^{31}P–^{31}P Spin–Spin Coupling in Complexes Containing Two Phosphorus Ligands

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Abstract: ^{31}P–^{31}P coupling constants ($^2J_{PP}$) for 30 coordination complexes containing two identical phosphorus ligands are reported. The values were obtained from their proton nmr spectra by (a) measurement of the separation of the $\chi = 1$ inner and outer lines, (b) double resonance techniques, or (c) computer simulation of the band shape. In some instances two techniques could be used as a check. From the available sign data (see preceding paper) it appears that $^2J_{PP}$ ranges from -26.2 to -78 Hz for *cis*-$Cr(CO)_4L_2$, -12.4 to -55 Hz for *cis*-$Mo(CO)_4L_2$, -13.4 to -38 Hz for *cis*-$W(CO)_4L_2$, -30 to $+34$ Hz for *trans*-$Cr(CO)_4L_2$, $+49$ to $+312$ Hz for *trans*-$Mo(CO)_4L_2$, $+65$ to $+315$ Hz for *trans*-$W(CO)_4L_2$, and $+65$ to $+300$ Hz for *trans*-$Fe(CO)_3L_2$. Among ligands involved in these complexes are PH_3, PR_3, $P(NR_2)_3$, $P(OR)_3$, and PF_3. Included in the ranges for $^2J_{PP}$ are the pertinent values available in the literature. The trends in these coupling constant ranges are shown to roughly parallel the increase in Pauling electronegativity of the atoms immediately bound to phosphorus in the substituents. Anomalies in these trends appear to occur only for those *cis* complexes which contain phosphorus ligands possessing an NR_2 group. Several such complexes have other unusual characteristics which may be associated with the anomalous coupling. Magnitudes of $^2J_{PP}$ are also reported for several Pt(II), Pd(II), and Ni(0) complexes. The new complexes *cis*-$Mo(CO)_4(P[N(CH_3)(C_6H_5)]_3)_2$, *cis*-$Mo(CO)_4(P[N(CH_3)_2]_3)_2$, and *trans*-$Cr(CO)_4[P(OCH_3)_3]_2$ are described. Chemical shifts and other coupling parameters for all of the complexes for which we obtained $^2J_{PP}$ are also reported.

Many aspects of the nature of the metal–phosphorus bond in coordination compounds remain obscure and the circumstances surrounding this problem have been described in the recent literature.[2–5] Because spin–spin coupling information is transferred by electron density between two coupling nuclei, the trends and magnitudes of metal–phosphorus coupling constants constitute a potentially valuable source of data for use in more fully interpreting changes in metal phosphorus bonding under varying conditions of stereochemistry, oxidation state of the metal, nature of the ligand, etc. Such studies are restricted, however, to nuclei with sufficient abundance of an isotope of nonzero (usually $^1/_2$) spin. Moreover the phosphorus ligands employed in these investigations have been limited for the most part to alkyl or aryl phosphines in the cases of ^{199}Hg[6] and ^{195}Pt[7–10] although a variety of ligands have been used in the case of ^{183}W.[4,11–13] The interpretation of the results of these researches centers on the importance of the Fermi contact term[8–11] although coupling *via* π-electron density arising out of π backdonation from the metal is not ruled out.[7,12,13]

Phosphorus–phosphorus coupling through a metal atom in a complex containing two dissimilar phosphorus ligands should also reflect the character of the phosphorus–metal bond. Although a somewhat larger variety of complexes becomes available because of the loss of the requirement that the metal nucleus be of nonzero spin, mixed ligand complexes are comparatively difficult to synthesize. This problem is made the more serious when it is noted that the complexes must be sufficiently soluble for obtaining ^{31}P spectra, unless facilities are available for spectral accumulation. Because of the fact that there are two different phosphorus ligands in such systems, it is not possible to apportion the coupling constants between them. Although several such constants have been measured,[14,15] this information at present is only useful (see Discussion) when ^{31}P–^{31}P coupling constants are known for the analogous compounds in which both ligands are identical.

Coupling constant studies of two ^{31}P nuclei through a metal atom in a complex containing two identical phosphorus ligands afford the advantage of investigating a wider range of metals inasmuch as the metal atom need not possess a nuclear spin and the synthetic problems are minimal. A further advantage accrues from the higher sensitivity of the ^1H nucleus in the proton nmr spectra from which the ^{31}P–^{31}P couplings are obtained. Thus solubility problems are reduced considerably. In this paper are recorded our attempts to correlate the magnitudes of ^{31}P–^{31}P coupling constants with the bonding character of ligands such as $P(NMe_2)_3$, PMe_3, $P(OMe)_3$, $P(OCH_2)_3CR$, and PF_3 in a variety of complexes.

Because the ligands we have studied in this work also possess protons, the complexes containing two identical ligands yield ^1H and ^{31}P nmr spectra of the type $X_nAA'X_n'$. Although it is in principle possible to cal-

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Table I. Proton Nmr Data for Compounds of $P(CH_3)_3(L)$

Compound	N, Hz	$^2J_{PH}$, Hz[a]	$^4J_{PH}$, Hz[a]	δH, ppm[b]	Solvent
L[c]		$+2.7 \pm 0.1$		0.89	Neat
cis-$Cr(CO)_4(L)_2$	-6.9 ± 0.1	-7.1 ± 0.2	$+0.2 \pm 0.2$	0.99	C_6H_6
trans-$Cr(CO)_4(L)_2$	-7.4 ± 0.1	-7.7 ± 0.2	$+0.3 \pm 0.2$	1.18	C_6H_6
cis-$Mo(CO)_4(L)_2$	-6.3 ± 0.1	-6.6 ± 0.2	$+0.3 \pm 0.2$	0.99	C_6H_6
cis-$W(CO)_4(L)_2$[d]	-7.09 ± 0.02	-7.34 ± 0.05	$+0.25 \pm 0.05$	1.08	C_6H_6
cis-$PdCl_2(L)_2$[e]	± 10.6	± 11.7	∓ 1.1	1.73	CH_2Cl_2
trans-$PdI_2(L)_2$	-7.0 ± 0.1	-10.0 ± 0.2	$+3.0 \pm 0.02$	1.85	$CDCl_3$
O=L[f]		13.4		1.93	D_2O
S=L[c]		-13.0 ± 0.1		1.74	Neat

[a] Values of $^2J_{PH}$ and $^4J_{PH}$ were determined by using $^2J_{PP}$, obtained from observation of the weak intensity wing peaks or double resonance methods, and the computer program to simulate the observed ^1H spectra. [b] Downfield from tetramethylsilane. [c] Reference 43. [d] $^1J_{WP} = \pm 209.8$ Hz, $^3J_{WH} = \pm 1.9$ Hz. [e] Reference 38. [f] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

culate $^2J_{AA'}$ (*i.e.*, $^2J_{PP}$) from the ^{31}P spectra using equations developed by Mowthorpe and Chapman,[16] the complexity of the spectra and solubility considerations render this method impractical for extensive studies. $^2J_{PP}$ can, however, be assessed by using high radiofrequency power to observe weak-intensity ($\chi = 1$) wing peaks in the ^1H spectrum as suggested by Finer and Harris,[17] by double resonance techniques,[18,19] or by computer simulation of the observed band shapes formed by overlapping lines[20] in the proton spectrum using the equations of Harris.[21] We have employed all three of these techniques and in some cases more than one of them were used on the same complex to serve as a check or to point up a difficulty in certain instances.

