR spectrum of *cis*-$[PtCl_2(PEt_3)_2]$.

difficult to observe in solution. With line widths, $\nu_{1/2} \sim 120$ Hz, the possibility of observing $^2J(^{31}P,^{31}P)$ in this class of compounds in the solid state is very remote, thus making differentiation between the two possible cases impossible spectroscopically. A sample of $[PtCl_2(PPh_3)_2]$, prepared by reaction of $[PtCl_2(NCPh)_2]$ with 2 equiv of PPh_3, gave rise to a CP/MAS ^{31}P NMR spectrum consisting of four central components, two with coupling to ^{195}Pt of ca. 2600 Hz and two with coupling of ca. 3700 Hz. In this case, the spectrum shows that the complex has crystallized as a mixture of cis and trans isomers, each giving rise to two central components with characteristic values of $^1J(^{195}Pt,^{31}P)$. The data for $[PtCl_2(PR_3)_2]$ complexes are summarised in Table II.

In order to assess the sensitivity of the isotropic chemical shift to solid-state effects, a series of complexes, *cis*-$[PtCl_2(CO)(PR_3)]$ containing a variety of tertiary phosphines, were examined. The data are summarized, with comparative high-resolution solution data, in Table III. These measurements confirm that values of δ and $^1J(^{195}Pt,^{31}P)$ obtained by solution measurements may be used in comparison with solid-state values in geometry assignments.

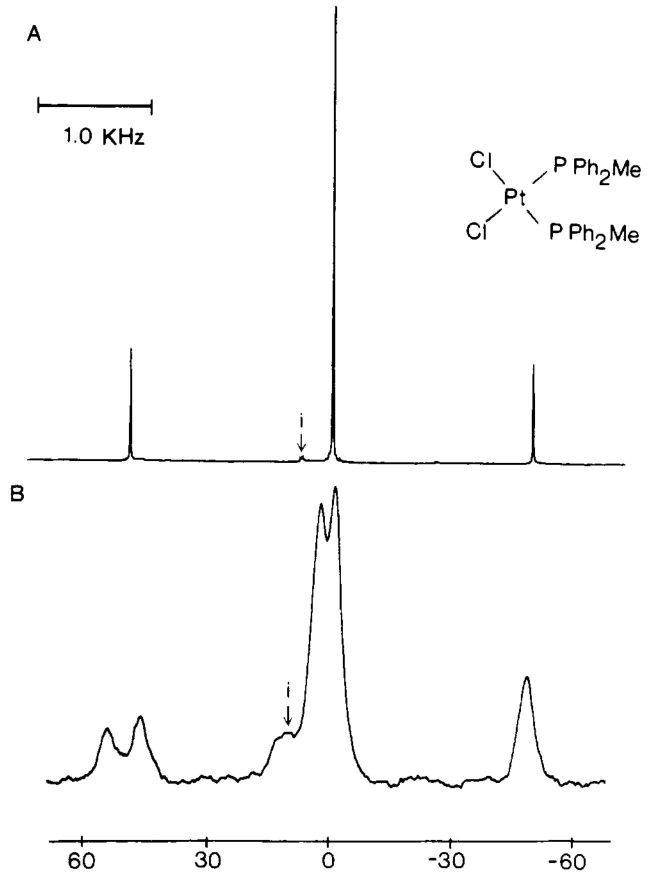

Figure 4. (A) High-resolution solution ^{31}P NMR spectrum of *cis*-$[PtCl_2(PPh_2Me)_2]$. (B) CP/MAS ^{31}P NMR spectrum of *cis*-$[PtCl_2(PPh_2Me)_2]$.

