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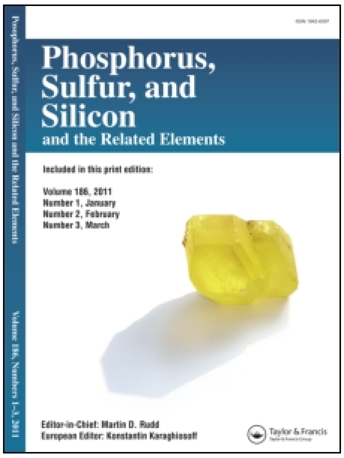

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Electrochemical Reduction of Phosphaallenes: Electron Spin Resonance and Theoretical Studies

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Electrochemical Reduction of Phosphaallenes : Electron Spin Resonance and Theoretical Studies

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In order to check to what extent allenic systems containing one or two phosphorus atoms are likely to accept an electron, solutions of $ArP{=}C{=}C\Phi_2$ (Ar: Phenyltri^{t}butyl; Φ: benzene) and ArP=C=PAr have been electrochemically and chemically reduced. Cyclic voltammetry shows that $ArP{=}C{=}C\Phi_2$ undergoes irreversible reduction at –2266mV in THF while an irreversible reduction takes place at –1900 mV (THF) for ArP=C=PAr

EPR spectroscopy was used to identify the reduction products. Electrolysis of the phosphaallene, in situ, inside the EPR cavity leads to spectra exhibiting well-resolved 31P structure. The same spectra were obtained by chemical reduction: 1) by reacting $ArP{=}C{=}C\Phi_2$ with naphtalenide ions 2) by reacting ArP=C=PAr on a potassium mirror under high vacuum. More specific information on the structure of the reduction compounds could be obtained from ^{13}C-enriched molecules: $ArP{=}^{13}C{=}C\Phi_2$, $ArP{=}C{=}^{13}C\Phi_2$, $ArP{=}^{13}C{=}PAr$. The resulting isotropic hyperfine constants (MHz) measured at room temperature are: $ArP{=}C{=}C\Phi_2$: ^{31}P: 262, ^{13}C (central): 33, ^{13}C (terminal):34 ; ArP=C=Par: ^{31}P (two nuclei): 215, ^{13}C: 27. Whereas no EPR response could be obtained with a frozen electrolyzed solution of ArP=C=Par, clear spectra were recorded at 105 K with reduced solutions of monophosphaallenes. Decomposition of the resulting tensors into isotropic and anisotropic coupling constants is consistent with the A_{iso} values measured in liquid solutions; the resulting anisotropic coupling constants ^{31}P. $\tau_{//}$ =465, $\tau_{\perp}$= -232.5, ^{13}C (central)$\tau_{//}$: 15 , $\tau_{\perp}$=-7.5 , ^{13}C (terminal) $\tau_{//}$: 43 , $\tau_{\perp}$ = -21.5. leads to the following spin densities: ^{31}P ρ_s= 0.019, ρ_p= 0.616, ^{13}C(central)ρ_s=0.008, ρ_p=0.059 ; ^{13}C (terminal) ρ_s= 0.009, ρ_p=0.202.

Ab initio (MP2/6-311+G**, MC/6-31+G**) and DFT calculations were used to predict the equilibrium geometry and the electronic structure of the model radicals $(HP{=}C{=}PH)^{\cdot -}$,$(HP{=}C{=}CH_2)^{\cdot}$ and $HP\text{-}CH{=}CH_2$. Two conformations are obtained for each anion: 1) the *cis*-like conformation which is characterized for $(HP{=}C{=}PH)^{\cdot -}$ by a HPPH torsion angle close to 40° and for $(HP{=}C{=}CH_2)^{\cdot}$ by a HPCH torsion angle close to 50°, 2) the *trans*-like conformation which is characterized for $(HP{=}C{=}PH)^{\cdot -}$ by a HP...PH torsion angle close to 150° and for $(HP{=}C{=}CH_2)^{\cdot}$ by a HP...CH torsion angle close to 120°.Comparison between calculated and experimental spin densities shows that the reduction products for the diphosphaallene and the monophosphaallene are respectively the radical anion and the phosphaallylic radical.