obtained under these conditions. As is seen in its electronic spectrum (Figure 3), the 457.9-nm line is almost at the center of the strong band V. Thus, this band is mainly responsible for the large enhancement of the $Mo{=}O$ stretching mode at 910 cm^{-1} relative to other vibrations. As stated before, the peak position of band V in the MoO(OEP)L series is very sensitive to the nature of the axial ligand, L. These observations suggest that band V of MoO(OEP)(OMe) is mainly due to a CT transition.

In general, the total scattering intensity is proportional to the absorption intensity in a pure radiative process. Thus, we expect that the total scattering intensity of MoO(MEC) by the 457.9-nm excitation should be larger than that by the 587.0-nm excitation. Although we cannot estimate the Rayleigh scattering intensity, it is generally proportional to the total Raman intensity. We observed that the total Raman intensity by the 457.9-nm excitation is much less than that by the 587.0-nm excitation. This result may imply that the internal energy transfer from the CT excited state to the higher vibronic π^* states is occurring rapidly while the molecule is irradiated by the 457.9-nm line.[14]

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Registry No. MoO(MEC), 63621-40-9; MoO(OEP)(OMe), 39048-14-1.

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Low-Power CO_2 Laser Induced Chemistry of SF_6-Sensitized Diborane

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Inverse quantum yields for B_2H_6 conversion and H_2, B_5H_9 + B_5H_{11}, and $B_{10}H_{14}$ formation were measured as a function of B_2H_6 initial partial pressure for constant 5 Torr of SF_6 with the CO_2 CW laser operating on the P–16 (947.75 cm^{-1}) line at 6.1 W and at an intensity of 15.9 W/cm^2. Sensitization with SF_6 was found to increase laser-induced conversion and formation efficiencies by a factor of 2–3 relative to the neat B_2H_6 case. Percent yield by weight for $B_{10}H_{14}$ production was found to be as high as 23% of the B_2H_6 reacted. Power and intensity studies demonstrated measurable product yields at 3.5 W and 9 W/cm^2. Average initial inverse quantum yields were measured for B_2H_6 conversion and H_2, B_5H_9 + B_5H_{11}, and $B_{10}H_{14}$ formation and found to be 46, 49, 112 and 3100, respectively. B_2H_6 conversion and B_5H_9 + B_5H_{11} and $B_{10}H_{14}$ formation yields were measured as a function of wavelength for laser lines between P32 (933 cm^{-1}) to P12 (951.2 cm^{-1}) for 400 Torr of B_2H_6 and 5 Torr of SF_6 at a power of 6.1 W and 15.9 W/cm^2 intensity. "Red shifting" relative to the room-temperature absorption spectrum of the ν_3 band of SF_6 was noted. All "red shifting" was interpreted as resulting from laser heating of SF_6 and indicated temperatures of 500–550 K.

Introduction

Recently, considerable attention has been focused on the infrared laser induced chemistry of diborane.[2-4] This attention may be partially attributed to the interest in applying lasers to demonstrate vibrationally enhanced synthesis of boron hydride cages. Of general importance are the aspects of the work that elucidate the nature of low-power laser-induced processes in laser-enhanced synthetic chemistry at high reactant pressures. There is both supportive and nonsupportive evidence that under these experimental conditions vibrationally controlled processes, and not only thermolysis, may be encountered.[2,4-7]

Reasons for the present study are twofold. First, regardless of the nature of the processes, can we improve on the efficiency of product formation over that of the neat B_2H_6 laser experiments?[3] Second, the sensitized experiments should shed light upon the question of predominance of laser-induced vibrationally controlled processes vs. laser-induced thermolysis under low-intensity CW infrared laser illumination.

Experimental Section

Details regarding the laser cells, sample preparation, postirradiation analysis, the laser, and tuning have been outlined previously.[3] In all the CW experiments 5 Torr of SF_6 was used which was added to the measured diborane sample in the cell from a calibrated volume by condensation with liquid nitrogen in the side vial of the cell. The room-temperature infrared spectrum of SF_6 was obtained using a Digilab Model 20B Fourier transform spectrophotometer at 0.5 cm^{-1} resolution with 6-cm cells. Data reproducibility was dependent upon maintaining a homogeneous 7 mm diameter laser beam. This was aided by adjusting the laser to oscillate in the TEM 00 mode in all experiments. Beam diameter was controlled by a variable aperture and determined from the burn spot and the image on an Optical Engineering CO_2 laser thermal image plate, Model 22A, No. 4.

