of a substitutionally inert outer-sphere oxidant devoid of Brønsted basic (pseudo)halide ligands, X, appears to be beneficial in avoiding postoxidation transfer of hydride ligands to X^-, which confuses quantification by producing a nonstoichiometric mixture of H_2 and HX products. It is for this reason that we have not examined $Fe(CN)_6^{3-}$ as an oxidant.

This study discloses an analytical technique that can be useful for quantitative assay of hydride ligands. On the basis of the systems studied, the procedure appears to be most useful when the highest accessible metal oxidation state is fairly low (e.g. Cu) and thus there is no question of failing to oxidize to a d-electron configuration where hydrogen elimination becomes quantitative. In cases where hydrogen evolution is incomplete, careful attention to identification of the oxidized nonvolatile products (e.g. coordinated hydride or protonated ligand) may still permit the total number of hydride ligands to be established. The method also warrants evaluation for quantifying ligands such as CO_2, O_2, N_2, light olefins[22] and alkynes, oxalate, NO, alkyl, and even perhaps BH_4. In the last two cases, and in general, mass and/or infrared spectral analysis of the identity and purity of the evolved gas is recommended.

The mechanistic details of certain of these oxidative hydrogen evolution reactions are currently under study.

Acknowledgment. This work was supported by the U.S. National Science Foundation (Grant No. 83-05281) and by the Canadian Natural Sciences and Engineering Research Council. We also thank Johnson Matthey, Inc., and Rhenium Alloys for material support and Stadt Wien for the inception of the idea developed here.

Registry No. $Fe(bpy)_3(PF_6)_3$, 28190-88-7; $ReH_5(PMe_2Ph)_3$, 65816-70-8; [*cis,mer*-$IrH(MeCN)_2(PMe_2Ph)_3](BF_4)_2$, 104155-37-5; *fac*-$H_3IrP_3$, 12099-83-1; MoH_4P_4, 40209-71-0; $Co_2(CO)_8$, 10210-68-1; $(HPMe_2Ph)BF_4$, 104155-38-6; H^-, 12184-88-2; CO, 630-08-0.

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(21) Self-exchange in the $Fe(bpy)_3^{3+/2+}$ couple proceeds near the diffusion-controlled rate.

(22) Compare the oxidative (Pb^{4+}, Ag^+, or Ce^{4+}) release of olefins from metal complexes in: Merk, W.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 4787.

Contribution from The BFGoodrich Research and Development Center,
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^{31}P and ^{13}C Solid-State NMR of Tertiary Phosphine–Palladium Complexes Bound to Silica

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Received December 26, 1985

Phosphorus-31 and carbon-13 NMR spectra with cross polarization and magic-angle spinning are used to characterize palladium–tertiary phosphine complexes and their precursors covalently bound to silica. Phosphorus-31 NMR is a good probe of complex formation and geometry, whereas ^{13}C NMR is a good probe of ligand structure. The 36.44-MHz ^{31}P spectrum of $(\equiv SiOSiCH_2CH_2PPh_2)_2PdCl_2$ shows two, barely resolved peaks at about 21 and 30 ppm assigned to the trans and cis complexes, respectively. These assignments are based on the chemical shifts of model compounds in both solution and the solid state. Uncomplexed phosphine and phosphine oxide are observed when complexes are prepared from phosphinated silica but not when the complexes are preformed and then attached to silica. The palladium dichloride complexes of bis(diphenylphosphino)methane, -ethane, and -propane, all of which have an approximately square-planar configuration, were examined as solid-state models for strained cis complexes on the silica surface. As in solution, the solid-state ^{31}P chemical shifts of these compounds occur over a range of 127 ppm while the P–Pd–P angle varies from 73 to 91°. Hence, the ^{31}P chemical shift is a very sensitive measure of strain in such complexes and confirms that the structures in solution are similar to those in the solid state. Applying these models, we find that the surface-bound complexes have mainly unstrained, trans configurations. Other species that have been examined on surfaces or as models include (dicyclohexylpropyl)phosphino complexes, for which cis and trans surface-bound complexes are observed, trimethylsilyl-capped samples, and phosphine oxides. Evidence is found for hydrogen bonding between bound phosphine oxide groups and silanol groups on the silica surface. Both the chemical shift anisotropy powder pattern and P–H cross-polarization rates indicate that the Pd–phosphine complex is rigidly bound to the silica surface.

Introduction

Considerable attention has been given recently to the chemical modification of organic and inorganic surfaces to increase their usefulness in catalytic processes. The materials resulting from such modifications are being explored as alternatives to conventional homogeneous and heterogeneous catalysts.[1] The chemical composition, conformation, and mobility of the molecular species existing at surfaces are important factors for establishing the relationship between heterogeneous catalytic processes and the corresponding ones in homogeneous solution.[2]

Analytical techniques for characterization of molecular structures at surfaces are few. X-ray photoelectron spectroscopy (XPS) is a powerful tool for surface characterization, but it provides atomic composition and oxidation state only. Infrared spectroscopy is commonly used to study surfaces.[1] Other techniques such as secondary ion mass spectrometry (SIMS), fast atom bombardment (FAB) mass spectrometry, and X-ray absorption using synchrotron radiation (EXAFS) are also available.

In certain situations NMR spectroscopy can be useful for studying molecules on surfaces. NMR has the advantages of spectral simplicity and ease of interpretation, as well as sensitivity to molecular mobility. Standard high-resolution NMR has been used for some time to characterize the absorption (physisorption) of molecules on surfaces.[3] This has been possible because the mobility of the adsorbed molecules on the surface or the exchange of the adsorbed molecule with unbound molecules in solution yields a relatively narrow NMR line whose features depend on the nature of the adsorption. In certain cases, swelling of the substrate can provide enough mobility to allow a standard high-resolution NMR spectrum to be obtained. It is only since the advent of solid-state

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NMR techniques [dipolar decoupling, cross polarization, magic-angle spinning (CPMAS)] that we can unambiguously observe resolved spectra of chemisorbed species on surfaces.[4,5]

NMR is generally not a good technique for characterizing the surface of materials. Because NMR is a bulk technique, it is usually not possible to distinguish the surface from the rest of the sample. This is not a problem for samples where the surface is significantly different from the substrate or the substrate is transparent to the technique (does not contain the observed nucleus). The question then becomes one of sensitivity. Due to the low sensitivity of NMR relative to other spectroscopic methods, it is necessary to use materials of high surface area and sometimes isotopic enrichment.

A number of reports have appeared on the characterization of surfaces using solid-state NMR techniques.[5-42] The nuclei commonly observed have been ^{13}C, ^{31}P, ^{29}Si, and ^{1}H. The advantage of ^{13}C NMR for studying organometallic complexes on surfaces chiefly has been in the ability to characterize organic ligand structure. Silicon-29 NMR has been used to observe different species of silicon atoms on silica surfaces. These atoms can originate from either the substrate or bound ligands. For example, ^{29}Si NMR can detect and quantify single, vicinal, and geminal hydroxyls[36] as well as the degree of condensation of multifunctional reagents on silica surfaces.[28] Both ^{13}C and ^{29}Si are isotopically dilute nuclei; hence, only materials of very high surface area can be examined without enrichment.

Phosphorus-31 NMR is an excellent probe for bound molecules containing phosphorus. The ^{31}P nucleus is 100% naturally abundant and has a large magnetic moment. These two features make ^{31}P NMR a more sensitive technique than either ^{13}C or ^{29}Si NMR. The ^{31}P chemical shift is a sensitive probe of organometallic complexes in the crystalline state or on surfaces since the P atom will usually be bound directly to the metal atom. Of particular interest here are the pioneering ^{31}P CPMAS studies of Fyfe and co-workers on immobilized transition metal–tertiary phosphine complexes, for the most part based on Pt(II).[14,15,21,26] These workers determined the composition and geometry of phosphine–Pt (and Pd and Ni) complexes in the crystalline state or bound to silica gel, high-surface-area glass beads or cross-linked polystyrene. They found both ^{31}P chemical shifts and one-bond P–Pt coupling constants to be useful for determination of the structure and geometry of the complexes on the surface. However, they did not explore ^{13}C NMR to characterize the structure of the ligands in the complexes.

