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On the Electronic Structure of Phosphorus- (III)-p- π -Bonded Systems: UV-and PE- Spectroscopic Investigations of Phosphaalkenes

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On the Electronic Structure of Phosphorus- (III)-p- π -Bonded Systems: UV- and PE- Spectroscopic Investigations of Phosphaalkenes

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UV- and He-I-p.e. spectra of phosphaalkenes 1 are discussed.

$$\frac{1}{2}$$
 R - P = C(SiMe₃)₂

$$R = C1$$
, F, OBu^{t} , SBu^{t} , $NHBu^{t}$, $NHSiMe_{3}$, NEt_{2} , NPr^{i}_{2} , $2,2,6,6-Me_{4}C_{5}H_{6}$, $N(Bu^{t})SiMe_{3}$, $N(SiMe_{3})_{2}$, Me , Bu^{t}

Assignment of $\pi(P=C)$ - and n(P)- ionization potentials agrees with u.v. data as well as semiempirical MNDO - calculations. The alkyl-substituted species exhibit a sequence of $\pi(P=C)$ and n(P)-i.p.'s which is unusual for phosphaalkenes (i.p. (n) < i.p. (π)). Introduction of RO- and RS-substituents results in formation of a mesomeric 3-center-4-electron π -system. Two different conformers of amino-phosphaalkenes can be distinguished which depend on the steric demand of the substituent, and differ in the orientation of the amine-ligand in relation to the plane of molecular symmetry. Coexistence of both isomers is proved in the case of R = NPr $\frac{i}{2}$ by temperature dependant u.v. studies.

D. Gudat, E. Niecke, W.Sachs, and P. Rademacher, Z. anorg. allg. Chem., in press.