

Correlation between Phosphorus–Tungsten Coupling Constants and Carbonyl Stretching Frequencies in Phosphorus-ligand Derivatives of Tungsten Hexacarbonyl

By SAMUEL O. GRIM,* PATRICK R. McALLISTER, and ROGER M. SINGER

(Department of Chemistry, University of Maryland, College Park, Maryland 20742)

WE reported earlier that there is a correlation between the most intense (*E* mode) carbonyl stretching frequencies in tertiary phosphine–tungsten pentacarbonyl compounds and the tungsten-183–phosphorus-31 nuclear spin–spin coupling constants in the compounds.¹ All the ligands were tertiary phosphines: hence, J_{W-P} varied by only 80 Hz while the CO stretching frequencies (*E* mode) had a range of only 8 cm.⁻¹.

We have extended the study over a significantly larger range of J_{W-P} (211 Hz) and ν_{CO} (25 cm.⁻¹) by including tertiary phosphites, mixed phenylalkoxyphosphines, and tris(dialkylamino)phosphines as ligands. The results are given in the Table and the data are plotted in the Figure. The least-squares line for all the points is shown by the solid line: ν_E (cm.⁻¹) = 1918 + 0.087 J (Hz), with a standard deviation (σ) of 3.7 cm.⁻¹. The correlation of all the

data collectively is not as good (correlation coefficient, $r = 0.86$) as that of the data for the individual classes of ligands. For example, the tertiary phosphines give $r = 0.97$ and $\sigma = 0.6 \text{ cm.}^{-1}$, whereas the phosphites have $r = 0.98$ and $\sigma = 1.2 \text{ cm.}^{-1}$. The qualitative relationship is, however, clear. Thus, the less basic ligands of phosphorus (the poorer σ -donors and better π -acceptors) have the larger phosphorus-tungsten coupling constants. Since the use of carbonyl stretching frequencies for determining the π -acceptor ability of ligands has been under attack recently,² the fact that there is a correlation between ν_{CO} and $J_{\text{W-P}}$ does not prove that $J_{\text{W-P}}$ is a measure of π -acceptor ability. One would expect the best σ -donors to have the largest coupling constants, because it is generally supposed that the coupling mechanism is transmitted through σ -bonds with s -electronic character.³ The experimental results indicate the opposite. Until theoretical developments show otherwise, we conclude that the σ -bond is strengthened by a synergic π -interaction and/or

The carbonyl stretching frequency (*E* mode) and phosphorus-tungsten coupling constant in $\text{LW}(\text{CO})_5$

	Ligand	<i>E</i> (cm.^{-1})	$J_{\text{W-P}}$ (Hz)
1	$(\text{PhO})_3\text{P}$	1959	411
2	$(\text{MeO})_3\text{P}$	1953	398
3	$(\text{EtO})_3\text{P}$	1949	391
4	$(\text{Bu}^n\text{O})_3\text{P}$	1947	390
5	$(\text{Pr}^i\text{O})_3\text{P}$	1944	378
6	$(\text{MeO})_2\text{PhP}$	1950	323
7	$(\text{Me}_2\text{N})_3\text{P}$	1950	297
8	$(\text{Et}_2\text{N})_3\text{P}$	1948	296
9	$\text{MeO}\cdot\text{Ph}_2\text{P}$	1945	280
10	Ph_3P	1942	280
11	MePh_2P	1939	245
12	EtPh_2P	1938	240
13	$\text{Ph}_2\text{Pr}^i\text{P}$	1937	240
14	$\text{Ph}_2\text{Bu}^n\text{P}$	1938	250
15	$\text{Ph}_2\text{Bu}^t\text{P}$	1937	240
16	PhBu_2^nP	1937	235
17	Bu_3^nP	1934	200

there is coupling transmitted *via* π -bonds or another mechanism.

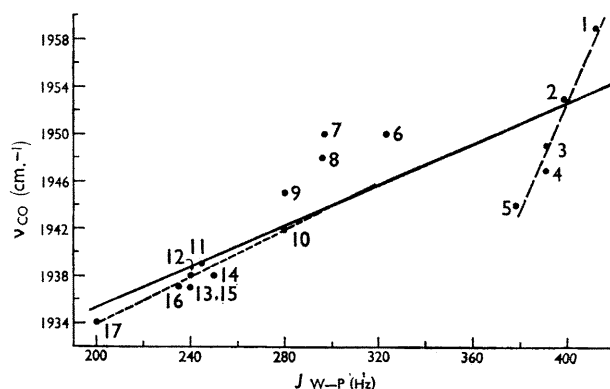


FIGURE. Correlation of ν_{CO} (*E* mode) and $J_{\text{W-P}}$ for $\text{LW}(\text{CO})_5$ compounds (—, all compounds; ---, phosphites; ·····, phosphines). The numbers correspond to the compounds in the Table

It seems (Figure) that $J_{\text{W-P}}$ is a better measure of π -acceptor ability (or inversely as σ -donor ability) than ν_{CO} . In particular, $J_{\text{W-P}}$ increases as follows: $\text{R}_3\text{P} < \text{RPh}_2\text{P} < \text{Ph}_3\text{P} \sim (\text{RO})\text{Ph}_2\text{P} < (\text{R}_2\text{N})_3\text{P} < (\text{RO})_2\text{PhP} < (\text{RO})_3\text{P} < (\text{PhO})_3\text{P}$, which appears to be a quite reasonable order based on inductive effects of the substituents on phosphorus. However, the order of increasing ν_{CO} is not the same. Indeed, the amino-phosphines and dimethoxyphenylphosphine are included in the span of phosphites, which is not expected.

We thank the U.S. Air Force Office of Scientific Research for support of this work and NASA for a traineeship (to P.R.M.).

(Received, October 29th, 1968; Com. 1474.)

¹ S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, 1967, **89**, 5573.

² M. Bigorgne, *J. Inorg. Nuclear Chem.*, 1964, **26**, 107.

³ R. J. Angelici and M. D. Malone, *Inorg. Chem.*, 1967, **6**, 1731.

⁴ D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, 1968, **7**, 959.

⁵ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Oxford, 1965, vol. 1, ch. 5.