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THE *trans*-INFLUENCE: ITS MEASUREMENT AND SIGNIFICANCE

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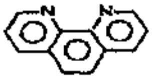
CONTENTS

ABBREVIATIONS

M	metal
X^-	anionic ligand
L or Z	will be used throughout to indicate the ligand whose *trans*-influence is being studied
A	will denote the "indicator" ligand which is being used to determine the *trans*-influence of L or Z
R	alkyl group
Ar	aryl group
Cp	cyclopentadienyl, $C_5H_5^-$
Cy	cyclohexyl, C_6H_{11}
en	ethylenediamine, $NH_2CH_2CH_2NH_2$
py	pyridine, C_5H_5N
bipy	2,2'-bipyridyl, 
phen	1,10-phenanthroline, 

terpy	
acac	acetylacetonate, $CH_3COCHCOCH_3^-$
BAE-H$_2$	bis(acetylacetone)ethylenediimine
DMG	dimethylglyoximate, $CH_3C(NO)^-{-}C(NOH)CH_3$
COD	1,5-cyclooctadiene
diphos	$Ph_2PCH_2CH_2PPh_2$
THF	tetrahydrofuran, C_4H_8O
DMSO	dimethylsulfoxide, $(CH_3)_2SO$
TMS	tetramethylsilane, $(CH_3)_4Si$

A INTRODUCTION

The "*trans*-influence" of a ligand in a metal complex was defined in 1966 by Pidcock et al.[1] as the extent to which that ligand weakens the bond *trans* to itself in the equilibrium state of that complex The term has gained wide (though not unanimous) acceptance among inorganic chemists since it conveniently and unambiguously distinguishes this bond-weakening effect of a ligand from its *trans*-effect[2], which is the effect of a coordinated group A upon the rate of substitution reactions of the group opposite to A. The *trans*-effect of a ligand thus describes a kinetic phenomenon and is a partial description of the transition state in a substitution reaction: it may or may not be related to its *trans*-influence in the equilibrium state of a complex.

In all of the following discussion, the two terms "*trans*-effect" and "*trans*-influence" are used carefully to distinguish between these kinetic and thermodynamic concepts.

This review attempts to describe the growth in our understanding of the *trans*-influence that has occurred since the review of the *trans*-effect by Basolo and Pearson[2] in 1962, with particular emphasis on the period since the distinction between the *trans*-influence and the *trans*-effect was made in 1966 No attempt has been made to provide a completely comprehensive coverage of all papers where the *trans*-influence has been mentioned, but it is hoped that all papers which have made a major contribution to our understanding of it have been included

B. THEORY OF THE *trans*-INFLUENCE

(i) Early theories

The earliest theory of the *trans*-influence was the "polarization theory"[3]. The dipole induced in L by the metal M in turn induces a dipole in M, which tends to repel negative charge in the *trans*-ligand, A, weakening the M—A bond but not greatly affecting ligands *cis* to L (Fig. 1). The main disadvantage of this theory is that it is essentially an electrostatic one, while metals for which the *trans*-influence appears to be most pronounced (e g. Pt^{II}) are those which form metal—ligand bonds with a high degree of covalency.

An explanation of the *trans*-influence in terms of hybridization of the metal was given

Fig. 1. Grinberg's polarization theory.

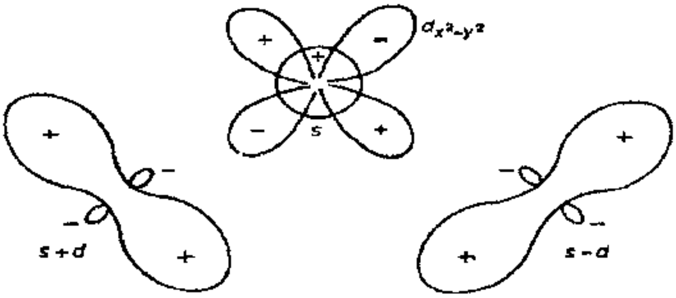


Fig 2 Syrkin's $s \pm d$ hybrid orbitals.

by Syrkin[4]. In a square planar complex a metal ion is considered to use $5d_{x^2-y^2}6s6p_xp_y$ hybrid orbitals (Fig. 2). If a ligand L forms a strong covalent bond with the metal, the hybrid orbital used by the metal in this bond will tend to contain a higher proportion of metal $5d$ and $6s$ orbitals and less $6p$ since the orbital energies are $5d \simeq 6s < 6p$. Since L and the ligand *trans* to it, A, must both share the same $s + d$ hybrid orbitals, additional d and s participation in the M—L bond will result in decreased availability of these orbitals for bonding by A, which results in a weaker M—A bond. The ligands *cis* to L use an independent s—d hybrid orbital and would be affected to a lesser extent. Syrkin predicted a slight strengthening of the bonds to the *cis* atoms. The theory can be extended to octahedral complexes.

(ii) π-Bonding and the trans*-influence*

During the 1950's and early 60's emphasis was given to metal—ligand π-back-bonding in discussing the behavior of metal complexes, especially when ligands such as phosphines were present which contain ligand orbitals of appropriate symmetry for overlap with filled metal d_π-orbitals. The stability of complexes of such ligands with "soft" metals (e.g. platinum and gold) was largely ascribed to π-back-bonding[5]. The ability of a ligand to withdraw electrons from the metal was recognized as possibly being important in stabilizing a transition state relative to the ground state in a substitution reaction[2,6,7]. In agreement with this hypothesis, ligands such as ethylene and CO, which were known to depend on π-back-bonding from a metal, had high *trans*-effects, and the high *trans*-effects of many other ligands, including phosphines, were ascribed to their π-bonding capacity. It was later recognized that this explanation could not hold for a few anions with very high *trans*-effects[8] such as H^- and CH_3^-, which were not π-acceptors.

It was observed that a metal—phosphine bond was less stable *trans* to another phosphine than when *trans* to a halide. For example, the enthalpies of the isomers *cis*-$PtX_2(PR_3)_2$ (X = halogen) were greater than the enthalpies of the *trans*-isomers[9] and $^1J(^{195}Pt—^{31}P)$ was much smaller for the *trans* than the *cis* isomer[10,11]. However, this was not considered as an example of a general *trans* bond-weakening effect of phosphines, which might be linked with their high *trans*-effect. An explanation was given in terms of competition by the phosphine ligands for available *d*-electrons. In the *trans* complexes the two phosphine ligands had to share the same metal d_π-orbital so that the Pt—P bonds were weakened In the *cis* isomer the two phosphines did not compete for the same metal d_π-orbital and since metal—halogen bonds were not considered to have a high π-component, more Pt—P π-back-bonding could occur, giving stronger M—P bonds.

Pidcock et al.[1] pointed out that the Pt—P bond strengths could equally well, or better, be explained in terms of phosphines having a strong σ-inductive effect (i.e. high *trans*-influence which does not depend on extensive Pt—P π-back-bonding). Phosphines would thus resemble[8] H^-. Although π-back-donation would be expected to be less important for Pt^{IV} complexes than for Pt^{II}, the ratio J(Pt—P) (*cis* isomer)/J(Pt—P) (*trans* isomer) is very similar for the complexes $PtCl_2(PR_3)_2$ and $PtCl_4(PR_3)_2$. X-ray structural determinations and NMR studies (discussed below) have since shown that phosphines do weaken bonds *trans* to themselves, irrespective of whether the *trans* ligand has a π-bonding capacity, and conversely that M—P bonds are, in turn, weakened when the phosphine itself is *trans* to a ligand of high *trans*-influence with no π-bonding capacity.

For some ligands (e.g. CO, olefins, which use synergic σ—π bonding to metals) the metal—ligand σ-bond, and thus the *trans*-influence of the ligand would be expected to depend on the availability of metal d_π-electrons for π-back-donation. However, it is now clear that metal—ligand π-back-bonding is less important in many metal complexes than was once thought.

(iii) Recent discussions of the theory of the trans-*influence*

Recent theoretical treatments of the bonding in metal complexes have emphasized the maximizing of metal—ligand orbital overlap.

A calculation[12] on hybrid orbitals composed of $3s$, $3p_x$, $3p_y$, $3d_{x^2-y^2}$ and $3d_z^2$ in square planar complexes showed that overlap with ligand orbitals was determined mainly by s, p, and $d_{x^2-y^2}$ orbitals (d_z^2 making little contribution). When $\mu\rho$ was moderately high (μ = effective metal atomic charge, ρ = internuclear distance) the contribution to total overlap was in the order $p_\sigma > s > d_{x^2-y^2}$. In this hypothetical situation, if a ligand L formed very strong covalent bonds at an optimum value of $\mu\rho$ which was moderately high, the M—L bond would contain a high proportion of p_σ and the bond to the *trans* ligand A, less p_σ. If optimum M—L bonding occurred at low $\mu\rho$, M—L *s*-character would increase and M—A *s*-character would decrease

Clearly, these results cannot easily be extrapolated to a metal ion such as Pt^{II} which has $5d_{x^2-y^2}$, $6s$ and $6p$ hybrid orbitals. Langford and Gray[13] emphasize the directional character of the metal p_σ orbitals. They examined theoretically a trigonal bipyramidal transition state, and ascribed the high *trans*-effects of ligands such as PR_3, CH_3^-, and H^- to unusually large overlap between these ligands and the Pt $6p_\sigma$ orbital, reducing its availability to the *trans* ligand.

Mason and coworkers[14, 15] consider that a ligand L will have a high *trans*-influence when the value of $S^2/\Delta E$ is large, where S is the overlap integral between the ligand orbital and the appropriate metal p_σ orbital, and ΔE is the absolute energy separation between these interacting orbitals. Since they predicted relatively high *trans*-influences for ligands with good π-acceptor properties, e.g. CO and $R_2C{=}CR_2$, which were found to have low *trans*-influences, they postulated that the σ-inductive effect was partially canceled by the metal–ligand charge drift associated with the π-back-donation. They considered that excess charge on the metal may be partially dissipated, by participation of metal s and d orbitals, isotropically through the complex giving rise to a *cis*-influence which would be relatively unimportant. An ordering of *trans*-influence of ligands from relative Pt–Cl bond lengths in square planar Pt^{II} complexes and a somewhat less satisfactory ordering for octahedral d_σ metal complexes supported these conclusions. The conclusion that Pt $6p_\sigma$ character increased in the M–L bond is the reverse of Syrkin's theory.

The most detailed calculation on the *trans*-influence in platinum(II) complexes was performed by Zumdahl and Drago[16], who carried out molecular orbital calculations on the series *trans*-$PtCl_2(L)(NH_3)$, where L = H_2O, NH_3, Cl^-, H_2S, PH_3, H^-, and CH_3^-. Their main conclusions were: (*i*) the Pt–N bond *trans* to L becomes progressively weaker as L changes in the above order from H_2O to CH_3^-, paralleling the *trans*-effect order; (*ii*) the Pt–Cl bonds *cis* to L also weaken in this order to an extent only slightly less than weakening of the Pt–N bond *trans* to L (i.e., the *cis*-influence is almost as great as the *trans*-influence); (*iii*) weakening of the bond *trans* to L is due primarily to weakening of Pt(6*s*)–N and $Pt(d_{x^2-y^2})$–N interaction, not to decreased availability of $Pt(6p_\sigma)$ (as with Syrkin's theory); (*iv*) metal–phosphine π-bonding is unimportant when L = PH_3; (*v*) ligands, L, which have high *trans*-effects stabilize a trigonal bipyramidal transition state by overlapping strongly with the $Pt(6p_\sigma)$ orbital which is shared with the potential leaving group (a possible exception is CH_3^-).