Results

B_5H_{11}, B_5H_9, $B_{10}B_{14}$, and $(BH)_n$ along with H_2 were found as products in all CW runs. Figures 1 and 2 show the inverse quantum yields (number of photons required per molecule) as a function of B_2H_6 partial pressure for H_2 and B_2H_6, B_5H_n (B_5H_9 + B_5H_{11}), and $B_{10}H_{14}$ using P-16 (947.75 cm^{-1}) illumination. Although smaller by a factor of 2–3, they follow the general trends as noted for the neat irradiations.[3] It should be pointed out that for a specific laser setting (power, frequency) energy is absorbed within the same volume at a given pressure of sensitizer, regardless of B_2H_6 partial pressures. Below approximately 200 Torr, for our cells, transmission occurred for the neat irradiations with the R-16 line and were corrected for proper ϕ^{-1}'s to be measured.[3] This was not necessary in the sensitized experiments since all energy is absorbed within a few tenths of a centimeter. Figure 3 depicts the percent yield by weight of $B_{10}H_{14}$ as a function of initial B_2H_6 partial pressure for the P-16 line. Taken throughout the entire pressure range, average yields for $B_{10}H_{14}$ were 2–3 times

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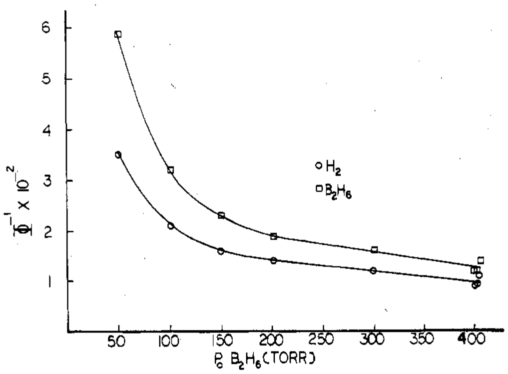

Figure 1. Inverse quantum yield (number of photons required per molecule) for H_2 formation (open circles) and B_2H_6 consumption (open squares) vs. initial B_2H_6 partial pressure for 5 Torr SF_6 sensitizer. Power was 6.1 W with 15.9 W/cm^2 intensity. Run time was 300 s with the P-16 (947.75 cm^{-1}) line.

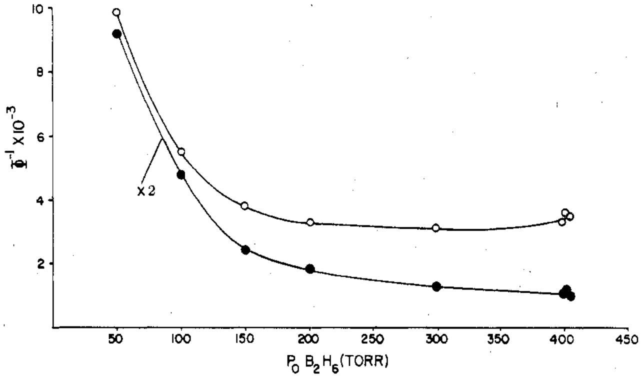

Figure 2. Inverse quantum yield for B_5H_n formation (solid circles) and $B_{10}H_{14}$ formation (open circles) vs. initial B_2H_6 partial pressure for 5 Torr SF_6 sensitizer. The solid circles have been multiplied by 2. Power was 6.1 W and intensity 15.9 W/cm^2. Run time was 300 s with the P-16 (947.75 cm^{-1}) line.

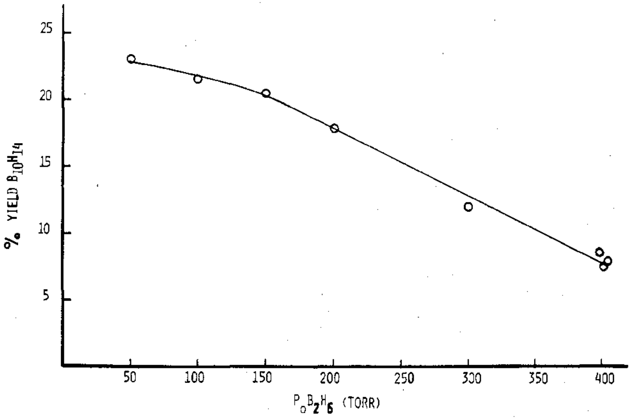

Figure 3. $B_{10}H_{14}$ percent yield by weight of B_2H_6 reacted vs. B_2H_6 initial partial pressure for 5 Torr SF_6 sensitizer. Power was 6.1 W and intensity 15.9 W/cm^2. Run time was 300 s with the P-16 (947.75 cm^{-1}) line.

higher than for the neat experiments. Interestingly, higher yields (up to tenfold) were found at the lower pressures.