Experimental Section

Infrared spectra were obtained on a Beckman Model 12 spectrometer. Mass spectra were obtained on an Atlas CH-4 single focusing spectrometer at an energy of 70 eV. Proton nmr spectra were obtained on Varian A-60 and HR-60 spectrometers. The preparations of most of the compounds have been described previously by King for metal carbonyl complexes of $P(N(CH_3)_2)_3$,[22a] Noth and Vetter for $HgI_2[P(N(CH_3)_2)_3]_2$,[22b] Vandenbroucke, *et al.*,[5] Verkade, *et al.*,[23] and Stanclift and Hendricker[24] for metal carbonyl complexes of $P(OCH_2)_3CR$, Mathieu and Poilblanc for *cis*-$Mo(CO)_4[P(OCH_3)_3]_2$,[25] Poilblanc and Bigorgne for *trans*-$Mo(CO)_4[P(OCH_3)_3]_2$,[26] and Jenkins and Verkade for the other complexes.[27] The few compounds that are not reported in the above references are given below.

N,N′,N′′-Trimethyl-N,N′,N′′-triphenylphosphorous Triamide. Attempts to prepare this ligand by a previously reported synthesis[28] failed in our hands but the following procedure proved successful. In 100 ml of liquid NH_3 was dissolved 6.9 g (0.3 mol) of sodium. A crystal of $Fe(NO_3)_3 \cdot 6H_2O$ was added to catalyze the formation of $NaNH_2$. To this was added dropwise 32.1 g (0.3 mol) of methylaniline. Anhydrous diethyl ether (125 ml) was added dropwise and the ammonia was allowed to evaporate after which the mixture was refluxed for 30 min to ensure complete removal of the ammonia. The mixture was then cooled to 0° and 13.7 g (0.1 mol) of phosphorus trichloride in 50 ml of anhydrous ether was added dropwise. After stirring the mixture at 25° for 3 hr, the sodium chloride was removed by filtration. The filtrate was taken to dryness yielding a white solid which was recrystallized from benzene in 34% yield (mp 208–210°; lit. mp 208–209°). The peak corresponding to the highest mass in the mass spectrum was at 106 (probably a $N(CH_3)(C_6H_5)$ fragment). The nmr spectrum consisted of a doublet at 2.67 ppm ($^3J_{PH} = 2.8$ Hz) and a complex multiplet at *ca* 7.1 ppm.

cis-$Mo(CO)_4(P[N(CH_3)(C_6H_5)]_3)_2$. A mixture of 2.0 g (7.5 mmol) of hexacarbonylmolybdenum and 6.0 g (17.2 mmol) of N,N′,N′′-trimethyl-N,N′,N′′-triphenylphosphorous triamide in 125 ml of toluene was refluxed for 16 hr. After cooling and filtering the mixture, its volume was reduced under reduced pressure until crystals began to form. Thirty milliliters of pentane was then added and the mixture was cooled to −20°. The complex, after separating by filtration, was recrystallized from an 80:20 toluene–pentane mixture in *ca.* 20% yield. The carbonyl stretching frequencies observed in chloroform were at 1911 (s), 1933 (sh), and 2125 (m) cm^{-1}.

cis-$Mo(CO)_4(P[N(CH_3)_2]_3)_2$. To 0.6 g (2.0 mmol) of tetracarbonyl(norbornadiene)molybdenum in 25 ml of pentane was added 1.0 g (6.1 mmol) of hexamethylphosphorous triamide. After stirring the mixture at 25° for 3 min, the complex was filtered off in 88% yield. The carbonyl stretching frequencies observed in chloroform were at 1894 (s), 1908 (sh), and 2012 (m) cm^{-1}.

trans-$Cr(CO)_4[P(OCH_3)_3]_2$. To 1.28 g (5.0 mmol) of tetracarbonyl(norbornadiene)chromium in 30 ml of pentane was added 2.0 g (16.1 mmol) of trimethyl phosphite. After stirring the mixture at 25° for 48 hr the complex was filtered off in 61% yield, washed with pentane, and used without further purification (mp 76–78°). The carbonyl stretching frequency observed in chloroform was at 1909 (s) cm^{-1}. Parent-ion peaks were observed in the mass spectrum at 412 and 413 corresponding to 83.5% and 9.5% natural abundance for ^{52}Cr and ^{53}Cr, respectively.

The method of obtaining $^2J_{PP}$ from observation of the weak outer peaks as well as the double resonance technique as applied to coordination complexes of the type discussed here have been presented earlier.[18,29] A description of the computer simulation of the proton spectra of several of these complexes has also been recorded.[20]

The proton nmr data are reported in Tables I–VI while the $^2J_{PP}$ values are recorded in Tables VII–IX. Because of the near-zero value of N ($N = |J_{AX} + J_{AX'}|$) in complexes of $P(CH_2O)_3CCH_3$ and $P(CH_2Cl)_3$, the methylene proton spectrum appeared as one unresolved peak in each case. Thus no solution of $^2J_{PP}$ was obtained from these spectra and so these complexes have been omitted from Tables VII–IX. The divalent platinum and palladium complexes of $P(N(CH_3)_2)_3$ have also been omitted from Tables VII–IX, the reason for which will be discussed later. Published values of $^2J_{PP}$[14,15,30–38] pertinent to the present study have been included in Tables VII–IX as well as those measured in this work.

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Table II. Proton Nmr Data for Compounds of $P(CH_2O)_3CCH_3$ (L)

Compound	N or $^2J_{PH}$, Hz[a]	δH, ppm[b]	Solvent
L	8.0	4.30	CCl_4
cis-$PdCl_2(L)_2$	0	4.70	CH_3CN
trans-$PdCl_2(L)_2$	0	4.70	CH_2Cl_2
O═L[c]	7.3	4.40	$CDCl_3$
S═L[c]	5.6	4.49	$(CH_3)_2CO$

[a] $N = {}^2J_{PH} + {}^4J_{PH}$ for the palladium complexes, $N = {}^2J_{PH}$ for the other compounds. [b] Chemical shifts of the methylene protons downfield from tetramethylsilane. The chemical shifts of the methyl proton (*ca.* 1.3 ppm) are not given. [c] E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, **7**, 165 (1968).

Table III. Proton Nmr Data for Compounds of $P(CH_2Cl)_3$ (L)

Compound	N or $^2J_{PH}$, Hz[a]	δH, ppm[b]	Solvent
L	6.1	3.78	CCl_4
cis-$Mo(CO)_4(L)_2$	0	3.38	C_6H_6
trans-$PdCl_2(L)_2$	0	4.14	CH_2Cl_2
trans-$PdI_2(L)_2$	0	3.77	C_6H_6

[a] $N = {}^2J_{PH} + {}^4J_{PH}$ for the complexes, $N = {}^2J_{PH}$ for $P(CH_2Cl)_3$. [b] Downfield from tetramethylsilane.