Conclusion (*ii*), that the *cis*-influence was comparable to the *trans*-influence, was unexpected, since most previous discussions had stressed the stereospecific nature of the *trans*-influence. Zumdahl and Drago cited a number of physical observations, chiefly infrared spectroscopic data for *cis* and *trans* isomers, which supported this conclusion, but the bulk of the experimental data presented in this review indicate that the *trans*-influence of a ligand is, in fact, much greater than its *cis*-influence.

In summary, the concept of metal rehybridization induced by a ligand, L, forming strong covalent bonds with the metal seems to be well established. Theoretical treatments have, however, given no general agreement on the particular type of metal orbital which tends to concentrate in the M–L bond at the expense of the M–A bond *trans* to it. Vibrational stretching frequencies show the existence of the *trans*-influence, but provide few clues as to the details of orbital rearrangements behind it. A beginning has been made in deducing metal hybridization from X-ray bond lengths[17] (see discussion later). If this interpretation and the explanation of NMR spin–spin coupling constants in terms of Fermi contact (discussed later) are correct, however, the M–L bond gains *s*-character at the expense of the *trans*-M–A bond when L has a high *trans*-influence.

C. EXPERIMENTAL OBSERVATIONS OF THE *trans*-INFLUENCE

In the following pages the results which have been obtained through the use of X-ray crystallography, vibrational spectroscopy, nuclear magnetic resonance, nuclear quadrupole resonance and photoelectron spectroscopy will be discussed in turn. Correlations and differences between the *trans*-influence series obtained by these different techniques will then be discussed.

(i) X-ray crystallography

If a bond M—A *trans* to a ligand L is "unusually long" compared with the sum of the covalent radii, or with "normal" bond lengths found in other crystal structures, a high *trans*-influence is usually ascribed to the ligand L (on the other hand, "unusually short" M—A bond distances have often been ascribed to M—A multiple bonding[18]).

Mason and Randaccio[17], however, have pointed out the inadequacy of using a fixed "hard-sphere" metal covalent radius for different types of ligands. Rather, the metal covalent radius varies according to the particular metal hybridization which provides maximum metal—ligand overlap. They concluded that, in general, for the metals considered, metal—phosphorus bonds require more metal *s*-character for maximum overlap than metal—chlorine bonds.

Some other factors that should be taken into account are.

(*i*) Differences in lengths of a bond M—A caused by variation of a *trans*-ligand L are small and often of the same order as the experimental error in bond length determination.

(*ii*) Intermolecular interactions in crystals can appreciably affect bond lengths. Significant variations can occur in different crystal structures of the same compound[19,20] and by changing the counter-ion[20]. Bonds which are chemically equivalent in solution but which are crystallographically distinct (i.e., not related by symmetry in crystal lattice) often show significant differences in length[21,22].

(*iii*) Intramolecular steric effects can substantially affect bond lengths, for example, in the ion $OsNCl_5{}^{2-}$, the Os—Cl bond *trans* to the nitrido ion is significantly longer than the *cis* Os—Cl bond lengths[23].

(*iv*) Many of the earlier X-ray method structural determinations were two-dimensional only and were not sufficiently refined to provide reliable bond length data.

Some of the conclusions reached from earlier determinations have been shown to be incorrect by the more accurate apparatus and techniques employed today. For example, the initial determination[24] of the structure of $[Co(NH_3)_5Cl]Cl_2$ showed a significantly shorter Co—N bond *trans* to Cl compared with the bonds *trans* to NH_3, but a more accurate determination[25] showed that this was not so. Many other earlier results, such as the bond length of 2.7 Å reported[26] for Pt—Br *trans* to NH_3 in $K[PtBr_3(NH_3)]\cdot H_2O$ have also been called into question[21].

One important crystal structure with an interesting history is that of Zeise's salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$. From earlier two-dimensional structural determinations[27] it was concluded that the Pt—Cl bond *trans* to ethylene was significantly longer than the other two Pt—Cl bonds. A redetermination of the structure[21] showed that, after allowing for thermal motion, this bond no longer differed significantly from one of the *cis* bonds.

A more recent redetermination using a different space group[28] suggests that a significant difference does exist between *cis* and *trans* Pt—Cl bond lengths (2.305 and 2.327 Å respectively).

Despite the substantial agreement between some independent determinations on the same compound carried out nearly simultaneously (e.g., for the black form of [Co(NO)-$(NH_3)_5$]Cl_2 (ref. 29), *trans*-$PdCl_2(DMSO)_2$ (ref. 30) and *cis*-$FeH_2\{P(OEt)_2Ph\}_4$ (ref. 31)) the crystal quality, and the details of data collection and refinement used by different workers can affect details of the structure.

Crystal structure determinations which tend to provide the least ambiguous information on the relative *trans*-influences of ligands L and L′ are those on complexes of the type *cis*-MA_2LL', which provide two different M—A bond lengths. Results from a number of such studies are listed in Table 1. Structural determinations of isomeric pairs, e.g., *cis*- and *trans*-MA_2L_2, allow comparisons of the *trans*-influences of A and L. Similarly, determinations of very closely related complexes such as *trans*-$MLAX_2$, where L is changed, provide a quantitative comparison of the *trans*-influences of L. These results are listed in Table 2 together with some isolated crystal structures showing "unusually long" bond lengths.

By comparing Pt–Cl bond lengths in a number of Pt^{II} complexes, Mason et al.[15] have placed a number of ligands in order of their structural *trans*-influence, $R_3Si^- > H^- > R_3P > H_2C{=}CH_2, Cl^- > O(acac)$. This order was correlated with ligand electronegativities and calculated overlap between ligand and $Pt(6p_\sigma)$. Since many Pt^{II}—Cl bond lengths are available for comparison, this ordering is probably valid, though it would be preferable if the compounds considered were structurally analogous, e.g., all of the type *trans*-PtClL-$(PR_3)_2$. From the results in Tables 1 and 2 the series can be extended somewhat to give an order of structural *trans*-influence. $R_3Si^- \simeq \sigma\text{-C} \simeq H^- \geqslant$ carbenes $\simeq PR_3 \geqslant AsR_3 >$ $CO \simeq RNC \simeq C{=}C \simeq Cl^- \simeq NH_3 > O(acac)$. It is clear from Tables 1 and 2 that the structural *trans*-influence is by no means limited to square planar complexes of Pt^{II}. Significant effects have been observed in square planar Rh^I, Ir^I, Pd^{II}, Ni^{II} and Au^{III} complexes, octahedral Fe^{II}, Cr^{III}, Re^{III}, Os^{II}, Os^{III}, Rh^{III}, Ir^{III}, and Pt^{IV} complexes and square pyramidal Ir^I complexes. Many other metals will probably be included when the necessary structural data have been obtained. Until there is definite evidence to the contrary, it is dangerous to assume that the *trans*-influence is completely absent in metal complexes[89].

Mason and Towl[14] have attempted to determine orders of structural *trans*-influence for Pt^{IV}, Ir^{III}, Rh^{III} and Co^{III}, but their ground is much less firm here than with Pt^{II}. They propose that the relative lengthening of a given metal ligand (A) bond, expressed as a fraction of the value of the bond length when the *trans* ligand is A itself (or if this is not known, as a fraction of the sum of the covalent radii) is a measure of the *trans*-influencing ability of the *trans*-ligand L′. It is difficult to see why this should provide a valid criterion, since if A has a high *trans*-influence itself, the M—A bond *trans* to A would be expected to be longer than M—A *trans* to a ligand of low *trans*-influence, such as Cl^- (e.g., Pt—P distances (refs. 18, 70) in *cis*- and *trans*-$PtCl_2(PR_3)_2$). The problem is illustrated by the structure[90] of $K_3[(HC_2F_4)Co(CN)_5]$. The Co—CN bond *trans* to $HC_2F_4^-$, 1.927(14) Å is slightly longer than that *trans* to CN^-, 1.894(14) Å. This enables one to decide that $-C_2F_4H^-$ has a high *trans*-influence comparable to or slightly greater than cyanide. But since the *trans*-influence of the cyanide ion for Co^{III} relative to other ligands is not known from other crystal structures, it does not allow one to place $-C_2F_4H^-$ relative to ligands such as

TABLE 1

X-ray crystal structure determinations on molecules in which two ligands A^1 and A^2 are *trans* to different ligands

Complex	M–A^1 bond length	Ligand *trans* to A^1	M–A^2 bond length [a]	Ligand *trans* to A^2	Ref.
K[PtCl$_3$(C$_2$H$_4$)]·H$_2$O	Pt–Cl 2.29 2.34	Cl	Pt–Cl 2.34	C$_2$H$_4$	21
PtCl$_3$(*trans*-MeCH=CHCH$_2$NH$_3$) [b]	Pt–Cl 2.307(6) 2.288(7)	Cl Cl	Pt–Cl 2.339(7)	C=C	32a
[PtCl$_3$(*trans*-NH$_3$CH$_2$CH=CHCH$_2$NH$_3$)]Cl	Pt–Cl 2.293(2) 2.311(2)	Cl	Pt–Cl 2.342(2)	C=C	33
cis-PtCl$_2$(PEt$_3$)L{:C(OEt)(NHPh)}	Pt–Cl 2.368(7)	PEt$_3$	Pt–Cl 2.365(5)	:C(OEt)(NHPh)	34
cis-PtCl$_2$(PEt$_2$Ph)(CNEt)	Pt–Cl 2.390(8)	PEt$_2$Ph	Pt–Cl 2.314(10)	EtNC	35
[Cl(tetramethylallene)PtCl]$_2$	Pt–Cl (bridge) 2.342(5)	Cl	Pt–Cl (bridge) 2.381(5)	Tetramethylallene	36
[Cl(AsMe$_3$)PtCl]$_2$	Pt–Cl (bridge) 2.312(5)	Cl	Pt–Cl (bridge) 2.394(6)	AsMe$_3$	37
[Cl(PPr$^n_3$)PtCl]$_2$	Pt–Cl (bridge) 2.315(8)	Cl	Pt–Cl (bridge) 2.425(8)	PPr$^n_3$	38
[(Dicyclopentadiene–OMe)PtCl]$_2$	Pt–Cl (bridge) 2.34	C=C	Pt–Cl (bridge) 2.51	σ-C	39

TABLE 1 (continued)

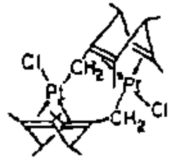
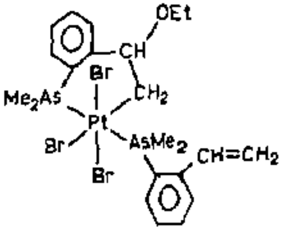
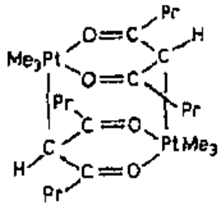
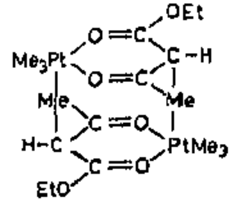
Complex	M–A^1 bond length	Ligand *trans* to A^1	M–A^2 bond length ^{a}	Ligand *trans* to A^2	Ref.
[(MeCO)$_2$CH–]PtCl(Acac)	Pt–O 1.968(14)	Cl	Pt–O 2.072(14)	σ-C	40
cis-Pt(Ph)(GePh$_2$OH)(PEt$_3$)$_2$	Pt–P 2.317(5)	–C$_6$H$_5$	Pt–P 2.328(5)	–GePh$_2$(OH)	41
	Pt–C (olefin) 2.36(2) 2.31(2)	σ-CH$_2$–	Pt–C (olefin) 2.18(2) 2.17(2)	Cl	42
	Pt–Br 2.460(5)	Br	Pt–Br 2.570(5)	σ-CH$_2$–	43
Pt(CH$_3$)$_3$[-CH(COCH$_3$)$_2$](bipy)	Pt–CH$_3$ 2.03(2) 2.07(2)	bipy	Pt–CH$_3$ 2.05(2)	σ-C (acac)	44a
	Pt–CH$_3$ 2.04(3) 2.02(4)	O	Pt–CH$_3$ 2.00(3)	σ-C (acac)	44b
	Pt–CH$_3$ 1.96(7) 2.14(9)	O	Pt–CH$_3$ 2.17(10)	σ-C (acetoacetate)	44c