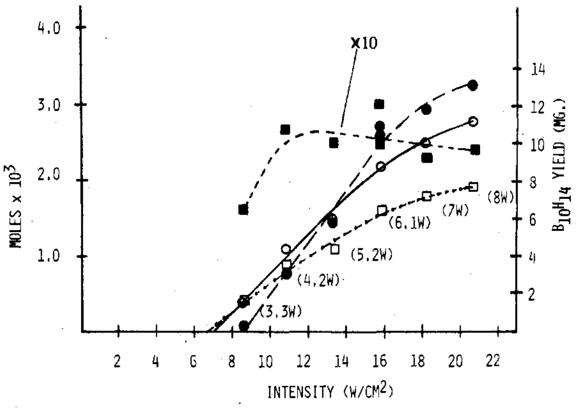

Figure 4. Yields or conversion vs. intensity. Solid squares and short dashed curve designate B_5H_n which have been multiplied by 10 for display. Open squares and dot–dash curve represent B_2H_6 conversions. The open circles and solid line designate H_2 production. B_5H_n, B_2H_6, and H_2 refer to the left ordinate. The solid circles and long dashed line represent $B_{10}H_{14}$ yields relative to the right ordinate. The numbers in parentheses denote the laser power to the sample for the sequential data points.

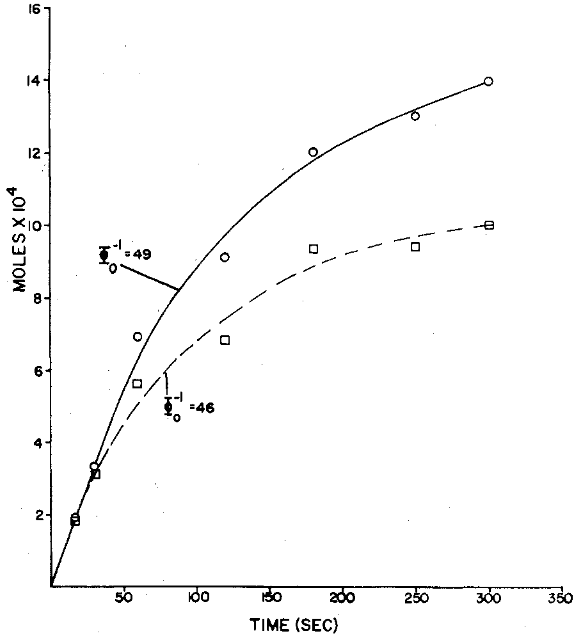

Figure 5. B_2H_6 reacted (open squares and dashed curve) and H_2 produced (open circles and solid curve) vs. time for 300 Torr B_2H_6 and 5 Torr SF_6. Power was 6.1 W and intensity 15.9 W/cm^2 with the P-16 (947.75 cm^{-1}) line. ϕ_0^{-1} = 46 and 49 are the average initial inverse quantum yields for B_2H_6 and H_2, respectively.

Figure 4 presents conversion yields as a function of laser intensity (to the sample) for B_2H_6, H_2, B_5H_n, and $B_{10}H_{14}$. The runs were 10 min long and carried out with the P-18 (946 cm^{-1}) line. Extrapolation of the intensity–yield curves for H_2 and B_2H_6 in Figure 4 to zero yield shows that about 7 W/cm^2 or 2.7 W with a 7-mm diameter beam is necessary to attain the conversion of B_2H_6 and formation of H_2 in measurable amounts (2–3 Torr sensitivity). Also shown is the fact that production of B_5H_n is relatively independent of laser power and intensity above 10 W/cm^2 (~4 W to the sample with a 7-mm beam). The $B_{10}H_{14}$ yield curve of Figure 4 indicates the minimum power and intensity requirements to produce measurable $B_{10}H_{14}$ for a 10-min run with our detection sensitivity (≃0.3 mg) to be 3.3 W and 8.6 W/cm^2.