In this report we describe the application of high-resolution, solid-state ^{31}P and ^{13}C NMR for the study of tertiary phosphine–palladium complexes bound to silica, their precursors, and model compounds. We have identified the composition and stereochemistry of species existing at the surface and have made an assessment of strain in the palladium complexes. Some information was also obtained concerning the interaction and mobility of bound molecules at the surface.

Experimental Section

Sample Preparation. Silica Diphenylphosphine Surface Coating (2 and 12). A mixture of 120 g of silica (Davison grade 56) (0.4 mmol of OH/g) and 350 mL of toluene was refluxed under argon for 16 h to remove water in a 3-neck, 1000-mL round-bottom flask with a mechanical stirrer and Dean–Stark trap. Then 10 g of (2-(diphenylphosphino)ethyl)triethoxysilane (**1**) (Petrarch Systems) in 50 mL of toluene was added dropwise over 1–2 h to the dried toluene–silica mixture at room temperature, and the resultant mixture refluxed 16 h. During the initial 3 h of reflux, four 25-mL fractions of toluene were removed through the Dean–Stark trap. The solid was filtered and washed with deaerated toluene (3 × 250 mL). It was extracted with deaerated toluene under argon for 16 h. It was then dried under vacuum at 50 °C for 16 h. Anal. Found C, 4.75; H, 1.01; P, 0.59.

Silica Coating Procedure for 4, 6, and 14. A mixture of 5.0 g of silica gel in toluene (250 mL) was refluxed for 1 h with removal of 50 mL of toluene in small portions. The mixture was cooled to room temperature, and a solution of 2.0 g (large excess) of $(EtO)_3Si(CH_2)_3P(O)(C_6H_{11})_2$ (**13**), $(EtO)_3Si(CH_2)_2P(O)Ph_2$ (**3**), or $[(EtO)_3Si(CH_2)_2PPh_2]_2PdCl_2$ (**7**) in 50 mL of toluene was added. The mixture was refluxed and 50 mL of toluene removed in small portions during the initial 3 h. Refluxing continued for 16 h. The mixture was cooled and the filtered solid extracted in a Soxhlet with dichloromethane for 16 h under argon. The silica was dried in a vacuum oven for 16 h at room temperature.

Surface-Bound Palladium Complexes (6 and 15). A mixture of 60.0 g of derivatized silica (approximately 11 mmol of P) in 150 mL of deaerated dichloromethane and 1.46 g (2.08 mmol) of $(Ph_3P)_2PdCl_2$ (**5**) was heated to 40 °C for 6 h and then allowed to stand at room temperature for 16 h. The solid was extracted with dichloromethane under argon for 16 h to remove triphenylphosphine and then dried in a vacuum oven for 11 h at room temperature.

Bis(((dicyclohexylphosphino)propyl)triethoxysilane)palladium Dichloride. To a solution of 8.42 g of ((dicyclohexylphosphino)propyl)-

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Table I. ^{13}C NMR Chemical Shifts[a] and Coupling Constants[b] of Model Compounds in Solution

	Ph or C_6H_{11}		CH_2P		CH_2		CH_2Si		CH_2	CH_3
compd[c]	δ	J	δ	J	δ	J	δ	J	δ	δ
$(EtO)_3SiCH_2CH_2PPh_2$ (**1**)	C-1, 139.0	15.1	20.6	14.1			6.3	12.6	58.5	18.3
	C-2,6, 132.9	18.1								
	C-3,5, 128.5	7.5								
	C-4, 128.6									
$(EtO)_3SiCH_2CH_2P(O)Ph_2$ (**3**)	134.0, 131.8, 131.1, 131.0, 128.8, 128.6[d]		22.9	70.9			1.3	3.0	58.6	18.3
$(EtO)_3Si(CH_2)_3P(C_6H_{11})_2$ (**11**)	C-1, 30.6	14.7	25.2	17.4	22.1	21.4	12.7	12.0	58.3	18.4
	C-2,6, 27.1	32.8								
	C-3,5, 33.6	13.3								
	C-4, 29.2	8.2								
$(EtO)_3Si(CH_2)_3P(O)(C_6H_{11})_2$ (**13**)	27.7, 26.9, 26.7, 26.1, 25.7[d]		36.5	63.4	16.1	3.0	12.7	12.6	58.5	18.3

[a] In ppm from Me_4Si. [b] Carbon–phosphorus coupling constants in hertz. [c] In $CDCl_3$. [d] Peak positions; resonances not assigned.

triethoxysilane (**11**) (0.0209 mol) in 50 mL of deaerated dichloromethane was added a solution of 4.0 g of bis(benzonitrile)palladium dichloride (0.104 mol) in 50 mL of deaerated dichloromethane immediately after preparation. This mixture was stored for 16 h under argon at room temperature. The dichloromethane was removed and the yellow oil redissolved in a mixture of 25 mL of ethanol and 5 mL of water. The yellow precipitate that formed was filtered immediately. The solid was dried overnight at room temperature under vacuum (yield 7.4 g (77.5%), mp 76–77 °C).

Bis(((diphenylphosphino)ethyl)triethoxysilane)palladium Dichloride (7). This complex was prepared as the cyclohexyl complex above, except that a yellow precipitate formed on addition of ethanol (yield 6.8 g, mp 119–124 °C).

((Dicyclohexylphosphino)propyl)triethoxysilane (11). To a stirred solution of 25 g of dicyclohexylphosphine (0.126 mol) in 300 mL of THF under argon at 0 °C was slowly added 52.9 mL of *n*-BuLi (2.4 g, 0.126 mol). The mixture was stirred for $^1/_2$ h at 0 °C after addition. The solution was cooled to −78 °C and a mixture of 30.36 g of (3-chloropropyl)triethoxysilane (0.1260 mol) in 60 mL of deaerated THF slowly added. After addition was complete, the temperature was allowed to rise slowly to room temperature. The solution was stirred for 16 h. To this mixture was added 50 mL of ethanol and the resultant solution stirred for an additional 1 h. The volume was reduced with an aspirator while the sample was warmed to 60 °C. To the residue was added 100 mL of dichloromethane with stirring. The mixture was filtered under argon. The filtrate was distilled to yield 33.0 g (65.1%), bp 150 °C (15.0 mm).

((Triethoxysilyl)propyl)dicyclohexylphosphine Oxide (13). To a stirred solution of ((dicyclohexylphosphino)propyl)triethoxysilane (**11**) (0.0124 mol) at 0 °C in 100 mL of toluene was added a solution of 2.14 g of *m*-chloroperbenzoic acid in 30 mL of toluene. After addition was complete, the solution was warmed to room temperature and stirred for 5 h. The toluene solution was washed with saturated Na_2CO_3 solution (3 × 100 mL), dried over $MgSO_4$, and distilled under vacuum (yield 5.0 g (96.3%), bp 166–170 °C (0.2 mm)).

((Triethoxysilyl)ethyl)diphenylphosphine Oxide (3). The compound was prepared in the same manner as **13** except that it gave a white, waxy solid on distillation; mp 68–72 °C.

Capping of Silica. To a mixture of 125 g of derivatized silica gel (0.7% P) in 500 mL of toluene was slowly added a large excess, 23.87 g, of trimethylsilyl chloride (0.219 mol) dissolved in 100 mL of toluene. This was heated at 50 °C for 16 h. The solid was then extracted with toluene in a Soxhlet under argon for 16 h and dried under vacuum at 50 °C for 16 h.

