Correlation of Nuclear Magnetic Resonance Coupling Constants with Transition Metal–Ligand Bond Lengths in Tertiary Phosphine Complexes

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N.m.r. coupling constants ${}^1J$(M–P) are reported for complexes of W^{IV}, Pt^{I}, and Pt^{IV}. Results for ${}^1J$(Pt–P) in the complexes $[PtCl_{4-n}(R_3P)_n]^{(n-2)+}$ and $[PtCl_{6-n}(R_3P)_n]^{(n-2)+}$ (n = 1—3) are discussed in terms of the M.O. expression for the Fermi contact interaction. Interpretation of coupling constants in terms of the s-orbital bond order is supported by the correlation of bond lengths with ${}^1J$(Pt–P) for Pt^{II} complexes and by the similarity of trends in bond lengths and M–P coupling constants in *mer*-tris(phosphine) complexes of W^{IV}, Rh^{I}, Rh^{III}, Pt^{II}, and Pt^{IV}. It is also shown that, for both ${}^1J$(Pt–P) and ${}^2J$(PtCH), ratios of coupling constants in related Pt^{IV} and Pt^{II} complexes reflect bond-length differences in the two oxidation states.

ALTHOUGH approximate M.O. expressions for the Fermi contact contribution to n.m.r. coupling constants involve many variables, when coupling constants in complexes of a given metal and ligand are compared it appears that the s-characters of the orbitals involved in the metal–ligand bond and its covalency are usually the most important variables.[1] Thus, to a good approximation, coupling constants between a metal nucleus and a directly bonded phosphorus atom are given by equation (1) and for a given metal and phosphorus ligand the

$${}^1J(\text{M–P}) = \gamma_M\gamma_P\frac{64\pi^2}{9}\beta^2\frac{|S_M(0)|^2}{\Delta E}|S_P(0)|^2(P'_{s_Ms_P})^2 \qquad (1)$$

terms involving the phosphorus lone pair and $|S_M(0)|^2/\Delta E$ appear to undergo little variation. In the form of equation (1) chosen, the s-characters of the orbitals and the M–P covalency are contained in the M.O. bond order between the s-orbitals, $(P'_{s_Ms_P})^2$.[1,2] The suggestion[3] that the coupling constants ${}^1J$(Pt–P) are dominated by the Fermi contact term was supported by approximate calculations of other contributions,[4] but more recently experimental evidence has become available. Contributions other than from the Fermi term to couplings involving ${}^1H$ are insignificant,[2] and this is probable for ${}^1J$(Pt–P) also in view of the good correlations[5] between ${}^1J$[*Pt*–*P*O(OPh)$_2$], ${}^1J$(Pt–H), and

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[1] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 346.

[2] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[3] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1707.

[4] W. G. Schneider and A. D. Buckingham, *Discuss. Faraday Soc.*, 1962, **34**, 147.

[5] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.

particularly ^2J(PtCH) in the series of compounds with varying anionic ligands X: *trans*-[PtX{(PhO)$_2$PO}(Bu$_3$P)$_2$], *trans*-[PtHX(Et$_3$P)$_2$], and *trans*-[Pt(CH$_3$)X(Et$_3$P)$_2$].

The much greater dependence of ^1J(Pt–P) on the *trans*- compared with the *cis*-ligand was originally suggested on the basis of relatively few results [3] but is of importance because of the implication that orbital changes and not variations in $|S_{Pt}(0)|^2/\Delta E$ are responsible for changes in the coupling constants. Subsequent studies have shown that appreciable changes in the coupling constants can be induced by varying the nature of *cis*-ligands, so it is therefore not absolutely clear whether some significant variation of $|S_{Pt}(0)|^2/\Delta E$ can occur in some circumstances or whether *cis* ligands can induce appreciable changes in Pt–P bonding.[6,7] Where two coupling constants in a single complex are compared, however, variations in $|S_M(0)|^2/\Delta E$ must be relatively unimportant.[1,6]

We now report measurements of ^1J(Pt–P) for complexes of W^{IV}, Pt^{II}, and Pt^{IV}. These and values of metal–ligand coupling constants from the literature are examined for internal consistency and are compared with bond lengths in identical or isostructural complexes. We are interested to determine whether there is any indication of significant variation in $|S_M(0)|^2/\Delta E$ in different complexes of a transition metal.