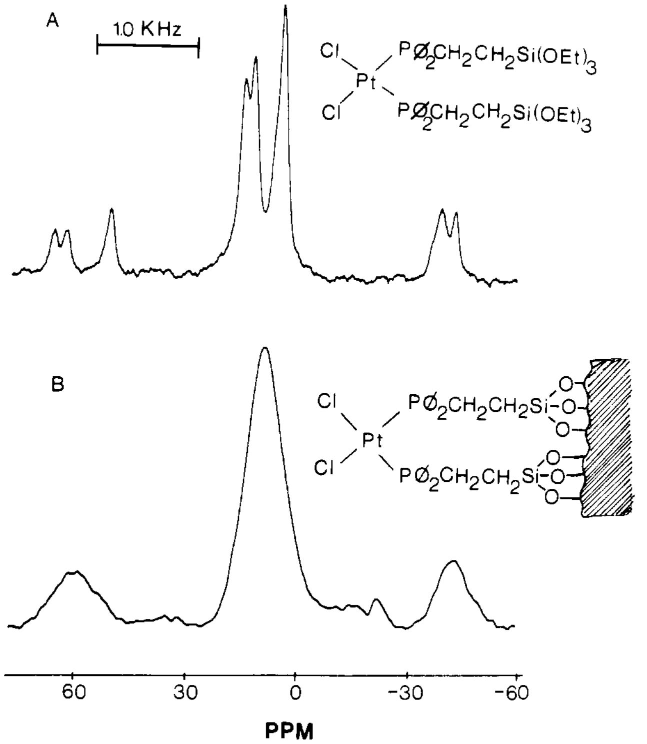

Figure 5. (A) CP/MAS ^{31}P NMR spectrum of *cis*-[$PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$]. (B) CP/MAS ^{31}P NMR spectrum after immobilization on silica gel.

The ease with which cis and trans isomers could be differentiated in the solid state suggested that the magnitude of $^1J(^{195}Pt,^{31}P)$ may be sensitive enough to identify chemically inequivalent phosphorus nuclei within a single molecule. This possibility was examined by comparing the spectra of *cis*-[$PtCl_2(PMePh_2)_2$] (δ -2.1, 1.6; $^1J(^{195}Pt,^{31}P)$ = 3466, 3759 Hz) and *cis*-[$PtMe_2(PPh_3)_2$] (δ 27.9, 31.4; $^1J(^{195}Pt,^{31}P)$ = 1835, 1963 Hz) with the spectrum of [$PtClMe(Ph_2P\{CH_2\}_2PPh_2)$]. The latter complex exhibits two central components in its CP/MAS ^{31}P NMR spectrum, δ 45.6 and 37.5, with coupling, $^1J(^{195}Pt,^{31}P)$ = 4277 and 1768 Hz, respectively. Although no coupling between the inequivalent cis phosphorus nuclei is observed as before, the magnitude of $^1J(^{195}Pt,^{31}P)$ again provides an unambiguous probe of geometry, clearly differentiating P trans to Cl and P trans to Me within the molecule.

The complex [$PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$] is of particular interest in this study as this complex was later immobilized on silica gel and high-surface-area glass beads and examined by CP/MAS ^{31}P NMR (vide infra). The free complex could be obtained as the pure cis isomer by slow crystallization of the product from the reaction of [$PtCl_2(NCPh)_2$] with 2 equiv of the ligand in benzene solution. Alternatively, rapid evaporation of such a solution in vacuo led to the isolation of a mixture of cis and trans isomers. The trans isomer could be isolated alone from the reaction of $[K]^+[PtCl_3(C_2H_4)]^-$ with 2 equiv of the ligand in acetone/benzene solution.

Table IV. CP/MAS ^{31}P NMR Data of Palladium and Nickel Complexes with Comparative High-Resolution Solution ^{31}P NMR Data

complex	CP/MAS ^{31}P NMR δ	solution ^{31}P NMR δ
[$NiCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$]	9.9	13.2[a]
[$NiCl_2(PCy_3)_2$]	3.0	
[$NiCl_2(PPh_2Me)$]	1.6	
[$PdCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$]	40.2	35.0[b]
[$Pd(CN)_2(Ph_2PCH_2CH_2PPh_2)$]	60.9	53.8[c]
[$Pd(PPh_3)_4$]	15.0	18.4[d]

[a] Toluene-d_8 solution at 213 K; $\Delta\sigma \simeq 132$ ppm, asymmetric, $\Delta\sigma \equiv \sigma_{33} - \sigma_{11}$. [b] Benzene-$d_6$ solution at room temperature; $\Delta\sigma \simeq$ 110 ppm, asymmetric, $\Delta\sigma \equiv \sigma_{33} - \sigma_{11}$. [c] Solution spectrum in $CDCl_3$. [d] Reference 13; solution spectrum in toluene at 203 K.

