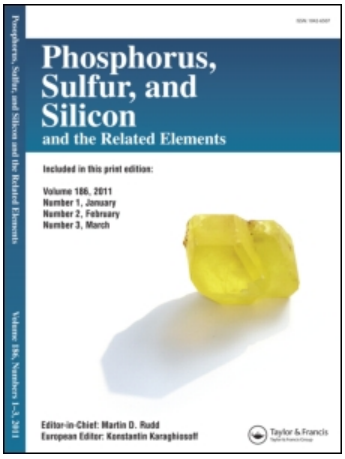

Phosphorus, Sulfur, and Silicon and the Related Elements

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Polarity of ^{3},λ^{5}-Phosphoranes

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POLARITY OF σ^3,λ^5-PHOSPHORANES

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Tricoordinated pentavalent phosphorus compounds - σ^3,λ^5--phosphoranes - present a new field in unusually (low) coordinated phosphorus chemistry. Our current interest in these compounds is stimulated by the possibility of actual determination of unknown phosphorus bond polarities, using electrical methods in subsequent investigations of the spatial and electronic structure of σ^3,λ^5-phosphoranes. We have studied the series of bis(imino)phosphoranes by the method of dipole moments $R^2N{=}P(R^1){=}NR^3$ (I-VI) R^1, R^2, R^3, $\mu_{exp.}$(D): (I) $N(SiMe_3)_2$, $SiMe_3$, $SiMe_3$, 2.16; (II) $N(SiMe_3)_2$, t-Bu, t-Bu, 2.36; (III) $N(SiMe_3)_2$, $SiMe_3$, t-Bu, 2.26; (IV) 2,4,6-$Me_3C_6H_2$, t-Bu, 2,4,6-t-$Bu_3C_6H_2$, 2.44; (V) t-Bu(Me_3Si)N, t-Bu, t-Bu, 2.74; (VI) c-2,2,6,6-$Me_4C_5H_6N$, $SiMe_3$, $SiMe_3$, 2.82 and defined P=N bond polarity (3.14D). Dipole moments (I-VI) are described by the given values, the group moments R-P and R-N were previously found from dicoordinated phosphorus compounds. The tendency of increasing μ_{exp} with the growth of n,Π-donor abilities of substituent R^1 in row (I-III)-(V)-(VI) is possibly caused by the increase of the conjugative effect contribution in stabilization of the 4-electron 3-centre Π-system N=P=N.