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**Registry No.** $[\mathrm{Ni(napy)_4](ClO_4)_2}$, 36202-33-2; $[\mathrm{Co(napy)_4](ClO_4)_2}$, 41202-96-4.

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## "Through-Space" Spin Coupling between Phosphorus and Hydrogen in $\pi$-$\mathrm{C_5H_5W(CO)_2PR_3X}$

*Sir:*

Nuclear spin-spin coupling in a freely tumbling molecule is normally transmitted by the electrons associated with the chemical bonds.[1] However, it sometimes happens that a pair of nuclei which are physically close but which are separated by a number of bonds will have an abnormally large coupling constant, and in such cases it is believed that a "through-space" coupling mechanism predominates.[2] This phenomenon is not well understood and the criteria for demonstrating its existence are not well established. Reports of the effect must therefore be examined carefully, especially when the number of bonds separating the coupled nuclei is not large and independent evidence (such as abnormal temperature variation of the coupling constant) is not available.[3]

It has recently been suggested[4] that in *trans*-$\pi$-$\mathrm{C_5H_5W(CO)_2PR_3X}$ [$\mathrm{R = CH_3, C_6H_5, OCH_3}$, etc.; $\mathrm{X = I, Sn(CH_3)_3}$] the observed couplings of 1-2 Hz between $^{31}$P and the protons of the $\pi$-cyclopentadienyl rings [$^{3}J(^{31}\mathrm{P}\cdots\mathrm{H})$] are primarily "through-space" in origin. The main evidence for this is that $^{2}J(^{31}\mathrm{P}\cdots{}^{13}\mathrm{C})$ which involves some of the same bonds as the $^{31}$P-H coupling is apparently zero, and the authors of ref 4 believe that this would not be so if there were appreciable electronic interaction between phosphorus and the cyclopentadienyl ring. We wish to offer an alternative interpretation and suggest that the observed coupling constants can be accounted for satisfactorily by a mechanism which involves the normal chemical bonds.

Firstly, $^{3}J(^{31}\mathrm{P}\cdots\mathrm{H})$ in these species is *not* abnormally large. It is, in fact, rather small, and this is probably due to the presence of the bulky tungsten atom and to essentially free rotation of the cyclopentadienyl ring which will lead to conformational averaging.[5] This process can also account for the zero value for $^{3}J(^{31}\mathrm{P}\cdots\mathrm{H})$ which has been found in *cis*-$\pi$-$\mathrm{C_5H_5W(CO)_2PR_3X}$.

Secondly, studies of a range of organophosphorus species have shown that $^{2}J(^{31}\mathrm{P}\cdots{}^{13}\mathrm{C})$ changes sign as the hybridization of phosphorus changes from essentially $\mathrm{p^3}$ to $\mathrm{sp^3}$, whereas $^{3}J(^{31}\mathrm{P}\cdots\mathrm{H})$ remains positive throughout and may increase in magnitude somewhat.[6] For example, in $\mathrm{(CH_3O)_3P}$ $^{2}J(^{31}\mathrm{P}\cdots{}^{13}\mathrm{C})$ and $^{3}J(^{31}\mathrm{P}\cdots\mathrm{H})$ are +9.9 and +10.0 Hz, respectively, and in $\mathrm{(CH_3O)_3PS}$ they are −5.6 and +12.9 Hz. Furthermore, metal complexes of phosphines can be regarded as being intermediate between the two above extremes [this is supported especially by measurements of $^{1}J(^{31}\mathrm{P{-}H})$ in $\mathrm{PH_3}$, $\mathrm{(PH_3)_2W(CO)_4}$, and $\mathrm{PH_4^+}$] and so should exhibit values of $^{2}J(^{31}\mathrm{P}\cdots{}^{13}\mathrm{C})$ which are close to zero since this coupling constant can vary monotonically from positive to negative as the hybridization of phosphorus changes.[5] The lack of coupling between phosphorus and the cyclopentadienyl ring carbons is therefore not abnormal and does not imply an absence of electronic interaction. In the light of this, the observed $^{3}J(^{31}\mathrm{P}\cdots\mathrm{H})$ most reasonably arises from a mechanism involving the normal chemical bonds and there is no reason to postulate "through-space" interaction.

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