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^{31}P Magnetic Resonance of Triphenylphosphine Oxide Complexes with Silicon Compounds

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Introduction

Organophosphine oxides behave as weak donor ligands to Lewis acids by coordination of oxygen to a vacent, valence shell orbital of the acid. In some cases (*e.g.* $SiCl_4$ [1], Me_2SnX_2 (X = Cl, Br, I) [2]) complexes may be isolated as a solid substance which precipitated simply by mixing the reagents. Generally, characterization of the complex involves examination of differences in spectroscopic properties between reactants and the complex. Often complexes do not exhibit the same spectroscopic properties in solution as in the solid phase. For example, $SiCl_4$ and Ph_3PO form a 1:2 complex which exhibits a large decrease in phosphoryl stretching frequency ($\Delta\nu_{PO}$ = -45 cm^{-1}) as a Nujol mull [2]. However, when the complex is dissolved in organic solvents, no frequency shift is observed. This suggests either appreciable dissociation or a weakened dative bond interaction of the complex in solution. Interestingly, complexes of Ph_3PO and organochlorsilanes (*viz.* Me_nSiCl_{4-n}, n = 1–3) have been neither isolated nor detected by physical or spectroscopic methods, yet such complexes have been proposed as intermediates in Ph_3PO catalyzed redistribution of chlorosilane monomers with cyclic polydimethylsiloxanes [3].

It has recently been shown by Grim *et al.* [4, 5] that ^{31}P nmr is a sensitive probe for the detection of complexes involving phosphorus containing mono- and bidentate ligands coordinated to transition metals. In each case a sizeable decrease in chemical shift ($\delta_{complex} - \delta_{ligand}$) is observed and has been interpreted in terms of inductive effects resulting from a decrease in electron density at phosphorus through oxygen coordination. In our pursuit of support for the existence of phosphine oxide–silicon bonded complexes in solution we have examined the ^{31}P nmr spectra of Ph_3PO solutions containing a variety of silanes and siloxanes (Me_nSiCl_{4-n}, n = 0–4; $(Me_2SiO)_3$, $Cl(Me_2SiO)_3SiCl_3$).

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Experimental

The monomeric silanes (Me_nSiCl_{4-n}, n = 0–4) (Alfa Inorganic Inc.) and $(Me_2SiO)_3$ (Union Carbide Corp.) were purified by distillation. $Cl(Me_2SiO)_3SiCl_3$ was prepared by established procedures and purified by gas chromatography.** ^{31}P nmr spectra were recorded with a Jeol PFT-100 spectrometer operating at a proton frequency of 100 MHz in a Fourier transform mode for phosphorus at 40.48 MHz. Nmr sample tubes containing a solution of the silane or siloxane and triphenylphosphine oxide in toluene (90%)–acetonitrile (10%) solvent mixture† were prepared immediately before the spectra were recorded. $(MeO)_3PO$ was used as an external reference. Additionally, a sample of $Ph_3POH^+Cl^-$ in the same solvent mixture was prepared by saturating a solution of triphenylphosphine oxide with hydrogen chloride gas under anhydrous conditions. The ^{31}P nmr data are summarized in Table I.

TABLE I. ^{31}P nmr Chemical Shift Data of Ph_3PO in the Presence of Chlorosilanes and Siloxanes.

Compound	δ_{ppm}[a]	$\Delta\delta_{ppm}$[b]
0.1*M* Ph_3PO	−24.8	0.0
0.1*M* Ph_3PO + 0.3*M* $(Me_2SiO)_3$	−25.0	−0.2
0.1*M* Ph_3PO + 0.3*M* $SiCl_4$	−32.8	−8.0
0.1*M* Ph_3PO + 0.3*M* $MeSiCl_3$	−33.0	−8.2
0.1*M* Ph_3PO + 0.3*M* Me_2SiCl_2	−33.9	−9.1
0.1*M* Ph_3PO + 0.3*M* Me_3SiCl	−34.0	−9.2
0.1*M* Ph_3PO + 0.3*M* Me_4Si	−24.8	0.0
0.1*M* Ph_3PO + ~0.3*M* I	−33.6	−8.8
0.1*M* Ph_3PO + $HCl_{(g)}$ (satd.)	−46.3	−21.5

[a]In 10% acetonitrile in toluene relative to $OP(OMe)_3$ as an external standard. [b]$\Delta\delta = \delta_{complex} - \delta_{Ph_3PO}$.

Results and Discussion

The experimental results indicate that a solution of compounds containing the Si–Cl bond and Ph_3PO exhibit a downfield ^{31}P nmr chemical coordination shift ($\delta_{complex} - \delta_{ligand}$) of approximately 8–9 ppm. Such data clearly substantiate the bonding interaction between phorphoryl oxygen and silicon in compounds which contain chlorine. No chemical shift change was found with either Me_4Si or $(Me_2SiO)_3$. This may be expected since it has been concluded by Ebsworth that at least one electron withdrawing

**Unequivocal structural characterization will be reported elsewhere.

†The solvent mixture is the same as that reported in redistribution studies [3].

substituent with electronegativity greater than that of oxygen is necessary for silicon to possess observable acceptor properties [6].

Although the molecularity of the complex in solution (*i.e.,* 1:1 and/or 1:2) has not as yet been confirmed, the ^{31}P nmr does attest to the coordinate nature of the complex(es). Grim and co-workers [4, 5] noted that a comparatively large change in chemical shift occurs when a phosphine oxide coordinates through oxygen to a metal in an ionic environment (*e.g.,* $[Bu_3PO)_4Zn](ClO_4)_2$, $\Delta\delta = -25.7$ ppm). Contrastly, small changes are observed where the complex is molecular in nature (*e.g.,* $(Ph_3PO)_2$-$HgBr_2$, $\Delta\delta = -5.8$ ppm; $[(Ph_2P(O))_2CH_2]MCl_2$, $\Delta\delta_{Zn} = -5.4$ ppm; $\Delta\delta_{Cd} = -5.0$ ppm; $\Delta\delta_{Hg} = -4.5$ ppm). They interpreted the larger change in shift in terms of the stronger Lewis acid properties of Zn(II) ion compared to the molecular moieties, $ZnCl_2$, $HgBr_2$, $CdCl_2$ and $HgCl_2$. Furthermore, in a separate study, it was reported that a large ^{31}P chemical shift change occurs when Ph_3PO is saturated with HBr ($\Delta\delta = -27.7$ ppm) and that the magnitude of the change is a result of the protonated form, Ph_3POH^+-Br^- [7]. A similar observation on a solution of Ph_3PO saturated with HCl under anhydrous conditions ($\Delta\delta = -23.5$ ppm) has been made in the present study. The ionic nature of such solutions has been verified by conductance measurements [8]. Finally, it is noteworthy that the molecular complex of the bidentate ligand, $[Ph_2P(O)]_2CH_2$, and another organometallic compound of a group IV element, Me_2SnCl_2, exhibits a shift change of -5.5 ppm [5]. The magnitude of the change is both consistent with a dative interaction in a molecular complex and comparable to the aforementioned silicon complexes.

Further studies are currently underway to utilize concentration dependent ^{31}P nmr data to confirm the number of complexes in solution and formation constants.

Attempts to detect complexation by UV spectroscopy were unsuccessful. No measurable changes in the region from 285–385 nm were observed even at high $Ph_3PO/SiCl_4$ ratios.

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