The CP/MAS ^{31}P NMR spectrum of *cis*-[$PtCl_2(Ph_2PCH_2CH_2\{SiOEt\}_3)_2$] is shown in Figure 5A. The spectrum consists of three central components over a shift range of ca. 10 ppm, each exhibiting scalar coupling to ^{195}Pt. The data are summarized in Table II. In an attempt to determine whether the inequivalence of the phosphorus nuclei arises because of symmetry constraints within the crystal lattice or because two or more different crystal polymorphs are present, a series of CP/MAS ^{31}P NMR spectra were obtained with the recycle time varying from 0.5 to 20 s. No relative intensity enhancement of any of the central resonances was observed, indicating that the presence of different crystalline polymorphs in the same sample is unlikely and that the observed inequivalence is probably due to constraints within a single crystalline form. Most importantly, the spectrum of *cis*-[$PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$] shows that the environment of a single type of ^{31}P nucleus may induce large and sensitive changes in the value of δ. In the case of surface immobilized systems, a wide variety of environments are expected to be present for a given type of nucleus due to disordering and hence a substantial shift dispersion, or line broadening, must be anticipated.

The spectrum of a stationary sample of solid *cis*-[$PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$] shows that the chemical shift anisotropy, $\Delta\sigma \simeq 70$ ppm, lies between the values obtained for tertiary phosphines and phosphine oxides. Thus, for samples of this type, three diagnostically useful parameters, δ, $^1J(^{195}Pt,^{31}P)$, and $\Delta\sigma$, may be obtained.

In the case of the mixture of *cis*- and *trans*-[$PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$] the initially complex spectrum, which contained overlapping central components due to the two isomers, could be readily interpreted by subtraction of the known spectrum of the cis isomer. The resulting spectrum showed a single peak due to the trans isomer, exhibiting coupling to ^{195}Pt. The data, shown in Table II, were confirmed by obtaining the spectrum of the pure trans isomer for comparison. The spectrum of the trans isomer, Figure 6A, shows a single central component, exhibiting coupling to platinum, $^1J(^{195}Pt,^{31}P)$ = 2616 Hz.

Complexes of palladium(II) and nickel(II) display no coupling between ^{31}P and the metal center, necessitating greater reliance upon the values of δ and $\Delta\sigma$ and providing less structural information. All the nickel and palladium complexes that we have so far examined display only a single resonance and no environmental inequivalence of chemically equivalent ^{31}P nuclei has yet been observed in complexes of these metals. Data for the two complexes, *trans*-[$MCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$] (M = Pd, Ni), with comparative data for related species are presented in Table IV. The nickel(II) complexes are evidently square planar (diamagnetic), this having been confirmed by X-ray crystallography for *trans*-[$NiCl_3(PCy_2)_3$].[33] No high-resolution solution ^{31}P NMR spectrum of [$NiCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$] could be obtained at room temperature, but cooling to 213 K gave rise to a spectrum consisting of a single resonance at 13.2 ppm. The solid-state spectrum exhibited a single resonance at 9.9 ppm. The solution behavior of the nickel(II) complex is indicative of a dissociative process occurring at ambient temperatures. The consequences of this on attempts to support this complex on silica surfaces are discussed below.

Immobilized Phosphine Ligands and Transition-Metal Complexes. In the preparation of supported catalysts, a wide variety of support materials have been utilized, including cross-linked polymer matrices, silica gels, and high-surface-area glasses. The inorganic supports possess a rigid structure and so are less affected by the nature of the solvent used in a catalytic reaction. Also, it is believed that the rigid supports may stabilize coordinatively unsaturated complexes, which tend to oligomerize when more mobile supports are employed.