Table IV. Proton Nmr Data for Compounds of $P[N(CH_3)_2]_3$ (L) and $P[N(CH_3)(C_6H_5)]_3$ (L′)

Compound	$^3J_{PH}$, Hz[a]	δH, ppm[b]	Solvent
L	+8.8 ± 0.1[c]	2.42	Neat
L′	2.8	2.67[d]	$CDCl_3$
trans-$Cr(CO)_4(L)_2$	+9.84 ± 0.02	2.65	C_6H_6
cis-$Mo(CO)_4(L)_2$	10.9	2.60	C_6H_6
cis-$Mo(CO)_4(L')_2$	9.2	3.10[d]	$CDCl_3$
trans-$Mo(CO)_4(L)_2$	+10.2 ± 0.1	2.67	C_6H_6
trans-$W(CO)_4(L)_2$	+10.4 ± 0.1	2.56	C_6H_6
trans-$Fe(CO)_3(L)_2$	+9.6 ± 0.1	2.67	C_6H_6
$Ni(CO)_2(L)_2$	9.3	2.47	C_6H_6
cis-$PdCl_2(L)_2$	9.7	2.63	C_6H_6
trans-$PdCl_2(L)_2$	10.1	2.77	C_6H_6
trans-$PdI_2(L)_2$	10.3	2.40	C_6H_6
cis-$PtCl_2(L)_2$	9.4	2.78	CH_2Cl_2
trans-$PtCl_2(L)_2$	10.1	2.83	CH_2Cl_2
trans-$PtI_2(L)_2$	10.0	2.81	CH_2Cl_2
$HgI_2(L)_2$	Broad[e]	2.83	$CDCl_3$
O═L	+9.30 ± 0.03[c]	2.62	Neat
S═L[f]	11.0	2.62	

[a] Values obtained at the ambient temperature of the probe (*ca.* 30°). [b] Downfield from tetramethylsilane. [c] Reference 18. [d] Chemical shift of the methyl protons. The chemical shifts of the phenyl protons were *ca.* 7.1 ppm. [e] Ligand exchange is occurring. [f] R. Burgada, G. Martin, and G. Mavel, *Bull. Soc. Chim. Fr.*, 2154 (1963). The solvent used (if any) was not given.

Table V. Proton Nmr Data for Compounds of $P(OCH_3)_3$ (L)

Compound	$^3J_{PH}$, Hz	δH, ppm[a]	Solvent
L[b]	+10.0 ± 0.1	3.69	Neat
trans-$Cr(CO)_4(L)_2$	+11.26 ± 0.05	3.47	C_6H_6
cis-$Mo(CO)_4(L)_2$	+11.6 ± 0.1	3.68	$CDCl_3$
trans-$Mo(CO)_4(L)_2$	+11.6 ± 0.1	3.65	$CDCl_3$
cis-$PdCl_2(L)_2$	+12.9 ± 0.2	3.89	$CDCl_3$
$PdI_2(L)_2$[c]	Broad	3.45	C_6H_6
cis-$PtCl_2(L)_2$[d]	12.7	3.88	$CDCl_3$
cis-$PtI_2(L)_2$[e]	12.9	3.82	CH_2Cl_2
O═L[b]	+10.5 ± 0.1	3.46	Neat
S═L[b]	+12.9 ± 0.1		Neat

[a] Downfield from tetramethylsilane. [b] Reference 43. [c] Far-infrared studies indicate the compound is *cis* in the solid state but nmr studies indicate that an exchange process is occurring probably giving a *cis–trans* mixture in solution. [d] $^4J_{PtH} = 2.5$ Hz. [e] $^4J_{PtH} = 2.2$ Hz.

Table VI. Proton Nmr Data for Compounds of $P(OCH_2)_3CR$[a]

Compound	$^3J_{PH}$, Hz	δH, ppm[b]	Solvent
L	2.00	3.93	$CDCl_3$
cis-$Cr(CO)_4(L)_2$	4.65	4.23	$(CH_3)_2CO$
trans-$Cr(CO)_4(L')$	4.11	4.29	$(CH_3)_2CO$
cis-$Mo(CO)_4(L'')_2$	4.30	4.21	$(CH_3)_2CO$
trans-$Mo(CO)_4(L'')_2$	4.20	4.28	$(CH_3)_2CO$
cis-$W(CO)_4(L'')_2$	4.50	4.23	$(CH_3)_2CO$
trans-$W(CO)_4(L'')_2$	4.40	4.17	$CDCl_3$
trans-$Fe(CO)_3(L')_2$	4.92	4.35	$(CH_3)_2CO$
trans-$PdI_2(L''')_2$	~2[c]	4.37	CH_2Cl_2
cis-$PdCl_2(L''')_2$	5.50	4.42	CH_2Cl_2
cis-$PtI_2(L''')_2$	5.70	4.42	CH_2Cl_2
cis-$PtCl_2(L''')_2$	5.65	4.47	DMSO
$Ni(CO)_2(L)_2$	4.00	4.10	$CDCl_3$
O═L[d]	6.00	4.48	CH_3CN
S═L[d]	7.00	4.48	CH_3CN

[a] R = CH_3 (L), R = C_2H_5 (L′), R = C_3H_7 (L″), R = C_5H_{11} (L‴). [b] Chemical shifts of the methylene protons downfield from tetramethylsilane. The chemical shifts of the alkyl chains (*ca.* 1 ppm) are not given. [c] Poor resolution of the apparent triplet did not permit the accurate determination of $^3J_{PH}$. [d] J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962).

Discussion

Stereochemistry

Unusual stereochemical properties of molybdenum complexes were observed with the ligands $P(N(CH_3)_2)_3$ and $P(N(CH_3)(C_6H_5))_3$. King was unable to prepare any *cis* complexes with $P(N(CH_3)_2)_3$.[23a] By reacting tetracarbonyl(norbornadiene)molybdenum and tricarbonyl(cycloheptatriene)molybdenum with this ligand, he obtained only the *trans*-$Mo(CO)_4L_2$ species instead of the expected *cis*-$Mo(CO)_4L_2$ and *fac*-$Mo(CO)_3L_3$ complexes, respectively. He attributed the reluctance of $P(N(CH_3)_2)_3$ to occupy *cis* positions to the bulk of the ligand. Although we have been able to prepare the *cis*-$Mo(CO)_4L_2$ complex with $P(N(CH_3)_2)_3$ we have found that it isomerizes to the *trans* isomer in benzene solution at room temperature in 30 min. In contrast, the ligand $P(N(CH_3)(C_6H_5))_3$ which should be similar to $P(N(CH_3)_2)_3$ in chemical properties and steric requirements forms a stable *cis*-$Mo(CO)_4L_2$ compound which could not be isomerized to the *trans* by refluxing it for 24 hr in a toluene solution. Complexes of $P(N(CH_3)_2)_3$ show other unusual properties which will be discussed later and it is possible that the bulk of this ligand is not the only reason for its reluctance to form *cis* complexes.