TABLE 1 (continued)

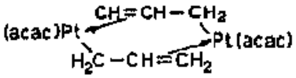
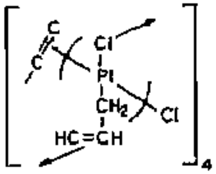
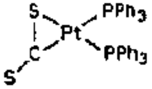
Complex	M–A^1 bond length	Ligand *trans* to A^1	M–A^2 bond length [a]	Ligand *trans* to A^2	Ref.
	Pt–O 1.98(2) 1.99(2)	π-C=C	Pt–O 2.07(2) 2.07(2)	σ-CH$_2$	46
	Pt–Cl (mean) 2.37(1)	π-C=C	Pt–Cl (mean) 2.49(1)	σ-CH$_2$	46
	Pt–P 2.240(15)	S	Pt–P 2.346(10)	C	45

TABLE 1 (continued)

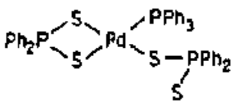
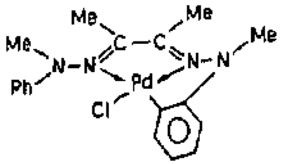
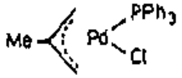
Complex	M–A^1 bond length	Ligand *trans* to A^1	M–A^2 bond length^a	Ligand *trans* to A^2	Ref.
	Pd–S (chelate) 2.35	S	Pd–S (chelate) 2.47	PPh$_3$	47
	Pd–N 2.00(2)	Cl	Pd–N 2.11(2)	σ-C	48
	Pd–C 2.14(3)	Cl	Pd–C 2.28(3)	PPh$_3$	49

TABLE 1 (continued)

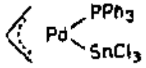
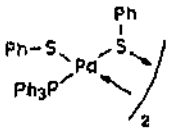
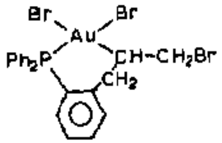
Complex	M–A^1 bond length	Ligand *trans* to A^1	M–A^2 bond length [a]	Ligand *trans* to A^2	Ref
	Pd–C 2.201(16)	$SnCl_3$	Pd–C 2.193(12)	PPh_3	50
	Pd–S (bridging) 2.358(7)	S–Ph	Pd–S (bridging) 2.432(7)	PPh_3	51
 [c]	Au–Br 2.460(6)	P	Au–Br 2.510(6)	σ-C	52

TABLE I (continued)

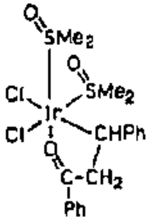
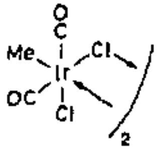
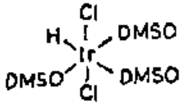
Complex	$M-A^1$ bond length	Ligand *trans* to A^1	$M-A^2$ bond length [a]	Ligand *trans* to A^2	Ref.
	Ir–Cl 2.380(5)	DMSO	Ir–Cl 2.490(5)	σ-C	53
	Ir–Cl (bridge) 2.38	CO	Ir–Cl (bridge) 2.52	$-CH_3$	54
	Ir–S 2.25	DMSO	Ir–S 2.39	H	54a

TABLE 1 (continued)

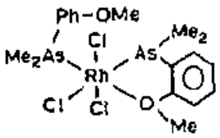
Complex	M–A^1 bond length	Ligand *trans* to A^1	M–A^2 bond length [a]	Ligand *trans* to A^2	Ref.
mer-$IrCl_3(PMe_2Ph)_3$	Ir–Cl 2.277 (6)	Cl	Ir–Cl 2.361 (6)	PMe_2Ph	55
	Ir–P 2.363 (6)	Cl	Ir–P 2.429 (6)	PMe_2Ph	
mer-$OsCl_3(PMe_2Ph)_3$	Os–Cl 2.347 (6)	Cl	Os–Cl 2.439 (6)	PMe_2Ph	55
	Os–P 2.350 (5)	Cl	Os–P 2.408 (6)	PMe_2Ph	
mer-$ReCl_3(PMe_2Ph)_3$	Re–Cl 2.353 (6)	Cl	Re–Cl 2.454 (6)	PMe_2Ph	55
	Re–P 2.401 (6)	Cl	Re–P 2.458 (6)	PMe_2Ph	
	Rh–Cl 2.35 (1) 2.33 (1)	Cl	Rh–Cl 2.39 (1)	As	56

TABLE 1 (continued)

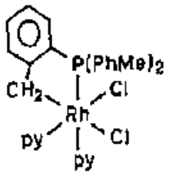
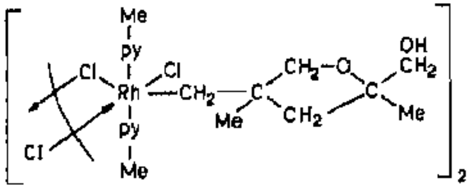
Complex	M–A^1 bond length	Ligand *trans* to A^1	M–A^2 bond length ^{a}	Ligand *trans* to A^2	Ref.
	Rh–Cl 2.339(4) Rh–N 2 122(14)	py Cl	Rh–Cl 2.531(4) Rh–N 2.123(13)	σ-C py	14
	Rh–Cl (bridge) 3.365(6)	Cl	Rh–Cl (bridge) 3.632(6)	σ-C	57
$[Rh(C_2H_5)(NH_3)_5]Br_2$	Rh–N 2.072(7)	NH_3	Rh–N 2 256	$-C_2H_5$	58

TABLE 1 (continued)

Complex	$M-A^1$ bond length	Ligand *trans* to A^1	$M-A^2$ bond length [a]	Ligand *trans* to A^2	Ref
$[Rh(H)(NH_3)_5](ClO_4)_2$	Rh–N 2.048(11) 2.071(6) 2.079(14) 2.086(8)	NH_3	Rh–N 2.244(13)	–H	59
$RhCl(PPh_3)_3$ [d]	Rh–P 2.218(8)	Cl	Rh–P 2.327(8)	PPh_3	60
$Rh(acac)(C_2H_4)(C_2F_4)$	Rh–O 2.027(8)	C_2H_4	Rh–O 2.047(8)	C_2F_4	61
$[CoCl(NH_3)_5]Cl_2$ [e]	Co–N 1.962(4) 1.978(6) 1.998(6)	NH_3	Co–N 1.964	Cl	25
$[Co(N_3)(NH_3)_5](N_3)_2$	Co–N 1.957(5) 1.960(5) 1.943(5) 1.976(5)	NH_3	Co–N 1.977(5)	N_3	62
$[Co(NO_2)(NH_3)_5]Br_2$	Co–N 1.985(15) 1.972(16)	NH_3	Co–N 1.976(19)	$-NO_2$	63
$[Co(NH_3)_5O_2Co(NH_3)_5](SO_4)_2 \cdot 4H_2O$	Co–N 1.962(9)	NH_3	Co–N 1.983(9)	O_2	64
$[Co(NO)(NH_3)_5]Cl_2$ [f]	Co–N 1.93	NH_3	Co–N 2.28	NO^-	29a

TABLE 1 (continued)

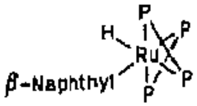
Complex	M–A¹ bond length	Ligand *trans* to A¹	M–A² bond length [a]	Ligand *trans* to A²	Ref.
$[Co(NH_3)_5\text{-}NC\text{-}Co(CN)_5] \cdot H_2O$	Co–N (NH_3) 1.976(3) 1.969(3) 1.956(3) 1.960(3)	NH_3	Co–N 1.935(3)	–NC	65
	Ru–P 2.280(5) 2.300(5)	P	Ru–P 2.330(5)	H	65a
$\widehat{PP} = Me_2P(CH_2)_2PMe_2$			2.300(5)	β-Naphthyl	
mer-Os(H)Br(CO)$(PPh_3)_3$	Os–P 2.34	PPh_3	Os–P 2.56	–H	66

TABLE I (continued)

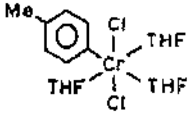
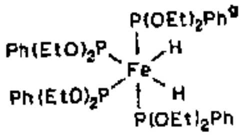
Complex	$M-A^1$ bond length	Ligand *trans* to A^1	$M-A^2$ bond length [a]	Ligand *trans* to A^2	Ref.
	Cr–O 2.044(7) 2.046(8)	THF	Cr–O 2.214(7)	σ-C	67
	Fe–P 2.134(2) 2.119(2)	$P(OEt)_2Ph$	Fe–P 2.153(2) 2.151(2)	–H	31

TABLE I (continued)

Complex	M–A[1] bond length	Ligand *trans* to A[1]	M–A[2] bond length [a]	Ligand *trans* to A[2]	Ref.
$GaCl_3$(terpy)	Ga–Cl 2.235(3)	N	Ga–Cl 2.329(3) 2.403(2)	Cl	68

[a] Bond lengths in angstroms with estimated standard deviations in last figure in parentheses (if given).

[b] A slightly smaller *trans*-bond weakening effect was observed for the *cis*-olefin (ref. 32b).

[c] Analogous results were obtained for a similar complex (ref. 43)

[d] Distorted toward tetrahedral.

[e] No significant difference between Co–N bonds was found for the SiF_6^- salt (ref. 88)

[f] Black form. Similar results were obtained independently (ref 29b).

