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## NMR Properties of SePPh<sub>3</sub> in the Solid State

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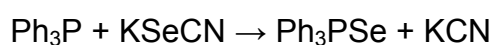
### Introduction

Spectroscopic and structural studies of phosphane chalcogenides R<sub>3</sub>PE (E = O, S, Se) have played an important role in the development of a model for the phosphoryl bond. Nevertheless, the phosphoryl systems continue to attract attention and the nature of the P-E bond is a point of much discussion by theoreticians and experimentalists.<sup>1-3</sup> On the experimental side, crystal structures and data of vibrational spectroscopy provide valuable evidence to assess the nature of the phosphoryl bond. In the case of selenophosphoranes, R<sub>3</sub>PSe, the phosphoryl bond connects two NMR active nuclei with spin 1/2, i.e. <sup>31</sup>P (100% natural abundance) and <sup>77</sup>Se (8% natural abundance). In principle NMR data such as <sup>1</sup>J<sub>PSe</sub> coupling constants should also render some information about the P-Se bond. For some selenophosphoranes such as SePPh<sub>3</sub> the NMR spectroscopic parameters in solution are available from the literature. We were interested to check whether these parameters remain the same in the solid state or whether there are differences due to polarity and solvation effects.



## Results and Discussion

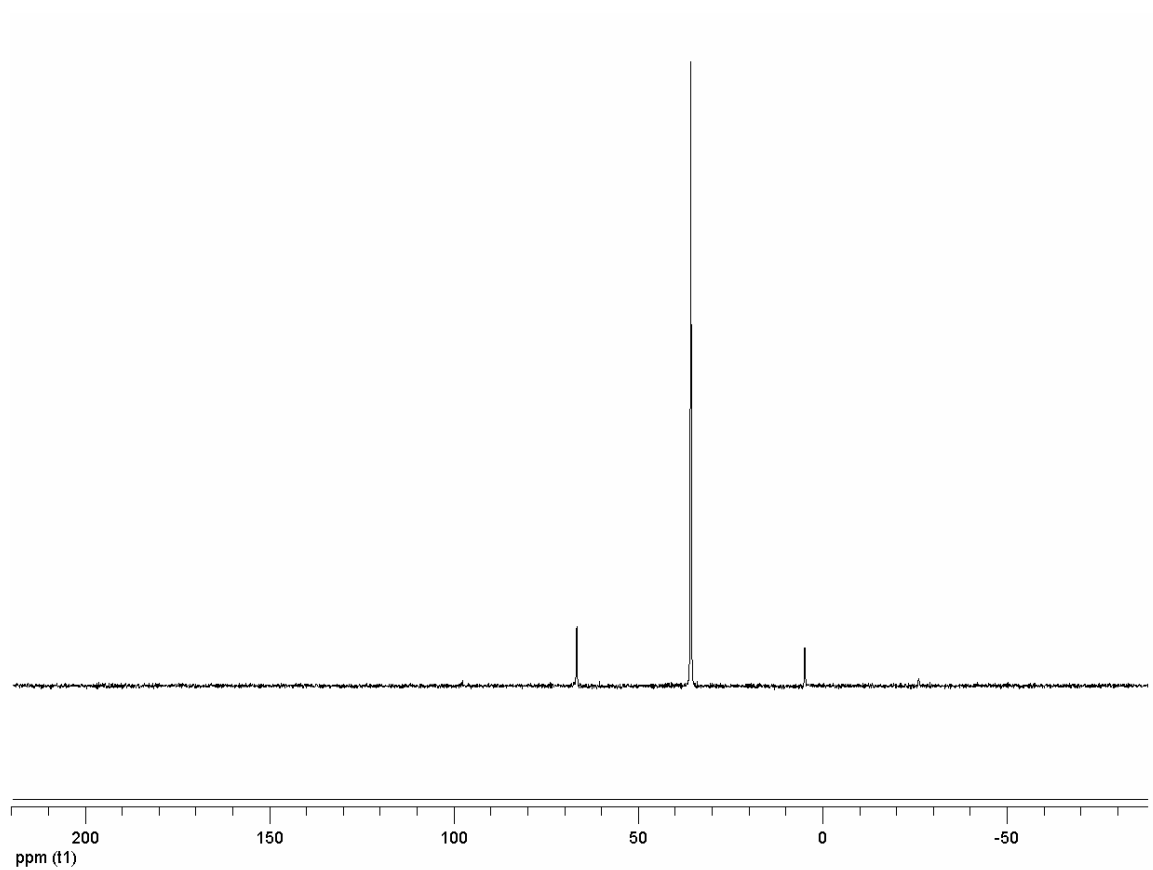
The title compound, triphenylselenophosphorane (SePPh<sub>3</sub>), has been prepared by oxidation of triphenylphosphane (PPh<sub>3</sub>) with potassium selenocyanate (KSeCN) in acetonitrile according to a published procedure (Scheme 1).<sup>4</sup> Owing to its high melting point of 188°C it should be suitable for the MAS (magic angle spinning) NMR technique, even at higher rotation frequencies.



