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Preliminary communication

THE DETECTION AND CHARACTERIZATION OF SURFACE IMMOBILIZED PHOSPHINE LIGANDS AND TRANSITION METAL CATALYSTS BY HIGH RESOLUTION ^{31}P SOLID STATE NMR USING MAGIC ANGLE SPINNING TECHNIQUES

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Summary

High-power proton decoupling, cross-polarization and magic angle spinning techniques have been used to obtain high resolution ^{31}P NMR spectra of solid *cis*-$[PtCl_2(PR_3)_2]$ ($PR_3 = PPh_2Me$ (I); $PR_3 = PPh_2(CH_2)_2Si(OEt)_3$ (II)) complexes. Solid-state effects result in non-equivalent ^{31}P shieldings within a single solid sample and the magnitude of scalar couplings are comparable to those obtained in solution. Reaction of II with silica or glass surfaces yielded an immobilized complex whose geometry was determined by these methods. The utility of various preparative routes to phosphine-linked immobilized transition metal complexes on silica and glass surfaces have been evaluated.

The past decade has seen extensive research efforts in the investigation of analogs of homogeneous transition metal catalysts which have been attached to or "immobilized" on insoluble supports such as silica gel, high surface area glasses or cross-linked polymer matrices [1—3]. Such supported catalysts can potentially combine the advantages of both conventional homogeneous and heterogeneous systems.

A major disadvantage of such systems, which has severely restricted systematic research efforts, has been the lack of good analytical techniques for the detection and characterization of surface immobilized species. Of the few techniques currently available, Fourier transform infrared spectroscopy has been among the most useful [3], but is still severely limited in the characterization of unknown species. Part of the difficulty in studying such systems comes from the low volume concentration of surface attached species, but also from the fact that their spectroscopic properties approximate closely those of completely

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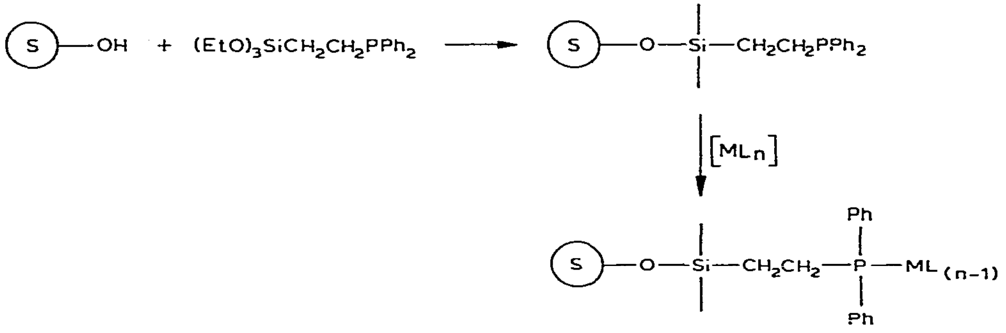
solid species, eliminating the possible use of high resolution NMR techniques.

It has recently been shown [4] that by a combination of high-power decoupling, cross-polarization [5] and "magic angle" spinning techniques [6], "high-resolution" NMR spectra of dilute nuclei may be obtained from solid materials. These techniques have been applied in several diverse areas of chemistry [7] and their potential utility in studies of surface immobilized species in general has been shown [8]. Maciel and co-workers have recently discussed [7i] the application of solid-state ^{31}P NMR to the study of bidentate tertiary phosphines and their rhodium(I) complexes. In that report the possibility of studying polymer-supported rhodium(I) phosphine complexes by such methods was mentioned. The purpose of the present work is to describe an evaluation of the utility of such techniques in the detection and characterization of surface-immobilized transition metal phosphine complexes and to comment on the nature of such species prepared by different routes.

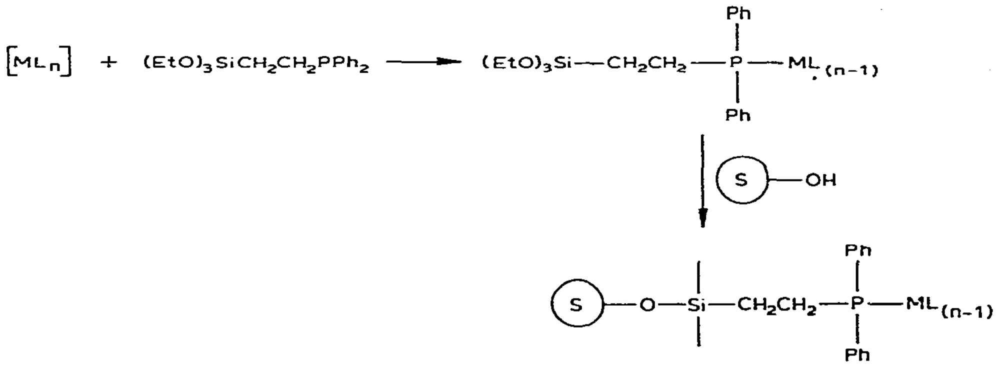
The choice of ^{31}P ($I = ½, N = 100\%$) as the observed nucleus gives a probe known from solution NMR studies [9] to be sensitive to structural variation in transition metal phosphine complexes. The high sensitivity of this nucleus to NMR detection removes many of the problems which arise from low complex concentrations in supported systems.