Bis((diphenylphosphino)alkane)palladium Dichloride (8–10). The preparation of complexes **8–10** was based on procedures described by Jenkins and Verkade[43] and Steffen and Palenik.[44] The recrystallization method is that reported by Westland.[45] A 100-mL Erlenmeyer flask was charged with 5.03 mmol of $PdCl_2(PhCN)_2$ and 5.27 mmol of the bis((diphenylphosphino)alkane). The mixture was stirred under nitrogen as 30 mL of benzene was added. After 30 min of stirring at room temperature, 20 mL of pentane was added. The mixture was filtered and the solid washed three times with 20 mL of pentane and then dried at room temperature in a vacuum oven. This crude product was dissolved in a minimum amount of dimethylformamide at 85 °C. It was filtered hot, and on cooling, ether was added until the solution became very turbid. It was then cooled in ice, giving well-formed crystals. With (diphenylphosphino)methane (dpm), a single crystallization gave 2.10 g (5.27 mmol, 63% yield) of bis((diphenylphosphino)methane)palladium dichloride (**8**) as very pale yellow, almost white crystals. With (diphenylphosphino)ethane (dpe), the combined product from two crops of crystals was 2.32 g (4.03 mmol, 80% yield) of bis((diphenylphosphino)ethane)palladium dichloride (**9**) as very pale, almost white crystals. Finally, with (diphenylphosphino)propane (dpp), the combined product from two crops of crystals was 2.22 g (3.76 mmol, 75% yield) of bis((diphenylphosphino)propane)palladium dichloride (**10**) as pale yellow, fibrous crystals.

NMR. High-resolution, solid-state NMR spectra were acquired by using cross polarization, dipolar decoupling, and magic-angle spinning (CPMAS) on a Bruker SXP spectrometer retrofitted with a BDR-90C unit. Several spectra were acquired with cross polarization and dipolar decoupling but without MAS. The Bruker solids ^{13}C NMR probe was modified for operation in the approximate range of 32–37 MHz (^{119}Sn–^{31}P). Solid-state ^{31}P spectra were acquired at 36.44 MHz with 9-mm-o.d. Delrin rotors of the Andrew geometry.[4] Magic-angle spinning was performed from 3.5 to 4 kHz. Typical conditions for the silica-supported complexes were as follows: recycle time, 1 s; P–H contact time, 2–3 ms; data acquisition time, 50 ms; spectral width, 10 kHz; 90° rf pulse, 4.5–5 μs. Typical conditions for the crystalline compounds were as follows: recycle time, 5–60 s; P–H contact time, 3–5 ms; acquisition time, 100 ms. The P–H cross-polarization time was measured in the usual manner by variation of the contact time. Chemical shifts were measured relative to powdered triphenylphosphine sulfide (43.96 ppm from 85% aqueous H_3PO_4) added to the sample or to the instrument frequency set according to the above as an external reference. Solution ^{31}P spectra were run with the standard high-resolution probe head or the MAS probe head without spinning. All ^{31}P chemical shifts are reported relative to 85% aqueous H_3PO_4. All line widths are reported as the full width at half-height.

Solid-state ^{13}C CPMAS spectra were acquired at 22.63 MHz by using a probe of double-bearing design purchased from Doty Scientific, Inc., Columbia, SC. Samples were spun at about 3 kHz in 5-mm-o.d. cylindrical sapphire rotors. Typical conditions were as follows: recycle time, 1 s; C–H contact time, 2 ms; data acquisition time, 50 ms; spectral width, 10 kHz; 90° rf pulse, 2.5 μs; number of scans for silica-immobilized species, 15 000–50 000. The solid-state ^{13}C chemical shifts were not measured relative to a Me_4Si standard placed in the MAS sample. Approximate ^{13}C chemical shifts were obtained by referencing to the output of the frequency synthesizer of the spectrometer. Solution ^{13}C spectra were acquired in $CDCl_3$ at 50.3 MHz on a Bruker WH-200 spectrometer.

Results and Discussion

(2-(Diphenylphosphino)ethyl)silane Ligands Bound to Silica. Figure 1 shows the high-resolution CPMAS ^{13}C NMR spectrum of the reaction product **2** of silica with (2-(diphenylphosphino)ethyl)triethoxysilane (**1**) (eq 1). This phosphinated silica **2**

$$3-n(\equiv SiOH) + \underset{\mathbf{1}}{(EtO)_3SiCH_2CH_2PPh_2} \longrightarrow \underset{\mathbf{2}}{(\equiv SiO)_{3-n}(EtO)_n Si(CH_2CH_2PPh_2)} \quad (1)$$

contained about 0.8 wt % phosphorus. Assignments were made on the basis of typical ^{13}C shifts and by comparison with the ^{13}C spectrum of **1** in solution at 50.3 MHz (Table I). As expected, the peaks in the solid-state spectrum are considerably broader than those in solution. For example, the approximate line widths of the CH_2O and CH_2Si peaks are about 70 and 130 Hz, respectively. The carbon–phosphorus scalar couplings (about 15 Hz or less)

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Table II. ^{31}P Chemical Shifts (ppm) of Solid Phenylphosphines[a]

	this work		previous work[c]	
	δ	$\sigma_{11} - \sigma_{33}$	δ	$\sigma_{11} - \sigma_{33}$
Ph_3P	-8.8	53	-7.2	50
$Ph_2P(CH_2)_2Si(OEt)_3$ (**1**)	-10.3[b]		-10.25[b]	
$Ph_3P{=}O$	26.7	~210	29.2	200
$Ph_3P{=}S$ (TPPS)	43.96	170		
$Ph_2P(O)(CH_2)_2Si(OEt)_3$ (**3**)	33.5			
$Ph_2P(CH_2)_2Si(OEt)_n(\equiv SiO)_{3-n}$ (**2**)				
phosphine	-9		-10.5	
phosphine oxide	43		42.05	
$Ph_2P(O)(CH_2)_2Si(OEt)_n(\equiv SiO)_{3-n}$ (**4**)	38			

[a] Relative to 85% aqueous H_3PO_4. Solid-state chemical shifts were measured vs. TPPS at 43.96 ppm. [b] Liquid state. [c] From ref 15.

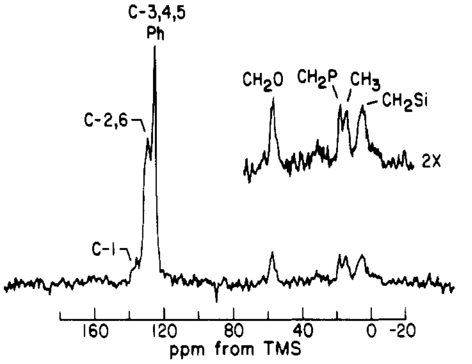

Figure 1. CPMAS ^{13}C NMR spectrum of silica derivatized according to reaction 1 with $(EtO)_3Si(CH_2)_2PPh_2$. The spectrum resulted from 15 430 acquisitions.

seen in the solution spectrum of **1** are not observed in the solid-state spectrum of **2**, but all carbon types are resolved in the aliphatic region. All chemical shifts obtained for **2** were within about 1 ppm of the values for **1** in solution, except for the methyl carbon, where the difference was about 3 ppm.

Three silanes, containing 0–2 residual ethoxy groups, are possible in **2**. Structures arising from condensation of neighboring silane ligands on the surface are also possible. Since the samples were prepared with the rigorous exclusion of H_2O, polymerization products of **1** are not expected to be present to any significant degree. The CPMAS ^{13}C spectrum confirms that the triethoxysilane lignds are bound to the silica gel and that residual ethoxy groups do remain. From the relative area of the peaks in Figure 1, we have determined that there is an average of about one residual ethoxy group remaining for each bound silane ligand in this sample. Maciel and co-workers[13,28] concluded previously that CPMAS ^{13}C NMR is an excellent method for detecting residual ethoxy and methoxy groups in such systems. However, the ^{13}C spectrum tells us nothing about the distribution of ethoxy groups in **2**. This information could be obtained, at least in part, by solid-state ^{29}Si NMR spectroscopy.[12,28] It is possible that this distribution of products, each with a slightly different chemical shift, is contributing to the solid-state NMR line widths for **2**, particularly for the CH_2Si carbon.

We know from ^{31}P solid-state NMR spectroscopy that the phosphine oxide corresponding to **2** (compound **4**) is also present on the silica surface (see below). However, we are unable to confirm its presence by ^{13}C NMR because the carbon spectrum of **1** and that of its phosphine oxide **3** are similar enough to be unresolved in the solid state (Table I), and there is relatively little phosphine oxide present. It is possible that the barely observable hump to the high-field side of the CH_2Si resonance of **2** arises from phosphine oxide.