^{1}H Nmr Line Shapes and Their Computer Simulation

It has been found that if $^2J_{PP}$ can be obtained by a method other than that of computer simulation of the envelope of overlapping ^{1}H spectra lines, more accurate

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Table VII. ^{31}P–^{31}P Coupling Constants in *cis*-Disubstituted Complexes

Compound	$^2J_{PP}$, Hz	Method^a
$Cr(CO)_4(PH_3)_2$	$-26.2^{b,c}$	A
$Cr(CO)_4[P(CH_3)_3]_2$	-36 ± 1	A^k
$Cr(CO)_4(PH_3)[P(C_6H_5)_3]$	33.0^b	E
$Cr(CO)_4[P(OCH_2)_3CCH_3]_2$	70 ± 10	D
$Cr(CO)_4[P(N(CH_3)_2)F_2]_2$	62 ± 2^d	B
$Cr(CO)_4[P(CCl_3)F_2]_2$	67 ± 1^d	B
$Cr(CO)_4(PF_3)_2$	78 ± 1^e	B
$Mo(CO)_4(PH_3)_2$	18.3^b	A
$Mo(CO)_4[P(CH_3)_3]_2$	-29.7 ± 0.1	A^k
$Mo(CO)_4[P(n\text{-}C_4H_9)_2(C_6H_5)][P(C_6H_5)_3]$	21^f	E
$Mo(CO)_4[PH(C_6H_5)_2]_2$	$\sim 19^g$	A
$Mo(CO)_4[P(N(CH_3)_2)_3]_2$	12.4 ± 0.2	A
$Mo(CO)_4[P(N(CH_3)(C_6H_5))_3]_2$	18.2 ± 0.2	A^l
$Mo(CO)_4[P(N(CH_3)_2)_3][P(OCH_2)_3CC_2H_5]$	39 ± 3^h	E
$Mo(CO)_4[P(OCH_3)_3]_2$	-40.5 ± 1	A^k
$Mo(CO)_4[P(OCH_3)_3][P(OCH_2)_3CC_2H_5]$	48 ± 3^h	E
$Mo(CO)_4[P(OCH_2)_3CC_3H_7]_2$	50 ± 10	D
$Mo(CO)_4[P(N(CH_3)_2)F_2]_2$	38 ± 2^i	B
$Mo(CO)_4[P(N(C_2H_5)_2)F_2]_2$	38 ± 1^i	B
$Mo(CO)_4[P(CH_2Cl)F_2]_2$	42.5 ± 0.5^i	B
$Mo(CO)_4[P(CCl_3)F_2]_2$	-48.0 ± 0.5^i	B
$Mo(CO)_4[P(CF_3)F_2]_2$	49 ± 1^i	B
$Mo(CO)_4(PF_3)_2$	55 ± 1^e	B
$W(CO)_4(PH_3)_2$	13.4^b	A
$W(CO)_4[P(CH_3)_3]_2$	-25.0 ± 0.1	A
$W(CO)_4[P(OCH_2)_3CC_3H_7]_2$	35 ± 5	D
$W(CO)_4[P(N(CH_3)_2)F_2]_2$	21 ± 1^d	B
$W(CO)_4[P(CH_2Cl)F_2]_2$	33 ± 1^d	B
$W(CO)_4[P(CCl_3)F_2]_2$	38.0 ± 0.5^d	B
$W(CO)_4(PF_3)_2$	38 ± 1^e	B^k
$PdCl_2[P(CH_3)_3]_2$	8^j	A
$PdCl_2[P(OCH_3)_3]_2$	$+79.9 \pm 0.2$	A^k
$PdCl_2[P(OCH_2)_3CC_5H_{11}]_2$	65 ± 10	D
$PtCl_2[P(N(CH_3)_2)_3]_2$	~ 0	F
$PtCl_2[P(OCH_3)_3]_2$	10 ± 2	D
$PtI_2[P(OCH_3)_3]_2$	~ 0	F
$PtCl_2[P(OCH_2)_3CC_5H_{11}]_2$	35 ± 10	D
$PtI_2[P(OCH_2)_3CC_5H_{11}]_2$	14 ± 5	D

[a] Methods of obtaining values of $^2J_{PP}$ are A, separation of $\chi = 1$ inner and outer lines in the ^1H spectrum; B, separation of $\chi = 1$ inner and outer lines in the ^{19}F spectrum; C, double resonance techniques; D, computer simulation of the band shape; E, direct observation of the ^{31}P spectrum; F, perturbation of main doublet was not observed, thus $^2J_{PP}$ must be undetectably small. [b] Reference 31. [c] J. F. Nixon, private communication. [d] Reference 32. [e] Reference 30. [f] Reference 14. [g] Calculated from spectrum in J. G. Smith and D. T. Thompson, *J. Chem. Soc.*, *A*, 1694 (1967). [h] Reference 15. [i] Reference 33. [j] Reference 38. [k] Reference 18. [l] R. D. Bertrand, personal communication.

values are obtained. Anomalous line shapes in nmr spectra can arise from a number of causes, the most obvious of which is from poor resolution of the instrument used. Non-Lorentzian band shapes can also occur if slow passage conditions are not obtained and the presence of paramagnetic impurities will cause a broadening of the lines. Although the band shape can be simulated for these cases it is doubtful that the ^{31}P–^{31}P coupling constants so derived have any significance.

Broadening of lines can also result from intermolecular exchange. Fackler, *et al.*,[39a] have discussed this problem for the $X_nAA'X'_n$ system. They have shown that a broad apparent triplet, a singlet, or a doublet can result, depending on the rate of exchange. An example

Table VIII. ^{31}P–^{31}P Coupling Constants in *trans*-Disubstituted Complexes

Compound	$^2J_{PP}$	Method^a
$Cr(CO)_4[P(CH_3)_3]_2$	-28.5 ± 1	A^h
$Cr(CO)_4[P(n\text{-}C_4H_9)_3][P(C_6H_5)_3]$	25^b	E
$Cr(CO)_4[P(n\text{-}C_4H_9)_3][P(OC_6H_5)_3]$	30^b	E
$Cr(CO)_4[P(N(CH_3)_2)_3]_2$	-17 ± 5	C^h
$Cr(CO)_4[P(OCH_3)_3]_2$	-15.0 ± 0.1	A^h
$Cr(CO)_4[P(OCH_2)_3CC_2H_5]_2$	9 ± 3	D
$Cr(CO)_4(PF_3)_2$	34 ± 1^c	B
$Mo(CO)_4[P(n\text{-}C_4H_9)_3][P(C_6H_5)_3]$	50^b	E
$Mo(CO)_4[P(n\text{-}C_4H_9)_2(C_6H_5)][P(C_6H_5)_3]$	49^b	E
$Mo(CO)_4[P(n\text{-}C_4H_9)_3][P(OC_6H_5)_3]$	112^b	E
$Mo(CO)_4[P(N(CH_3)_2)_3]_2$	$+101 \pm 1$	A^h
$Mo(CO)_4[P(N(CH_3)_2)_3][P(OCH_2)_3CC_2H_5]$	141 ± 3^d	E
$Mo(CO)_4[P(OCH_3)_3]_2$	$+162 \pm 5$	C^h
$Mo(CO)_4[P(OCH_3)_3][P(OCH_2)_3CC_2H_5]$	185 ± 3^d	E
$Mo(CO)_4[P(OCH_2)_3CC_3H_7]_2$	210 ± 30	D
$Mo(CO)_4(PF_3)_2$	312 ± 1^c	B
$W(CO)_4[P(n\text{-}C_4H_9)_3][P(C_6H_5)_3]$	65^b	E
$W(CO)_4[P(n\text{-}C_4H_9)_3][P(OC_6H_5)_3]$	120^b	E
$W(CO)_4[(n\text{-}C_4H_9)_2(C_6H_5)][P(OC_6H_5)_3]$	112^b	E
$W(CO)_4[P(N(CH_3)_2)_3]_2$	$+81 \pm 5$	C^h
$W(CO)_4[P(OCH_2)_3CC_3H_7]_2$	140 ± 25	D
$W(CO)_4(PF_3)_2$	315 ± 1^c	B
$Fe(CO)_3[P(N(CH_3)_2)_3]_2$	$+65 \pm 10$	C^h
$Fe(CO)_3[P(N(CH_3)_2)_3][P(OCH_2)_3CC_3H_7]$	183 ± 1^d	E
$Fe(CO)_3[P(OCH_2)_3CC_2H_5]_2$	300 ± 40	D
$PdI_2[P(CH_3)_3]_2$	$+572 \pm 5$	C^h
$PdI_2[P(CH_3)_3][P(C_2H_5)_3]$	565^e	E
$PdI_2[P(n\text{-}C_4H_9)_3][P(CH_3)_2(C_6H_5)]$	551^f	E
$PdI_2[P(n\text{-}C_4H_9)_3][P(OC_6H_5)_3]$	758^f	E
$PdI_2[P(CH_3)_2(C_6H_5)][P(OC_6H_5)_3]$	829^f	E
$PdCl_2[P(C_6H_5)_2(CF_3)]_2$	1100 ± 50^g	D