The catalytic activity of a variety of transition-metal-complex-supported or functionalized silica surfaces has been examined

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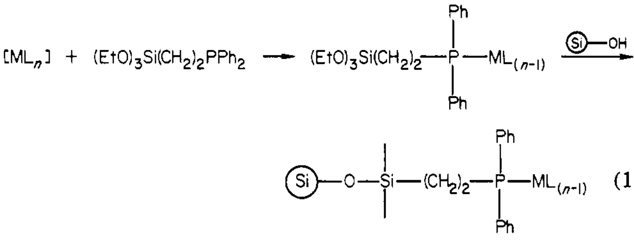
Table V. CP/MAS ^{31}P NMR Data of Supported Species

species[a]	support	δ	$\nu_{1/2}$, Hz	$^1J(^{195}Pt, ^{31}P)$, Hz
L	silica gel	−10.5	110	
L	glass beads	−10.5	225	
cis-$[PtCl_2L_2]$	silica gel	10.2	500	3633
cis-$[PtCl_2L_2]$	glass beads	10.4	400	3721
trans-$[PtCl_2L_2]$	silica gel	18.3	215	2656
trans-$[PdCl_2L_2]$	silica gel	37.0	410	
trans-$[NiCl_2L_2]$	silica gel	9.4	400	

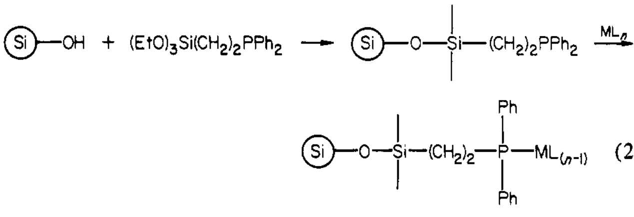
[a] L = supported group derived from $Ph_2PCH_2CH_2Si\{OEt\}_3$ by condensation.

in detail;[34-37] the routes most commonly used in the preparation of the catalysts are shown schematically in eq 1 and 2.



$$[ML_n] + (EtO)_3Si(CH_2)_2PPh_2 \longrightarrow (EtO)_3Si(CH_2)_2P(Ph)_2{-}ML_{(n-1)} \xrightarrow{Si{-}OH} Si{-}O{-}Si{-}(CH_2)_2{-}P(Ph)_2{-}ML_{(n-1)} \quad (1)$$

1



$$Si{-}OH + (EtO)_3Si(CH_2)_2PPh_2 \longrightarrow Si{-}O{-}Si{-}(CH_2)_2PPh_2 \xrightarrow{ML_n} Si{-}O{-}Si{-}(CH_2)_2{-}P(Ph)_2{-}ML_{(n-1)} \quad (2)$$

1

In both cases, the supported complex, **1**, is the supposed product. In the present work we have examined the merits of both routes using CP/MAS ^{31}P NMR to characterize the products from a knowledge of the solid-state spectra presented above.

The condensation of *cis*-$[PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ with activated silica gel was examined as a typical example of the route described by eq 1. The CP/MAS ^{31}P NMR spectrum of such a sample is shown in Figure 5B and consists of a single central resonance exhibiting scalar coupling to ^{195}Pt. The line width of the central component ($\nu_{1/2} \simeq 500$ Hz) indicates a very disordered environment for the surface-immobilized species, as anticipated from the shift dispersion observed for the free complex *cis*-$[PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ discussed above and presented in Figure 5A. The profile of the central component of the spectrum is symmetrical and indicates that only a single type of phosphorus(III) nucleus is present. The magnitude of $^1J(^{195}Pt,^{31}P)$ demonstrates that the complex maintains a cis geometry on the surface of the support.

There is no direct evidence to exclude the presence of species attached to the surface by only one bridging group, but the general efficiency of the reaction and the symmetrical appearance of the spectrum indicate that the structure shown in Figure 5B is a good representation of the surface-immobilized complex. Using glass beads as the support material for this reaction led to the identification of the same immobilized species. Data for the supported complexes are given in Table V.