Figure 2A shows the ^{31}P CPMAS NMR spectrum of **2**. The predominant peak at about -9 ppm is assigned to phosphorus atoms in bound phosphine on the basis of model phosphines in both solution and the solid state (Table II). The agreement between the chemical shift of this peak and that of the models (PPh_3 and **1**) is good, given the line width of the resonance (180 Hz) of the bound group and the possibility of small solvent, crystal-packing, or susceptibility effects on the ^{31}P shifts. In addition, our results for these models and for **2** are in good agreement with those previously obtained by Bemi et al. (Table II).[15] The widths of the chemical shift anisotropy (CSA) powder patterns for PPh_3 and $OPPh_3$ (Table II) are also in agreement with those reported previously.[15]

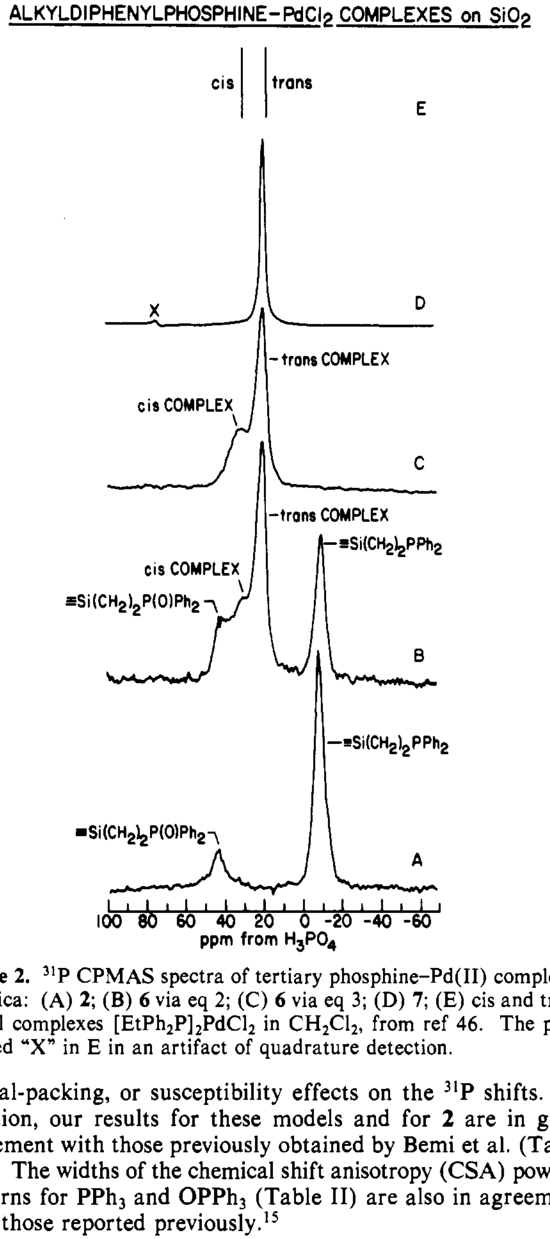

Figure 2. ^{31}P CPMAS spectra of tertiary phosphine–Pd(II) complexes on silica: (A) **2**; (B) **6** via eq 2; (C) **6** via eq 3; (D) **7**; (E) cis and trans model complexes $[EtPh_2P]_2PdCl_2$ in CH_2Cl_2, from ref 46. The peak labeled "X" in E in an artifact of quadrature detection.

The peak at about 43 ppm is assigned to bound phosphine oxide, as suggested previously.[15] In this case, however, the agreement between the chemical shifts of the best monomeric model, the oxide **3**, and the bound group is not particularly good. The oxide **3** has a ^{31}P chemical shift of 33.5 ppm in crystalline form, about 10 ppm upfield of the peak due to bound phosphine oxide in Figure 2A. Attachement of **3** to silica yielded a single peak with a ^{31}P chemical shift of 38 ppm (compound **4**, Table II), still about 5 ppm removed from the position in **2**. We tentatively attribute this remaining difference to hydrogen bonding of the small fraction of phosphine oxide in **2** to residual silanol groups on the surface (see below).

Table III. ^{31}P Chemical Shifts[a] of Phenylphosphine–Palladium Dichloride Complexes in the Solid State and in Solution

	this work	previous work
trans-$[Ph_3P]_2PdCl_2$ (**5**)	23.1	
trans-$[(EtO)_3Si(CH_2)_2Ph_2P]_2PdCl_2$ (**7**)	21.1 (125[e])	40.2[b]
trans-$[EtPh_2P]_2PdCl_2$		19.3[c]
cis-$[EtPh_2P]_2PdCl_2$		30.2[c]
(dpm)$PtCl_2$		−64.3[d]
(dpm)$PdCl_2$ (**8**)	−63.3 (314[f])	
(dpe)$PdCl_2$ (**9**)	63.7 (212[f])	68.3[d]
(dpp)$PdCl_2$ (**10**)	10.6, 22.7 (148[f])	12.9[d]
$[(\equiv SiO)_{3-n}(OEt)_nSi(CH_2)_2PPh_2]_2PdCl_2$ (**6**) (prepared from **2** and **5**)		
trans	21.3	
cis	30	
$[(\equiv SiO)_{3-n}(OEt)_nSi(CH_2)_2PPh_2]_2PdCl_2$ (**6**) (prepared from silica and **7**)		
trans	20.3	37[b]
cis	29.9	

[a] In ppm from 85% aqueous H_3PO_4. [b] From ref 15. [c] From ref 46; in solution. [d] From ref 53; in solution. [e] $\sigma_{11} - \sigma_{33}$ in ppm. [f] Approximate width of full pattern without MAS, in ppm.

The spectrum in Figure 2A represents a typical amount of phosphine oxide on the surface for preparations of this type, which are performed under relatively mild conditions with the exclusion of oxygen. Less care to exclude oxygen or more vigorous conditions produced a larger proportion of bound phosphine oxide. It is clear from the spectrum in Figure 2A that ^{31}P NMR is an excellent method to assess the degree of oxidation of the surface-bound ligands, as also concluded by Bemi et al.[15] This knowledge is important since only the phosphine will form the transition-metal complex.

Bis(ethyldiphenylphosphine)palladium Dichloride Complexes on Silica. Figure 2B is the solid-state ^{31}P spectrum of the product from the reaction described in eq 2. Sufficient dichlorobis(triphenylphosphine) palladium (**5**) was used to complex with about 90% of the ligands in **2**. Much information is immediately evident. The peak at about −9 ppm is due to uncomplexed ligands, and the shoulder at about 43 ppm is assigned to phosphine oxide. The two new peaks at about 30 and 21 ppm are due to complex **6** with the major peak at 21.3 ppm (line width 230 Hz) being assigned to the trans complex on the basis of model compounds. Table III lists the ^{31}P shifts of a number of tertiary phosphine–palladium dichloride complexes. Figure 2D shows the spectrum of the pertinent model compound **7** (the palladium dichloride complex of **1**) having a chemical shift of about 21 ppm and a line width of 110 Hz.

$$\underset{\sim}{2} + (Ph_3P)_2PdCl_2 \longrightarrow$$

$$\underset{\underset{\sim}{6}}{[(\equiv SiO)_{3-n}\,Si(EtO)_n\,CH_2CH_2P(Ph)_2]_2PdCl_2} + 2PPh_3 \qquad (2)$$

Cross-polarization-time measurements for the bound complex (see below) and limited CP data for the bound ligand alone indicate that the ^{31}P spectra can be used for the relative quantitation of the various surface species.

The possiblity of a mixed-ligand complex with triphenylphosphine is ruled out by the ^{13}C spectrum (Figure 3). The observed ratio for phenyl carbons to CH_2Si carbon is 15, in good agreement with the value of 12 expected for complex **7** but in poor agreement with the value of 30 required of the mixed complex with 1:1 triphenylphosphine and **2**.

We assign the peak at 30 ppm in the ^{31}P spectrum to the cis isomer of **6**. We have not prepared the cis isomer of **7** as a model, but the ^{31}P chemical shifts of several cis and trans pairs of bis(alkyldiphenylphosphine) palladium dichloride complexes in dichloromethane solution have been reported by Grim and Keiter.[46] The pair $[(C_2H_5)Ph_2P]_2PdCl_2$ was reported at 30.2 ppm for cis and 19.3 ppm for trans (Table III and Figure 2E). We have reversed the chemical shift sign convention of Grim and Keiter[46] to conform to that used here. On this basis the assignment of the peak at 30 ppm on the surface to cis complex is reasonable. The ^{13}C spectrum of the bound complex (Figure 3) is not sensitive to stereochemistry.