Figures 5 and 6 depict the time–yield curves of B_2H_6 conversion, and H_2, B_5H_n, and $B_{10}H_{14}$ formation at 300 Torr partial pressure of B_2H_6 for the P-16 line. In Figure 5 the initial slope for B_2H_6 conversion was found by averaging over the first 15 s of illumination and gave an average initial rate of 1.15×10^{-5} mol/s, corresponding to an average inverse quantum yield of 46 photons per B_2H_6 molecule converted. Applying a similar treatment to the H_2 curve resulted in a value for H_2 production of 1.09×10^{-5} mol/s and an average initial inverse quantum yield of 49. In Figure 6 the initial slope for B_5H_n production was determined by averaging over the first 12.5 s and corresponded to a rate of 4.80×10^{-6} mol/s and an average initial inverse quantum yield of 112. The time–

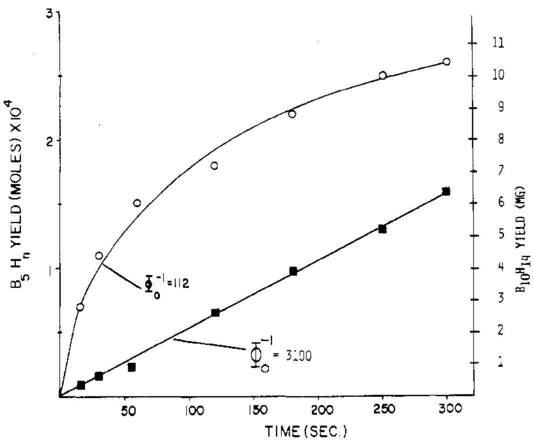

Figure 6. B_5H_n yield (open circles) and $B_{10}H_{14}$ yield (solid squares) vs. time for 300 Torr B_2H_6 and 5 Torr SF_6. Open circles refer to left ordinate and solid squares to right ordinate. Power was 6.1 W and intensity 15.9 W/cm^2 with the P-16 (947.75 cm^{-1}) line. ϕ_0^{-1} = 112 and 3100 are the average initial inverse quantum yields for B_5H_n and $B_{10}H_{14}$, respectively.

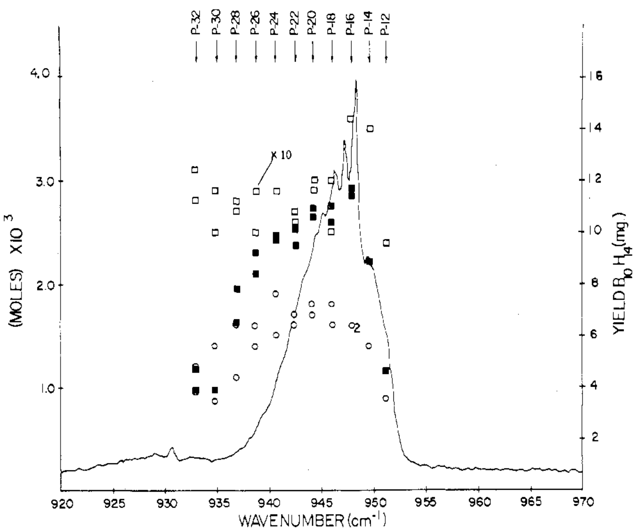

Figure 7. Yields or conversion vs. laser wavenumber for 400 Torr B_2H_6 with 5 Torr SF_6. Open squares designate B_5H_n yield multiplied by 10 for display. Open circles represent B_2H_6 conversion. B_5H_n and B_2H_6 both refer to left ordinate. Solid squares denote $B_{10}H_{14}$ yields with reference to the right ordinate. The solid line is the superimposed room-temperature absorption spectrum of the ν_3 band of SF_6 at 0.5 cm^{-1} resolution for 0.2 Torr in a 6-cm cell. Power was 6.1 W and intensity 15.9 W/cm^2. Runs were for 600 s.

yield curve for $B_{10}H_{14}$ also depicted in Figure 6 was linear over a 5-min period. A least-squares fit resulted in a constant rate of 1.74 × 10^{-7} mol/s and an inverse quantum yield of 3100 for the 5 min. There appears to be a few seconds delayed onset for $B_{10}H_{14}$ formation.

Figure 7 shows conversion or yields of B_2H_6, B_5H_n, and $B_{10}H_{14}$ as a function of wavenumber of the CO_2 laser line superimposed upon the absorption spectrum of the ν_3 band of SF_6 at room temperature. Initial partial pressure of B_2H_6 was 400 Torr for these experiments. In all three cases there is a definite "red shift" showing enhanced product formation at photon energies less than the absorption peak of the ν_3 band at room temperature.