[g] Arrangement of phosphorus atoms approaches tetrahedral

TABLE 2
Comparisons of M–A bond lengths in different molecules

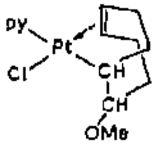
Complex	M–A bond length ^{a}	*Trans* ligand	Ref.	Comparison complex	M–A bond length ^{a}	*Trans* ligand	Ref.
trans-$PtCl_2(NH_3)_2$	Pt–Cl 2.32(1)	Cl	69	*cis*-$PtCl_2(NH_3)_2$	Pt–Cl 2.328(9) 2.330(9)	NH_3	69
	Pt–N 2.05(4)	NH_3	69		Pt–N 2.05(4) 1.95(3)	Cl	69
cis-$PtCl_2(PMe_3)_2$	Pt–Cl 2.364(8) 2.388(9)	PMe_3	70				
				trans-$PtCl_2(PEt_3)_2$	Pt–Cl 2.294(9)	Cl	18
trans-$Pt(H)Cl(PEtPh_2)_2$	Pt–Cl 2.422(9)	–H	71				
trans-$Pt(H)Br(PEt_3)_2$	Pt–Br 2.56(4)	–H	72	*trans*-$PtBr_2(PEt_3)_2$	Pt–Br 2.428(2)	Br	18
	Pt–N 2.20(2)	σ-C	73	Covalent radii	Pt–N 2.05		73
	Pt–Cl 2.341(8)	C=C	73				
				trans-$PtCl_2(NH_3)_2$	Pt–Cl 2.32(1)	Cl	69

TABLE 2 (continued)

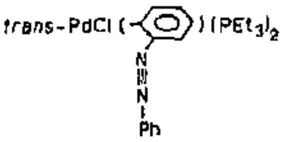
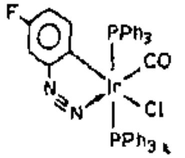
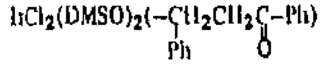
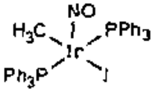
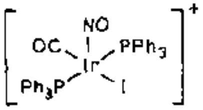
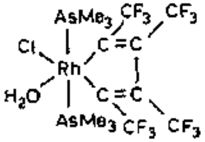
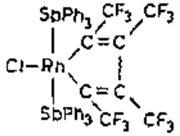
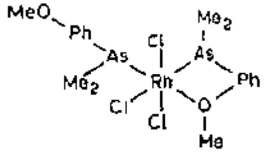
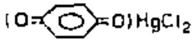
Complex	M–A bond length^a	*Trans* ligand	Ref.	Comparison complex	M–A bond length^a	*Trans* ligand	Ref.
cis-$PtCl_2(CNC_6H_5)_2$	Pt–Cl 2.313(4)	CNC_6H_5	35	*cis*-$PtCl_2(CO)(PEt_3)$	Pt–Cl 2.31(2)	CO	74a
trans-$PtCl_2(NH_2-Ph-Me)$ $(Bu^t-C{\equiv}C-Bu^t)$	Pt–N 2.104(10)	C≡C	74	*cis*-$PtCl_2(NH_3)_2$	Pt–N 2.01(4) 2.02	Cl	69
cis-$Pt(CN)(-C{\equiv}C-CN)(PPh_3)_2$	Pt–P 2.33(1) 2.32(1)	 –CN –C≡C–CN	 75	$Pt(CO_3)(PPh_3)_2$	Pt–P 2.24	CO_3	76
	Pd–Cl 2.381(5)	σ-C	77				
trans-$Pd(H)Cl(PPr^i_3)_2$	Pd–Cl 2.39	–H	79	*trans*-$PdCl_2(DMSO)_2$	Pd–Cl 2.290(2)	Cl	30
cis-$PdCl_2(PMe_2Ph_2)$	Pd–Cl 2.362(3)	PMe_2Ph	78				
	Pd–P 2.260(2)	Cl	78	*trans*-$PdI_2(PMe_2Ph)_2$	Pd–P 2.333(7)	PMe_2Ph	19
trans-$Ni(H)Cl(PPr^i_3)_2$	Ni–Cl 2.21	–H	79				
	Ir–Cl 2.44(1)	σ-C	80	 $IrCl_2(DMSO)_2(-\underset{Ph}{C}H-CH_2CH_2\underset{\|O}{C}-Ph)$	Ir–Cl 2.380(5) 2.490(5)	DMSO σ-C	 53

TABLE 2 (continued)

Complex	M–A bond length [a]	*Trans* ligand	Ref	Comparison complex	M–A bond length [a]	*Trans* ligand	Ref.
	Ir–I 2.726(2)	CH_3	81		Ir–I 2.666(3)	CO	82
	Rh–Cl 2.446(5) Rh–O 2.243(11)	σ-C σ-C	83		Rh–Cl 2.381	Trigonal bipyramidal	84
	Rh–C 2.051(16) Rh–C 2.007(16)	Cl H_2O			Rh–Cl 2.35(1) 2.33(1)	Cl	56
trans-$[CoCl(NO)(en)_2]ClO_4$	Co–Cl 2.575(3)	NO^-	85	$[CoCl(NH_3)_5]Cl_2$	Co–Cl 2.281(4)	NH_3	25
$(EtO)_2(O)P\text{-}HgCl$	Hg–Cl 2.370(17)	$P(O)(OEt)_2$	86		Hg–Cl 2.30	Cl	87

[a] In angstroms. Standard deviations, where given, in parentheses

other σ-C bonded groups. Another difficulty is that different "indicator" groups might have different sensitivities towards the structural *trans*-influence. In a metal carbonyl bond, the effect of synergic σ—π bonding on the M—CO bond length could well outweigh changes induced by variation of the *trans*-influence of the ligand *trans* to CO. It is consequently difficult to interpret a result such as the observation of essentially equivalent Mn—CO bond lengths in $HMn(CO)_5$, and small variations in ν_{M-CO} in related complexes[90a]. Frenz and Ibers[90a] have suggested that in these complexes CO has a slightly higher *trans*-influence than H^-.

It thus appears premature to attempt a fine grading of ligands until more structural data are available; in particular, rather extensive series of M—Cl bond lengths *trans* to different ligands. For all of the metals studied it appears quite clear that σ-alkyl groups have a high structural *trans*-influence; and that halides and nitrogen donors have low *trans*-influences.

An exception to this rule appears to be the σ-C bonded β-diketonate ligands, in Pt^{IV} complexes both in monomeric[44a] and dimeric[44b, c] complexes, since $Pt—CH_3$ bond lengths *trans* to these ligands are not significantly different from $Pt—CH_3$ bond lengths *trans* to N- or O-donors. This contrasts with the apparent high *trans*-influence[40] of the C-bonded acetylacetonate in "$[Pt(acac)_2Cl]^-$".

A rather unexpected result[14] was obtained from the crystal structure of the complex $RhCl_2(py)_2\{P(o\text{-tolyl})_2(\sigma\text{-}C_6H_4\text{-}CH_2)\}$. The Rh—N distance *trans* to P is not significantly different from that *trans* to Cl, which suggests that the phosphine has a low structural *trans*-influence for Rh^{III}. (Arsines, which in Pt^{II} complexes have a *trans*-influence slightly less than phosphines[37, 38], appear to have a moderately high *trans*-influence[56] for Rh^{III}.) More data on the structural *trans*-influence of phosphines for Rh^{III} would be helpful.

For Co^{III}, Cl^-, NH_3, N_3^-, and NO_2^- all appear[25, 62, 63] to have similar low structural *trans*-influences, with peroxide showing a slight *trans* bond-weakening effect[65]. NO^- appears to have a high structural *trans*-influence[29, 85] for Co^{III}, and from the structures of vitamin B_{12} derivatives and analogues[14, 20, 91], the methyl group and other σ-C bonded groups have a high *trans*-influence in complexes of this type.

Results on Pd^{II} complexes[78] suggest that phosphines have a high structural *trans*-influence comparable to that in Pt^{II} complexes. The complex[45] $Pt(CS_2)(PPh_3)_2$ provides an example of an apparent structural *trans*-influence in a formally Pt^0 complex. The Pt—P bond "*trans*" to the carbon atom is significantly longer than that "*trans*" to S. The authors suggest that this is due to more efficient overlap of metal d_π with carbon p_π orbitals than with sulfur p_π orbital, giving rise to less Pt—P π-bonding in the bond *trans* to C.

The crystal structure[68] of $GaCl_3(terpy)$ apparently indicates a significantly higher *trans*-influence for Cl^- than for terpy-N, the first observed for a main group metal ion. It is, however, unfortunate that steric effects cause a considerable difference in the two Ga—Cl bond lengths *cis* to terpy, leaving the possibility open that part, at least, of the difference between Ga—Cl bond lengths *cis* and *trans* to terpy may also be steric in origin.

While X-ray structural data have been extremely useful in providing many examples of the structural *trans*-influence, reliable quantitative comparisons between ligands will only be possible as crystallographers systematically determine the structures of closely related compounds. Some series which could be profitably extended are $[Co(L)(NH_3)_5]^{n+}$, *trans*-$PtCl(L)(PR_3)_2$ and $[Cl(L)PtCl_2Pt(L)Cl]$. Since it is synthetically possible to prepare many analogous complexes of Ni^{II}, Pd^{II} and Pt^{II}, systematic comparisons of the structural *trans*-influence for this triad should also be possible.

(ii) Metal–ligand stretching vibrations

The assumption is usually made that a decrease in the force constant for an M–A stretching vibration indicates a weakening of the M–A bond. For most complexes that have been examined by vibrational spectroscopy, force constants are not available and stretching frequencies are used instead, it being considered that a lower M–A stretching frequency corresponds to a weaker bond Even where force constants have been calculated, the physical significance of the results has been questioned for all but the simplest molecules[92]. One difficulty which occurs when the relative *trans*-influences of donor atoms of very different masses are examined (e.g., Cl^-, Br^-, I^-, PR_3, AsR_3, SbR_3), arises from the possibility of a mass effect on the "indicator" frequency of the ν_{M-A} vibration. As the mass of other ligands L attached to M increases, the "effective mass" of an $-ML_n$ unit will increase, which will tend to reduce ν_{M-A} even if the M–A force constant does not change. This is occasionally considered a possible source of some "*cis*-influences"[93] and "*trans*-influences"[94] but is often ignored. Interpretation of M–A stretching frequencies is also complicated by the possibility of vibrational coupling between ν_{M-A} and other molecular vibrations. From the normal coordinate analysis of $PtCl_2(NH_3)_2$, Nakamato et al.[95] suggested that almost no coupling exists between various vibrational modes in this complex. Most authors consider that vibrational coupling can be ignored provided that the frequency ν_{M-A} is well separated from that of other vibrational modes that are likely to couple, especially when M is a heavy metal like platinum[96]. An example of vibrational coupling where this condition is not met is provided by ν_{M-H} when the hydride is *trans* to CO (refs. 97, 98), RNC (ref. 97) and CN^- (ref 99)

Another problem arises from lattice effects on vibrational modes when the spectra are obtained from solid samples. The spectra may then contain bands which are not observed for solutions[100], and additionally solid state effects sometimes cause band splittings[101]. On the other hand, close agreement is often found between spectra measured for solids and in solution[94, 102]. In ionic complexes the counter-ion can also have an effect on the metal–ligand stretching frequency[20, 103]

(a) Metal–halogen stretching frequencies

Platinum(II) complexes. Complexes of platinum(II) and platinum(IV) have been more thoroughly studied by vibrational spectroscopy, or indeed any other technique, than those of any other metal, at least as far as examination of *trans*-influences is concerned The largest group of platinum compounds studied are halide derivatives, in which variations of ν_{Pt-X} (where X = Cl or Br) with changes in the ligand, L, *trans* to X are interpreted in terms of the *trans*-influence of L The assignment of Pt–I stretching frequencies often tends to be difficult[92] and these frequencies do not clearly show the same trends[104] as ν_{Pt-Cl} and ν_{Pt-Br}. Complexes of the type *trans*-PtL_2X_2, where X = Cl or Br, give[94, 95, 105–107] only a single Pt–X stretching band in the far infrared region, whose frequency is virtually independent of L (ca. 340 cm^{-1} for X = Cl and ca. 250 cm^{-1} when X = Br) except for L = NH_3 (331 cm^{-1} for X = Cl and 227 cm^{-1} for X = Br). These low values for amine complexes have been attributed[105] to intermolecular hydrogen bonding.