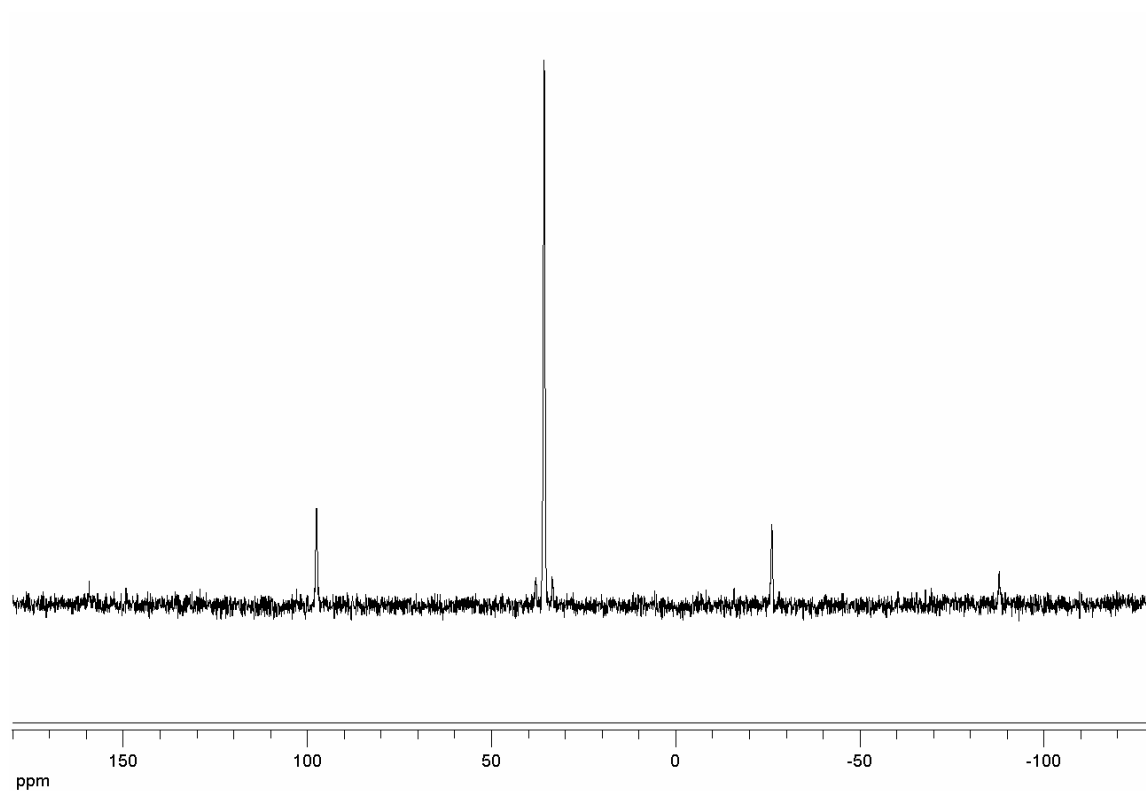
**Scheme 1:** Synthesis of Ph<sub>3</sub>PSe.