[a] Methods of obtaining values of $^2J_{PP}$ are A, separation of $\chi = 1$ inner and outer lines in the ^1H spectrum; B, separation of $\chi = 1$ inner and outer lines in the ^{19}F spectrum; C, double resonance techniques; D, computer simulation of the band shape; E, direct observation of the ^{31}P spectrum; F, perturbation of main doublet was not observed, thus $^2J_{PP}$ must be undectectably small. [b] Reference 14. [c] Reference 30. [d] Reference 15. [e] Reference 36. [f] Reference 38. [g] A. J. Rest, *J. Chem. Soc.*, *A*, 2212 (1968). The value, however, is considered dubious since the effect of ^{31}P–^1H coupling was not taken into account. [h] Reference 18.

Table IX. ^{31}P–^{31}P Coupling Constants in Miscellaneous Compounds

Compound	$^2J_{PP}$	Method^a
mer-$Mo(CO)_3[P(C_2H_5)_3]_3$	$\leq 15^b$	E
mer-$Mo(CO)_3[P(OCH_3)_3]_3$	47^b	E
mer-$Mo(CO)_3[P(OC_2H_5)_3]_3$	51^b	E
$Fe(CO)_3(PF_3)_2{}^c$	98 ± 1	B
mer-$RhCl_3[P(n\text{-}C_3H_7)_3]_3$	22 ± 3^d	E
mer-$RhCl_3[P(n\text{-}C_4H_9)_3]_3$	21 ± 3^d	E
mer-$RhCl_3[P(C_2H_5)_2(C_6H_5)]_3$	30 ± 8^d	E
mer-$RhCl_3[P(n\text{-}C_4H_9)_3]_2[P(OC_6H_5)_3]$	30.3^e	E
$Ni(CO)_2[P(N(CH_3)_2)_3]_2$	~ 0	F
$Ni(CO)_2[P(OCH_3)_3]_2$	10 ± 3^f	A
$Ni(CO)_2[P(OCH_2)_3CCH_3]_2$	~ 0	F
$Ni(CO)_2[P(CF_3)_3]_2$	$\sim 0^g$	F
$Ni(CO)_2[P(N(CH_3)_2)F_2]_2$	$\sim 0^h$	F
$Ni(CO)_2[P(N(C_2H_5)_2)F_2]_2$	$\sim 0^h$	F
$Ni(CO)_2(PF_3)_2$	38 ± 1^i	B

[a] Methods of obtaining values of $^2J_{PP}$ are A, separation of $\chi = 1$ inner and outer lines in the ^1H spectrum; B, separation of $\chi = 1$ inner and outer lines in the ^{19}F spectrum; C, double resonance techniques; D, computer simulation of the band shape; E, direct observation of the ^{31}P spectrum; F, perturbation of main doublet was not observed, thus $^2J_{PP}$ must be undetectably small. [b] Reference 34. [c] This molecule apparently undergoes intramolecular exchange. The value obtained would therefore be a time average of all possible isomers (ref 30). [d] Reference 35. [e] Reference 36. [f] Calculated from spectrum given in R. Mathieu and R. Poilblanc, *C. R. Acad. Sci., Paris, Ser. C*, **265**, 388 (1967). [g] Reference 37. [h] Reference 32. [i] Reference 30.

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(39) (a) J. P. Fackler, J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, **91**, 1941 (1969); (b) R. A. Newmark, A. D. Norman, and R. W. Rudolf, *Chem. Commun.*, 893 (1969). It is interesting that molecules of the type Me_2PGPMe_2 (where G = S, SiR_2, and GeR_2) also have ^1H nmr spectra which are temperature dependent.

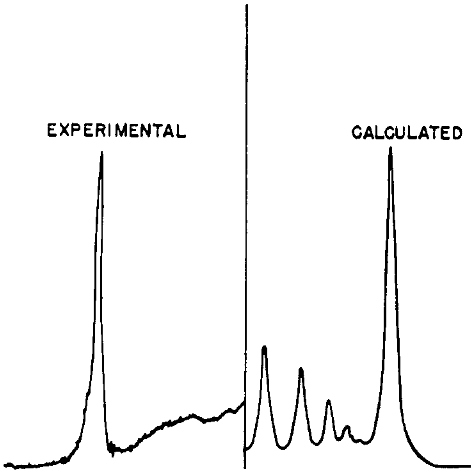

Figure 1. Comparison of experimental and calculated spectra for *cis*-$Mo(CO)_4[P(OCH_3)_3]_2$ using $^2J_{PP}$ = 40 Hz. One-half of each spectrum is shown.

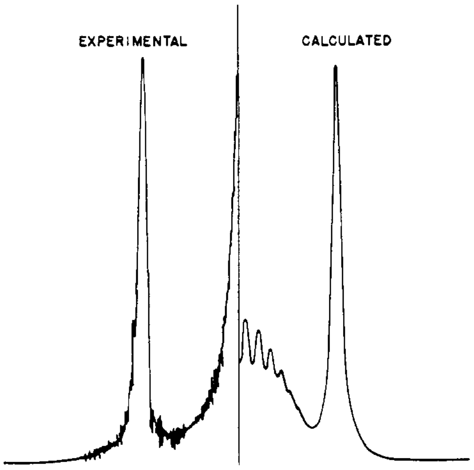

Figure 2. Comparison of experimental and calculated spectra for *trans*-$Fe(CO)_3[P(N(CH_3)_2)_3]_2$ using $^2J_{PP}$ = 65 Hz. One-half of each spectrum is shown.

of this phenomenon was encountered in this work with $HgI_2[P(N(CH_3)_2)_3]_2$ for which a broad singlet was observed. The origins of anomalous line shapes due to the above causes can generally be readily detected.

Other anomalies in ^1H spectral line shapes are not so easily explained. In Figure 1 is a comparison of the experimental and calculated spectrum for *cis*-$Mo(CO)_4(P(OCH_3)_3)_2$ using $^2J_{PP}$ = 40 Hz which was obtained from observation of the weak-intensity wing peaks. Although the width at half-height of the intense doublet is small in the experimental spectrum, the central lines are broad and lacking in resolution regardless of the instrument used to obtain the spectrum. Straightforward spectral calculations assuming uniform line widths do not account for the observed band shapes. Finer, *et al.*,[40] have made similar observations with other compounds and have postulated a number of reasons for this phenomenon. Two of their postulates that seem most likely to account for the poor resolution of the central lines are that in theory each transition can have its own transverse relaxation time T_2 and secondly that off-diagonal elements of the relaxation matrix can cause overlapping lines to give band shapes which are not simply sums of Lorentzian lines.

