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Preliminary communication

Tungsten-183–phosphorus-31 spin–spin coupling interactions in phosphorus trihalide pentacarbonyltungsten complexes

E.O. FISCHER and L. KNAUSS
Inorganic Chemistry Laboratory, Technical University, Munich (Germany)

R.L. KEITER
Department of Chemistry, Eastern Illinois University, Charleston, Illinois (U.S.A.)

J.G. VERKADE
Department of Chemistry, Iowa State University, Ames, Iowa (U.S.A.)

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It has been shown previously that a good correlation exists between the magnitudes of ^{183}W–^{31}P nuclear spin–spin coupling constants and the electronegativity of the substituent atoms bound to phosphorus* in $LW(CO)_5$ complexes where $L = PF_3$, $P(OCH_2)_3CC_5H_{11}$, $P[N(CH_3)CH_2]_3CC_5H_{11}$, $P(SCH_2)_3CC_5H_{11}$, $P(CH_2O)_3C$–n-Bu and $(C_4H_9)_3P)$[1]. The four caged ligands and PF_3 were chosen[1] for inclusion in the calculation of the correlation coefficients (Tables 1 and 2) and to establish the least-squares line in Fig. 1 (circled points in lower line) because they minimized possible coupling changes induced by steric effects of the phosphorus substituents**. The rest of the organophosphorus ligands are seen to generate points which are reasonably close to the lower line in Fig. 1 and interestingly, phenyl α-carbons do not appear to be grossly different in electronegativity from alkyl α-carbons.

Complexes of the type $LW(CO)_5$ where $L = PCl_3$, PBr_3 and PI_3 have been prepared recently[2,3] and although it is gratifying to note from the upper line in Fig. 1 that an excellent correlation of their $^1J(W$–$P)$ values with electronegativity is demonstrated (Table 2) a distinctly different slope is generated. The Pople–Santry MO theory shows that coupling constants between directly bonded atoms arise from the Fermi contact term and

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*No correction was made for atoms β, γ, etc. to phosphorus[1].

**Tributyl phosphine was included when it was found that its coupling is only slightly different from $P(CH_2O)_3C$–n-Bu and this similarity indicates that electronic effects beyond the α atom on the *P*-substituent as well as general steric effects are not very important.

the resultant expression for complexes of high symmetry is

$$ {}^1J(\text{P–M}) = \gamma_P\gamma_M \frac{\hbar}{2\pi}\,\frac{256\pi^2}{9}\,\beta^2\,|\,S_P(O)\,|^2\,|\,S_M(O)^2\,|\times\frac{\alpha^2(1-\alpha^2)}{n}\,\alpha^2\times\frac{1}{\Delta E\psi\psi}\,* $$

where it is assumed that only the valence shell *s* orbital of the metal contributes to the bonding[5]. In this equation it is seen that as *s* character (α^2) increases, *J*(P–M) becomes larger, which is consistent with the two sets of results taken independently. According to the Pople–Santry expression, however, *J*(P–M) is directly proportional to the square of the value of the valence state *s* orbital densities on the coupling nuclei and inversely

TABLE 1

${}^1J$(W–P) COUPLINGS IN W(CO)$_5$L COMPLEXES

	L	${}^1J$(W–P) (Hz)	Ref.		L	${}^1J$(W–P) (Hz)	Ref.
1	PF_3	485	1	14	$P(NEt_2)_3$	296	8
2	PCl_3	426	[a]	15	$P(OMe)Ph_2$	280	8
3	PBr_3	398	[a]	16	$P(SCH_2)_3C$-n-Pent	276	1
4	PI_3	334	[a]	17	PPh_3	280	8
5	$P(OPh)_3$	415	7	18	$PBuPh_2$	250	8
6	$P(OMe)_3$	398	8	19	$PMePh_2$	245	8
7	$P(OCH_2)_3C$-n-Pent	393	1	20	$PEtPh_2$	240	8
8	$P(OEt)_3$	391	8	21	P(i-Pr)Ph_2	240	8
9	P(O-n-Bu)$_3$	390	8	22	P(t-Bu)Ph_2	240	8
10	P(O-i-Pr)$_3$	378	8	23	PBu_2Ph	235	8
11	$P(OMe)_2Ph$	323	8	24	$P(CH_2O)_3C$-n-Bu	234	1
12	$P(NMeCH_2)_3C$-n-Pent	318	1	25	PBu_3	227	7
13	$P(NMe_2)_3$	297	8				