Platinum Complexes.—Coupling constants ^1J(Pt–P) have been measured for $[PtCl_{4-n}(R_3P)_n]^{(n-2)+}$ and $[PtCl_{6-n}(R_3P)_n]^{(n-2)+}$ (n = 1—3) (Table 1). They show considerable dependence on the nature of the *trans*-ligand, but remarkably little dependence on the *cis*-ligands: for a given *trans*-group and oxidation state of platinum the variation about the mean value is always less than 4%, and the values for the *trans*-arrangement R$_3$P–Pt^{IV}–Cl are within a total range of 1·5%. Since both Pt^{II} and Pt^{IV} series include *mer*-tris(phosphine) complexes, where differences in ^1J(Pt–P) can to a good approximation only be ascribed to differences in $(P'_{s_{Pt}s_P})^2$,[1,6] it is probable that in these complexes the nature of the Pt–P σ-bonds is almost completely determined by the oxidation state of platinum and the nature of the *trans*-group, and that any variations of $|S_{Pt}(0)|^2/\Delta E$ are small.

TABLE 1

Coupling constants ^1J(Pt–P)/Hz in trialkylphosphine complexes of platinum(II) and platinum(IV) (P = phosphine) [a]

Complex:	$[PtCl_3P]^-$	*cis*-$[PtCl_2P_2]$	$[PtClP_3]^+$	*trans*-$[PtCl_2P_2]$
P = Et$_3$P	3704 $(+111\cdot_2)$	3520 [b]	3499 (+103),[c] 2233 (+94) [d]	2400 [b]
P = Bu$_3$P	3686 $(+118\cdot_9)$	3504 [e]	3459,[c] 2266 [d,f]	2386 [e]

Complex:	$[PtCl_5P]$	*cis*-$[PtCl_4P_2]$	$[PtCl_3P_3]^+$	*trans*-$[PtCl_4P_2]$
P = Et$_3$P	2059 $(+92\cdot_3)$		2049 (+98·0),[c] 1374 $(+104\cdot_0)$ [d]	
P = Bu$_3$P	2038 $(+98\cdot_8)$	2069 [c]		1474 [e]

[a] Chemical shifts in p.p.m. are given in parentheses relative to external P$_4$O$_6$ (a positive shift implies a sample resonance to high field of the reference). [b] Ref. 13. [c] P *trans* to Cl. [d] P *trans* to P. [e] Ref. 1. [f] F. N. Allen and S. N. Sze, *J. Chem. Soc.* (*A*), 1971, 2054.

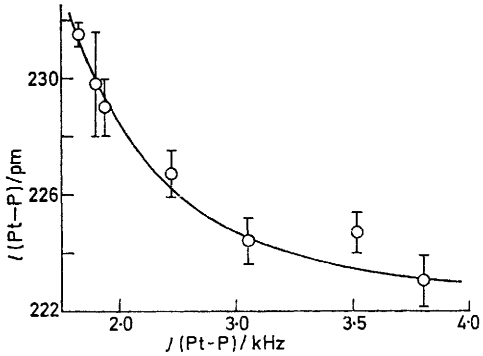
The coupling constants for R$_3$P–Pt^{II}–Cl decrease slightly with increasing number of phosphine substituents, but this trend is absent from the data for R$_3$P–Pt^{IV}–Cl. It is possible that in the platinum(II) compounds the s-components of the Pt–P bonds are slightly reduced by the electronic effects of *cis* phosphine ligands or by distortions of the kind observed in *cis*-[PtCl$_2$(Me$_3$P)$_2$] where the angle between the Pt–P bonds is 96° and nearest ligand neighbours are displaced *ca.* 0·1 Å from the best least-squares plane.[8] In platinum(IV), even though the Pt–P bonds are *ca.* 0·1 Å longer and therefore somewhat weaker than in platinum(II) (see Table 2 and later discussion),[9,10] the presence of the extra two ligands probably inhibits distortion of angles about platinum(IV). Explanations in terms of variation of other parameters of equation (1) do not account satisfactorily for this difference between platinum(II) and platinum(IV), but it is also possible that the approximations involved in the derivation of equation (1) may preclude discussion of such small differences in coupling constants especially for complexes of low symmetry.[1]