Discussion

Laser-augmented synthesis of cage-structure boron hydrides from B_2H_6 with an SF_6 sensitizer was found to be more efficient relative to the neat synthesis. This may be attributed to the greater absorption coefficient of SF_6 and is particularly evident at lower B_2H_6 pressures. The increase in efficiency of synthesis of desirable products was accompanied by an increase in the yield of undesirable $(BH)_n$ polymeric solids. However, the production of the undesirable boron hydride solids may be eliminated by interrupting the laser beam at faster than the minimum pressure-dependent rate.[8] Chopping results in a decreased yield of the other products too. However, one could in principle increase the yield of desired products by reflecting the stopped portion of the chopped beam into a second reaction cell. We interpret this as resulting, at least in part, from a drop in laser thermolysis temperature for the chopped system relative to the unchopped. The time–yield curve for B_5H_n formation in Figure 6 is qualitatively similar to that found for B_5H_9 + B_5H_{11} when B_2H_6 undergoes heterogeneous pyrolysis, but on a compressed time scale.[9] Other data (not presented) show that while the $B_{10}H_{14}$ yield is linear over the 300-s reaction interval shown in Figure 6, it does change slope and finally saturates. The least-squares fit of Figure 6 comes close to, but does not pass through, the origin. Comparison with the neat B_2H_6 to $B_{10}H_{14}$ conversion should be reserved to the linearly ascending portion of Figure 4 of ref 3. It is satisfying to note that the determined average ϕ^{-1} for B_5H_n was about 2.5 times that of B_2H_6 in agreement with reaction stoichiometry.

Figure 7 shows that reaction yields are increased when the irradiation is carried out at the low-frequency side of the room-temperature ν_3 band of SF_6; i.e., a "red shift" effect is seen. Neat B_2H_6 does not react when irradiated with the laser lines used in our experiments. The room-temperature absorption spectrum of B_2H_6 peaks at 973 cm^{-1}. The transmission of a beam with 8 W power at 12.6 W/cm^2 intensity (to the sample) through 200 Torr of neat B_2H_6 increases by a factor of 2.5 for the R-8 (967.72) cm^{-1}) line relative to R-16 (973.3 cm^{-1}). Under our experimental conditions the rate of collisions exceeds the rate of photon absorption per unit volume by many orders of magnitude. One would expect that intermolecular relaxation is complete and that thermolysis is responsible for the reactions. The "red shifting" of SF_6 may be explained by the work of Nowak and Lyman.[10] They have shown that triple degeneracy and strong anharmonicity of the ν_3 normal mode coupled to a nearly continuum of rotational states lead to a large spectral shift of the absorption peak toward longer wavelengths with increasing temperature. Using Figure 7 and the data of Nowak and Lyman[10] we can estimate the equilibrium temperature for the thermal processes involved. The "red shifting" of the B_2H_6 conversion is consistent with heating of SF_6 to approximately 500–550 K. Other workers have noted "red shifting" of product yields under low photon density, collision-dominated conditions[6,11,12] and have associated it with evidence for nonthermal, vibrationally enhanced reaction paths. We see no reason for this interpretation under our experimental conditions.

B_4H_{10} is the only stable product found in pyrolysis of B_2H_6 not yet reported with laser-induced thermolysis. Recent laser experiments in our laboratory using the R-16 (973 cm^{-1}) line on high-pressure ($\geq$760 Torr) neat B_2H_6 in a jacketed cell cooled to −75 °C indicate that small amounts of B_4H_{10} are produced. The experiment is similar to that of Klein, Harrison, and Solomon[13] except that the heater is replaced with a CW-CO_2 laser beam. B_4H_{10} formation is only favored during very high pressure thermolysis.[13,14] B_5H_{11} has always been a product in our experiments although it was not found by Bachmann et al.[2] When the jacketed cell is cooled to −75 °C and irradiated for 20 min with R-16 (973 cm^{-1}) line at 8 W power and 20.8 W/cm^2 intensity, the only product found is B_5H_{11} for room-temperature pressures of B_2H_6 $\leq$400 Torr.

At pressures in excess of ~20 Torr, laser chemistry is dominated by collisions. However, the unique property of the laser for homogeneous flash heating of reactants still offers promise for driving selected reaction channels preferentially or at least improving yields of desirable products relative to those obtained under standard heterogeneous pyrolysis conditions. In preliminary experiments we have found that appropriate chopping can control $(BH)_n$ formation. On–off fast heating by laser pulsing or chopping and the subsequent effect upon convection flow patterns and reactant replenishment can lead to different quantitative results. Application of these effects to alter the reaction product distribution in synthesis is currently being investigated.

