the size and polarizing power which will allow this ion to coordinate effectively and simultaneously to both species.

The bond distance Mn4–O2 = 2.3 Å suggests that site II may be partially occupied by both $Mn^{2+}$ and residual water, or that the bonding of $Mn^{2+}$ in this site to the O2's in the adjacent six-ring is weakened by the association of the cation with the sorbed species.

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# The Signs of $^1K_{PC}$ and Other Coupling Constants in Phosphorus and Selenium Compounds

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**Abstract:** The changes in signs of $^1K_{PC}$ and $^2K_{PCH}$ over a wide range of phosphorus compounds, as well as the signs of PH, SeC, and SeCH couplings, are explained by a model which has been successful in accounting for changes in sign of $^1K_{NN'}$ across the periodic table.

It has been found that it is possible to account for the changes in sign across the periodic table of the reduced spin–spin coupling constants, $K_{NN'}$, of directly bonded nuclei by attributing the changes to nuclear spin–electron spin contact contributions, $\mathcal{A}_N$ and $\mathcal{A}_{N'}$, each of which is composed of two parts[1]

$$\mathcal{A}_N = \mathcal{A}_N(\text{s}) + \mathcal{A}_N(\text{core pol})$$

$\mathcal{A}_N(\text{s})$ is the direct Fermi contact term caused by the s density of the bonding electrons at the nucleus and $\mathcal{A}_N$(core pol) is an indirect Fermi contact interaction due to polarization of the s electrons in the core. For an s orbital there is evidence that the core polarization term is positive while for atomic orbitals with nodes at the nucleus the core polarization term is usually negative.[1,2] If the atom employs ns orbitals in the bond, the direct interaction term, $\mathcal{A}_N(\text{s})$, which is positive, dominates. The bonding of group VII and, to a lesser degree, group VI atoms employs primarily p orbitals. In such atoms the model predicts that the dominant nuclear spin–electron spin interaction is the indirect one, $\mathcal{A}_N$(core pol), and probably negative. While both mechanisms $\mathcal{A}_N(\text{s})$ and $\mathcal{A}_N$(core pol) would be in operation in every case, the sign of the coupling constant is determined by the dominant nuclear spin–electron spin interactions for N and N′, since

$$K_{NN'} \propto \mathcal{A}_N\mathcal{A}_{N'}$$

It was stated previously that the borderline region where the dominant term is expected to change is in groups V and VI.[1] If the model is valid, we should expect that there should be related but different compounds containing atoms in groups V and VI in which $^1K_{NN'}$ changes sign for a given pair of nuclei N and N′, where N belongs to group V or VI. In agreement with the model proposed in ref 1, hereafter referred to as I, both positive and negative coupling constants are observed for $^{31}P$–$^{13}C$ coupling. While the model has been successful in explaining the changes in sign across the periodic table, the transition in sign of the coupling constant between any two given nuclei should likewise be consistently explained by the model. We show that this can be done in compounds of P and Se in agreement with intuitive arguments based on hybridization and the effect of ligand electronegativity on hybridization.

The coupling for which the changing sign over a variety of compounds has been observed is $^{31}P$–$^{13}C$. The $^{77}Se$ couplings are included in this discussion as a representative of group VI since it is the only one of group VI in which signs of coupling constants have been determined in an extensive number of compounds. The signs and magnitudes of these coupling constants are shown in Tables I and II. Values of $^2K_{PCH}$ and $^2K_{SeCH}$, as well as $^1K_{PH}$ and $^1K_{SeH}$ in the same and related compounds, are included. It is noted that for P(III) compounds, the P–C coupling constant is small negative, becoming positive in $P^+$(IV) compounds and P(V) compounds, and increasingly positive as more electronegative atoms are bonded to P. At the same time, the geminal PCH coupling is positive for P(III) compounds, becoming negative in $P^+$(IV) and P (V) compounds. It might be useful to point out that HCH and CCH couplings in saturated systems are negative. The PH coupling is small positive for P(III) compounds, increasing to more than threefold in P(V) compounds. $^1K_{SeC}$ is

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[1] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, in press.