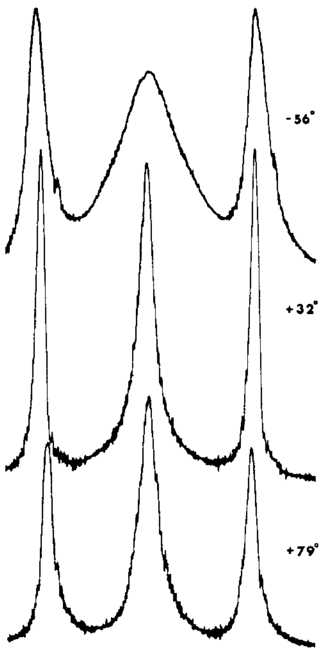

Figure 3. Proton nmr spectra of *trans*-$Fe(CO)_3[P(N(CH_3)_2)_3]_2$ in toluene-d_8 at −56°, +32°, and +79°.

A totally different phenomenon was observed for all the complexes of $P(N(CH_3)_2)_3$. For the compounds of Finer, *et al.*, the energies of the transitions were similar to those calculated in spite of the anomalous line shapes. Such agreement is not necessarily expected, however,[40] and indeed in our complexes of $P(N(CH_3)_2)_3$ these energies are not the same as those calculated. Thus values of $J_{AA'}$ obtained by curve fitting are much larger than those observed by the observation of the weak outer lines or by double resonance techniques. This is illustrated in Figure 2 which is a comparison of the experimental and calculated spectrum for *trans*-$Fe(CO)_3[P(N(CH_3)_2)_3]_2$ using a value of $^2J_{PP}$ of 65 Hz obtained by the double resonance method. A value of 320 Hz for $^2J_{PP}$ is required to simulate the observed spectrum. Values as high as 4500 Hz for $^2J_{PP}$ in *trans*-$PdCl_2[P(N(CH_3)_2)_3]_2$ were needed to simulate the observed spectra in this compound. For *cis*-$Mo(CO)_4[P(N(CH_3)_2)_3]_2$ a value of 90 Hz was calculated for $^2J_{PP}$ whereas a value of 12.4 Hz was obtained from the observation of the outer lines. In contrast, very good agreement was obtained between the calculated (20 Hz) and observed value (18.2 Hz) for $^2J_{PP}$ in the similar complex *cis*-$Mo(CO)_4[P(N(CH_3)(C_6H_5))_3]_2$.

In addition we found that the proton nmr spectrum of *trans*-$Fe(CO)_3[P(N(CH_3)_2)_3]_2$ is temperature dependent as can be seen in Figure 3. As the temperature falls, the central portion becomes broader and the separation of the doublet increases. This separation which can be assigned to $^3J_{PH}$[18] rises from 9.0 Hz at +79° to 10.0 Hz at −56°. For this temperature dependence to be observed, some change in the molecule must be occurring during an interval which is of the order of nmr detection time (10^{-2} sec). An intermolecular exchange can be ruled out because as the temperature is increased, such exchange would increase causing the lines to

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[40] E. G. Finer, R. K. Harris, M. R. Bond, R. Keat, and R. A. Shaw, submitted for publication. We are grateful to Professor Harris for this information in advance of publication.

broaden rather than sharpen. Intramolecular exchange between *cis* and *trans* isomers is unlikely because the infrared spectrum at room temperature showed only one ν(CO) absorption at 1876.5 ± 1 cm^{-1}. If a *cis–trans* equilibrium were established it should be detectable by infrared spectroscopy since the detection time is of the order of 10^{-12} sec. This indeed has been found to be the case with $Fe(CO)_3(PF_3)_2$ which is known to undergo intramolecular exchange.[41] It is possible that there is hindered internal rotation of the phosphorus substituents in the ligand. If this were the case, the rotation should stop upon sufficient cooling (perhaps below −56°) and the methyl groups should then become nonequivalent. Because of this, splitting of each line separated by N should be observed and it is probable that two apparent triplets would result. Moss and Shaw[42] have observed a similar effect in *trans*-NiBr(O-tolyl)[$P(C_6H_5)(CH_3)_2]_2$ in which the phosphine methyl resonances at room temperature consist of two well-defined 1:2:1 triplets showing that the two methyl groups on the same phosphine ligand differ considerably in their time-averaged magnetic environments. If hindered rotation occurs, however, it seems highly fortuitous that the value of $^2J_{PP}$ obtained by computer simulation compares so well with that observed from the separation of the $\chi = 1$ outer and inner lines in the spectrum of *cis*-$Mo(CO)_4[P(N(CH_3)(C_6H_5))_3]_2$ (Table VII). Because of this anomalous line shape for complexes of $P(N(CH_3)_2)_3$, only the values of $^2J_{PP}$ which were obtained by observing the weak intensity $\chi = 1$ outer lines or by double resonance techniques are included in Tables VII–IX. However, it should be noted that since the inner lines show a temperature dependence, it is probable that the outer lines of weak intensity are also temperature dependent. Therefore any value obtained for $^2J_{PP}$ from observation of these outer lines or from double resonance methods may only be appropriate for the temperature at which they were obtained. Because of this, the comparison discussed later of $^2J_{PP}$ values for complexes of $P(N(CH_3)_2)_3$ with those for the other complexes are taken to be valid only at the ambient probe temperature of the HR-60 (~30°). Further experiments on the temperature dependences[39b] of proton spectra of these and other complexes are planned.

Proton Chemical Shifts and ^{31}P–^1H Couplings

In general the chemical shifts of the protons on the carbons nearest to the phosphorus atom follow the trend L (ligand) < Cr, Mo, and W complexes of L < Pd, and Pt complexes of L < L-sulfide < L-oxide < RL$^+$ as shown in Tables I–VI. It is conceivable that the increased deshielding of these protons is a result of the increase in electronegativity of the metal moiety and the dominance of this effect over any tendency toward back-donation from the metal. The presence of several discrepancies in this trend, however, admits of the possibility of one or more subtle influences which at times may override the inductive effect. Moreover the use of different solvents may cause minor variations in the chemical shift.

The trends in the phosphorus–proton coupling constants are more fully discussed elsewhere.[18,43] As more electronegative groups are bound to the fourth site on phosphorus $^3J_{PNCH}$ and $^3J_{POCH}$ increase. In trialkyl phosphines $^2J_{PCH}$ is positive but changes to negative in quinquivalent phosphorus species.

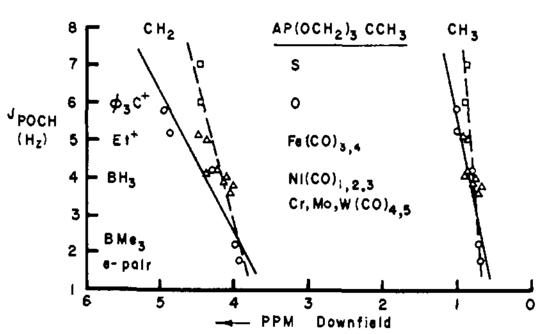

Figure 4. Correlation of proton chemical shifts with $^3J_{PH}$ in derivatives of $P(OCH_2)_3CCH_3$.