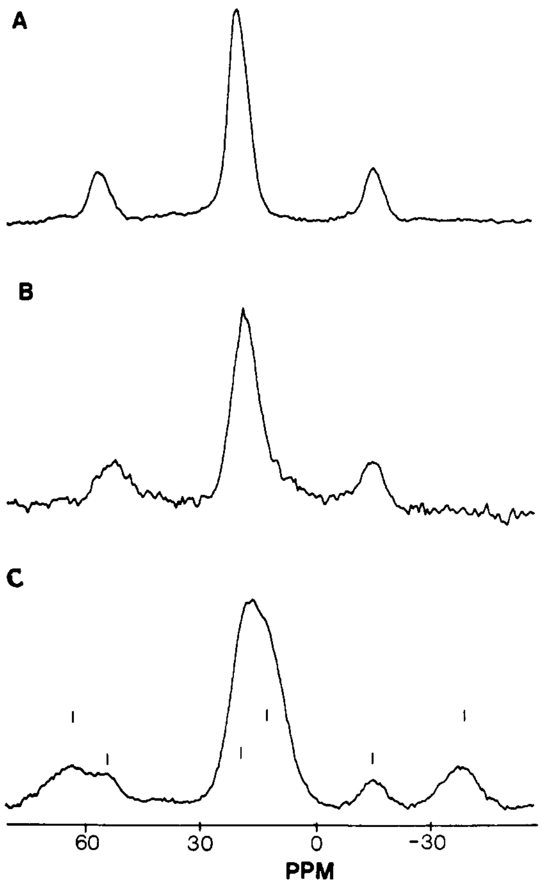


Figure 6. (A) CP/MAS ^{31}P NMR spectrum of *trans*-$[PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$. (B) CP/MAS ^{31}P NMR spectrum after immobilization on silica gel. (C) CP/MAS ^{31}P NMR spectrum of a mixture of *cis*- and *trans*-$[PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ after immobilization on silica gel.

In order to investigate the effects of geometry at the metal center, the complex *trans*-$[PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ was also condensed with silica gel. The CP/MAS ^{31}P NMR spectrum of the product is shown in Figure 6B. The value of $^1J(^{195}Pt,^{31}P)$, Table V, demonstrates that the geometry is maintained and that the surface-immobilized species was of trans configuration. Thus, both cis and trans isomers of the supported complex could be prepared and readily identified. During these reactions, no phosphorus(V) species were observed (vide infra) and only a single isomer of the surface-immobilized species was produced.

A mixture of *cis*- and *trans*-$[PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ (1:1 molar ratio) was also condensed with silica gel. The CP/MAS ^{31}P NMR spectrum, Figure 6C, is indicative of the presence of both isomers on the surface, leading to a rather complex spectrum due to the overlapping of the relatively broad central components. Subtraction of the spectrum of the cis isomer supported on silica gel confirmed that both cis and trans geometries of the immobilized species were present, although the ratio of peak heights may indicate some preferential condensation of the cis isomer.

The condensation of the palladium(II) complex, *trans*-$[PdCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$, with silica gel was also straightforward, the CP/MAS ^{31}P NMR spectrum of the product, Table V, indicating that immobilization occurred with retention of geometry about the metal center. No oxidation products were detected (vide infra). Both the immobilized platinum(II) and palladium(II) complexes were found to be rigidly bound to the surface of the support; extensive Soxhlet extraction with benzene or toluene did not affect the CP/MAS ^{31}P NMR spectra of these species, indicating that no dissociative processes occur in the presence of these solvents.