[2] Unrestricted Hartree–Fock calculations of s hyperfine interactions in 3d ions and atoms show that the electron with spin parallel to that of the net spin (3d) is attracted into the 3d region, the regions outside (including the nucleus at $r = 0$) having opposite spin: R. E. Watson and A. J. Freeman, "Hyperfine Interactions," A. J. Freeman and R. B. Frankel, Ed., Academic Press, New York, N. Y., 1967. On the other hand, calculations by D. A. Goodings (*Phys. Rev.*, **123**, 1706 (1961)) show that polarization due to s electrons gives only positive spin densities at the nucleus. A possible explanation for this is the following. Inner s electrons are attracted into the regions of high probability for the ns electron, and since these regions include the nucleus at $r = 0$, the core polarization by ns electrons leads to positive contributions to $\mathcal{A}_N$(core pol).

large negative, and ${}^2K_{\mathrm{SeCH}}$ is positive. ${}^1K_{\mathrm{SeH}}$ is small positive, smaller than ${}^1K_{\mathrm{PH}}$ in P(III). It will be shown that these observations on these borderline cases are consistent with the predictions of the model presented in I.

**Table I.** Reduced Coupling Constants in Phosphorus Compounds in Which ${}^1K_{\mathrm{PC}}$ Has Been Measured[a]

| Compound | ${}^1K_{\mathrm{PC}}$ | ${}^2K_{\mathrm{PCH}}$ | ${}^1K_{\mathrm{PH}}$ | Ref |
|---|---|---|---|---|
| $P(CH_2O)_3P$ | −20 | +1.9 | | *b* |
| $CH_3PH_2$ | | +0.82 | +38.62 | *c* |
| $(CH_3)_2PH$ | | +0.69 | +39.28 | *c* |
| $(CH_3)_2C_6H_5P$ | −11.4 | +0.62 | | *d* |
| $(CH_3)_3P$ | −11.1 | +0.56 | | *e* |
| $CH_3PCl_2$ | (+)36.8 | (−)3.6 | | *f, g* |
| $Et_4P^+Br^-$ | +39.7 | −2.61 | | *e* |
| $(CH_3)_4P^+I^-$ | +45.4 | −3.17 | | *e* |
| $(CH_3)_3HP^+$ | | −3.23 | +103.9 | *h* |
| $(CH_3)_2H_2P^+$ | | −3.50 | +106.2 | *h* |
| $(CH_3)H_3P^+$ | | −3.62 | +108.4 | *h* |
| $(CH_3)_2C_6H_5P^+HBr^-$ | +45.8 | −3.19 | | *d* |
| $(CH_3)_3PSe$ | +39.7 | −2.67 | | *e* |
| $(CH_3)_3PS$ | +45.9 | −2.67 | | *e* |
| $CH_3P(S)Cl_2$ | (+)66.2 | | | *f* |
| $CH_3P(O)Cl_2$ | (+)85.0 | | | *f* |
| $(EtO)_2P(O)C^*H_2COMe$ | (+)103.8 | | | *f* |
| $HP(O)(OCH_3)_2$ | | | +143.0 | *i* |
| $CH_3P(O)(OCH_3)_2$ | +116.3 | −3.58 | | *e* |
| $CH_3P(O)F_2$ | (+)120.2 | | | *f* |
| $(EtO)_2P(O)C^*{\equiv}CMe$ | (+)248.6 | | | *f* |

[a] In units of $10^{20}$ cm$^{-3}$. [b] W. McFarlane and J. A. Nash, *Chem. Commun.*, 127 (1969). [c] S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966). [d] W. McFarlane, *Chem. Commun.*, 58 (1967). [e] W. McFarlane, *Proc. Roy. Soc.*, **A306**, 185 (1968). [f] G. Mavel and M. J. Green, *Chem. Commun.*, 742 (1968). [g] G. Mavel, *J. Chim. Phys.*, **65**, 1692 (1968). [h] H. Dreeskamp, H. Elser, and C. Schumann, *Ber. Bunsenges. Physik. Chem.*, **70**, 751 (1966). [i] W. McFarlane, *J. Chem. Soc., A*, **305**, 1148 (1967).