TABLE 3

Platinum—chloride stretching frequencies (cm^{-1}) and the *trans*-influence [a]

A Complexes[b] *of the type* trans-*$PtXClL_2$*

CO (344) (ref. 97) $\leq$ *t*-BuNC (341) (ref 97) $\leq$ Cl^- (340) (ref. 105) $\leq$ Py (337) (ref. 114) $\leq$ *p*-$MeOC_6H_4NC$ (335) (ref. 97) $<$ $P(OPh)_3$ (316) (ref 97) $\simeq$ $P(OMe)_3$ (316) (ref. 97) $\leq$ $SnCl_3^-$ (315, PPh_3 complex) (ref 112) $<$ $C_6F_5^-$ (310) (refs. 115, 116) $<$ $AsPh_3$ (306) (ref. 114) $\leq$ PPh_3 (298) (ref. 114) $\simeq$ $SnPh_3^-$ (298, PPh_3 complex) (ref 112) $\leq$ PEt_3 (295) (ref. 97) $<$ $PbPh_3^-$ (286, PPh_3 complex) (ref. 112) $<$ $SnMe_3^-$ (278, PPh_3 complex) (ref 113) $<$ CH_3^- (274) (ref. 105) $\simeq$ $SiCl_3^-$ (274*) (ref. 110) $\simeq$ $Si(C_6F_5)_3^-$ (276*) (ref. 110) $\leq$ $SnEt_3^-$ (272*) (ref. 110) $\leq$ $C_6H_5^-$ (270) (ref. 105) $\leq$ H^- (269) (ref. 105) $<$ $GePh_3^-$ (263*) (ref. 110) $<$ $Si(p\text{-}C_6H_4CF_3)_3^-$ (258*) (ref 110) $\simeq$ $Si(m\text{-}C_6H_4CF_3)_3^-$ (258*) (ref 110) $<$ $Si(p\text{-}C_6H_4Me)_3^-$ (256*) (ref. 110) $\simeq$ $Si(p\text{-}C_6H_4F)_3^-$ (256*) (ref. 110) $\simeq$ $Si(m\text{-}C_6H_4Cl)_3^-$ (256*) (ref. 110) $\leq$ $Si(m\text{-}C_6H_4Me)_3^-$ (255*) (ref 110) $\leq$ $Si(p\text{-}C_6H_4Cl)_3^-$ (253*) (ref 110) $<$ $Si(m\text{-}C_6H_4F)_3^-$ (250*) (ref 110) $\leq$ $GeMe_2Ph^-$ (248*) (ref. 110) $<$ $SiMe_2Ph$ (242*) (ref. 110) $\leq$ $SiPh_3^-$ (239*) (ref. 110) $\simeq$ $Si(p\text{-}C_6H_4OMe)_3^-$ (239*) (ref. 110) $\simeq$ $Si(p\text{-}C_6H_4NMe_2)_3^-$ (239*) (ref. 110) $\leq$ $SiMe_3^-$ (238) (ref. 111) $\leq$ $GeMe_3^-$ (235) (ref. 111)

B Complexes of the type cis-*$PtCl_2L_2$ (mean frequencies)*

Phen (347) (ref. 117) $\leq$ bipy (345) (ref 121) $<$ py (336) (ref. 105, 118) $\simeq$ SMe_2 (336) (ref. 107) $<$ COD (327) (ref. 105) $\leq$ en (325) (ref. 119) $\simeq$ $SeEt_2$ (325) (ref. 105) $\leq$ SEt_2 (324) (ref 105) $<$ NH_3 (321) (ref. 95) $\leq$ $NH_2CH_2CH_2CH_2NH_2$ (318) (ref. 124) $<$ $Ph_2PC{\equiv}CPPh_2$ (315) (ref 122) $\leq$ $Ph_2AsCH_2CH_2AsPh_2$ (313) (ref 117) $<$ PPh_3 (305) (ref 117) $\simeq$ $Ph_2PCH_2CH_2PPh_2$ (305) (ref 117) $\leq$ $AsMe_3$ (303) (refs. 92, 120) $\simeq$ $SeMe_2$ (303) (ref. 107) $\simeq$ $SbMe_3$ (303) (ref. 120) $\leq$ $AsEt_3$ (301) (ref. 105) $<$ $AsPr^n_3$ (298) (ref 105) $\leq$ $SbPr^n_3$ (296) (ref. 105) $\leq$ PEt_3 (294) (refs. 106, 107, 115) $\leq$ $TeMe_2$ (293) (ref. 107) $\simeq$ $TePr^n_2$ (293) (ref. 105) $\leq$ $TeEt_2$ (292) (ref. 105) $\simeq$ PPr^n_3 (292) (ref 105) $\leq$ PMe_3 (290) (refs 94, 120)

C Complexes of the type [$PtCl_3L$] (ref. 127)

CO (322) $<$ SMe_2 (310) $\leq$ C_2H_4 (309) $\leq$ SEt_2 (307) $\ll$ $AsEt_3$ (280) $\leq$ PPh_3 (279) $<$ PMe_3 (275) $\leq$ $AsMe_3$ (272) $\leq$ PEt_3 (271) $\leq$ PPr^n_3 (270)

D. Complexes of the type $Pt_2X_4L_2$ [c] *(refs 102, 104)*

Cl^- $<$ CO $<$ $TeEt_2$ $<$ $TePr^n_2$ $\sim$ *p*-toluidine $\simeq$ C_3H_6 $<$ C_2H_4 $\leq$ PCl_3 $\ll$ PEt_3 $\simeq$ PPr^n_3 $\simeq$ PPh_3 $\simeq$ PMe_3 $\simeq$ $AsPr^n_3$ $\simeq$ $AsEt_3$ $\simeq$ $AsMe_3$ $\simeq$ $P(OEt)_3$

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[a] *Trans*-influence is the reverse order of ν_{Pt-Cl} frequencies

[b] $L = PEt_3$ except where denoted by an asterisk when $L = PMe_2Ph$.

[c] The order shown is that of decreasing ν_{Pt-Cl}, as well as ν_{Pt-Br} where available.

Thus, any *cis*-influence of L on ν_{Pt-X} is small.

As shown in Table 3A, ν_{Pt-Cl} stretching frequencies in the complexes *trans*-$PtXClL_2$ indicate[105, 108, 109] that $X = H^-$, CH_3^- or $C_6H_5^-$ has a high *trans*-influence; this is also true for cases where R contains a Group IV metalloid, so that groups such as $SiMe_3^-$ have *trans*-influences[110–113] higher than H^- or CH_3^-. The values of ν_{Pt-Cl} in a series of complexes *trans*-$[PtClL(PEt_3)_2]^+ClO_4^-$, where L is a neutral ligand, have been determined by infrared[97] and Raman[114] spectroscopy. Since ν_{Pt-Cl} in *trans*-$[PtCl(PEt_3)_3]ClO_4$ (295 cm^{-1})[97] is comparable to that[115] in *cis*-$PtCl(C_6H_5)(PEt_3)_2$ (290 cm^{-1}) and *cis*-$PtCl(C_6F_5)(PEt_3)_2$ (302 cm^{-1})[115, 116], it appears that data for cationic and neutral Pt^{II} complexes can be integrated, hence giving the *trans*-influence series shown in Table 3A. It will be noted that the magnitudes of the changes in ν_{Pt-Cl} are greater at the high *trans*-influence end of the series. Also, note that the low value[110] of ν_{Pt-Cl} in *trans*-$PtCl(SiPh_3)$-

$(PMe_2Ph)_2$ (239 cm^{-1}) appears anomalous by comparison with other aryl—silyl complexes, although within the silyl—platinum series there is a general trend for the *trans*-influence to decrease as the electronegativity of the silyl substituent increases. However, electronegativity alone does not determine the *trans*-influence of MX_3^-, since the *trans*-influence order is $SiX_3^- \geq GeX_3^- > SnX_3^-$, which is not the order which would be predicted from electronegativities[110].

Complexes of the type *cis*-$PtCl_2L_2$ show[105] two Pt—Cl stretching absorptions corresponding to the asymmetric (higher frequency) and the symmetric (lower frequency) stretching modes. These frequencies, and hence presumably the metal—chlorine bond strengths, are very dependent on the nature of L, as seen in Table 3B, and thus a *trans*-influence series is obtained. There is some disagreement about the assignment of ν_{Pt-Cl} in the complex $PtCl_2$en. Boschi et al.[119] assign the Pt—Cl stretching modes to bands at 334 and 315 cm^{-1}, while Watt and Cuddeback[117] assign them to bands at 311 and 290 cm^{-1}. The higher-frequency assignments seem more compatible with that expected for a nitrogen donor and are in agreement with the ν_{Pt-Cl} frequencies observed[123] for the closely related complexes $PtCl_2$(substituted trimethylenediamine) (e.g., 325 and 312 cm^{-1} for $PtCl_2(NH_2CH_2CH_2CH_2NH_2)$ (ref 124).

Where frequencies for ν_{Pt-Br} are available for the complexes *cis*-$PtBr_2L_2$, similar trends are observed[92,104,105,119,120] to the chlorides Again there are some disagreements over assignments; Adams et al.[105] and Clark and Williams[125] assigned ν_{Pt-Br} in *cis*-$PtBr_2(py)_2$ to the bands at 219 and 211 cm^{-1}, compared with 251 cm^{-1} in the *trans* isomer. However, Durig et al.[118] showed that the spectrum near 250 cm^{-1} was complicated by the presence of a Pt—N stretching band, and by using the deuterated pyridine complex assigned the Pt—Br stretching modes to bands at 252 and 235 cm^{-1}, thus removing an anomaly.

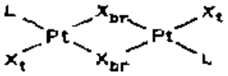
In considering this series, several possible complications should be noted. (*i*) intermolecular hydrogen bonding may affect ν_{Pt-Cl} frequencies when L contains N—H bonds[105] (though Durig et al.[126] consider this unimportant in related palladium complexes); (*ii*) vibrational coupling may affect the results where ν_{Pt-L} has a frequency similar to that of ν_{Pt-X}, e.g., $\nu_{Pt-AsMe_3}$ is thought to be of the same order[94] as ν_{Pt-Cl}; (*iii*) with heavy donor atoms such as Sb or Te, mass effects as well as actual changes in bond strength will lower ν_{Pt-X}. Note also that for the organosulfur and organoselenium complexes, the results suggest an appreciable substituent effect; for the dimethylchalconide series, the *trans*-influence order is S < Se < Te, which parallels the order of M—L bond strengths[107], while for the diethyl series, the order is Se ≤ S < Te. Adams et al.[105] noted that COD had a low *trans*-influence despite its high *trans*-effect.

For the ions $PtCl_3L^-$, three metal—chlorine stretching bands are expected, the asymmetric and symmetric stretching of the Pt—Cl bonds *cis* to L, and stretching of the Pt—Cl bond *trans* to L. However, the two ν_{Pt-Cl}(*cis*) bands are usually almost coincident and except for L = CO (343 cm^{-1}), their frequencies are insensitive to L (i e., usually 329 ± 4 cm^{-1}). The ν_{Pt-Cl} (*trans*) frequency varies with L as shown in Table 3C.

For Zeise's salt, $K[PtCl_3(C_2H_4)] \cdot H_2O$, bands observed at 339, 331 and 310 cm^{-1} have been assigned to ν_{Pt-Cl} (*cis*)(*asym*), ν_{Pt-Cl} (*cis*)(*sym*) and ν_{Pt-Cl} (*trans*) respectively[128]. The force constants of 1.82 and 1.78 for Pt—Cl (*cis*) and Pt—Cl (*trans*), respectively, obtained from their normal coordinate analysis, suggest a slight *trans*-bond weakening effect by ethylene.