An attempt to correlate the chemical shifts of the protons and the values of $^3J_{PH}$ in the complexes of $P(OCH_2)_3CCH_3$ was of interest in view of the apparent linear correlations of these parameters in $AP(OCH_2)_3CCH_3$ where A = electron pair, $B(CH_3)_3$, BH_3, $CH_3CH_2^+$, and $(C_6H_5)C^+$.[44] The plot in Figure 4 shows these correlations for the CH_2 and CH_3 protons of the boron and carbon acceptor adducts as solid lines, and the new apparent linear correlations for some monosubstituted carbonyl complexes of $P(OCH_2)_3CCH_3$ are shown as dashed lines. Although the monosubstituted carbonyl derivatives were chosen because of the better comparison of an $M(CO)_n$ than an $M(CO)_{n-1}L$ acceptor to Lewis acids like BR_3 and R$^+$, the disubstituted derivatives also cluster on the dashed lines. Previously[44] it was noticed that the chalcogenides of $P(OCH_2)_3CCH_3$ did not fall near the line generated by the BR_3 and R$^+$ adducts. The latter adducts, which fall on the solid lines in Figure 4, form single bonds with phosphorus whereas the chalcogenides can form multiple bonds. The fact that there is a linear correlation of the transition metal complexes and the chalcogenides would seem to indicate that there is some degree of double bond character in the phosphorus–metal bond. The solid line correlations were obtained from the nmr spectra taken in CD_3CN whereas the dashed line correlations were obtained using $(CH_3)_2CO$, DMSO, $CDCl_3$, and CH_2Cl_2 solutions because of solubility considerations. The observations are believed to be valid in spite of the variation in solvents because the ligand shows only minor variations in its proton chemical shifts in these solvents.

^{31}P–^{31}P Couplings

The data in Tables VII–IX show that the magnitudes of $^2J_{PP}$ depend on four factors: (1) the stereochemistry of the complex, (2) the metal atom, (3) the ligands other than phosphorus in the complex, and (4) the nature of the phosphorus ligand. These factors will now be discussed in sequence.

The repeated observation in a variety of systems[45] that ^{31}P–^{31}P couplings of *trans* oriented ^{31}P nuclei are large and are characterized by apparent triplets in the

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(41) C. A. Udovich, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969).

(42) J. R. Moss and B. L. Shaw, *J. Chem. Soc., A*, 1793 (1966).

(43) W. McFarlane, *Proc. Roy. Soc., Ser. A*, **306**, 185 (1968).

(44) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).

(45) P. R. Brookes and B. L. Shaw, *J. Chem. Soc., A*, 1079 (1967).

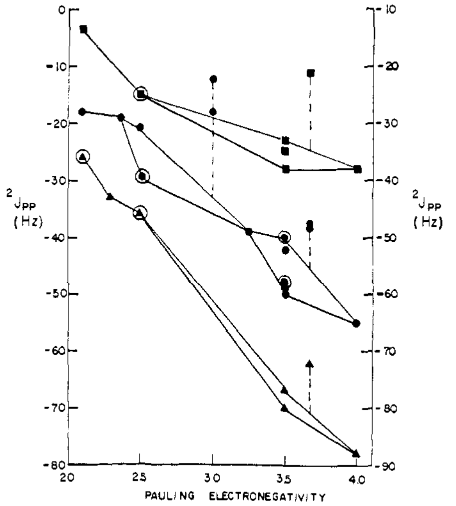

Figure 5. A plot showing the progression of $^2J_{PP}$ for *cis*-M(CO)$_4$L$_2$ (where M = Cr (▲), Mo (●), or W (■)) as a function of the electronegativity of the ligand. The left ordinate applied to the Cr and Mo complexes and the right to the tungsten systems. See text for the ligands employed and the method of calculating their electronegativity.

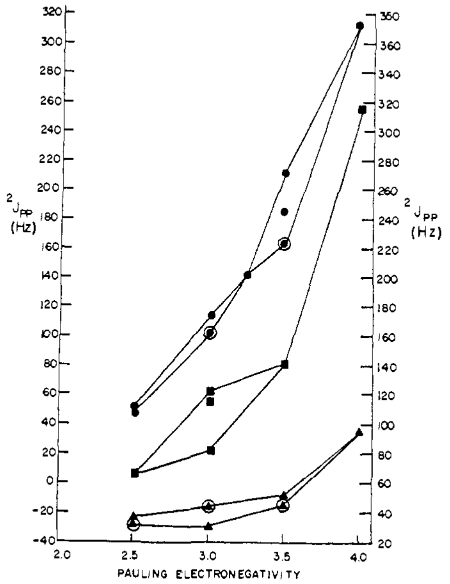

Figure 6. A plot showing the progression of $^2J_{PP}$ for *trans*-M(CO)$_4$L$_2$ (where M = Cr (▲), Mo (●), or W (■)) as a function of the electronegativity of the ligand. The left ordinate applies to the Cr and Mo complexes and the right to the tungsten systems. See text for the ligands employed and the method of calculating their electronegativity.

^{1}H spectrum while *cis* couplings are small, leaving the J_{AX} doublet unperturbed, has served as a criterion for determining the geometrical relationships of phosphorus ligands in many complexes. However considerable caution should be taken in using this criterion in assigning the stereochemistry of complexes. Many *cis* complexes have appreciable phosphorus–phosphorus coupling and from preliminary data it appears that the magnitudes of $^2J_{PP}$ in *cis* and *trans* manganese complexes of the type Mn(CO)$_3$L$_2$X (X = Cl, Br, I) are approximately equal. Indeed in chromium complexes the magnitude of $^2J_{PP}$ is even greater in *cis* compounds than in *trans* (Tables VII and VIII). It should be pointed out that weak ^{31}P–^{31}P coupling can lead to apparent triplets when J_{AX} is small. Other than in chromium and manganese compounds, phosphorus–phosphorus couplings are generally larger in *trans* compounds than in their *cis* isomers. This appears to be true especially with palladium and platinum systems.

The nature of the metal atom plays a definite role in determining the magnitude of $^2J_{PP}$. The most intensely studied series with the same stereochemistry consists of group VI complexes. The data show that the order of magnitude for *cis* couplings is Cr > Mo > W. For the *trans* couplings there appears to be less order other than that the $^2J_{PP}$ values in Mo and W complexes are much larger than in their Cr analogs. From the few results for other groups, it is difficult to observe meaningful trends but it does appear that couplings in palladium complexes are greater than in platinum compounds.

From the limited data available, the other ligands in a given complex appear to effect the value of $^2J_{PP}$ relatively slightly. Results for compounds in which only the halides are varied suggest that $^2J_{PP}$ increases in magnitude from I to Cl. A similar small effect has been observed for $^1J_{PtP}$ in some platinum complexes.[9]

The most significant factor affecting ^{31}P–^{31}P coupling appears to be the electronegativity of the substituents on phosphorus. In Figures 5 and 6 are plots of $^2J_{PP}$ *vs.* a crude estimate of the overall Pauling electronegativity of the substituent groups on the phosphorus ligands. The electronegativity of the ligands was taken to be that of the hydrogen in PH$_3$, fluorine in PF$_3$, oxygen in P(OR)$_3$ or P(OAr)$_3$, carbon in PR$_3$ or PAr$_3$, and nitrogen in P(NR$_2$)$_3$ or P(NRAr)$_3$. Thus no correction was attempted due to effects of atoms further away than the first one bound to phosphorus. Where ligands contained two different substituents (*e.g.*, PN(CH$_3$)F$_2$ or P(CF$_3$)F$_2$, the overall electronegativity was estimated by taking a weighted mean of the electronegativities of the three atoms bound to phosphorus. For mixed ligand complexes (*e.g.*, *trans*-Mo(CO)$_4$[P(OCH$_3$)$_2$CC$_2$H$_5$][P(N(CH$_3$)$_2$)$_3$]), the average of the electronegativities of the two ligands was used. Although these estimates are admittedly quite crude, three rather interesting features become apparent in Figures 5 and 6. Firstly, when the known signs[18] are taken into account (circled points), it is clear that the overall progression of $^2J_{PP}$ with electronegativity in the *trans* chromium complexes parallels that of the molybdenum and tungsten systems. Secondly, $^2J_{PP}$ appears to increase positively with electronegativity in the *trans* complexes while in the *cis* systems it is seen to increase negatively. Thirdly, the points connected to the *cis* curves by dotted lines appear to lie anomalously far off the main progression in most instances. It is worthy of note that these points represent ligands containing NR$_2$ groups. It may be that the bulk of such ligands distorts the P–M–P angle to a value greater than 90° and thus allows $^2J_{PP}$ to rise toward a more positive value. The normal value of (OC)$_4$Mo[P(N(CH$_3$)$_2$)$_3$][P(OCH$_2$)$_3$CCH$_3$] (39 Hz, Figure 5) seems to bear out this postulate.