**Table II.** Reduced Coupling Constants in Selenium Compounds ($10^{20}$ cm$^{-3}$)

| Compound | ${}^1K_{\mathrm{SeC}}$ | ${}^2K_{\mathrm{SeCH}}$ | ${}^1K_{\mathrm{SeH}}$ | Ref |
|---|---|---|---|---|
| HDSe | | | +28.5 | *a* |
| $CH_3SeH$ | −83.3 | +4.58 | +19.5 | *a* |
| | | +4.10 | +19.1 | *b* |
| $(CH_3)_2Se$ | −107.6 | +4.58 | | *a* |
| $(CH_3Se)_2$ | −130.2 | +5.19 | | *b* |
| $C_6H_5SeSeCH_3$ | | +5.32 | | *b* |
| $C_6H_5CH_2SeH$ | | +5.59 | +18.4 | *c* |
| $(CH_3)_3Se^+I^-$ | −86.8 | +4.06 | | *d* |

[a] H. Dreeskamp and G. Pfisterer, *Mol. Phys.*, **14**, 295 (1968). [b] W. McFarlane, *J. Chem. Soc., A*, 670 (1969). [c] W. McFarlane, *Chem. Commun.*, 963 (1967). [d] W. McFarlane, *Mol. Phys.*, **12**, 243 (1967).

Consider a localized valence-bond description for a bond in which only s and p orbitals are used on each of the bonded atoms.

$$\psi = \mathrm{N}\{\phi_{\mathrm{N}}(1)\phi_{\mathrm{N'}}(2) + \phi_{\mathrm{N}}(2)\phi_{\mathrm{N'}}(1) + \lambda_{\mathrm{N}}\phi_{\mathrm{N}}(1)\phi_{\mathrm{N}}(2) + \lambda_{\mathrm{N'}}\phi_{\mathrm{N'}}(1)\phi_{\mathrm{N'}}(2)\}$$

$$\phi_{\mathrm{N}} = \alpha_{\mathrm{N'}}{}^{\mathrm{N}}\phi_{\mathrm{s}}(\mathrm{N}) + \sqrt{1 - (\alpha_{\mathrm{N'}}{}^{\mathrm{N}})^2}\,\phi_{\mathrm{p}}(\mathrm{N})$$

This supposes perfect pairing. We can then ask qualitatively what happens to ${}^1K_{\mathrm{NN'}}$ as $\alpha^{\mathrm{N}}$ and $\alpha^{\mathrm{N}'}$ change independently. As $\alpha^{\mathrm{N}}$ decreases from 1 to 0, we proceed from large s density at nucleus N (for which $\mathcal{A}_{\mathrm{N}}(\mathrm{s})$ is positive and large, and $\mathcal{A}_{\mathrm{N}}$(core pol) is also positive), through intermediate states (where the direct Fermi contact interaction of bonding s electrons plus bonding s orbital core polarization competes with a negative core polarization by the p bonding electrons), to the limit where $\alpha^{\mathrm{N}} \simeq 0$ (where $\mathcal{A}_{\mathrm{N}}$ is due entirely to spin polarization of the core s electrons by the p bonding electron).

It is generally accepted that in the localized description of bonds, use of an s atomic orbital (or one with s-like properties: relatively high density near the nucleus) in bonding allows the bonding electrons to have greater density near the nucleus of the atom in question, whereas use of p or d orbitals (or those with p-like properties: relatively high density along certain directions away from the nucleus, zero density at the nucleus) in bonding allows the bonding electrons to have greater density near the nucleus of the other atom, to which the atom in question is bonded. Thus, it is usually assumed in the localized description of bonds that the atom uses an orbital with relatively more s character for lone pairs or for bonds toward more electropositive atoms, and an orbital with relatively more p character for bonds toward more electronegative atoms (relative, that is, to its other bonds in the same molecule).