TABLE 2

Bond lengths in platinum(II) and platinum(IV) complexes

Complex	l(Pt–Cl)/Å	l(Pt–P)/Å	Ref.
trans-[PtCl$_2$(Et$_3$P)$_2$]	2·294(9)	2·298(18) [a]	9
trans-[PtCl$_4$(Et$_3$P)$_2$]	2·332(5)	2·393(5)	10

[a] The distance is known with greater accuracy in the dibromo-complex (Table 3).



Correlation between l(Pt–P) and ^1J(Pt–P). Results are from Table 3. The error limits indicated for the bond lengths are the quoted standard deviations (*i.e.*, $l \pm 1\sigma$)

In the absence of significant variations of terms other than $(P'_{s_{Pt}s_P})^2$ of equation (1) a correlation may be expected between ^1J(Pt–P) and Pt–P bond length for compounds of given co-ordination number. The term

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[6] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.

[7] B. T. Heaton and A. Pidcock, *J. Organometallic Chem.*, 1968, **14**, 235; G. Socrates, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1667.

[8] G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 725.

[9] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1775.

[10] L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Comm.*, 1970, 30.

$(P'_{s_{Pt}s_P})^2$ is expected to decrease with increasing Pt–P length whether this is lengthening due to a reduction of covalency of the Pt–P bond or to a reduced contribution of the platinum 6*s*-orbital.[11] Ideally results used for the correlation should be taken only from a single class of phosphines such as the trialkylphosphines, because the bond lengths[12] and coupling constants[13] are sensitive to the nature of the groups on phosphorus. However, the standard deviations in the bond lengths are a significant fraction of the total variation, so use of the primary data (Table 3) including that for phenylphosphines is not expected to affect the Figure to a significant extent.

The correlation (Figure) reveals no significant anomaly. The form of the correlation curve is not accurately defined at any point, but this is especially so for the shorter Pt–P bonds. Inspection of the Figure suggests that the entry for *cis*-[$PtCl_2(R_3P)_2$] may lie above the best correlation curve for the other entries. This could be a consequence of the distortion in the structure of this complex,[8] and it would be of interest to have structural data for [$PtCl_3(R_3P)$]$^-$ where distortions are presumably relatively small. The existence of the rough correlation supports the view that, even when *trans*-ligands are as various as chloride, carbene, and phosphine, the term $|S_{Pt}(0)|^2/\Delta E$ of equation (1) is not a very significant variable. Grim *et al.* have also shown that the larger W–P coupling constant in *trans*-[$W(CO)_4\{(PhO)_3P\}_2$] than in [$W(CO)_5(PhO)_3P$] corresponds in the expected manner with Cr–P bond lengths in isostructural Cr^0 complexes.[12,14]

TABLE 3

Coupling constants ^1J(Pt–P) and bond lengths *l*(Pt–P) in platinum(II) complexes

Complex	^1J(Pt–P)/Hz	Ref.	Complex	*l*(Pt–P)/Å	Ref.
cis-[$PtCl_2(Et_3P)(PhNC)$]	3049	*a*	*cis*-[$PtCl_2(Et_2PhP)(EtNC)$]	2·244(8)	*b*
cis-[$PtCl_2(Et_3P)_2$]	3520	13	*cis*-[$PtCl_2(Me_3P)_2$]	2·247(7) [c]	8
trans-[$PtHCl(Et_3P)_2$]	2723	7	*trans*-[$PtHCl(EtPh_2P)_2$]	2·267(8) [c]	*d*
trans-[$PtCl_2(Et_3P)$- $\{CN(Ph)CH_2CH_2N(Ph)\}$]	2440	*e*	*trans*-[$PtCl_2(Et_3P)$- $\{CN(Ph)CH_2CH_2N(Ph)\}$]	2·29(1)	*c*
trans-[$PtCl_2(Et_3P)_2$]	2400	13	*trans*-[$PtCl_2(Et_3P)_2$]	2·298(18)	9
trans-[$PtBr_2(Bu_3P)_2$]	2327	*f*	*trans*-[$PtBr_2(Et_3P)_2$]	2·315(4)	9
sym-trans-[$Pt_2Cl_4(Bu_3P)_2$]	3800	1	*sym-trans*-[$Pt_2Cl_4(Pr_3P)_2$]	2·230(9)	*g*

