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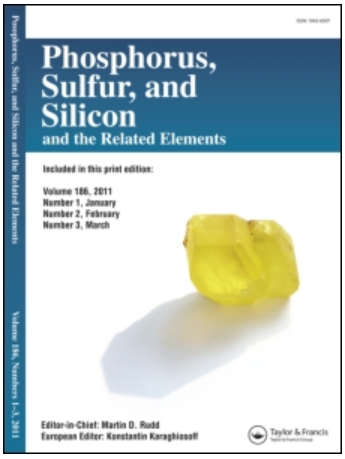

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Single Crystal ESR Study of Phosphoranyl Radicals Obtained by Electron Capture of Four-Coordinated Phosphorus Compounds

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Single Crystal ESR Study of Phosphoranyl Radicals Obtained by Electron Capture of Four-Coordinated Phosphorus Compounds

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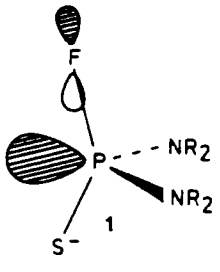
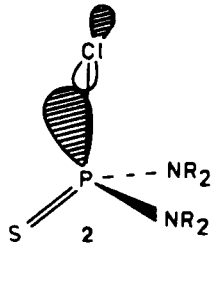
x-Irradiation of four-coordinated phosphorus compounds at low temperature yields phosphoranyl radicals formed by electron capture. The structure of these radicals is elucidated at low temperature via single crystal ESR. Analysis of the isotropic and anisotropic contributions to the phosphorus and substituent hyperfine couplings gives an accurate description of the populations (ρ_s and ρ_p) and the directions of the atomic orbitals participating in the single occupied molecular orbital. It is found that radical **1** possesses a deformed trigonal bipyramidal structure with the unpaired electron in an equatorial position (TBP-e) whereas in **2** the unpaired electron resides in an antibonding σ orbital between P and Cl (σ*). For tetrasubstituted diphosphine disulfides (methyl, ethyl and phenyl) a variety of coexisting configurations is established. Structure **3a** possesses a symmetrical distribution of the unpaired electron over the two phosphorus atoms (P_1 and P_2 both 43%). In contrast, an asymmetric spin density distribution is found for radical **3b** (P_1 49% and P_2 29%) and for radical **3c** in which the extra electron is found in a σ* P-S orbital.



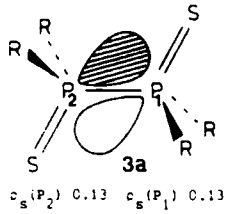
1

ρ_s(P) 0.23 ρ_s(F) 0.02
ρ_p(P) 0.42 ρ_p(F) 0.15



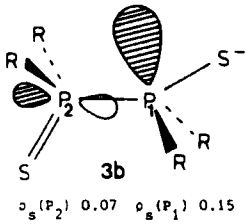
2

ρ_s(P) 0.19 ρ_s(Cl) 0.02
ρ_p(P) 0.52 ρ_p(Cl) 0.17



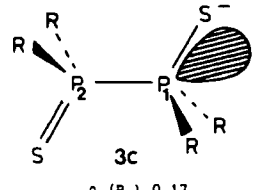
3a

$\rho_s(P_2)$ 0.13 $\rho_s(P_1)$ 0.13
$\rho_p(P_2)$ 0.30 $\rho_p(P_1)$ 0.30



3b

$\rho_s(P_2)$ 0.07 $\rho_s(P_1)$ 0.15
$\rho_p(P_2)$ 0.22 $\rho_p(P_1)$ 0.34



3c

$\rho_s(P_1)$ 0.17
$\rho_p(P_1)$ 0.55