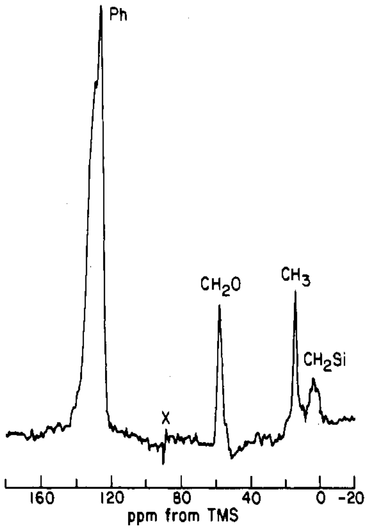

Figure 3. ^{13}C CPMAS spectrum of the surface-bound Pd(II) complex prepared according to reaction 2. The center line artifact is marked by "X".

We also prepared the silica-bound complex **6** from palladium dichloride complex **7** (eq 3). The ^{31}P spectrum of this material

$$\underset{\underset{\sim}{7}}{trans[(EtO)_3Si(CH_2)_2PPh_2]_2PdCl_2} + (\equiv SiOH) \longrightarrow \underset{\sim}{6} \qquad (3)$$

is shown in Figure 2C. As expected, no uncomplexed phosphine or phosphine oxide are present on the surface, as reported by Bemi et al.[15] for the analogous platinum complex. Both isomers are detected in about the same ratio as for the sample prepared via reaction 2. Hence, the configuration of the complex is not totally retained, though it is for the analogous Pt complex.[15] We do not know the equilibrium ratio of cis and trans isomers of **7** in solution, but Grim and Keiter[46] reported a cis:trans ratio of about 1:3 for the $[(C_2H_5)Ph_2P]_2PdCl_2$ pair in CH_2Cl_2 at ambient temperature. This result is similar to our finding of about 20–25% cis isomer on the surface for either preparation. Therefore, we speculate that the value for the surface-bound complex represents the equilibrium ratio for **7** at the temperature of preparation in toluene and is not significantly influenced by immobilization on silica (see below).

We must rely on chemical shifts alone to distinguish stereoisomers of Pd–phosphine complexes by NMR. For Pt–phosphine complexes, the one-bond spin–spin coupling between ^{31}P and ^{195}Pt

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(46) Grim, S. O.; Keiter, R. L. *Inorg. Chim. Acta* **1970**, *4*, 56.

($I = {}^1/_2$, 33.8% natural abundance) is a more sensitive measure of cis–trans isomerism than the chemical shift.[47] However, we observe no P–Pd spin–spin coupling for any of the phosphine complexes of Pd (for ^{105}Pd, $I = {}^5/_2$, 22.2% natural abundance) either in solution or in the solid state. No such coupling has ever been observed to our knowledge.[48] We attribute this to a short spin–lattice relaxation time (T_1) for the quadrupolar ^{105}Pd nuclei relative to $1/(2\pi{}^1J_{\mathrm{PPd}})$, which will average the coupled multiplet into the center line (arising from P atoms bonded to nonmagnetic isotopes of Pd).

Another consideration, peculiar to solid-state spectra, is the effect of the ^{105}Pd quadrupole moment on the dipolar coupling between ^{105}Pd and ^{31}P. In certain cases, such as ^{14}N ($I = 1$) coupled to ^{13}C, MAS will not average the ^{13}C peak into a single, narrow line for the carbon directly bonded to nitrogen. Complicated patterns are seen that arise from residual ^{13}C–^{14}N dipolar coupling not removed by MAS because of the ^{14}N quadrupolar interaction.[49] The magnitude of the effect depends on ther ratio of the quadrupole coupling constant to the Zeeman frequency of the quadrupolar nucleus and hence is more pronounced at lower magnetic fields. The effect has been observed at low magnetic field for ^{31}P in copper(I)–triphenylphosphine complexes, for which ^{31}P–^{63,65}Cu scalar coupling was also seen.[50] Such behavior might also be expected to occur for the case of interest here. However, although the magnitude of the ^{105}Pd quadrupole coupling is probably quite large, the magnitude of the ^{105}Pd–^{31}P dipolar coupling is small (~200 Hz) in the complexes of interest here, given the typical bond distance of 2.25 Å and the low magnetic moment of ^{105}Pd. No evidence for this effect was seen even at high signal-to-noise ratio (see Figure 2D). We attribute this also to a short T_1 for ^{105}Pd, which leads to self-decoupling of the dipolar interaction between ^{31}P and ^{105}Pd.[51] The residual effect may be small and contribute as a broadening at the peak base.

Bemi et al.[15] also have reported the ^{31}P chemical shifts of complex **7** and bound complex **6**. Our results are not in agreement with their results for similar samples. They reported the shift of the model at 40.2 ppm and that of the bound complex at 37 ppm (Table III). Given the internal consistency of our results, the two methods of preparation that we used for **6**, and the agreement with previously published work on similar compounds, we feel that the results of Bemi et al.[15] are in error in these two cases. These authors used a similar preparation to obtain the complex **7**, but starting with $(PhCN)_2PdCl_2$ instead of **5**. They then attached this preformed complex to the silica gel similarly to our preparation in reaction 3, which explains the internal consistency of their two reported results. In some of our early work, we attempted to prepare bound complex **6** using reaction 2 but starting with $(PhCN)_2PdCl_2$ instead of $(Ph_3P)_2PdCl_2$. We obtained a spectrum considerably different from that in Figure 2B. The largest peak appeared at 34 ppm, which is relatively close to that at 37 ppm reported by Bemi et al.[15] Elemental analysis showed this sample to contain a significant amount of nitrogen.

An interesting question is why the trans complex is the dominant species on the surface. It should be the most stable isomer in solution. It is intuitively reasonable to expect that the cis isomer could be relatively more stable on a locally flat surface with pendant phosphine ligands. However, there must be an abundant population of interligand distances that are suitable for trans complexation on the derivatized silica surface. That the complexes are bound in an unstrained fashion is demonstrated in the next section.

Bidentate Phosphine Complexes as Models for *cis*-Bis(alkyldiphenylphosphine)palladium Dichloride Complexes on Silica. Considering the ratio of cis to trans complex present on the surface, one might inquire about the extent of distortion in the geometries of the surface complexes relative to those in solution or in the pure crystalline state. One approach to assess this would be to determine the distribution of interligand distances and how well an ideal cis or trans complex could accommodate these restrictions, allowing for possible conformational changes in the chemical bonds from silica surface to the metal atom. The ^{13}C spectrum of bound complex **6** (Figure 3) shows no clear evidence for any significant conformational changes at the methylene carbon bonds upon complexation as measured by the ^{13}C chemical shifts. For example, the broad CH_2Si carbon resonance does not shift significantly upon forming the organometallic complex on the surface.

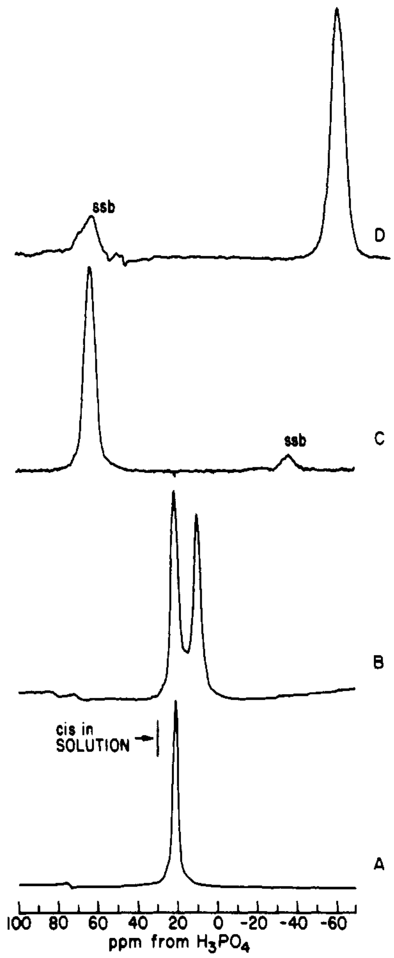

Figure 4. ^{31}P CPMAS spectra of bis((diphenylphosphino)alkane)palladium dichloride model complexes for cis coordination: complex **7** and the value for *cis*-$[(C_2H_5)Ph_2P]_2PdCl_2$ solution (from ref 46) shown for comparison in (A); (B) **10**; (C) **9**; (D) **8**. The peaks labeled "ssb" are spinning sidebands.

