Sign of $^1J(^{31}P–^{183}W)$ in Octahedral Complexes of Tungsten(0)

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Summary $^1J(^{31}P–^{183}W)$ is positive in octahedral complexes of tungsten(0), suggesting dominance by the Fermi contact interaction and that the use of the mean excitation energy approximation is valid.

NUCLEAR spin coupling constants involving phosphorus display remarkable variations in sign and magnitude according to the valency and substituents of the phosphorus atom.[1] The one-bond reduced coupling constants between four-co-ordinate phosphorus and the nuclei of elements which are not very electronegative are normally positive, while for very electronegative elements (*e.g.* fluorine) ^1K is normally negative.[2] This behaviour can be explained in terms of the inavailability of open *s*-shell configurations for the electronegative elements, and this leads to a small *s*-overlap integral for the P–X bond.[3] In three-co-ordinate phosphorus compounds an open *s*-shell configuration may not be accessible to the phosphorus atom itself, and this can account for the occurrence of negative reduced coupling constants between P^{III} and relatively electropositive elements.[4] In metal complexes of trivalent phosphorus donors the situation appears to be intermediate between that in phosphorus(III) and phosphonium species. For example, in PH_3, PH_4^+, and *cis*-$(PH_3)_2W(CO)_4$ $^1J(^{31}P–H)$ has values of 182, 550, and 338 Hz respectively, and the differences can be ascribed to changes in the effective nuclear charge on phosphorus and/or in the *s*-character of the hybrid orbitals used to form the P–H bonds.[5] These three (P–H) coupling constants are known to be positive, but the sign of only one phosphorus–transition-metal coupling constant [$^1J(^{31}P–^{195}Pt)$–positive[6]] has been established, although semi-theoretical discussions of the others have usually assumed that these are positive also.[5] The sign of $^1J(^{31}P–^{183}W)$ is of special importance in this connexion because the magnitudes which have been observed[7] for this coupling constant are rather small [typically $^1K(PW) = 1{\cdot}3 \times 10^{23}\,cm^{-3}$ compared with $2{\cdot}4 \times 10^{23}\,cm^{-3}$ for $^1K(PPt)$ in complexes of similar phosphorus ligands], and because $^1K(WF)$ can change sign without any accompanying change in the oxidation state of tungsten.[8] We now report $^1H–\{^{13}C\}$, $^1H–\{^{31}P\}$, and $^1H–\{^{183}W\}$ heteronuclear double resonance experiments which give the sign of $^1J(^{31}P–^{183}W)$ in the octahedral complex dimethylphenylphosphinepentacarbonyltungsten(0). The results given in the Table were obtained using a JEOL spectrometer operating at a proton frequency of 60 MHz from a sample of $Me_2PhPW(CO)_5$ which contained the isotopes ^{13}C and ^{183}W in natural abundance (1·1 and 14·3% respectively) and the signs of the coupling constants are relative to $^1J(^{13}C–H) > 0$. The sign of $^1J(^{31}P–^{183}W)$ and hence of $^1K(PW)$ is thus positive since $\gamma(^{183}W) > 0$, and the trends in the magnitude of this coupling constant displayed by a range of phosphorus complexes of tungsten(0)[5] [in particular the correlation with $^1J(^{31}P–H)$ in protonated species] indicate that this is always so. The value of $^1J(^{13}C–^{31}P)$ which is intermediate between that found in Me_2PhP ($-14{\cdot}5$ Hz) and that found in Me_2PhP^+H ($+56$ Hz) confirms that the bonding is intermediate between that in a phosphine and a phosphonium salt.

TABLE. *N.m.r. parameters of dimethylphenylphosphine pentacarbonyltungsten*(0)

$^1J(^{13}C–H)$ (Me)	$+130{\cdot}0 \pm 0{\cdot}5$ Hz	δ (H) (Me)	$1{\cdot}91 \pm 0{\cdot}01$ p.p.m.[a]
$^1J(^{31}P–^{13}C)$ (Me	$+30 \pm 10$ Hz	δ (H) (Ph)	7·3—7·6 p.p.m.[a]
$^1J(^{183}W–^{31}P)$	$+230 \pm 3$ Hz	Ξ (^{13}C) (Me)	25, 145, 518 Hz[b]
$^2J(^{31}P \cdots H)$ (Me)	$-\ 7{\cdot}6 \pm 0{\cdot}1$ Hz	Ξ (^{31}P)	40, 479, 759 Hz[b]
$^3J(^{183}W \cdots H)$ (Me)	$+\ 2{\cdot}2 \pm 0{\cdot}2$ Hz	Ξ (^{183}W)	4, 152, 557 Hz[b]

[a] To low field of Me_4Si. [b] Ξ is the resonant frequency corrected to a magnetic field strength at which Me_4Si would give a proton resonance at 100 MHz.

It thus appears that theoretical treatments of phosphorus–tungsten coupling in complexes of tungsten(0) which assume dominance by the Fermi contact interaction together with the mean excitation energy approximation may be adequate.[7] That is, the *s*-overlap integral between phosphorus and tungsten must be reasonably large, and the observed variations in the coupling constant must arise mainly from changes in the effective nuclear charge of phosphorus and to some extent from changes in the *s*-character of the hybrid orbitals used by phosphorus to form the P–W bond. By contrast, in tungsten(VI) species the *s*-overlap integrals may be small, and so relatively large changes in them (and hence in the signs of the mutual polarisabilities) can occur when the substituents of tungsten change, and these can lead to changes in the signs of coupling constants involving tungsten, as is found in derivatives of WF_6.[8]

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