[a] This work. The ${}^1J$(W–P) values for L=PCl_3 and PBr_3 reported incorrectly earlier (Ref. 2) are corrected here.

TABLE 2

CORRELATION COEFFICIENTS OF ${}^1J$(W–P) *versus* ELECTRONEGATIVITY FOR W(CO)$_5$L COMPLEXES

L	Electronegativity scale	Correlation coefficient
PBu_3, $P(CH_2O)_3C$-n-Bu, PO_3Y, PS_3Y, $P(NMe)_3Y$ (Y = $(CH_2)_3C$-n-Pr or $(CH_2)_3C$-n-Pent)	Sanderson	0.996 [a]
	Pauling	0.983 [a]
	Allred–Rochow	0.961 [a]
PI_3, PBr_3, PCl_3, PF_3	Sanderson	0.995
	Pauling	0.941
	Allred–Rochow	0.949

[a] These correlation coefficients are improved over those reported previously (Ref. 1) because of the inclusion of a more precise value for PBu_3 (Ref. 7) than that reported earlier (Ref. 9).

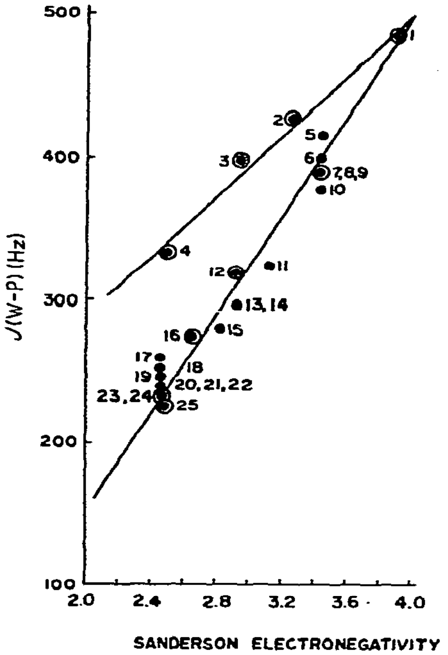

Fig. 1. Plot of $^1J(W-P)$ *versus* the Sanderson Electronegativity of the ligand in a series of $W(CO)_5L$ complexes where L is the compound correspondingly numbered in Table I. The circled points were used to construct the least-squares lines.

proportional to the triplet electronic excitation energy between the ground and excited states. The trends in these variables in the PX_3 and organophosphine series may be sufficiently different to produce the different slopes in the correlations of $J(P-M)$ with electronegativity[★].

The intersection of the two slopes at PF_3 may or may not be fortuitous. If it is not a coincidence, a regular periodicity of $^1J(W-P)$ with the α *P*-substituent is suggested[★★]. The recent synthesis of the $P(GeMe_3)_3$ and $P(SnMe_3)_3$ pentacarbonyl tungsten complexes[6][★★★] may shed further light on this question.

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[★] The postulate that the organophosphines fall on the greater slope because of an overestimation of the α-substituent atom electronegativity owing to the presence of an electron inductive β-carbon moiety seems untenable. Thus the α-carbon for $P(n\text{-}Bu)_3$ would have to have an effective electronegativity of less than zero for its $^1J(W-P)$ value to fall on the PX_3 line.

[★★] If this is true the necessary exclusion of $P(SCH_2)_3C$–n-pentane from the least-squares calculation of lower line does not alter the slope appreciably.

[★★★] Attempts to measure $^1J(W-P)$ on these complexes are presently underway in the laboratories of Professor Schumann (H. Schumann, private communication to J.G.V.).

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