If we consider P and Se compounds in the light of the above arguments, we see that in P(III) compounds the P bonds to the three groups are closer to p$^3$ than sp$^3$ in description, since the fourth pair of electrons (lone pair) has a higher probability of being found in the region close to the P nucleus (describable by more s character). In P$^+$(IV) and P(V) compounds the P bonds to the C and H are closer to sp$^3$, with increasing $\alpha_{\mathrm{C\,(or\,H)}}$ as electronegative atoms like O are bonded to P (phosphorus bonds to electronegative atoms are describable by more p than sp$^3$). The description of the P and Se compounds based on these arguments are correlated with the observed coupling constants in Table III. Both mechanisms for P nuclear spin–electron spin interaction are in operation when there is participation of both s and p orbitals in bonding to other atoms. As the lone pair is replaced by more electron-withdrawing groups, the electron distribution around the P nucleus changes, and shows in bonds to carbon, the changeover of the dominant mechanism from being core polarization predominant over valence s electron density in P(III), over to the reverse in P$^+$(IV) and P(V) compounds.

The electronegativity difference between C and H is small (2.6 *vs.* 2.1) but apparently enough to show up the changing dominance of the two mechanisms of nuclear–electron coupling in P as well as in Se. The P–H coupling in P(III) compounds and the Se–H coupling are relatively small and positive, whereas the P–C coupling in P(III) compounds and the Se–C coupling are negative. The order $(\alpha^{\mathrm{F}})^2 < (\alpha^{\mathrm{Se}})^2 < (\alpha^{\mathrm{P}})^2$ is to be expected from their ground configurations of ns$^2$np$^5$, ns$^2$np$^4$, and ns$^2$np$^3$. Indeed the Se–H couplings are smaller compared to the P–H couplings in P(III) compounds, in spite of the larger atomic number and $\phi_{\mathrm{s}}(0)^2$ for Se compared to P.

The geminal coupling constant ${}^2K_{\mathrm{XYZ}}$ is found to be sensitive to the bond angle and the nature of substituents on the coupled nuclei or the intervening atom Y, as well as to rather subtle differences in environment.[3]

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(3) See, for example, R. M. Lynden-Bell, *Mol. Phys.*, **6**, 537 (1963); F. J. Weigert and J. D. Roberts, *J. Phys. Chem.*, 73, 449 (1969); G. Mavel, *J. Chim. Phys.*, **65**, 1692 (1968).

**Table III.** Correlation of the Reduced Coupling Constants with the Nature of Bonding in Phosphorus Compounds

| M coordination (M = P, Se) | Possible explanation | | | |
|---|---|---|---|---|
| | M hybridization in bonds | M s character, $(\alpha^P)^2$, in diff bonds | Dominant mechanism for for M nuclear–electron interaction[a] | Consistent with the following observations |
| P(III) | Closer to $p^3$ than to $sp^3$, more s in lone pair | $\alpha^2$ lone pair $\gg 1/4 \gg \alpha_C^2$,<br>$\alpha^2$ lone pair $\gg \alpha_H^2 > \alpha_C^2$<br>substitution at P by highly electroneg X increases $\alpha_C^2$ | $\mathcal{A}_P$(core pol) for bonds to carbon $\mathcal{A}_P$(s) for bonds to H | ${}^1K_{PH}$ is small positive, ${}^1K_{PC}$ is small negative, ${}^2K_{PCH}$ is positive, ${}^1K_{PC}$ probably becomes positive with increasing electronegativity (X) |
| P$^+$(IV) | $\sim sp^3$ | $\alpha_H^2 > \alpha_C^2 \sim 1/4$ | $\mathcal{A}_P$(s) | ${}^1K_{PC}$ is positive, ${}^2K_{PCH}$ is negative, ${}^1K_{PH}$ is positive |
| P(V) | $\sim sp^3$ with more p in P(O) | $\alpha_H^2 > \alpha_C^2 > 1/4 \gg \alpha_O^2$<br>$\alpha_{Se}^2 > \alpha_S^2 > \alpha_O^2$ | $\mathcal{A}_P$(s) | ${}^1K_{PC}$ is largest and positive, ${}^2K_{PCH}$ is negative, ${}^1K_{PH}$ is largest and positive, ${}^1K_{PC}$ in P(O) > in P(S) > in P(Se) |
| Se(II) | Closer to $p^2$ than to $sp^3$ | $\alpha_H^2 > \alpha_C^2 \ll 1/4$ | $\mathcal{A}_{Se}$(core pol) for bonds to carbon more dominant than in P(III), $\mathcal{A}_{Se}$(s) for bonds to hydrogen | ${}^1K_{SeC}$ is negative, ${}^1K_{SeH}$ is small positive and smaller than ${}^1K_{PH}$, ${}^2K_{SeCH}$ is positive |
| Se(III) | Closer to $p^3$ than to $sp^3$ | $\alpha_C^2 \ll 1/4$ | $\mathcal{A}_{Se}$(core pol) | ${}^1K_{SeC}$ is negative and about the same magnitude as in Se(II) |

[a] For carbon and hydrogen the dominant mechanism is $\mathcal{A}$(s), positive.