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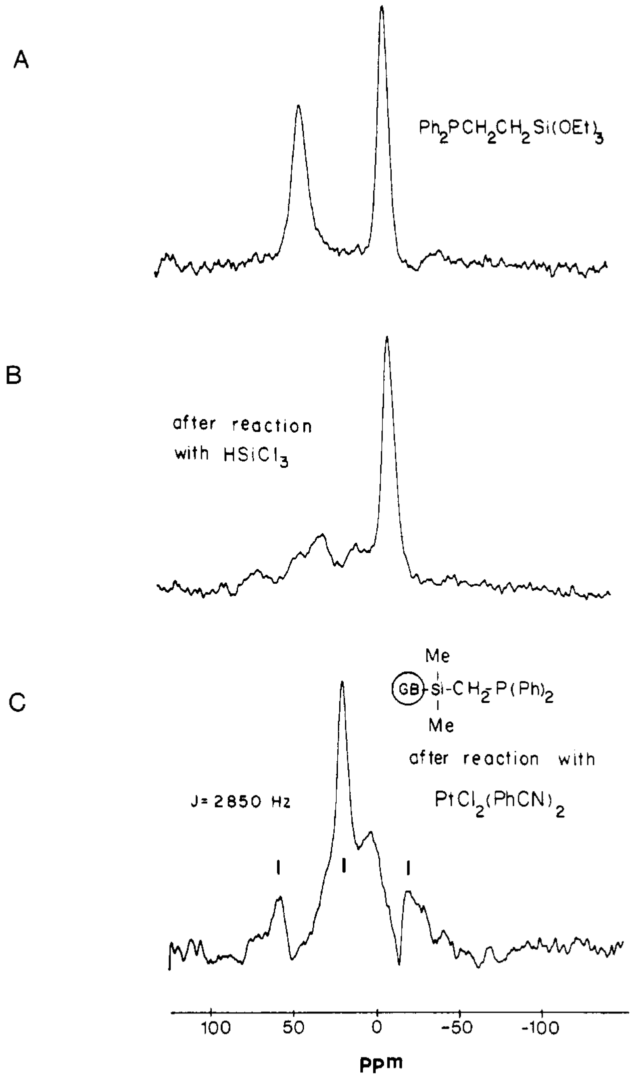
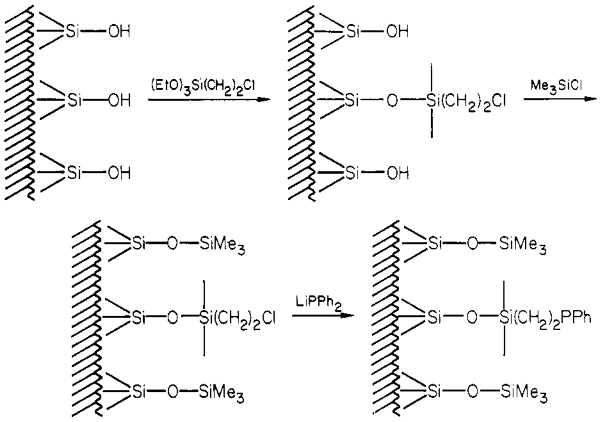


Figure 7. (A) CP/MAS ^{31}P NMR spectrum of $Ph_2PCH_2CH_2Si\{OEt\}_3$ after immobilization on silica gel. (B) CP/MAS ^{31}P NMR spectrum after reduction with $HSiCl_3$. (C) CP/MAS ^{31}P NMR spectrum of a "capped" surface after treatment with $[PtCl_2(NCPh)_2]$.

The complex *trans*-$[NiCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ exhibited solution ^{31}P NMR behavior indicative of a dissociative process at ambient temperatures which could be prevented by cooling (vide supra). Attempts to condense this complex with high-surface-area glass beads at room temperature yielded a sample whose CP/MAS ^{31}P NMR spectrum consisted of two resonances at 42.9 and −8.8 ppm in the ratio of ca. 2:1. The former is attributed to an oxidation product of the tertiary phosphine (vide infra) and the latter to the supported phosphine ligand itself. No resonances with shifts similar to that of the free nickel(II) complex (9.9 ppm as a solid, 13.2 ppm as a toluene-d_8 solution at 213 K) were observed. The room-temperature condensation with silica gel gave a similar spectrum, but with a minor resonance at 10.5 ppm which may be indicative of the immobilized nickel(II) species. Further attempts to absorb the nickel(II) complex onto the support material in toluene soluiton at 273 K, followed by drying the sample at low temperatures and then forcing the condensation by heating the dried solid at 373 K in vacuo, shed some light on these results. The CP/MAS ^{31}P NMR spectrum of such a sample supported on silica gel showed two resonances at 43.4 and 9.4 ppm in a ratio of ca. 1:1. The former is indicative of a ligand oxidation product and the latter of the supported nickel(II) complex.

Undoubtedly, the complexity of the nickel(II) system arises because of dissociative processes which occur in solution at ambient temperature. Oxidation of the free phosphine leads to the production of substantial amounts of the phosphorus(V) species (vide infra), while some free phosphine itself is also grafted to the surface. At lower temperatures, the dissociative processes are inhibited (as indicated by the high-resolution solution ^{31}P NMR data) and the amount of nickel(II) complex on the surface in increased.