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Registry No. B_2H_6, 19287-45-7; SF_6, 2551-62-4; B_5H_9, 19624-22-7; B_5H_{11}, 18433-84-6; $B_{10}H_{14}$, 17702-41-9.

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Phosphorus-31 NMR of Triphenylphosphine Oxide Complexes with Compounds of Silicon, Germanium, and Tin

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Phosphorus-31 NMR of equimolar mixtures of Ph_3PO and compounds of the main group 4 elements in toluene exhibits downfield coordination shifts from the free base. The data are interpreted in terms of the formation of adduct complexes in solution. Analysis of the concentration dependency of the chemical shift permits the determination of the formation constant of the 1:1 complex and the change in chemical shift upon complexation where the 1:1 complex is the predominant species in solution. Thus, $K(Ph_3PO{:}Me_3SiCl) = 60 \pm 5\ M^{-1}$, $\Delta_c = 7.8$ ppm, and $K(Ph_3PO{:}Me_3SnCl) = 100 \pm 5\ M^{-1}$, $\Delta_c = 3.2$ ppm, where $\Delta_c = \delta_{complex} - \delta_{Ph_3PO}$. More complicated data, observed for $SiCl_4$–Ph_3PO solutions, suggest multiple equilibria. Data analysis at very low concentration gives $K(Ph_3PO{:}SiCl_4) \approx 180\ M^{-1}$ with $\Delta_c \approx 16$ ppm. Additionally, an effect of added MeCN on the chemical shift of Ph_3PO–Me_3SiCl solutions has been observed and interpreted in terms of a coordinate interaction between the nitrilic group and silicon.

Introduction

Tertiary phosphine oxides are known to be weak bases. It has been suggested that the weak donor character may be due to $d\pi$–$p\pi$ bonding[1] which reduces the electron density on oxygen. That these oxides interact with protic acids to give hydroxyphosphonium salts and that they behave as weak donor ligands to Lewis acids by coordination through oxygen attest to their basic properties.[2-6] Many such complexes with strong acceptors have been isolated and exhibit a characteristic shift in the phosphoryl stretching (P→O) frequency. Similar complexes of $SiCl_4$ with Ph_3PO and $(Me_2N)_3PO$, which have been suggested as intermediates in chlorosilane–siloxane redistribution reactions,[7] have been isolated as solids;[4,8] however, the decrease in $\nu(P{\rightarrow}O)$ observed for the complexes as a mull ($\sim$45 cm^{-1}) is not detected when the complexes are dissolved in either polar or nonpolar solvents.[8,9] Furthermore, the UV spectrum of Ph_3PO remains unchanged in the presence of a chlorosilane. It has been suggested that the lack of an observable change in the solution spectra (IR or UV) results from either a lack of complexation, appreciable dissociation of the complex, or a weak dative interaction giving rise to a shift too small to be detected.[9]

It has recently been shown by Grim et al. that ^{31}P NMR is a sensitive probe for the detection of complexes in solutions containing mono- and bidentate phosphorus ligands coordinated to transition metals.[10,11] In each case sizable increases in chemical shift ($\delta_{obsd} - \delta_{ligand}$) have been observed and interpreted in terms of inductive effects resulting from a decrease in the electron density at phosphorus owing to oxygen coordination. In this paper we will describe the detection of Ph_3PO complexes with various silanes, siloxanes, and stannanes and tetrachlorogermane in solution by ^{31}P NMR. Importantly, analysis of concentration-dependent ^{31}P NMR chemical shifts provides a facile method for the determination of the formation constant for 1:1 addition complexes.

Experimental Section

Toluene and MeCN (Fisher Scientific, reagent grade) were purified by distillation under anhydrous conditions. Ph_3PO (Eastman Kodak, reagent grade) was purified by recrystallization from acetone. $SiCl_4$ (Fisher Scientific, reagent grade), Me_3SiCl, Me_2SiCl_2, and $MeSiCl_3$ were purified by distillation. $Cl_3Si(OSiMe_2)_3Cl$ was prepared according to methods described earlier.[7] The stannanes (Alfa Inorganics) were purified by recrystallization for solids and by distillation for liquids. All other chemicals were reagent grade and used without

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[†] In partial fulfillment of the requirements for the Ph.D. degree in Chemistry at the Polytechnic Institute of New York.