Density Functional Theory (DFT) Calculations of Indirect Nuclear Spin-Spin Coupling Constants $^1J(^{31}P, ^{13}C)$ in $\lambda^3$-Phosphaalkynes

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The calculation of the spin-spin coupling constants $^1J(^{31}P, ^{13}C)$ of $\lambda^3$-1-phosphaalkynes $P\equiv C-R$ ($R = H, Me, 'Bu, Ph, SiMe_3$ and $NMe_2$) using density functional theory (DFT) have revealed a positive sign of this coupling constant in agreement with the experiment for $P\equiv C-tBu$. The calculations have shown that the Fermi contact (FC) contribution to this coupling is negative [in contrast to FC for $^1J(^{14}N, ^{13}C)$ in the corresponding nitriles], and that the positive sign of $^1J(^{31}P, ^{13}C)$ is the result of significant contributions arising from spin-dipole (SD) and paramagnetic spin-orbital (PSO) terms. Coupling constants were also calculated for some representative $\lambda^3$-phosphorus compounds containing two- and three-coordinate phosphorus, indicating the strong dependence of the FC term on the geometry at the phosphorus atom.

Key words: Phosphaalkynes, NMR, Coupling Signs, MO Calculations