[a] E. M. Badley, D.Phil. Thesis, Sussex, 1970. [b] B. Jovanović and Lj. Manojlović-Muir, *J.C.S. Dalton*, 1972, 1176. [c] Mean of two values. [d] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 773. [e] D. J. Cardin, B. Cetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400. [f] G. G. Mather, G. J. N. Rapsey, and A. Pidcock, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 567. [g] M. Black, R. H. B. Mais, and P. G. Owston, *Acta Cryst.*, 1969, **B25**, 1760.

TABLE 4

Metal–phosphorus coupling constants ^1J(M–P) and bond lengths *l*(M–P) in *mer*-tris(phosphine) complexes

	^1J(M–P)/Hz		$\frac{^1J(P\text{–}M\text{–}Cl)}{^1J(P\text{–}M\text{–}P)}$ [a]			*l*(M–P)/Å		
Complex	P–M–Cl	P–M–P		Ref.	Complex	P–M–Cl	P–M–P	Ref.
cis-mer-[$W(O)Cl_2(Me_2PhP)_3$] [b]	442	342	1·29	*c*				
					cis-mer-[$Mo(O)Cl_2(Me_2PhP)_3$] [d]	2·503	2·549	17
cis-mer-[$W(O)Cl_2(MePh_2P)_3$]	418	334	1·25	*c*				
mer-[$RhCl_3(Me_2PhP)_3$]	112·3	84·6	1·33	*e*	*mer*-[$IrCl_3(Me_2PhP)_3$]	2·277	2·363	10
[$RhCl(Ph_3P)_3$]	189	142	1·33	*f*	[$RhCl(Ph_3P)_3$]	2·218	2·321	18

[a] Ratios calculated from results in Table 1 are (complex, ratio): [$PtCl(Et_3P)_3$]$^+$, 1·57; [$PtCl(Bu_3P)_3$]$^+$, 1·53; *mer*-[$PtCl_3(Et_3P)_3$]$^+$, 1·49. [b] Chemical shifts (Table 1, footnote *a*) were $+136{\cdot}_0$ (P–W–Cl) and $+128{\cdot}_0$ (P–W–P). [c] Present work. [d] Blue isomer, see text. [e] B. E. Mann, C. Masters, and B. L. Shaw, *J.C.S. Dalton*, 1972, 704. [f] T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, 1970, **91**, 2359.

Tris(phosphine) Complexes.—Although tris(phosphine) complexes are undoubtedly subject to stronger interligand repulsions than complexes with fewer phosphines, complexes with meridional configurations have the desirable characteristic of containing non-equivalent phosphorus atoms, and comparison of the two M–P coupling constants is unlikely to have any significant contribution from differences in $|S_M(0)|^2/\Delta E$.[1,6] Table 4 lists bond lengths and coupling constants for closely related *mer*-tris(phosphine) complexes in which a chloride ligand is *trans* to the unique phosphine. Structural parameters for the complexes *cis-mer*-[$WOCl_2(Me_2PhP)_3$] and *mer*-[$RhCl_3(Et_3P)_3$] are not available for comparison with the coupling constants, but bond lengths have been determined for corresponding complexes of Mo^{IV} and Ir^{III}, and we assume that comparison with these structures is valid. Green and blue forms of the Mo^{IV} complexes are known[15] and they differ substantially in their metal–ligand bond lengths.[16,17] Since the green isomer spontaneously changes into the blue isomer in solution, we have also assumed that the

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[11] S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 1968, **90**, 6669; R. Mason and L. Randaccio, *J. Chem. Soc.* (*A*), 1971, 1150.