In the light of the model presented in I, the geminal coupling constant may be considered in three parts: $\mathcal{A}_X$, the transfer of nuclear spin information to the electrons in the X bonding orbital in the XY bond; $\gamma_{XYZ}$, the transfer of electron spin information from the X bonding orbital in the XY bond to the Z bonding orbital in the YZ bond; then, $\mathcal{A}_Z$, the transfer of spin information from the Z bonding orbital in the YZ bond to the Z nucleus.

$$ {}^2K_{XYZ} \propto \mathcal{A}_X \cdot \gamma_{XYZ} \cdot \mathcal{A}_Z $$

The interactions $\mathcal{A}_X$ and $\mathcal{A}_Z$ are of the same nature as those considered in coupling of directly bonded nuclei. $\gamma_{XYZ}$ is a function of one- and two-center exchange integrals which are sensitive to the bond angle and the nature of substituents on the coupled nuclei and the intervening nucleus. It is also expected to be sensitive to the rather subtle differences in environment due to differences in stereochemistry of the rest of the molecule.

However, in most cases, $K_{XCH}$ is found to be negative for bond angles between 90 and 110° for nuclei X which clearly belong to case A or B.[1] For example, ${}^2K_{HCH}$ is negative,[4] ${}^2K_{CCH}$, ${}^2K_{SnCH}$, ${}^2K_{SiCH}$, and ${}^2K_{PbCH}$ are negative,[5] and ${}^2K_{CdCH}$ and ${}^2K_{HgCH}$ are likewise negative.[6,7] If X is a case A or B nucleus, the nuclear spin–electron spin interaction $\mathcal{A}_X$ is positive, just as $\mathcal{A}_H$ is positive. Therefore, in these instances where ${}^2K_{XCH}$ is found to be negative, that is, for bond angles between 90 and 110°, the interaction $\gamma_{XCH}$ is negative. It is to be expected that in PCH, where the bond angles are between 90 and 110°, $\gamma$ is probably also negative.[8] Thus, ${}^2K_{PCH} \propto \mathcal{A}_P \cdot \gamma_{PCH} \cdot \mathcal{A}_H$, where the signs are$(\mathcal{A}_P)(-)(+)$. Therefore, in order for the geminal PCH and SeCH coupling constants to be consistent with the previous arguments stated for the PC and SeC couplings, the sign of the PCH coupling should be opposite that of the PC coupling, and likewise, the sign of the SeCH coupling should be opposite to that of the SeC coupling. This is indeed found to be the case, as seen in Tables I and II. The SeCH geminal coupling constants are all positive, opposite in sign to the SeC couplings which are all negative. The PCH geminal coupling constants are found to be positive in those compounds where PC coupling is negative, and negative in those compounds where PC coupling is positive.

It is thus seen that the model presented in I is consistent with the observed couplings in the borderline region of the periodic table.

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(4) H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, **38**, 3012 (1963).

(5) (a) H. Dreeskamp and E. Sackmann, *Spectrochim. Acta*, **21**, 2005 (1965); (b) W. McFarlane, *J. Chem. Soc., A*, 528 (1967); (c) H. Dreeskamp, H. Elser, and C. Schumann, *Ber. Bunsenges. Physik. Chem.*, **70**, 751 (1966).

(6) H. Dreeskamp and K. Hildenbrand, *Z. Naturforsch.*, **23a**, 940 (1968).

(7) R. R. Dean and W. McFarlane, *Mol. Phys.*, **13**, 343 (1967).

(8) That this is not necessarily so, is implied by Mavel.[3] While the average of $\gamma$ over all dihedral angles for X–P–C–H (where X may be a lone pair) is probably negative, values of $\gamma$ for various dihedral angles probably do not have the same sign.