<sup>31</sup>P MAS NMR spectra were recorded on finely powdered samples of SePPh<sub>3</sub> using a cross polarization pulse sequence with a ramp shaped contact pulse. Even at lower rotation frequencies of 5 kHz the signal mainly consists of the central transition line with only few spinning side bands, indicating a rather small shift anisotropy (Figure 1). The chemical shift of the central transition closely matches the literature value of 35.8 ppm in solution.<sup>5</sup> Interestingly, no P-Se coupling can be seen in the spectrum at this rotation frequency, although the line width at half height ( $\nu_{1/2}$ ) is with *ca.* 40 Hz significantly lower than the <sup>1</sup>J<sub>PSe</sub> coupling constant. Then, at a higher rotational frequency of 10 kHz the <sup>1</sup>J<sub>PSe</sub> coupling becomes visible as satellite transitions of the central signal, although the signal to noise ratio is lower than at 5 kHz (Figure 2). The value of the coupling constant again is with 712 Hz close the value reported for solution NMR (730 Hz).<sup>3</sup> A further increase of the rotational frequency to 15 kHz increases the relative intensity of the central transition, while spinning side bands are still present (Figure 3). Also the satellite transitions due to <sup>31</sup>P-<sup>77</sup>Se coupling remain visible, although somewhat weaker than at 10 kHz.



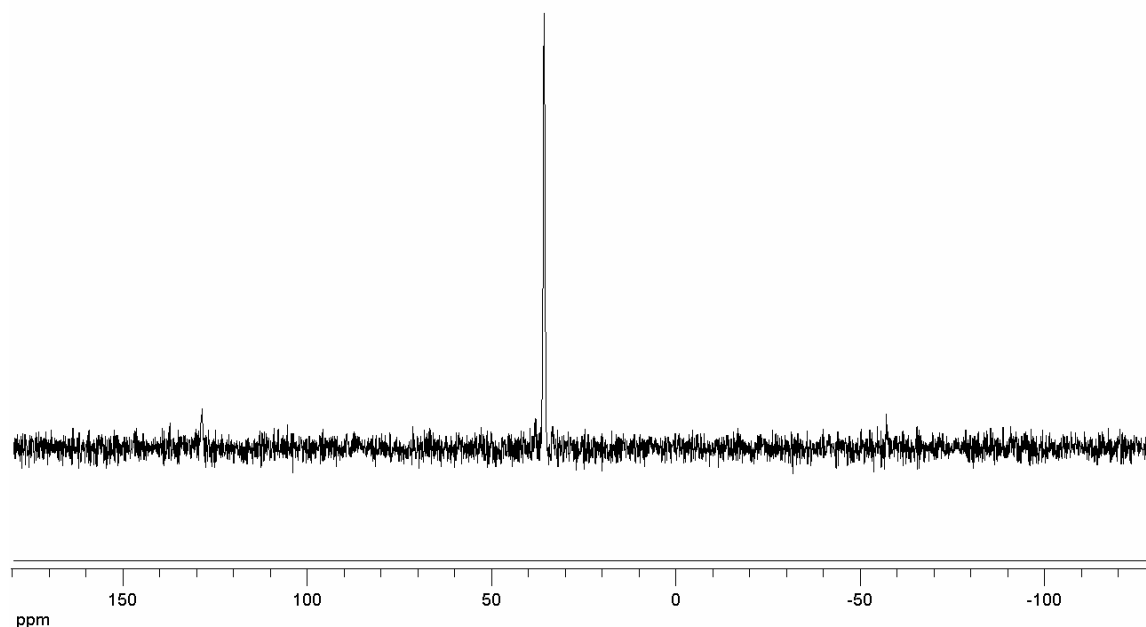


**Figure 1:**  $^{31}\text{P}$  solid state NMR spectrum of  $\text{SePPh}_3$  (rotation frequency 5 kHz).



**Figure 2:**  $^{31}\text{P}$  solid state NMR spectrum of  $\text{SePPh}_3$  (rotation frequency 10 kHz).





**Figure 3:**  $^{31}\text{P}$  solid state NMR spectrum of  $\text{SePPh}_3$  (rotation frequency 15 kHz).

## Conclusion

According to our findings the  $^{31}\text{P}$  NMR data of  $\text{SePPh}_3$  in the solid state are virtually the same as in solution. This indicates that the  $^{31}\text{P}$ - $^{77}\text{Se}$  coupling constant is not significantly affected by the polarity and/or solvation properties of the surrounding medium, as one might have anticipated based on semipolar bonding models for phosphoryl compounds.

## Solid-State-NMR

Solid state NMR MAS (magic angle spinning) spectra were recorded at 22°C on a Bruker DSX 400 spectrometer at 161.9 MHz ( $^{31}\text{P}$ ) with bottom layer rotors of  $\text{ZrO}_2$  (diameter 4 mm) containing ca. 75 mg of sample, using a rotation frequencies of 5, 10 and 15 kHz and a cross polarization pulse sequence with a ramp shaped contact pulse.

## Acknowledgements

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## References:

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