In the study of route 2, the prior condensation of $(EtO)_3Si(CH_2)_2PPh_2$ with silica gel and with high-surface-area glass beads was attempted. With both substrates, the CP/MAS ^{31}P NMR showed that two chemically distinct phosphorus-containing groups were grafted to the surface. Figure 7A shows the spectrum of functionalized silica gel; the two resonances have isotropic shifts of −10.5 and 42.0 ppm, with an intensity ratio of ca. 1:1. The assignment of the resonance at −10.5 ppm to supported phosphine is by comparison with the high-resolution solution spectrum of the free ligand, which has an isotropic shift of −10.25 ppm (Table I). The deshielded resonance at 42.0 ppm is indicative of a phosphorus(V) species. Performing the condensation reaction under the mildest possible conditions using all precautions to preclude the presence of air gave a sample with resonances in the intensity ratio 3:1, favoring the supported phosphine. The phosphorus(V) species, believed to be an oxidation product, could not be completely excluded using this preparative route. The extent of oxidation could be dramatically reduced, however, by immobilizing an organic group with an active halide and then "capping" all unreacted surface silanol groups by reaction with chlorotrimethylsilane, prior to functionalization with lithium diphenylphosphide, eq 3. The indication at this time is that the surface silanol groups are involved in oxidation of the tertiary phosphine. Interestingly, it has been observed that the "capping" of unreacted surface silanol groups in this fashion minimizes the occurrence of side reactions during the use of the supported catalysts in hydrogenation and hydroformylation reactions.[34-37]



(3)

A far simpler method to prepare oxide-free supports was developed by allowing the grafting reaction to proceed, producing both supported phosphine and supported oxide, and then treating the surface with the reductant $HSiCl_3$. In this manner, the phosphorus(V) species may be converted to tertiary phosphine almost quantitatively and the progress of this reaction monitored by solid-state NMR. The CP/MAS ^{31}P spectrum of a sample containing ca. 1:1 tertiary phosphine and oxide, Figure 7A, shows substantial removal of oxide after treatment with $HSiCl_3$, Figure 7B.

The reaction of the surface-immobilized phosphine with $[PtCl_2(NCPh)_2]$ was found to be highly dependent upon the reaction conditions. Either the very slow addition of $[PtCl_2(NCPh)_2]$ to the supported ligand or the addition of solvent to a mixture of solid $[PtCl_2(NCPh)_2]$ and the supported ligand led to the isolation of products with extremely complex CP/MAS ^{31}P spectra. The latter reaction conditions favor formation of species such as $[PtCl_2(NCPh)(PR_3)]$ and the corresponding dimeric product formed by elimination of NCPh. It seems likely that some, if not all, of these possible products can be formed, depending upon the precise reaction conditions employed. The most well-defined product was obtained using a "capped" functionalized surface, prepared according to eq 3. Reaction with $[PtCl_2(NCPh)_2]$ led to the isolation of a product whose CP/MAS ^{31}P spectrum is shown in Figure 7C. Undoubtedly, more than one species is present, but the complete disappearance of the resonance due to the supported phosphine indicates the efficiency of the reaction. The major species exhibits a coupling to ^{195}Pt of 2850 Hz, indicative of a *trans*-[$PtCl_2L_2$] moiety. A second species of unknown identity is also indicated by a resonance to slightly higher field. The complexity of the spectra we have obtained using this indirect route for immobilization cast considerable doubt upon the idealized structures often taken as representative of the nature of supported transition-metal phosphine complexes.[2]

Summary

These investigations demonstrate that CP/MAS ^{31}P NMR spectroscopy may be utilized to gain valuable information about surface-immobilized phosphine ligands and transition-metal complexes. Our studies of two of the common routes to supporting transition-metal complexes on silica and glass surfaces demonstrate that the simple schemes representing the course of these reactions, eq 1 and 2, are not sufficient to describe the chemistry that actually occurs. Equation 2 is misleading as the initial step results in substantial oxidation of the tertiary phosphine, while the product of the second step depends upon the exact reaction conditions and may well result in the production of more than one immobilized metal complex. The route described by eq 1 is more meaningful, but becomes invalid when the metal complex undergoes labile dissociative processes. In such cases, immobilization of the metal complex is accompanied by the formation of supported phosphine and phosphine oxide.

Currently we are expanding our work to include the study of rhodium(I) systems, using both inorganic and organic support materials, and to investigate the nature of supported catalysts before and after use in catalytic reactions.

Acknowledgment. Thanks are expressed to the Natural Science and Engineering Research Council of Canada for financial support in the form of operating grants (to H.C.C., C.A.F., R.E.W.) and to Johnson Matthey Limited for a very generous loan of platinum metal salts.