Our initial studies have concentrated on the immobilization of platinum metal complexes on silica gel and high surface area glass beads, using the established routes [10] (eq. 1 and 2).

As an example of the spectroscopic data obtained, Fig. 1 presents some results relating to the dichlorobis(phosphine)platinum(II) catalyst system used in homogeneous processes as a precursor in the catalytic hydrogenation and hydro-



(1)



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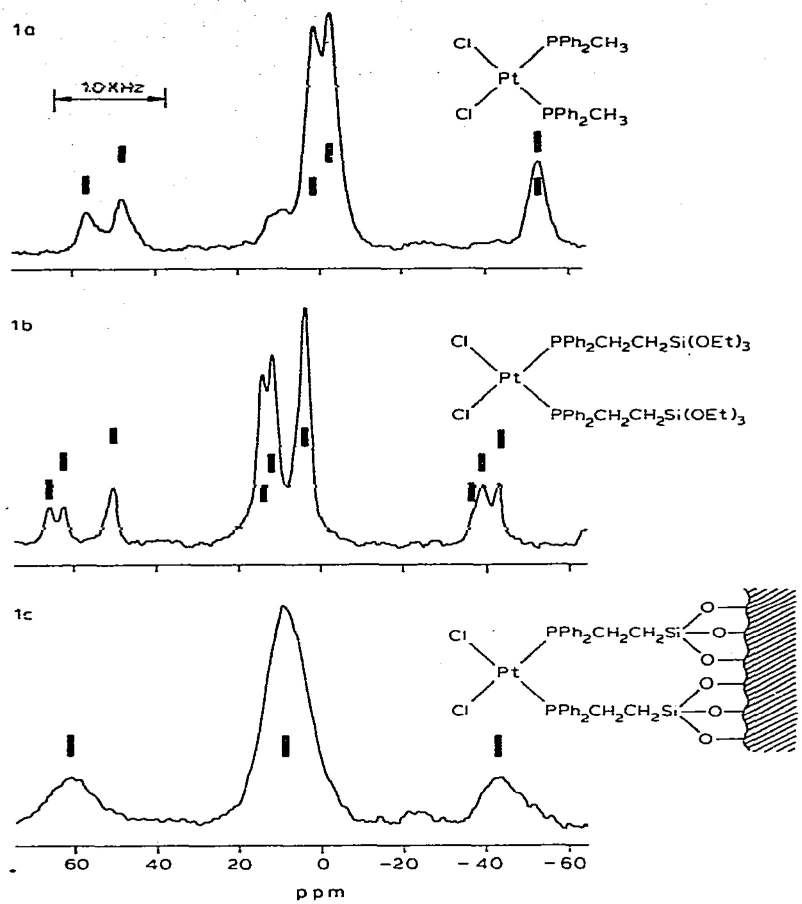

Fig. 1. 1a ^{31}P CP/MAS spectrum of solid complex I (250 mg) recorded at 36.442 MHz using matching and decoupling fields of approximately 10 G, spinning at 3 KHz in a delrin rotor; 3000 scans were accumulated with a 1 s recycle time and a 1 ms single CP contact. The FID was transformed with a 15 Hz line broadening and the spectrum is referenced to 85% external H_3PO_4 (aq). 1b ^{31}P CP/MAS spectrum of solid complex II, recorded as described for complex I except that 6000 scans were accumulated. 1c ^{31}P CP/MAS spectrum of II, covalently immobilized on glass beads (Porasil B, 125—250 m^2/g) after 14000 scans, transformed with a line broadening of 40 Hz.

formylation of olefins [10, 11]. Figures 1a and 1b show spectra of two crystalline platinum(II) complexes, investigated to determine the sensitivity of the ^{31}P chemical shifts and coupling constants to solid state effects. Figure 1a shows the spectrum of *cis*-$[PtCl_2(PPh_2Me)_2]$ (I). The central resonance consists of two components (δ —2.1 and δ +1.6 ppm [12]), each exhibiting coupling to ^{195}Pt ($I = ½$, N 33.8%), $^1J(^{195}Pt, ^{31}P)$ 3466 and 3759 Hz, respectively, which is characteristic of the *cis* geometry [13]. The observed difference in chemical shift may be due to an asymmetry, induced by the solid state, making the phosphorus nuclei inequivalent (the magnitude of $^2J(^{31}P, ^{31}P)$ in such *cis*-complexes is small and probably would not be detected) or may be due to there being two non-equivalent sites in the crystal lattice. It may be possible to distinguish between these two possibilities by X-ray diffraction and/or solid state ^{195}Pt NMR studies. In either case, the spectrum indicates the general sensitivity to solid state effects. This is further exemplified by the spectrum of the complex functionalized with the linking ligand, *cis*-[$PtCl_2(Ph_2PCH_2CH_2Si(OEt)_3)_2$] (II) (Fig. 1b). In this case, the central resonance consists of three components in the intensity ratio 1/1/2 (δ 15.6, 12.9 and 4.8 ppm) with the associated values of ${}^1J({}^{195}Pt, {}^{31}P)$ 3740, 3711 and 3418 Hz, respectively, indicative of the *cis*-geometry [13]. As before, the splittings observed may be due to permutations of non-equivalent sites and solid state induced non-equivalence of the phosphine ligands on a single metal atom and it is not possible to clearly distinguish these cases, where the magnitude of ${}^2J({}^{31}P, {}^{31}P)$ is small, without crystallographic data. All three components in this spectrum showed the same relative intensity on varying the recycle time in the cross-polarization-magic angle spinning experiment from 0.5 to 10.0 s. This result suggests the presence of only a single polymorphic form of II with possibly two different crystallographic sites, one of which has slightly inequivalent phosphine ligands.