Barring the possibility of unexpected sign reversals in complexes on which we were unable to perform double resonance experiments, the assignments of the unknown signs seem reasonable by analogy or by inference from the data on mixed complexes[15] (Tables VII and VIII). Thus it is expected that the values of $^2J_{PP}$ in the mixed ligand complexes should be intermediate in value between those for the two analogous complexes in which both ligands are the same. If a sign change between complexes of $P(OCH_2)_3CR$ and $P(N(CH_3)_2)_3$ or $P(OCH_3)_3$ were occurring, the magnitudes of $^2J_{PP}$ in the mixed ligand complexes should be less than $^2J_{PP}$ in complexes in which both ligands are the same. Since the values of the mixed complexes lie between those of the latter, our assignment is probably correct. Our trends correspond to the trend in absolute magnitude of $^2J_{PP}$ in a series of *cis*-$M(CO)_4(R_3PF_{3-n})_2$ complexes where M = Cr, Mo, or W.

The signs of $^2J_{PP}$ in both *cis*-$PdCl_2[P(OCH_3)_3]_2$ and *trans*-$PdI_2[P(CH_3)_3]_2$ were found to be positive. Trends cannot be constructed from the limited data for the palladium and platinum cases but it may be that $^2J_{PP}$ values for these metals in both the *cis* and *trans* configurations are positive, and become more positive as the electronegativity of the substituents on phosphorus increases.

Since ^{31}P–^{31}P couplings found in coordination compounds are transmitted *via* the metal atom, metal–phosphorus couplings might be expected to parallel the trends found for the $^2J_{PP}$ values. Although there are few metals with suitable nuclei in sufficient abundance for such studies, several papers dealing with metal–phosphorus couplings have been published.[6–13] Indeed the values of $^1J_{MP}$ are dependent upon the substituents on phosphorus, and the magnitudes of both $^1J_{WP}$ and $^1J_{PtP}$ in tungsten[11] and platinum[7] complexes, respectively, increase as the electronegativity of the substituents increase. Grim, *et al.*,[13] ascribed their observed linear correlation of $^1J_{WP}$ with ν(CO) in the series $W(CO)_5L$ (L = PR_3, $PR_2(C_6H_5)$, $PR(C_6H_5)_2$, $P(C_6H_5)_3$) to the increased π back-bonding expected from PR_3 to $P(C_6H_5)_3$. Over a larger range of electronegativity of substituents, however, the correlation between $^1J_{WP}$ and ν(CO) is apparently lost.[11]

Platinum–phosphorus coupling constants are greatly affected by the nature of the ligand *trans* to the phosphorus atom.[9] Grim and coworkers[7] discussed the large platinum–phosphorus coupling constants in terms of π bonding. The use of π bonding to explain coupling constants has been criticized by Schneider and Buckingham[46] who pointed out that large ^{195}Pt–^1H coupling constants are observed in platinum hydride complexes in which there can be no π bonding. A similar criticism could be made for any explanation using π bonding to account for ^{31}P–^{31}P couplings since $^2J_{PH}$ values in metal hydride complexes containing phosphorus ligands follow trends analogous to that observed for the $^2J_{PP}$ values.[47] If π bonding were a significant factor, $^2J_{PP}$ in *cis* complexes would be expected to be highly influenced by ligands *trans* to the phosphorus atoms. The closeness of $^2J_{PP}$ in *cis*-$Mo(CO)_4[P(OCH_3)_3]_2$ (40 Hz) and in *mer*-$Mo(CO)_3[P(OCH_3)_3]_3$ (47 Hz) suggests that π bonding is of little importance in the coupling mechanism. Pidcock and coworkers[9,10] have suggested that the dependence of $^1J_{PtP}$ on the ligand *trans* to phosphorus is due to an inductive effect. Ligands with a strong σ inductive character effectively reduce the positive charge on the platinum and thus weaken the overlap of the phosphorus and metal orbitals *trans* to the group in comparison to the case where the phosphorus ligands are *trans* to one another. Thus in compounds of the type $PtX_2(PR_3)_2$ where X is a phenyl or silyl group, $^1J_{PtP}$ is greater in *trans* compounds than in the *cis* analogs whereas the opposite observations were made on these isomers when X is an electronegative group such as a halogen. These arguments are based on all ^{195}Pt–^{31}P coupling constants being positive which is likely.[48] Inasmuch as a CO group is a poorer σ inducting group than a phosphine, the observation[4] that $^1J_{WP}$ is larger in *trans*-$W(CO)_4(PR_3)_2$ than in the *cis* compound would suggest that $^1J_{WP}$ is negative if the inductive arguments are correct or perhaps that π-bonding is important in determining the magnitude of $^1J_{WP}$.[4]

In valence bond formalism, the Fermi contact contribution to a coupling constant is dependent mainly upon the effective nuclear charges of the two coupling nuclei and the s character in the bonds between the nuclei.[49,50] In the series PH_3, $P(N(CH_3)_2)_3$, $P(OCH_3)_3$, $P(OCH_2)_3CR$, and PF_3, the effective nuclear charge on the phosphorus should increase as the electronegativity of the substituents increases. Thus the magnitude of $^2J_{PP}$ should increase because of the effective nuclear charge as more electronegative substituents are placed on phosphorus. However, using the arguments of Bent,[51] an increase in the s character in the metal–phosphorus bond should also result in an increase in $^2J_{PP}$. Bent contends that hybridizational changes will occur such that s character concentrates in orbitals directed toward electropositive substituents. Recently[30] we summarized available structural data on phosphorus ligands and their coordination compounds and the trends are consistent with the ideas that (a) the bond angles formed by the phosphorus and its substituents appear to open up upon coordination and (b) these angles in the coordinated complex decrease (placing more s character in the M–P bond) as the electronegativity of the substituents increases. Thus both s character and effective nuclear charge arguments favor the trends observed, but it is presently not possible to separate the two effects. The possible implications of our observations in qualitative molecular orbital terms are discussed in the previous paper.[52]

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(52) NOTE ADDED IN PROOF. Recently Fischer, *et al.*, (E. Moser, E. O. Fischer, W. Bathelt, W. Gretner, L. Knauss, and E. Louis, *J. Organometal. Chem.*, **19**, 377 (1969)) have calculated the value of $^2J_{PP}$ in *cis*-$(OC)_4Cr[P(n\text{-}C_4H_9)_3][P(C_6H_5)_3]$. The point represented by this coupling constant (33 Hz) and the calculated effective electronegativity (2.4) does not appreciably alter the graph shown in Figure 5.