Denning and Ware[129] studied the Raman (in aqueous solution) and solid state infrared spectra of the anions $[PtCl_3(NH_3)]^-$ and $[PtCl_3(CO)]^-$. For the former, all the Pt—Cl bands were degenerate at 325 cm^{-1}; this places NH_3 at the low end of the *trans*-influence order given in Table 3C. In rough agreement with Goodfellow et al.[127], $[PtCl_3(CO)]^-$ gave ν_{Pt-Cl} (*cis*) at 344 cm^{-1}, and ν_{Pt-Cl} (*trans*) at 318 cm^{-1}. From the calculated force constants, strengthening of the Pt—Cl (*cis*) bonds in $[PtCl_3(CO)]^-$ relative to the same bonds in the ammine complex is at least as important as weakening of the Pt—Cl(*trans*) bond by the *trans*-influence of CO. This *cis*-influence was attributed to an increased positive charge on platinum due to electron withdrawal from Pt *d*-orbitals to CO via π-bonding. On the other hand, Goggin and co-workers[92], from the Raman and infrared spectra of $[NPr^n{}_4][PtX_3L]$ (where X = Cl^-, Br^- or I^- and L = PMe_3, $AsMe_3$, PEt_3 or $AsEt_3$), obtained experimental values for the ratio ν_{Pt-X} (*cis*) (*asym*)/ν_{Pt-X} (*trans*). Comparison with values calculated on the basis of a very simple valence force field assuming both Pt—Cl stretching force constants are identical, showed that the force constant for the Pt—Cl bond *trans* to L was different from that for the Pt—Cl(*cis*) bond

Several workers[92,94,100,102,104,130,131] have examined the vibrational spectra of the halogen-bridged dimers $Pt_2X_4L_2$, which have a *trans*-structure I with the metal atoms and



I

bridging halides coplanar[37]. Assignments are based on those for the simple anions[96] $M_2X_6{}^{2-}$. In general, three Pt—X bands are observed in the infrared spectra, the highest-frequency band corresponding to stretching involving mainly the terminal halogens, $\nu_{Pt-X(t)}$. The remaining two Pt—X bands are associated with Pt—X_{br} stretching, the higher-frequency one being almost insensitive to L, while the lower band varies widely as L is changed. These two bands are thus assigned to Pt—X_{br} stretching involving the bridging halide *trans* to X_t and *trans* to L respectively. For the ligands so far studied[102,104] $\nu_{Pt-Cl(t)}$ varies from 330—368 cm^{-1} although the value of 330 cm^{-1} for *p*-toluidine seems anomalously low, perhaps owing to N—H······Cl bonding; if this case is ignored, the range is small, only 347—368 cm^{-1}. $\nu_{Pt-Cl(br)}$ *trans* to Cl^- varies over the range 312—331 cm^{-1} and $\nu_{Pt-Cl(br)}$ *trans* to L over the range 257—301 cm^{-1}, and from the latter the *trans*-influence series shown in Table 3D is obtained. Where data are available, this order is substantiated by $\nu_{Pt-Br(br)}$.

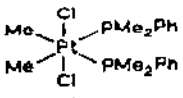
Adams and Chandler[104] noted that this ordering was similar to that obtained for *cis*-PtX_2L_2, except for the position of the tellurides for which the assignments are uncertain. Goggin and co-workers[102] considered that mixing of Pt—Cl and Pt—L modes could be important, at least for L = $AsMe_3$, and cautioned against drawing too definite conclusions from this ordering of ligands.

Palladium(II) complexes Palladium(II) complexes analogous to many of the platinum(II) complexes discussed above have been examined: *trans*-PdX_2L_2 (refs. 92, 93, 106, 107, 115, 118), *cis*-PdX_2L_2 (refs. 92, 94, 106, 107, 118, 120, 126), PdX_3L (refs. 93, 127),

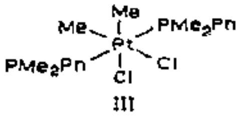
$Pd_2X_4L_2$ (refs 92, 94, 100, 102, 104), and *trans*-$[PdClL(PR_3)_2]^+$ (refs. 132, 133). In general, the results are very similar to those obtained for the corresponding platinum complexes; the *trans*-influence orders of ligands are similar, and the magnitude of the effect on Pd–X stretching frequencies is comparable, although occasionally the trends are less well defined for palladium complexes[104]. This may be due to greater vibrational coupling through the lighter Pd atom

Nickel(II) complexes. Various workers[106, 115, 134–137] have examined the infrared spectra of complexes *trans*-NiX_2L_2. A single Ni–X stretching band is observed in the range 400–410 cm^{-1} for X = Cl^-, and 310–340 cm^{-1} for X = Br^-. The only *cis* planar complexes NiX_2L_2 which have been examined are those of chelating phosphines Two Ni–Cl stretching bands are observed for $NiCl_2$(diphos)[134] at 330 and 320 cm^{-1}. These frequencies are considerably lower than those obtained for the *trans*-complexes indicating that the *trans*-influence of phosphines is much greater than that of Cl^- for square planar nickel(II) Similarly Ni–Br stretching bands occur at 264 and 250 cm^{-1} in $NiBr_2$(diphos).

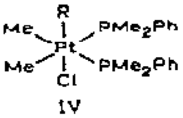
Platinum(IV) complexes Ruddick and Shaw[108, 109] found that $\nu(Pt^{IV}–Cl)$ was high when *trans* to Cl^- (e g , 332 cm^{-1} in II) but low *trans* to a methyl or an acetyl group (e g., 242 and 265 cm^{-1} in III, 244 cm^{-1} in IVa, 243 cm^{-1} in IVb).



II

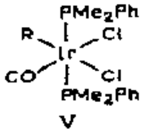


III



IV
(a) R = Me
(b) R = COMe

Iridium(III) complexes. Jenkins and Shaw[138] first noted that ν_{Ir-Cl} in iridium(III) complexes depended mainly on the ligand *trans* to Cl^- and relatively little on the *cis* ligands. This has been confirmed by subsequent work[101, 139–142]. Frequency ranges are given in Table 4 for those ligands for which a large number of complexes are available. Deeming and Shaw[101] compared the infrared spectra of a series of complexes of stereochemistry V with different R groups and the results are listed in Table 5 with the R groups listed in order of increasing *trans*-influence.



V

Rhodium(III) complexes The infrared *trans*-influence has been studied less extensively for Rh^{III} than for Ir^{III}. Data that are available suggest that ν_{Rh-Cl} is sensitive to changes in the ligand *trans* to Cl^-. For example, in the complex VI, ν_{Rh-Cl} (*trans* to CO) occurs[143] at 311 cm^{-1}, ν_{Rh-Cl} (*trans* to –COMe) at 230 cm^{-1} and in VII, ν_{Rh-Cl} (*trans* to CO) at 307 cm^{-1} and ν_{Rh-Cl} (*trans* to $-C_4H_7$) is at 245 cm^{-1}.

TABLE 4

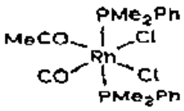
Effect of *trans* ligands on iridium–chlorine stretching frequencies

Trans ligands	ν(Ir–Cl)	*Trans* ligands	ν(Ir–Cl)
Cl^-	303–335	CH_3^-	255–270
CO	297–327	H^-	246–249
COD	290–305	$COCH_3^-$	215–247
PR_3 or AsR_3	262–290		

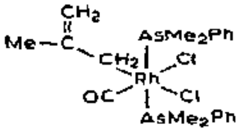
TABLE 5

Trans-influences of groups R from Ir–Cl stretching frequencies

R	ν(Ir–Cl) (cm^{-1}) *trans* to R	ν(Ir–Cl) (cm^{-1}) *trans* to CO
CH_3SO_2-	284	325
$NCCH_2-$	280	309
$PhSO_2-$	278	324
p-$MeC_6H_4SO_2-$	276	327
MeO_2CCH_2-	274	312
CCl_3-	272	320
Ph–	271, 251	315
Me–	260, 248	303
PhCO–	255, 242	299
PhN_2-	248	311
MeCO–	245	314
EtCO–	240	310



VI



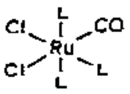
VII

Gold(I) complexes. Coates and Parkin[106] noted that ν_{Au-Cl} in the complexes L–Au–Cl decreased in the order PPh_3 (329 cm^{-1}) > Me_2S (324) > Me_3As (317) > PEt_3 (312) ≃ PMe_3 (311), which is then the order of increasing *trans*-influence, although the frequency for ν_{Au-Cl} *trans* to PPh_3 seems anomalously high. The overall frequency range is small so that the effect of the *trans* ligand on ν_{Au-Cl} is less pronounced than for other metals. It should be noted that the results of Goggin and co-workers[92] for Me_3PAuCl and $Me_3AsAuCl$ show a significant difference between solution and solid state values for ν_{Au-Cl} in both the infrared and Raman spectra (e.g., in the IR spectrum of the PMe_3 complex, ν_{Au-Cl} for the solid was assigned at 311 cm^{-1} and for a dichloromethane solution at 328 cm^{-1}) so that these frequencies are also somewhat sensitive to the environment of the molecule. The values of ν_{Au-Br} obtained[106] for the complexes LAuBr also show some anomalies but when a correction[92] is made for the assignment for ν_{Au-Br} in PMe_3AuBr, the order is similar to that for ν_{Au-Cl} (Goggin and co-workers[92] consider that there must be significant mixing between ν_{Au-Br} and $\delta(PC_3)_{sym}$ in the trimethylphosphine complex)

Gold(III) complexes. Coates and Parkin[106] also examined the infrared spectra of some gold(III) complexes, $LAuX_3$. In $pyAuCl_3$ a peak assigned to ν_{Au-Cl} is observed at 365 cm^{-1} with a shoulder at 357 cm^{-1}, but for Et_3PAuCl_3 bands are observed at 370, 301 and 296 (shoulder) cm^{-1}. Clearly, the low-frequency band in the phosphine complex corresponds predominantly to Au–Cl stretching involving the Cl^- *trans* to PEt_3. Analogous results were obtained for the bromide complexes (264 (sh) and 261 cm^{-1} for ν_{Au-Br} in $pyAuBr_3$; 263 and 215 cm^{-1} in Et_3PAuBr_3).

Liddle and Parkin[144], from the IR spectra of a number of aryl–gold(III) complexes, found that ν_{Au-Cl} *trans* to phenyl or substituted phenyl groups was very low. For example, in $[NBu^n{}_4][PhAuCl_3]$, the mutually *trans* Cl^- ligands give bands at 365 and 332 (weak) cm^{-1}, while ν_{Au-Cl} *trans* to phenyl occurs at 280 cm^{-1}. Complexes *cis*-$AuPhCl_2L$ give two Au–Cl stretching bands. For L = $SPr^n{}_2$, they occur at 328 cm^{-1} (*trans* to $SPr^n{}_2$) and 294 (*trans* to $-C_6H_5$) and for L = PMe_2Ph at 310 (*trans* to PMe_2Ph) and 286 cm^{-1} (*trans* to $-C_6H_5$).

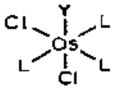
Ruthenium(II) complexes Lupin and Shaw[145] found that ν_{Ru-Cl} fell into three ranges, 347–299 cm^{-1} (*trans* to Cl^-), 311–266 cm^{-1} (*trans* to CO) and 262–229 cm^{-1} (*trans* to PR_3). For example, for the complex VIIIa, ν_{Ru-Cl} (*trans* to CO) occurs at 288 cm^{-1} and 229 cm^{-1} (*trans* to PMe_2Ph) For the $AsMe_2Ph$ analogue VIIIb ν_{Ru-Cl} (*trans* to $AsMe_2Ph$) is at 270 cm^{-1} although ν_{Ru-Cl}(*trans* to CO) is very similar (293 cm^{-1}). This suggests that arsines have lower *trans* influence for Ru^{II} than phosphines.