We have pursued the more limited goal of investigating the sensitivity of the ^{31}P chemical shifts to distortions at the Pd–P bonds and then drawing conclusions about the likelihood of distorted complexes being present. Certain bidentate phosphine ligands will force the cis geometry in complexes with palladium dichloride. We have examined the complexes $PdCl_2$(dpm) (**8**), $PdCl_2$(dpe) (**9**), and $PdCl_2$ (dpp) (**10**) of known crystal structures[44] as models for surface-bound cis complexes.

The compounds differ by having 1–3 bridging methylene groups between the diphenylphosphino groups. The CPMAS ^{31}P spectra of the three compounds are shown in Figure 4 along with those of cis and trans monodentate complexes for reference. The exact chemical shifts are listed in Table III. The chemical shift of complexes **8**–**10** are greatly different. The dpp complex, **10**, exhibits two peaks of equal intensity separated by about 12 ppm. Apparently, the ^{31}P chemical shift is extremely sensitive to small changes in the stereochemistry. From the X-ray structural analysis,[44] it is known that large changes occur in the P–Pd–P

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(47) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*, 1.

(48) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley-Interscience: New York, 1981.

(49) Zumbulyadis, N.; Henrichs, P. M.; Young, R. H. *J. Chem. Phys.* **1981**, *75*, 1603.

(50) Menger, E. M.; Veeman, W. S. *J. Magn. Reson.* **1982**, *46*, 257.

(51) Spiess, H. W.; Haeberlen, U.; Zimmermann, H. *J. Magn. Reson.* **1977**, *25*, 55.

angle in these structures and that P atoms can be forced from an exact square-planar arrangement. In the dpm complex, **8**, both P atoms are forced out of the plane, and the angle is 72.7°, well below the "ideal" square-planar angle (for identical ligands) of 90°. In the dpe complex, **9**, both P atoms are essentially in the plane, and the angle is 85.6°. In the dpp case, one P atom is in plane and the other out of plane. The P–Pd–P angle in this last case is 90.6°.

The observation of two ^{31}P resonances for the two P atoms in **10** can be explained by the fact that one P atom is in the plane and the other is out of plane. In **9**, both P atoms deviate very slightly from the plane formed by the Pd and the two chlorine atoms, and a single, narrow line is observed. Finally, for **8** both P atoms deviate from the plane, but one about twice as much as the other. In this last case only one line is observed, but it is measurably broader than for the dpe case, suggesting an unresolved nonequivalence.

The ^{31}P chemical shifts of the uncomplexed diphosphines in solution have been previously reported.[52] They are (dpm) −23.0, (dpe) −12.5, and (dpp) −17.3 ppm. The ^{31}P shifts of two of the complexes (**9** and **10**) and the Pt analogue of the third complex (**8**) in solution have been reported and are listed in parentheses in Table III.[53] Examination of these data shows that the chemical shifts in solution correspond reasonably well to those in the solid state. The possibility of bridged structures does exist.[53] Our results confirm that the structures of the complexes in solution are monomeric and have geometries similar to those of the corresponding complexes in the solid state. For compound **10**, the chemical shift in solution (12.9 ppm) corresponds reasonably well to the upfield peak (10.6 ppm) of the two seen in the solid-state spectrum. On this basis we tentatively assign the downfield peak at 22.7 ppm in the solid-state spectrum of **10** to the out-of-plane P atom in the crystal structure.[44]

The ^{31}P chemical shifts in transition metal–phosphine chelate complexes relative to those of the uncomplexed diphosphines have been interpreted in terms of ring contributions,[54] although this view has been challenged.[55] The large downfield shift occurring upon coordination of dpe is well documented.[55] Our immediate interest is not so much in the electronic origin of the particular chemical shifts observed but in the sensitivity of the ^{31}P shifts to the geometry of the complex. The results for the diphosphine chelate complexes show that the ^{31}P chemical shift in cis complexes is highly sensitive to the P–Pd–P angle and hence to strain in the complex.

The results for the model compounds lead to several conclusions concerning our ability to observe strained complexes on the surface. If such complexes are formed, they will be difficult to detect unless they are in sufficient concentration and at only one or a few discrete angles. Strained complexes having a range of angles would yield a broad, probably undetectable resonance due to the strong dependence of the chemical shift on angle. We saw no evidence for strained complexes in any of the derivatized silicas we examined. However, unstrained complexes having approximately the same angle as in *cis*-$[(C_2H_5)Ph_2P]_2PdCl_2$ are present, although most of the complexes have trans stereochemistry. Assuming that the ^{31}P shift of the trans complex would exhibit the same sensitivity to strain, we can conclude that trans complexes on the silica surface are also unstrained since the chemical shift of the surface-bound complex is close to that of the model.

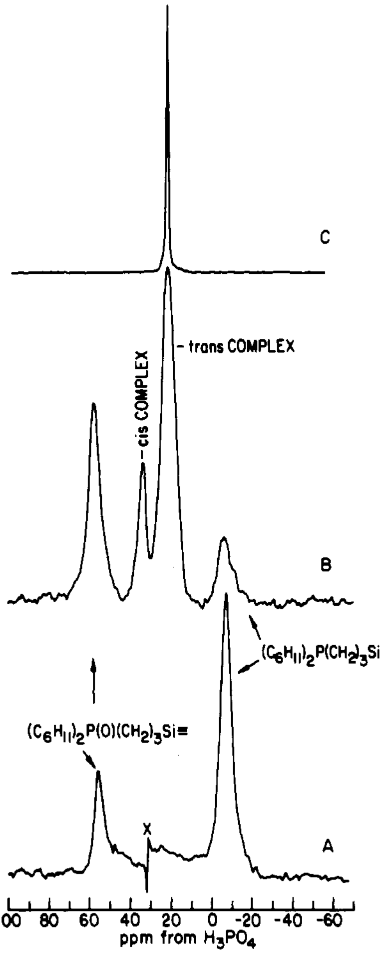

Figure 5. ^{31}P CPMAS spectra of silica-bound bis(propyldicyclohexylphosphine)palladium dichloride complexes: (A) silica derivatized with $(EtO)_3Si(CH_2)_3P(C_6H_{11})_2$, **12**; (B) $PdCl_2$ complex prepared from the sample in (A) according to reaction 4, **15**; (C) *trans*-$[(C_6H_{11})_2P(CH_2)_3Si(OEt)_3]_2PdCl_2$. The symbol "X" denotes a center line artifact.

Table IV. ^{31}P Chemical Shifts of Solid Cyclohexylphosphines and Complexes

$(C_6H_{11})_3P$	6.6 (7.5[a])
$(C_6H_{11})_2P(CH_2)_3Si(OEt)_3$ (**11**)	−7.6[b]
$(C_6H_{11})_2P(O)(CH_2)_3Si(OEt)_3$ (**13**)	50.1[b]
trans-$[(C_6H_{11})_3P]_2PdCl_2$	22.5
trans-$[(C_6H_{11})_2P(CH_2)_3Si(OEt)_3]_2PdCl_2$	19.7
$(\equiv SiO)_{3-n}(EtO)_nSi(CH_2)_3P(C_6H_{11})_2$ (**12**)	
phosphine	−6.7
phosphine oxide	56.6
$[(\equiv SiO)_{3-n}(EtO)_nSi(CH_2)_3P(C_6H_{11})_2]_2PdCl_2$ (**15**)	
trans	19.8
cis	32.9
$(\equiv SiO)_{3-n}(EtO)_nSi(CH_2)_3P(O)(C_6H_{11})_2$ (**14**)	56.7
	38[c]

[a] From ref 15. [b] In solution. [c] Of unknown origin.

