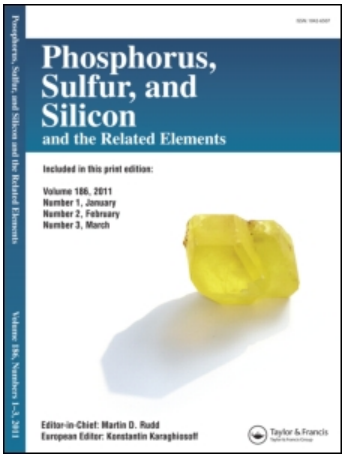

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Structure of Low-Coordinated Phosphorus (III) Compounds Including Phosphorus-Nitrogen Multiple Bond: ^{13}C, ^{15}N and ^{31}P NMR Investigation

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STRUCTURE OF LOW-COORDINATED PHOSPHORUS (III) COMPOUNDS INCLUDING PHOSPHORUS-NITROGEN MULTIPLE BOND: ^{13}C, ^{15}N AND ^{31}P NMR INVESTIGATION

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A wide series of low-coordinated phosphorus (III) compounds including iminophosphines **1**, two- **2** or mono-coordinated **3** phosphorus-containing cations, and anion **4**, where Mes* = 2,4,6-tris-(*tert*-butyl)phenyl, has been investigated by ^{13}C, ^{15}N and ^{31}P NMR spectroscopy. The spectral parameters obtained are considered in connection with the *ab initio* (6-31G*) calculation data of the model compounds.

Mes*-N=P-X **Mes*-NX-P^+-NR_2** **Mes*-N=P^+** **Mes*-N=P^-=NR** **Me_4N^+**

1 **2** **3** **4**

1 X= Alk, Ar, NR_2, OR, SR, PR_2, Hal; **2** X= H, $AlCl_3^-$, $GaCl_3^-$

In spite of the absence of the conjugation between the P=N and Mes* π-systems, essential ^{13}C shielding variation is found for all carbon-13 nuclei in Mes* moiety within the series **1-4**. The π-inductive nature of the ^{13}C shielding variation in the aromatic moiety is suggested. The found peculiarity of the Mes* substituent to be polarized by electronegative substituents seems to be an additional factor promoting the total stability of low-coordinated phosphorus (III) compounds involving the Mes* moiety. The ^{13}C NMR data analysis makes it possible to determine the isomers configuration for compounds **1,2**.

The ^{15}N and ^{31}P NMR chemical shifts of corresponding nuclei in Mes*-N=P-X moiety, as well as phosphorus-nitrogen coupling constants, are shown to be sensitive both to the hybridization type of the P and N atoms and to inductive and resonance properties of the X substituent. The largest deshielding of ^{15}N nuclei (δN=+163.6 ppm) is found for anion **4**. The P=N bonds have the double character in this compound but they are highly polarized to N atoms.

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