VIII

(a) L = PMe_2Ph

(b) L = $AsMe_2Ph$



IX

Osmium(II) complexes In osmium(II) complexes Chatt et al.[146] found that ν_{Os-Cl} (*trans* to Cl^-) occurred in the range 290–313 cm^{-1} and ν_{Os-Cl} (*trans* to CO) in the range 277–305 cm^{-1}. In the complexes IX, where L = PR_3 and Y = CO, N_2, RNC, PhNC, two ν_{Os-Cl} bands were observed The low-frequency band, 248–272 cm^{-1}, corresponded mainly to ν_{Os-Cl} (*trans* to PR_3) and the higher-frequency band 278–307 cm^{-1} mainly to ν_{Os-Cl} (*trans* to Y). By varying Y through a series of complexes IX and ordering the mean Os–Cl stretching frequency, a *trans*-influence order for Y was obtained: PhNC, MeNC > CO > N_2.

It was noted[145] that the ranges of ν_{Os-Cl} *trans* to particular ligands were close to or slightly lower (as expected from the mass effect) than the corresponding ranges of ν_{Ru-Cl}.

(b) Metal–hydride stretching frequencies

Platinum(II) complexes Chatt et al.[147, 148] first noted that ν_{Pt-H} in the complexes *trans*-$PtHX(PEt_3)_2$ was very dependent on X, decreasing with increasing *trans*-effect of X. Subsequent work has verified this finding for these[149] and analogous series of complexes *trans*-$PtHXL_2$, where L = PPh_3 (refs 150–153), PPh_2Me (ref. 154), PEt_3 (ref. 155) and $AsEt_3$ (ref. 156). A corresponding dependence of ν_{Pt-H} on L′ was found for the cationic complexes *trans*-$PtH(L')L_2^+$, where L = PEt_3 (ref 97), PPh_3 (ref. 153), $PMePh_2$ (refs. 154, 157) and $AsEt_3$ (ref. 156). For the carboxylate complexes *trans*-$PtH(O_2CR)(PEt_3)_2$, a linear relationship between J_{Pt-H}, τ_H, ν_{Pt-H}, and pK_a for RCO_2H has been found[158]. The correlation between the various spectroscopic parameters will be discussed later. The fact that ν_{Pt-H} decreases as pK_a increases implies a direct correlation between the σ-electron donation from RCO_2^- to Pt and the *trans*-influence of the carboxylate ligand.

Some caution is required in the detailed interpretation of ν_{Pt-H} since this frequency can be solvent-dependent[148, 158, 159], with the magnitude of the solvent effect depending on the nature of the *trans* ligand. Solid state effects may also influence the Pt–H stretching frequency. For example, the ν_{Pt-H} region for solid *trans*-$PtHCl(PPh_3)_2$ is very complex, and differences in ν_{Pt-H} led Bailar and Itatani[160] to believe that they had isolated *cis* and *trans* isomers of this complex, when in fact they had crystal modifications of the *trans* isomer[161]

Significant vibrational coupling can occur when hydride is *trans* to a ligand with a vibration close in frequency to ν_{Pt-H} (~ 2000 cm^{-1}), e.g , CN^- (ref. 99), CO (refs. 97, 167), and RNC (ref 97). Such vibrational coupling can be detected by examining the ligand frequency of the analogous deuteride complex. Since ν_{Pt-D} has a frequency quite different (∿ 1500 cm^{-1}) from that of the ligand vibration, coupling is minimal and the ligand band occurs at its "unperturbed" frequency. The ν_{Pt-H} frequency in the hydride may then be "corrected" by assuming that the coupling is first order, i.e., the true value of ν_{Pt-H} is obtained by the addition of (ν(ligand) deuteride complex – ν(ligand) hydride complex) to the observed value of ν_{Pt-H}. From results for both cationic and neutral complexes and for complexes with different phosphines (changing the phosphine has a relatively small effect on ν_{Pt-H}) the *trans*-influence order shown in Table 6 is obtained.

Gavrilova et al.[153] reported values of ν_{Pt-H} for *trans*-$[PtH(C_2H_4)(PPh_3)_2]ClO_4$ and *trans*-$[PtH(C_3H_6)(PPh_3)_2]ClO_4$ which would place ethylene and propene higher in the *trans*-influence series than any of the ligands of Table 6. These values appear to be erroneous.

Attempts in this laboratory[163] to prepare $[PtH(C_2H_4)(PPh_3)_2]ClO_4$ have been unsuccessful because of the extremely rapid insertion of ethylene into the Pt–H bond, and it seems likely that Gavrilova et al. actually examined $Pt(C_2H_5)(PPh_3)_2(ClO_4)$, which would give similar analyses. (The NMR spectrum was not reported.) The band that they observed may have been an overtone of a perchlorate mode. For the complex *trans*-$[PtH(C_2H_4)(PMePh_2)_2]PF_6$, which was definitely characterized, no clear assignment of ν_{Pt-H} could be made from the infrared spectrum as all bands in this region were weak. but τ_H and J_{Pt-H} suggest a lower *trans*-influence for ethylene than isocyanides (see later).

TABLE 6

Metal–hydride stretching frequencies (cm^{-1}) as a measure of the *trans*-influence

---

A *For platinum(II) hydrides,* trans-*$PtHXL_2$ or* trans-*$[PtHL'L_2]^+$* [a, b]
Acetone (2275*) (ref. 157) $\leq$ ClO_4^- (2312**) (ref. 153) < NO_3^- (2242 hexane; 2267 $CHCl_3$) (ref. 149) $\simeq$ $CF_3CO_2^-$ (2258 acetone) (ref. 158) < p-$MeC_6H_4COO^{2-}$ (2226 acetone, 2216 cyclohexane) (ref. 158) < NCO^- (2234 (ref. 162), 2200 $CHCl_3$ (ref. 149)) $\simeq$ NCS^- (2195 (ref. 162), 2210 $CHCl_3$ (ref. 149)) $\simeq$ N_3^- (2199 $CHCl_3$) (ref. 149) $\simeq$ Cl^- (2183 hexane (ref. 147); 2209 $CHCl_3$ (ref. 149)) $\simeq$ Br^- (2178 hexane (ref. 147), 2199 $CHCl_3$ (ref. 149)) $\simeq$ NH_3 (2202, 2087**) (ref 153) $\simeq$ py (2216 $CHCl_3$) (ref 97) $\simeq$ NH_2CH_3 (2195**) (ref 153) < I^- (2156 hexane (ref. 147), 2175 $CHCl_3$ (ref 149)) $\simeq$ SCN^- (2160 $CHCl_3$) (ref. 149) < $-S{=}C(NH_2)_2$ (2150**) (ref 153) $\simeq$ $-SCOMe^-$ (2140**) (ref 152) $\simeq$ NO_2^- (2150 hexane (ref. 147); 2165 $CHCl_3$ (ref. 149)) < CO (2129 "corrected" $CHCl_3$) (ref. 97) $\simeq$ $SbPh_3$ (2130**) (ref 153) < t-BuNC (2214 "corrected") (ref 97) < p-$MeOC_6H_4$-NC (2106 "corrected") (ref 97) $\simeq$ $SnCl_3^-$ (2105 hexane?) (ref. 155) $\leq$ PPh_3 (2100 $CHCl_3$) (ref. 97) $\leq$ $P(OPh)_3$ (2090 $CHCl_3$) (ref. 97) $\simeq$ PEt_3 (2090 $CHCl_3$) (ref. 97) $\leq$ $P(OMe)_3$ (2067 $CHCl_3$) (ref. 97) $\simeq$ CN^- (2095 "corrected") (ref 99) < $-C{\equiv}CPh^-$ (2020 not corrected for any coupling) (ref. 111)

B. *For palladium(II) hydrides*[165], trans-*$PdHX[P(Cy)_3]_2$*
NCS^- (2022) < Cl^- (2002) $\simeq$ BH_4^- (2002) < Br^- (1991) < I^- (1966)

C. *For nickel(II) hydrides*[164,165], trans-*$NiHX[P(Cy)_3]_2$*
I^- (1976) < NCS^- (1928) < BH_4^- (1920) < Br^- (1917) $\simeq$ Cl^- (1916) < CN^- (1870)

---

[a] *Trans* ligand is X or L′; L = PEt_3 except that one asterisk indicates L = $PMePh_2$ and two asterisks indicates L = PPh_3

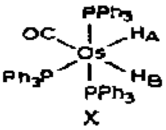
[b] Spectra obtained from samples prepared as Nujol mulls except where noted

Palladium(II) and nickel(II). Green et al.[164, 165] examined the nickel hydride complexes *trans*-$NiHX(PCy_3)_2$, from which ν_{Ni-H} frequencies give the *trans*-influence order of Table 6C. It is of interest that the ordering of the halogens, observed also for the analogous Ni^{II} tris(isopropyl)phosphine complexes, is the reverse of that obtained for Pt^{II} hydride complexes. However, the order of τ_H is the same as that for the Pt^{II} complexes (see later). For palladium(II), the halogen order is "normal" (Table 6B)[165, 166].

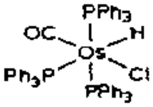
Iron, ruthenium and osmium complexes A number of iron(II) complexes of the type *trans*-$FeHX(\widehat{PP})_2$, where $\widehat{PP}$ is a chelating disphosphine, have been examined by Chatt and Hayter[168]. In the complex *trans*-$FeH_2[o\text{-}C_6H_4(PEt_2)_2]_2$, the Fe–H stretching frequency occurs at 1726 cm^{-1}, considerably lower than ν_{Fe-H} in *trans*-$FeHCl[o\text{-}C_6H_4(PEt_2)_2]$, 1870 cm^{-1}, which is consistent with the high *trans*-influence of H^- relative to Cl^-.

Chatt and Hayter[169] also examined a series of ruthenium (II) and osmium (II) complexes of the type *trans*-$MHX(\widehat{PP})_2$. The *trans*-influence order, determined from the decreasing order of M–H stretching frequencies for both metals, is $I^- < Br^- < Cl^- < SCN^- < NO_2^- < CN^- < H^-$. Chatt and Hayter noted that the overall sequence is similar to that obtained for Pt^{II}, namely halogens < SCN^- < NO_2^- < CN^-, but that the order of the halides is reversed. A similar reversal noted in the iron(II) complexes[168] was attributed to electronic effects; however, the order of τ values is normal[169, 170]. Since these complexes (like the nickel hydrides discussed above) are sterically crowded, steric constraints introduced by increasing halogen size may affect ν_{M-H}. There also seems to be a significant *cis*-influence of the chelating diphosphine or diamine on ν_{M-H}, considerably more pronounced than for Pt complexes[156].

Vaska[98] examined the infrared spectra of the complexes X and XI and their deuterated analogues. In X, ν_{Os-H_B} couples with ν_{CO} but ν_{Os-H_A} does not. Even



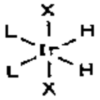
X



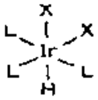
XI

allowing for this coupling, it is quite clear that ν_{Os-H_B} (1852 cm^{-1}) is considerably lower than ν_{Os-H_A} (2051 cm^{-1}) and ν_{Os-H} in XI (2097 cm^{-1}). These results suggest that in these complexes the *trans*-influence of CO is significantly greater than that of PPh_3, which reverses the order found for Pt^{II} cations[97].