Because of its directional nature, the chemical shift anisotropy is a better measure of the electronic environment of a nucleus than the isotropic chemical shift.[4] We have obtained the ^{31}P spectra of compounds **8**–**10** without MAS. The patterns do not conform to a typical powder pattern (see below) and vary substantially in width (Table III). The widths reported in Table III do not correspond to the true CSAs because of the contribution from intramolecular ^{31}P homonuclear dipolar coupling. The observed line shapes result from the convolution of the individual line shapes for the two interactions in each case. Calculations indicate that this contribution is on the order of 43, 29, and 25 ppm (at 36.44 MHz) for compounds **8**, **9**, and **10**, respectively. Hence, even after allowing for this contribution it is clear that the CSA varies substantially among the cis dichelate complexes. A more detailed interpretation must await measurement of the CSAs independently of the ^{31}P homonuclear dipolar coupling and the determination of the orientation of the CSA tensors in the molecules.

(3-(Dicyclohexylphosphino)propyl)silanes and Their Palladium Dichloride Complexes on Silica. Figure 5A is the ^{31}P spectrum of silica gel derivatized with $(C_6H_{11})_2P(CH_2)_3Si(OEt)_3$ (**11**),

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(52) Appleton, T. G.; Bennett, M. A.; Tompkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439.

(53) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1971.

(54) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(55) Hill, W. E.; Minahan, D. M. A.; Taylor, J. G.; McAuliffe, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 6001.

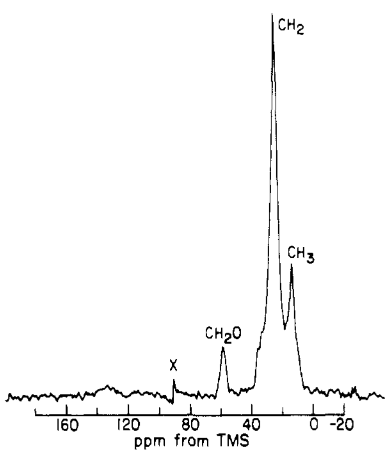
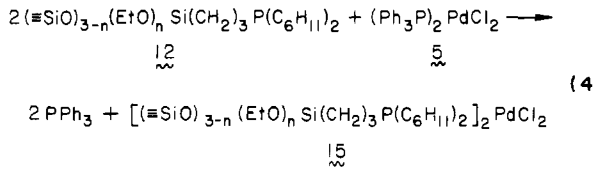


Figure 6. ^{13}C CPMAS spectrum of **15**, showing that essentially all the triphenylphosphine ligands have been replaced by bound propyldicyclohexylphosphine ligands. The center line artifact is marked by "X".

instead of **1**, as in reaction 1. The bound (3-(dicyclohexylphosphino)propyl)silane, **12**, occurs at about −7 ppm (Table IV and Figure 5A). However, the phosphine oxide derived from **12** occurs at about 57 ppm, well downfield from that for the diphenylphosphine oxide **4**. The assignments were made by examining the triethoxysilanes **11** and **13** as models. As with the case of ethyldiphenylphosphine oxide, the chemical shift of propyldicyclohexylphosphine oxide on the surface is somewhat downfield (6.5 ppm) from that of its model oxide **13**. The assignment of the peak at about 57 ppm to bound phosphine oxide was confirmed by reacting phosphine oxide **13** with silica gel to produce bound phosphine oxide **14** (Table IV). An additional, unidentified peak was observed at about 38 ppm for this last preparation.

Figure 5B shows the ^{31}P spectrum of surface-bound complex **15** (Table IV) prepared from the bound ((dicyclohexylphosphino)propyl)silane according to reaction 4. In addition to



$$\underset{\textbf{12}}{2(\equiv SiO)_{3-n}(EtO)_nSi(CH_2)_3P(C_6H_{11})_2} + \underset{\textbf{5}}{(Ph_3P)_2PdCl_2} \longrightarrow 2PPh_3 + \underset{\textbf{15}}{[(\equiv SiO)_{3-n}(EtO)_nSi(CH_2)_3P(C_6H_{11})_2]_2PdCl_2} \quad (4)$$

the peaks due to uncomplexes phosphine and phosphine oxide, two resolved peaks attributable to complex formation are seen. By analogy to ((diphenylphosphino)ethyl)silane complex **6**, we assign these to the cis (32.9 ppm) and trans (19.8 ppm) square-planar complexes. The ^{31}P chemical shifts of the two model complexes given in Table IV (see also Figure 5C) confirm the trans assignment. The cis assignment is made by analogy to complex **6** and the results of Grim and Keiter.[46] The better peak resolution in the ^{31}P spectrum of **15** permits a better estimate of the ratio of cis and trans isomers than for the case of **6**. As with ((diphenylphosphino)ethyl)silane complex **6**, the trans complex predominates (80%).

The ^{13}C spectrum of bound complex **15** is shown in Figure 6. This spectrum is little different from that of derivatized silica **12** (not shown). Peaks from residual ethoxy groups are resolved in the aliphatic region, but only one large resonance, possibly with downfield shoulders, is seen for the cyclohexyl carbons. The ^{13}C spectrum of **15** shows no significant fraction of aromatic carbons, indicating that triphenylphosphine has been totally displaced by bound dicyclohexylphosphine.

Complexes of Bound Tertiary Phosphines on Capped Silica. In the derivatization of silica gel according to reaction 1, not all of the silanol groups on the surface are reacted. There is some evidence that phosphine oxide is formed by reaction of the bound phosphine with the surface itself, presumably with the remaining OH groups.[15] For purposes of catalyst design, it may be desirable to minimize possible side reactions by capping as many of the remaining OH groups as possible by using a large excess of

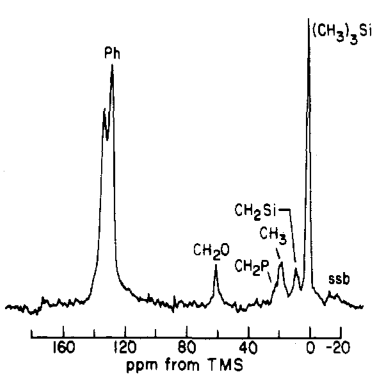


Figure 7. ^{13}C CPMAS spectrum of $[(\equiv SiO)_{3-n}(EtO)_nSi(CH_2CH_2PPh_2)]_2PdCl_2$ on silica capped with $(CH_3)_3SiCl$. The peak labeled "ssb" is a spinning sideband of the phenyl carbon resonance.

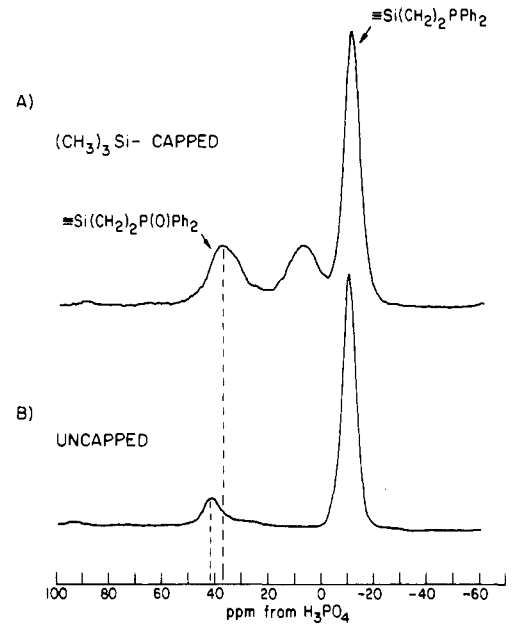


Figure 8. ^{31}P CPMAS spectra of silica (A) after being derivatized according to reaction 1 and capped with $(CH_3)_3SiCl$ and (B) before capping.