[12] H. J. Plastas, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, 1969, **91**, 4326.

[13] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 133.

[14] H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, 1972, **11**, 1927; See also G. G. Mather and A. Pidcock, *J. Chem. Soc.* (*A*), 1970, 1226.

[15] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

[16] Lj. Manojlović-Muir and K. W. Muir, *J.C.S.* (*Dalton*), 1972, 687.

[17] Lj. Manojlović-Muir, *J. Chem. Soc.* (*A*), 1971, 2796.

tungsten complex has a structure that corresponds with that of the more stable molybdenum compound.[17]

The ratio ^{1}J(P–M–Cl) : ^{1}J(P–M–P) is significantly larger than unity for all the complexes and, in accord with the discussion in the previous section, it is also found that the P–M bonds are shorter when *trans* to chloride than when *trans* to phosphine. Further, the results in Tables 1 and 4 give values for this ratio of coupling constants that increase from Group VI to Group VIII: (metal, ratio: W$^{\text{IV}}$, 1·27; Rh$^{\text{I}}$, 1·33; Rh$^{\text{III}}$, 1·33; Pt$^{\text{II}}$, 1·55; and Pt$^{\text{IV}}$, 1·49). This implies that $(P'_{s_\text{M}s_\text{P}})^2$ (*trans* to Cl)/$(P'_{s_\text{M}s_\text{P}})^2$ (*trans* to P) increases in the same order, and suggests that the difference in lengths of P–M bonds *trans* to chloride and *trans* to phosphine may increase as the Group number increases. Bond-length measurements for meridional platinum complexes are not available, but the trend is clearly seen from the differences in bond lengths from Table 4 and in meridional complexes of Re$^{\text{III}}$ and Os$^{\text{III}}$: [metal, M–P length difference: Mo$^{\text{IV}}$, 0·046 Å;[17] Re$^{\text{III}}$, 0·057 Å;[10] Os$^{\text{III}}$, 0·058 Å;[10] Ir$^{\text{III}}$, 0·086 Å;[10] Rh$^{\text{I}}$, 0·103 Å (distorted complex)].[18] The coupling constants, which depend on the *s*-components of the bonds, strongly suggest that the M–P bonds *trans* to Cl compared with those *trans* to P gain an increasingly greater share of the metal valence-state *s*-orbital as the Group number of the metal increases. The approximate calculations of Mason and Randaccio,[11] although carried out in detail only for *trans*-bis(phosphine) complexes, give a similar trend for M–P *s*-characters, and provide some support for this interpretation.

Comparison of Pt$^{\text{IV}}$ *and* Pt$^{\text{II}}$.—Here we compare platinum(II) complexes with platinum(IV) complexes formally derived from them by addition of two ligands X, Y above and below the square plane, and we consider only variations of ^{1}J(Pt–P) and ^{2}J(PtCH) because longer range couplings such as ^{3}J(PtPCH) may depend significantly on the conformation as well as the configuration of the molecules. With certain assumptions, ratios of coupling constants J(Pt$^{\text{IV}}$) : J(Pt$^{\text{II}}$), which would be 0·67 for d^2sp^3 and dsp^2 hybridised platinum orbitals,[3] but are found to depend significantly on the nature of the ligand involved in the coupling.[19] Results from Table 1 and elsewhere [6,19-21] give ratios for ^{1}J(Pt–P) in the range 0·56—0·68 with most values close to 0·60, whereas ratios ^{2}J(PtCH) in methyl complexes vary from 0·79 to 0·92. A single result for Pt–CF$_3$ gives a ratio for ^{2}J(PtCF) of 0·67.[19]

