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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Transmission of Molecular Structure on NMR Characteristics of Phosphorus-Nitrogen Double Bond Systems

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## Transmission of Molecular Structure on NMR Characteristics of Phosphorus-Nitrogen Double Bond Systems

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Elucidation of the origin for the large variability of  $^{31}\text{P}$  and  $^{15}\text{N}$  chemical shifts in compounds with P-N double bonds is a challenging task. We demonstrate here how trends in  $^{31}\text{P}$  and  $^{15}\text{N}$  chemical shifts of iminophosphines and ylène-iminophosphoranes can be explained by the use of quantum chemical model concepts.

✧ Iminophosphines  $\text{RO-P=NMe}_s^*$  display large variations of molecular geometries <sup>[1]</sup>. A characterization of  $^{31}\text{P}$  shielding tensors of five derivatives by CP-MAS experiments and model calculations clearly confirms a gradual change in P-N bond order from a formal double to a triple bond which follows closely the geometry deformations <sup>[2]</sup>.

✧  $\delta^{15}\text{N}$  in ylène-imino-phosphoranes  $\text{X-P(=Y)=NR}$  is influenced according to model calculations by both substituent effects and E/Z-isomerism of the double bond. Comparison of  $^{15}\text{N}$  shifts with model data revealed that in solution all P-N double bonds exhibit Z-configuration, and variations result alone from substituent effects. A correlation between  $\delta^{15}\text{N}$  and calculated bond polarities  $\Delta q = [q(\text{P}) - q(\text{N})]$  suggests that increased nitrogen shieldings indicate enhanced ylide character of P-N double bonds <sup>[3]</sup>.

✧ Marked changes of  $\delta^{31}\text{P}$  in compounds  $\text{R-P(=Y)=NMe}_s^*$  arise according to model calculations from sterically induced deformations of nitrogen valence angles, while P=N-Aryl- $\pi$ -conjugation is negligible. This hypothesis is experimentally confirmed by the low barrier for N-Mes<sup>\*</sup> rotation in  $\text{Mes}^*\text{P(=NH)=NMe}_s^*$  ( $\Delta H^\ddagger$  13 kcal/mol,  $\Delta S^\ddagger$  -12 e.u.).

In addition to providing detailed insight in the electronic structures of the studied compounds, the presented results emphasize that skeletal distortions are frequently of similar importance for the interpretation of  $^{31}\text{P}$  chemical shifts as electronic effects.

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