$(CH_3)_3SiCl$. Figure 7 shows the ^{13}C CPMAS spectrum of a sample for which this was done. This particular sample was first derivatized with **1**, capped with $(CH_3)_3SiCl$, and then reacted with **5** to form the surface-bound complex, **6**. The ^{13}C spectrum of bound ligand does not change significantly upon complex formation for the capped samples. The large peak at about zero ppm is due to the $Si(CH_3)_3$ groups. The ^{31}P CPMAS spectrum (not shown) of the same sample is very similar to that of an uncapped sample (Figure 2B) and has a prominent peak at about 21 ppm due to trans complex **6**. This confirms that capping has taken place without disrupting the ability to form the Pd complex. Spectra such as in Figure 7, when acquired under conditions permitting relative quantitation, can be used to estimate the degree of capping.

Figures 8A and 8B compare the ^{31}P spectrum of phosphine **2** bonded to capped and uncapped silica. The peak at about 38 ppm is assigned to surface-bound phosphine oxide. A new peak appears at about 9 ppm. Comparison of the peak areas in this spectrum with those in the spectrum of the derivatized but uncapped silica gel indicates that the new peak is derived in some way from the bound ligands **2** and not the phosphine oxide. The identity of this peak is not known for certain at this time. It may arise from formation of the phosphonium salt from $(CH_3)_3SiCl$ and bound phosphine, $[-SiCH_2CH_2PPh_2Si(CH_3)_3]Cl$. It is also possible that it represents unreacted phosphine ligands in a substantially new environment on the surface arising from the presence of capping groups. Because of the substantial difference between the chemical

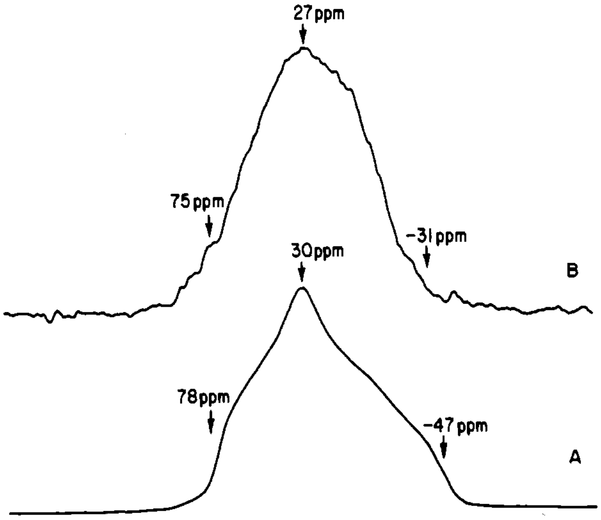


Figure 9. ^{13}C spectra taken with cross polarization and dipolar decoupling but without MAS, of (A) crystalline trans complex **7** and (B) trans Pd(II) complex **6** prepared via reaction 3.

shifts of the new peak and unreacted phosphine, we do not consider this latter possibility a likely one. In any event, it does not disappear upon formation of the $PdCl_2$ complex.

The spectra in Figure 8 show that the phosphine oxide peak has shifted from about 43 to about 38 ppm on capping. We attribute the change in chemical shift of the phosphine oxide on capping to the removal of hydrogen bonds between bound phosphine oxide and surface silanol groups. This would in large measure explain the 10-ppm disparity between the ^{31}P chemical shifts of the bound phosphine oxide present in **2** and the model **4** discussed earlier. The value of 38 ppm is also that obtained when phosphine oxide **3** is attached to silica to give **4**. However, the apparent absence of hydrogen bonding in **4** is likely due to stoichiometry. Unlike **2**, all of the phosphorus in **4** is present as phosphine oxide and there may be insufficient available silanol to produce a significant fraction of hydrogen-bonded phosphine oxide ligands. It is also possible that the chemical shift change of the phosphine oxide peak on capping arises from a relatively nonspecific change in surface environment and not a breakup of hydrogen bonds.

Cross-Polarization Time, CSA, and Mobility of a Bound Complex. The mobility of surface-bound species on silica can affect catalytic properties. Mobility in both the presence and absence of solvent is of interest. There are several ways to study mobility by solid-state NMR.[4] We have measured two parameters that are somewhat sensitive to mobility for bound complex **6** (prepared from silica and preformed trans complex **7**). Bound complex **6** is of particular interest since our chemical shift comparisons reveal no strain in the cis and trans complexes.

We have measured the $^{31}P-^{1}H$ cross-polarization (CP) times for the cis and trans isomers of complex **6**. The CP time is the characteristic time for transfer of spin energy from hydrogen to phosphorus in the P–H CP experiment. It depends on the magnitude of the residual P–H dipolar interaction, as determined by the internuclear distance and the presence of rotational or translational motion. The CP time can become relatively long when the static dipolar interaction is averaged by molecular motion or when the internuclear distance is relatively large. We have obtained average CP times of 75 and 70 μs for the cis and trans complexes, respectively. These values are relatively short and are comparable to those obtained for directly bonded CH pairs in rigid environments. By this very insensitive criterion, we conclude that the complexes are rigidly held on the surface in the dry state. Such may not be the case in the presence of solvent.[30] These CP results also indicate that under our conditions the solid-state spectra should be adequate for quantitation of the relative amounts of cis and trans complex and probably other surface species as well.

Another parameter that can be sensitive to mobility is the chemical shift anisotropy. If rotational motions of the order of the width of the CSA powder pattern or faster are present, the CSA pattern will be averaged, and the full static pattern will not be observed. Figure 9A shows the CSA pattern of trans complex **7**, with the principle values indicated. Since this is a crystalline substance with apparently no possibility of significant motion within the crystal, the CSA pattern of Figure 9A represents the full static pattern for the P atom in this environment. Figure 9B shows the CSA pattern for the same complex bound to the surface. The details of the pattern are not as clear as for the crystalline compound for several possible reasons. For example, the cis isomer is present and the heterogeneity of environments on the surface would tend to obscure the features of the CSA. In addition, bulk susceptibility effects for the surface species and homonuclear P–P coupling could be contributing. However, earlier results in this work indicate that a heterogeneous surface environment can contribute at most several ppm to the line width. Such is also the magnitude of the maximum contribution expected from susceptibility effects for diamagnetic systems. For the trans complex, homonuclear P–P coupling can be shown to be about 9 ppm. Because P–H dipolar broadening is removed by decoupling, we can conclude that the pattern in Figure 9B is overwhelmingly dominated by the CSA. A comparison of the two patterns in Figure 9 shows that little averaging of the static CSA pattern by rotational motion has occurred for the complex on the surface. The values of σ_{11} and σ_{22} for the surface complex are essentially the same as the corresponding values for the crystalline compound. It appears that σ_{33} may be averaged slightly, since this quantity changes from −47 to about −31 upon binding the complex. However, it is difficult to determine σ_{33} exactly in Figure 9B due to the low signal-to-noise ratio and the line shape. These results indicate that there is very little rotational motion of sufficient amplitude or frequency to average the CSA pattern of the bound complex.

Conclusions

Solid-state ^{13}C and ^{31}P NMR are well suited for studying Pd–phosphine complexes on silica (and possibly other surfaces), their precursors, and model compounds. Carbon-13 NMR provides information about the basic molecular structure of the ligands, whereas ^{31}P NMR monitors complex formation, geometry, the presence of byproducts such as phosphine oxides, and hydrogen bonding. The high-resolution, solid-state spectra, aided by additional information such as the chemical shift anisotropy and relaxation times, provide information on structure, mobility, and reactivity of catalytic complexes.

Acknowledgment. We thank John Shockcor for providing the 50.3-MHz ^{13}C spectra in solution.

Registry No. **1**, 18586-39-5; **3**, 104130-33-8; **5**, 28966-81-6; **7**, 79919-62-3; **8**, 38425-01-3; **9**, 19978-61-1; **10**, 59831-02-6; **11**, 104130-31-6; **13**, 104130-34-9; *trans*-$[(C_6H_{11})_3P]_2PdCl_2$, 78655-99-9; *trans*-$[(C_6H_{11})_2P(CH_2)_3Si(OEt)_3]_2PdCl_2$, 104130-32-7; $(CH_3)_3SiCl$, 75-77-4; bis(benzonitrile)palladium dichloride, 14220-64-5; dicyclohexylphosphine, 829-84-5; (3-chloropropyl)triethoxysilane, 5089-70-3.