Several terms from equation (1) (or its empirical extension for indirect couplings [19,22]) could contribute to the differences in these ratios, but there are strong indications that differences in the *s*-components of the platinum–ligand bonds in the two oxidation states are more important than differences in $|S_{\text{Pt}}(0)|^2/\Delta E$. First, the contribution to the ratios from the latter terms may be expected to depend significantly on X,Y, but for the methyl complexes there are sufficient data to establish that this dependence is slight or non-regular: for *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] ratios calculated from ^{2}J(PtCH) are 0·85 (X,Y = 2Cl), 0·84 (X,Y = Me, Cl), and 0·85 (X,Y = 2Me).[20] Secondly, the ratio for X,Y = Me,Cl is 0·80 for ^{2}J(PtCH) in *trans*-[PtMeCl(PMe$_2$Ph)$_2$] [20] but is 0·68 for ^{1}J(Pt–P) in the very similar triethylphosphine complexes.[6] Since variations in $|S_{\text{Pt}}(0)|^2$ would probably affect both ^{1}J(Pt–P) and ^{2}J(PtCH) equally, the probable explanation for this result is that the $(P'_{s_\text{Pt}s_\text{L}})^2$ terms of the Pt–C and Pt–P bonds undergo changes of different magnitudes on conversion from Pt$^{\text{II}}$ into Pt$^{\text{IV}}$. The absence of substantial changes in the platinum radial functions on oxidation is indicated by ESCA measurements.[23]

Appleton *et al.* have suggested that the large values of the ratio found for ^{2}J(PtCH) reflect a greater affinity of methyl groups for platinum 6*s*-orbitals in the higher oxidation state.[19] They support this suggestion by noting that the Pt–CH$_3$ bonds are probably stronger in the higher oxidation state in view of their greater resistance to acid cleavage. This is a doubtful argument because the cleavage reaction for Pt$^{\text{II}}$ probably proceeds *via* oxidative addition, whereas this is not possible for Pt$^{\text{II}}$. However, there is some evidence that Pt–C(sp^3) bonds are significantly shorter in the higher oxidation state. Although results are not available to enable comparison to be made between very closely related Pt$^{\text{II}}$ and Pt$^{\text{IV}}$ complexes, the more accurate of the Pt–C distances in the literature indicate that the range of Pt–C lengths is 2·07—2·11 Å in Pt$^{\text{II}}$ complexes [24] and 2·02—2·04 in Pt$^{\text{IV}}$ complexes.[25]

Precise comparison of coupling constants and bond lengths is possible for the Pt–P bonds in the *trans*-bis(triethylphosphine) complexes of the Pt$^{\text{II}}$ and Pt$^{\text{IV}}$ chlorides (Tables 1 and 2). The relatively small ratio for values of ^{1}J(Pt–P) (0·62) suggests that the Pt–P bond has a relatively low *s*-component in the higher oxidation state, and the *X*-ray structure determinations show that in Pt$^{\text{IV}}$ the Pt–P bond is longer by 0·1 Å (Table 2). Since other ratios of ^{1}J(Pt–P) for the two oxidation states calculated from Table 1 are similarly close to 0·6, the Pt–P bond lengthening on oxidation may be a fairly general phenomenon and not confined to situations where the phosphines are *trans*. Aslanov *et al.*[10] have also shown that M–Cl bonds are generally shorter in higher oxidation states and have noted that a

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[18] P. B. Hitchcock, M. McPartlin, and R. Mason, *Chem. Comm.*, 1969, 1367.

[19] T. G. Appleton, H. M. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 1786.

[20] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

[21] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 2349.

[22] G. W. Smith, *J. Chem. Phys.*, 1965, **42**, 435.

[23] D. T. Clark, D. B. Adams, and D. Briggs, *Chem. Comm.*, 1971, 602.

[24] M. R. Collier, C. Eaborn, B. Jovanović, M. F. Lappert, Lj. Manojlović-Muir, K. W. Muir, and M. M. Truelock, *J.C.S. Chem. Comm.*, 1972, 613; R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc.* (*A*), 1969, 485.

[25] H. S. Preston, J. C. Mills, and C. H. L. Kennard, *J. Organometallic Chem.*, 1968, **14**, 447; T. G. Spiro, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 2163; A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.*, 1960, **254***A*, 205; M. R. Truter and R. C. Watling, *J. Chem. Soc.* (*A*), 1967, 1955.

difference in the behaviour of anionic and neutral ligands is intuitively reasonable;[10] it is, however, difficult to give a more detailed explanation especially for the substantial changes in the Pt–P bonds.

