$^{1}J(^{13}C^{31}P)$ Sign Variation in Phosphorus(III) Heterocycles: Existence of Both Positive and Negative $^{1}J(^{13}C^{31}P)$ to the Same Phosphorus

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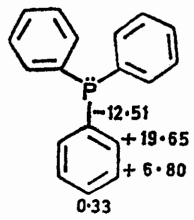
Summary A series of phosphorus heterocycles of various ring sizes has been studied with particular attention paid to the sign of the ^{13}C–^{31}P nuclear spin couplings; both positive and negative values are found along with the first reported cases of different signs of one-bond couplings to a central atom, of atoms in the same oxidation state.

All determinations of directly bonded ^{13}C–$^{31}P^{III}$ nuclear-spin coupling constant signs have resulted in negative signs.[1a—d] Theoretical treatments have also rationalized the negative sign, although in a qualitative manner.[2] This coupling varies widely in magnitude depending on the particular type of compound observed. Trialkyl-substituted P^{III} compounds have $^{1}J_{CP}$'s ranging from (−)10·7 to (−)33·9 Hz.[3] The $^{1}J_{CP}$ for the substituted phenyl carbon in mixed phenyl and alkyl phosphines has been reported to vary from (−)14·1 to (−)17·9 Hz.[3] In previous work[4] we have recorded J_{CP}'s in substituted four-membered phosphorus(III) heterocycles, compounds that showed very large differences in $^{1}J_{CP}$'s within the same molecule. For example, in 1-phenyl-2,2,3,4,4-pentamethylphosphetan the two observed $^{1}J_{CP}$'s were 41·3 (phenyl) and 5·9 (ring) for the *trans*-(C-3 methyl and phenyl) isomer, and 42·8 (phenyl) and 2·6 (ring) for the *cis*-isomer.[4] It is clear that these $^{1}J_{CP}$'s are unusual, based on the acyclic models.

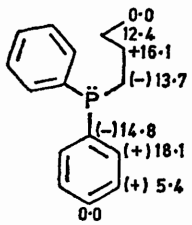
In order to explore this behaviour further we have examined compounds (**2**)—(**6**). Unfortunately, the unsubstituted analogue of (**6**) has not yet been synthesized, but the ring methylene in (**6**) can provide an analogue for those in (**2**)—(**5**). Signs of couplings were determined using the techniques developed by Jackobsen and co-workers[1b—d] which relate the sign of the ^{31}P–^{13}C coupling to that of the ^{31}P–^{1}H coupling for the proton on the carbon atom. For $^{n}J_{CP}$ and $^{n+1}J_{PH}$ of the same sign, a high (low) frequency ^{1}H decoupling field will enhance (or sharpen) the high (low) frequency component of the ^{13}C–^{31}P doublet under conditions close to, but not at, perfect decoupling. The very large dihedral-angle dependence for $^{2}J_{PCH}$ in phosphines[5] gives well-separated spin states in the proton spectrum. This coupling is large and positive for a proton *cis* to the P^{III} lone pair, much smaller and negative for a proton *trans* to the lone pair. The only cyclic phosphine for which a sign determination has been reported is compound (**7**).[1d]

The published[1b] signs and magnitudes for (**1**) provide a starting point which, in effect, allows confidence in sign assignment for the phenyl carbons in (**2**)—(**6**). The smooth progression of the phenyl $^{1}J_{CP}$ from -12.51 Hz to $(-)35{\cdot}4$ Hz in (**6**) hardly permits any change of sign. The *ortho* carbon retains its positive coupling (also primarily determined by its dihedral angle dependence with the lone pair).[6] These are the first experimental indications of positive $^{1}J_{CP^{III}}$. To our knowledge this is also the first demonstration of different signs of one-bond coupling to a central atom, of atoms in the same oxidation state.

The large $^{1}J_{CP}$ magnitudes seen earlier[4] in the phosphetans are now seen to be a natural consequence of ring formation and contraction. As the C–P–C interior angle contracts to the *ca.* 90° in (**6**) it is possible that a redistribution of *s*-character within the bonding phosphorus orbitals occurs, leading to a greater portion within that orbital directed toward the phenyl substituent. Dominance of the Fermi-contact mechanism would then predict a larger associated coupling, consistent with the experimental results.



1b
(1)



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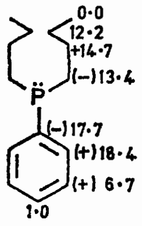

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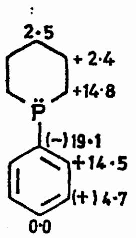

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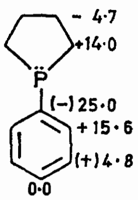

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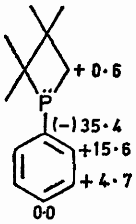

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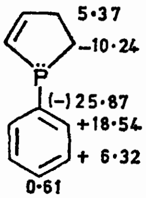

1d
(7)

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