The importance of these two examples is that they indicate that substantial dispersions of ${}^{31}P$ chemical shifts (ca. 12 ppm) must be anticipated in amorphous systems where a given type of phosphorus atom may be present in a wide variety of environments. This broadening due to environmental effects will not be further reduced by any line-narrowing technique.

Figure 1c shows the spectrum of complex II covalently immobilized on high surface area glass beads by reaction 2 [14]. There is clearly only a single species present (the peaks are symmetrical with $\delta(P)$ 10.45 ppm and $\nu_{1/2} \approx 500$ Hz), indicating that the reaction has been very efficient and the magnitude of ${}^1J({}^{195}Pt, {}^{31}P)$ 3721 Hz indicates a *cis*-geometry for the supported complex. The broadening of the resonances is as anticipated from the discussion above of the solid state spectra shown in Fig. 1a and 1b and indicates a very disordered environment on the surface for these immobilized species. Similar results are obtained by immobilization of other complexes on both glass beads and silica gel by this route.

The alternative route, eq. 1, was found to be very much less efficient. Preparations of the surface immobilized phosphine ligand were always found to contain a large proportion (up to 50% by peak heights) of the phosphine oxide, even when carried out under rigorous inert atmosphere conditions, using the mildest possible reaction conditions. The two species are readily distinguished by solid state ${}^{31}P$ NMR (δ −8.6 ppm for the supported ligand [13], δ 44.2 ppm for the corresponding oxide).

There are indications that the oxidation of the phosphine is caused, and possibly catalyzed by, the silica and glass surfaces. The only "oxide-free" ligand which we have obtained was prepared by immobilizing an organic group with an active chlorine and then "capping" all unreacted surface hydroxyls by reaction with chlorotrimethylsilane. Subsequent reaction with lithium diphenylphosphide then generated the surface-supported phosphine ligand. The ${}^{31}P$ NMR spectrum of this sample showed that levels of phosphorus containing side-products were low, certainly less than 20%. Interestingly, the "capping" reaction is known to lead to more efficient catalysis during hydrogenation and hydroformylation reactions [10].

The reaction of the supported ligand with [$PtCl_2(NCPh)_2$] does not yield a single product, as implied by eq. 1. The ${}^{31}P$ NMR spectrum is extremely complex, showing that at least two species are immobilized on the surface, possibly a mixture of isomers. We are currently investigating the preparative method in greater depth in order to elucidate the exact nature of the species present.

For a variety of systems, the synthesis decribed by eq. 2 was found to yield clea, easily characterized products whereas the alternative method, eq. 1, yields more than a single product and involves very substantial oxidation of the phosphine ligand. Polystyrene-immobilized tertiary phosphines, including commercial samples, were also found to contain very large amounts of phosphine oxide and it is felt that the direct incorporation of a pre-formed metal complex into the polymerization system will yield cleaner and much more reproducible catalyst systems. Investigations of this and other systems including a study of the catalytic activity of these well-characterized supported complexes are presently in progress.

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12 Chemical shifts are measured relative to 85% H_3PO_4 (external), more positive shifts represent deshielding.
13 Solution ^{31}P NMR data are: δ —1.3 ppm, $^1J(^{195}\text{Pt}, ^{31}\text{P})$ 3621 Hz for *cis*-$[\text{PtCl}_2(\text{PPh}_2\text{Me})_2]$, δ 10.45 ppm, $^1J(^{195}\text{Pt}, ^{31}\text{P})$ 3616 Hz for *cis*-$[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}\{\text{OEt}\}_3)_2]$ and δ —10.25 ppm for $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3$.
14 Although there is no direct evidence to rule out the contribution of species which are linked via only one silyl group to the surface, the reaction conditions and the observed sensitivity of the ^{31}P shifts to small environmental effects shown in Fig. 1a and 1b together with the symmetric shape and relatively small width of the observed ^{31}P signal makes it likely that the majority of the immobilized complexes are linked as indicated in Fig. 1c.