By the nature of equation (1), the coupling constants tend to focus attention on the *s*-component of the P–M bond and, as suggested by Appleton *et al.*,[19] it is possible that changes in relative *s*-affinities of ligands are the origin of the observed changes in bonding. However, changes in the *p*- or *d*-affinities of ligands will also affect the bond lengths and indirectly affect the $(P'_{s_M s_P})^2$ term in the expression for coupling constants. It is probable that changes of energy and radial functions of the metal σ-orbitals may alter the relative strength of bonds to P and Cl quite significantly in this region of the Periodic Table. We have noted [26] that for complexes containing approximately linear P–M–Cl arrangements *X*-ray structure determinations show that $l(\text{M–P}) < l(\text{M–Cl})$ for M = Pt^{II}, but $l(\text{M–P}) > l(\text{M–Cl})$ for Hg^{II}. Also, the considerable sensitivity of bond strengths to the nature of metal σ-orbitals is implied by the usefulness of the *trans*-influence concept.

EXPERIMENTAL

Complexes.—*cis*- and *trans*-Dichlorobis(phosphine)-platinum(II) were prepared by established methods.[27] The method of ref. 28 was used to obtain chlorotris(triethylphosphine)platinum(II) perchlorate, m.p. 125—128 °C (Found: C, 31·8; H, 6·75. Calc. for $C_{18}H_{45}Cl_2O_4P_3Pt$: C, 31·60; H, 6·65%). *Tetrapropylammonium salts* of trichloro(triethylphosphine)platinum(II) (Found: C, 36·0; H, 7·5; N, 2·4. Calc. for $C_{18}H_{43}Cl_3NPPt$: C, 35·65; H, 7·15; N, 2·30%) and trichloro(tributylphosphine)platinum(II) (Found: C, 42·8; H, 8·4; N, 2·2. Calc. for $C_{24}H_{55}Cl_3NPPt$: C, 41·75; H, 8·05; N, 2·05%) were prepared by addition of tetrapropylammonium chloride to dichloromethane solutions of the appropriate chlorine bridged complex *sym-trans*-$[Pt_2Cl_4(R_3P)_2]$ (R = Et or Bu). Platinum(IV) compounds were obtained after passage of chlorine through benzene or dichloromethane solutions of the ionic platinum(II) compounds. Obtained in this way were mer-*trichlorotris*(*triethylphosphine*)*platinum*(IV) *perchlorate*, m.p. 121—123 °C (Found: C, 29·3; H, 6·05. Calc. for $C_{18}H_{45}Cl_4O_4P_3Pt$: C, 29·6; H, 6·00%), *tetrapropylammonium pentachloro*(*triethylphosphine*)*platinum*(IV) (Found: C, 32·6; H, 7·1; Cl, 26·1; N, 2·2. Calc. for $C_{18}H_{43}Cl_5PPt$: C, 1·95; H, 6·40; Cl, 26·2; N, 2·05%), and *tetrapropylammonium pentachloro*(*tributylphosphine*)*platinum*(IV) (Found: C, 37·8; H, 7·8; Cl, 24·3; N, 1·90. Calc. for $C_{24}H_{55}Cl_5NPPt$: C, 37·9; H, 7·3; Cl, 23·3; N, 1·8%). The complexes *cis-mer*-oxodichlorotris(dimethylphenylphosphine)tungsten(IV), m.p. 150—151 °C (Found: C, 42·0; H, 4·9. Calc. for $C_{24}H_{33}Cl_2OP_3W$: C, 42·0; H, 4·8%), and *cis-mer*-oxodichlorotris(methyldiphenylphosphine)tungsten(IV), m.p. 135—140 °C (Found: C, 53·5; H, 4·6. Calc. for $C_{39}H_{39}Cl_2OP_3W$: C, 53·8; H, 4·5%) were obtained by the method of ref. 29.

Spectra.—^{31}P Spectra of dichloromethane solutions of the complexes were obtained as described in ref. 5.

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