Registry No. *trans*-[$PtCl_2(PPr_3)_2$], 15977-22-7; *cis*-[$PtCl_2(PMePh_2)_2$], 16633-72-0; *cis*-[$PtCl_2(PPh_3)_2$], 15604-36-1; *trans*-[$PtCl_2(PPh_3)_2$], 14056-88-3; *cis*-[$PtCl_2(Ph_2P(CH_2)_2Si(OEt)_3)_2$], 79919-60-1; *trans*-[$PtCl_2(Ph_2P(CH_2)_2Si(OEt)_3)_2$], 79980-82-8; *cis*-[$PtCl_2(CO)(P(p\text{-}CH_3C_6H_4)_3)$], 42958-15-6; *cis*-[$PtCl_2(CO)(P(p\text{-}FC_6H_4)_3)$], 76705-01-6; *cis*-[$PtCl_2(CO)(P(c\text{-}C_6H_{11})_3)$], 19618-81-6; *cis*-[$PtCl_2(CO)P(n\text{-}Bu)_3)$], 73320-20-4; *trans*-[$NiCl_2(Ph_2PCH_2CH_2Si(OEt)_3)_2$], 79919-61-2; *trans*-[$NiCl_2(PCy_3)_2$], 55333-16-9; *trans*-[$NiCl_2(PPh_2Me)$], 28665-20-5; *trans*-[$PdCl_2(Ph_2PCH_2CH_2Si(OEt)_3)_2$], 79919-62-3; [$Pd((N)_2\text{-}(Ph_2PCH_2CH_2PPh_2)$], 32288-97-4; [$Pd(PPh_3)_4$], 14221-01-3; *cis*-[$PtCl_2(PEt_3)_2$], 15692-07-6; [$PtCl_2(NCPh)_2$], 14873-63-3; *cis*-[$PtMe_2\text{-}(PPh_3)_2$], 17567-35-0; [$PtClMe(Ph_2P(CH_2)_2PPh_2)$], 27711-50-8; PPh_3, 603-35-0; $P(p\text{-}CH_3C_6H_4)_3$, 1038-95-5; $P(p\text{-}FC_6H_4)_3$, 18437-78-0; $P(p\text{-}MeOC_6H_4)_3$, 855-38-9; $P(c\text{-}C_6H_{11})_3$, 2622-14-2; $Ph_2PCH_2PPh_2$, 2017-20-7; $Ph_2PCH_2CH_2PPh_2$, 1663-45-2; $Ph_2PCH_2CH_2AsPh_2$, 23582-06-1; $Ph_2PCH_2CH_2Si(OEt)_3$, 18586-39-5; $OPPh_3$, 791-28-6; $OP(C_{14}H_{29})_3$, 72931-37-4.

Effects of Mg(II) on the Conformation of Tetracycline in Me_2SO Solution

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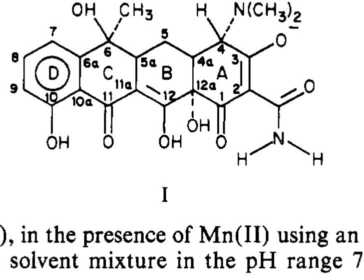
Contribution from the Department of Chemistry, The University of Kansas,
Lawrence, Kansas 66045. Received April 13, 1981

Abstract: Carbon-13 NMR and CD data are presented which show that tetracycline in Me_2SO solution undergoes a major conformation change upon addition of water. In Me_2SO/H_2O solvent mixtures, tetracycline is believed to be in a zwitterionic form. In addition, it is shown that Mg(II) is able to induce the same conformation change in Me_2SO in the absence of water, presumably by binding to the zwitterionic form of tetracycline. These results suggest that Mg(II) ions may effect the in vivo transport of tetracycline by their influence on the molecular conformation.

During the past decade there has been considerable interest in the tetracycline antibiotics with regard to their cation binding properties[1-4] and their molecular conformations in the crystalline[5-13] and solution phases.[14-15]

A recent paper from this laboratory reported the results of a ^{13}C NMR spin–lattice relaxation study of tetracycline, I (hereafter



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abbreviated TC), in the presence of Mn(II) using an 80:20 (v/v) $Me_2SO\text{-}d_6$:D_2O solvent mixture in the pH range 7–8.[16] The

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