Iridium(III) complexes Chatt et al.[171] found that ν_{Ir-H} in some hydride complexes of iridium(III) was dependent on the ligand *trans* to hydride Thus, in complexes of the type XII, where L is a tertiary phosphine or arsine and X is a halogen, ν_{Ir-H}

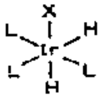


XII

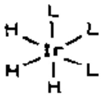


XIII

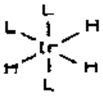
occurs in the range 2000–2100 cm^{-1} (2069 cm^{-1} for L = PEt_2Ph, X = Cl^-, 2076 cm^{-1} for L = $AsEt_2Ph$, X = Cl^-) and in the isomeric complexes XIII, ν_{Ir-H} occurs in the higher range 2195–2220 cm^{-1} (2186 cm^{-1} for L = PEt_2Ph, X = Cl^-). Dihydrides, XIV, show two ν_{Ir-H} bands near 2030 cm^{-1} (*trans* to halogen) and near 2170 cm^{-1} (*trans* to phosphine). The *fac*-trihydrido-complexes XV, where L = terti-



XIV



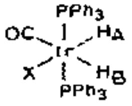
XV



XVI

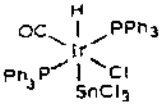
ary phosphine or arsine, show a strong band in benzene solution in the range 2020–2090 cm^{-1} (2025 for L = PEt_2Ph, 2058 for L = $AsEt_2Ph$). The *mer*-complexes XVI showed two ν_{Ir-H} bands, 2037–2104 cm^{-1} (*trans* to phosphine) and 1750 cm^{-1} for the ν_{Ir-H} (*trans* to H^-). This corresponds to a very high *trans*-influence for hydride.

For the complex[98] XVII (allowing for vibrational coupling between ν_{CO} and ν_{Ir-H_B}), ν_{Ir-H_B} is significantly lower ($\sim$ 2100 cm^{-1}) than ν_{Ir-H_A} (2196 cm^{-1}), in-



XVII

dicating a somewhat higher *trans*-influence for CO than for Cl^-. This is supported by the values of ν_{Ir-H} obtained by Chatt et al.[172] for the isomers of $IrHCl_2(CO)(PEt_2Ph)_2$. Wilkinson and co-workers[173], from an examination of some iridium(III) hydride complexes containing $SnCl_3^-$, concluded that $SnCl_3^-$ has a slightly higher *trans*-influence than Cl^-. For instance, the complex XVIII has ν_{Ir-H} (Nujol) at 2198,



XVIII

2160 cm^{-1} (solid-state splitting), while the corresponding chloride has ν_{Ir-H} at 2239 cm^{-1}. Some apparently contradictory results were also obtained, however, and the *trans*-influence of $SnCl_3^-$ for Ir^{III} does not appear[150, 155] to be as high relative to Cl^- as for Pt^{II}. The *trans*-influence series obtained from ν_{Ir-H} for Ir^{III} is thus $H^- \gg PR_3 \geq AsR_3 > CO \sim SnCl_3^- > Cl^-$

(c) Metal–carbon stretching frequencies

Platinum(II) complexes The ν_{Pt-CH_3} bands in the infrared spectra of complexes such as *trans*-$Pt(Me)X(PR_3)_2$ and *cis*-$PtMe_2L_2$ are characteristically weak but two bands have been assigned[174] for the *cis* dimethyl compounds and only one for *trans*-$PtMeX(PR_3)_2$. The Pt–C stretching frequencies are dependent on the nature of the ligand *trans* to the methyl group, decreasing in the order (with frequencies (cm^{-1}) for the PEt_3 complexes in benzene): NO_3^- (566) > NCS^-(556) > Cl^- (551) > Br^- (548) > NO_2^- (544) > I^- (540) > CN^- (516), the reverse order of which represents the *trans*-influence series. Some ambiguity is associated with the frequencies of ν_{Pt-CH_3} *trans* to NO_2^- and CN^- since the Pt–X stretching vibration, with which there could be appreciable vibrational coupling, is nearby. The $Pt-CH_3$ stretching frequency for *cis*-$PtMeCl(PEt_3)_2$ at 527 cm^{-1}, is considerably lower than that of the *trans* isomer, consistent with the high *trans*-influence of PEt_3.

Since the complexes *cis*-$PtMe_2L_2$ give two Pt–C stretching bands a comparison of results with those obtained for the *trans*-monomethyl compounds is difficult but where $L = PR_3$, the frequencies are low (526 and 506 cm^{-1} for $L = PEt_3$) and for $L = EtSCH_2CH_2SEt$, the frequencies are higher (555 and 548 cm^{-1}). Fritz and Sellmann[175] assigned a band at 550 cm^{-1} in the infrared spectrum of $PtMe_2(COD)$ to ν_{Pt-CH_3}, and a corresponding band appears[114] in the Raman spectrum at 545 cm^{-1}. Thus the expected two stretching modes are apparently degenerate, and the value of ν_{Pt-CH_3} indicates a *trans*-influence for COD similar to that of $EtSCH_2CH_2SEt$.

TABLE 7

Metal–carbon stretching frequencies (cm^{-1}) and the *trans*-influence

---

A *For the complexes* trans-*PtMeL* $(PMe_2Ph)_2^+$ *(with frequencies for representative ligands)*
L = Carbenes ($C(OCH_3)CH_3$, 514) (ref. 176) > phosphines (PMe_2Ph, 527; PPh_3, 528) (ref. 114) > $SbPh_3$ (531) (ref. 114) > isocyanides (CNEt, 537) (ref 177) > $CH_3{-}CH{=}CH_2$ (542) (ref 179) > CO (545) (ref. 114) $\simeq$ $CH_2{=}C{=}CH_2$ (545) (ref. 178) > $CH_3C{\equiv}CCH_3$ (547) (ref. 179) > C_2H_4 (549) (ref 179) $\simeq$ Ar_FCN (C_6F_5CN, 549) (ref 180) > $CH_2{=}CH{-}CH{=}CH_2$ (550) (ref. 178) $\geqslant$ iminoethers ($NH{=}C(OMe)C_6F_5$, 551) (ref. 180) > py (555) (ref 114) > ArCN (*p*-MeC_6H_4CN, 570) (ref. 180)

B *For the complexes* $[PtMe_3X]_4$ *and* $PtMe_3L_3^+$
$Me_3Pt(OH_2)_3^+$ (600) (ref. 181) < $[PtMe_3(OH)]_4$ (595) (ref 182, 183) < $Me_3Pt(NH_3)_3^+$ (584) (ref. 184) $\simeq$ $[Me_3Pt(NO_2)_3]^{2-}$ (583) (ref. 185) $\leqslant$ $[Me_3PtCl]_4$ (581) (ref. 186) < $[Me_3Pt(py)_3]^+$ (578) (ref. 185) $\simeq$ $Me_3Pt(NHMe_2)_3^+$ (577) (ref. 185) < $[Me_3PtBr]_4$ (574) (ref. 186) $\simeq$ $(\pi\text{-}C_5H_5)PtMe_3$ (594, 561) (ref 187) < $[Me_3PtSH]_4$ (563) (ref. 188) $\simeq$ $Me_3Pt(SCN)_3^{2-}$ (563) (ref 185) $\leqslant$ $[Me_3PtI]_4$ (560) (ref 186) < $Me_3Pt(p\text{-}MeC_6H_4NC)_3^+$ (555) (ref 189) $\leqslant$ $Me_3Pt(CN)_3^{2-}$ (553) (ref. 185) < $Me_3Pt(PMe_2Ph)_3^+$ (530, 525, 510) (ref. 189)

C *For the complexes* $PtMe_2(PMe_2Ph)_2L_2^{2+}$ (XIX) (higher frequency band) (ref. 190) *p*-MeC_6H_4CN (561) $\simeq$ bipy (562) $\simeq$ phen (560) < py (546) < *p*-MeC_6H_4NC (539) < diphos (536) < $P(OMe)_3$ (523) < *o*-$C_6H_4(AsMe_2)_2$ (513)

D *For the complexes* $PtMe_3(PMe_2Ph)_2L^+$ *(XX) (*trans *to L)* (ref 189)
py (569) < EtNC (546) < *p*-MeC_6H_4NC (541) < $SbMe_3$ (539) < PMe_2Ph (530)

E *For the complexes* $PtMe_3X(bipy)$ *(frequencies* trans *to X)*[185a]
NO_3^- (580) < $CH_3CO_2^-$ (577) $\simeq$ NCO^- (577) < Cl^- (575) < Br^- (570) $\simeq$ NO_2^- (569) < I^- (563) $\simeq$ NCS^- (562) $\ll$ CH_3^- (480)

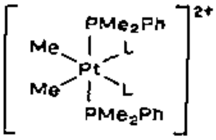
A comparison of ν_{Pt-CH_3} for corresponding complexes *trans*-$PtMeXL_2$, where L = PMe_2Ph (ref. 108) and $AsMe_2Ph$ (ref 109) suggests that this change in the *cis* ligand has little effect on this frequency.

Pt–CH_3 stretching bands have also been observed in the Raman spectra (where they occur as strong and polarizable bands) of some solid salts of the cationic complexes *trans*-$PtMeL(PMe_2Ph)_2^+$, to give the *trans*-influence order for L shown in Table 7A.

Platinum(IV) complexes. Many methylplatinum(IV) compounds contain more than one methyl group so that coupling between the various Pt–C stretches makes it impossible to assign a particular Pt–CH_3 stretching vibration. However, for the complexes $[PtMe_3X]_4$, where each Pt atom is attached to three triply bridging X groups, and $PtMe_3L_3^+$, the symmetric and antisymmetric Pt–Me stretching frequencies are often degenerate, which allows a direct comparison between X and L groups. The ν_{Pt-Me} bands are generally weak in the infrared, but strong in the Raman spectra, and the order of *trans*-influence in Table 7B can thus be obtained. Note that in the Raman spectra of $PtMe_3(PMe_2Ph)_3^+$, the molecular symmetry is apparently less than C_{3v} so the degeneracy of the *E* mode is removed and the expected three bands are observed[189]. It is also noteworthy that although X^- ions are triply bridging in

$[PtMe_3X]_4$, their relative *trans*-influences seem comparable to those expected for monodentate X^-.

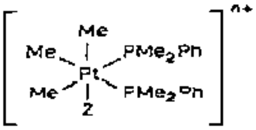
For the platinum (IV) cations XIX, Clark and Manzer [190] observed two Pt—Me



XIX

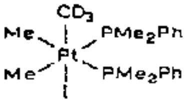
stretching bands, in most cases, in the Raman spectra corresponding to symmetric and asymmetric stretching. The frequencies are dependent on L and are given in Table 7C. Some anomalies in this sequence (e.g., the large difference between bipy and py, and the very low value for the diarsine ligand compared with diphos), suggest that the (reverse) *trans*-influence order is not accurately defined by these values. It seems clear [190] that severe steric crowding occurs in the diphos complex, which is probably largely responsible for the anomalous position of this ligand.

For the trimethylplatinum (IV) compounds, XX, Clark and Manzer [189] observed three Pt—Me stretching vibrations. A comparison of the solid state Raman spectra



XX

(a) $Z = I^-$, $n = 0$
(b) $Z = L$, $n = +1$



XXI

of XXa and XXI (Fig. 3) indicates that ν_{Pt-Me} (*trans* to I) is virtually independent of the two stretching modes involving methyl groups *trans* to phosphine since the first mode on deuteration shifts to lower frequency by the factor $(15/18)^{1/2}$ with the other two bands being virtually unchanged (Fig. 3). Thus it would be expected that ν_{Pt-Me} (*trans* to L) in XXb would be sensitive to L, while the two ν_{Pt-Me} (*trans* to PMe_2Ph) would not. Experimental results confirm this expectation [190] (Table 7B). A similar situation [185a] holds for $PtMe_3X(bipy)$.

Ruddick and Shaw [108] found that in the complex $PtMe_4(PMe_2Ph)_2$, the mutually *trans* Pt—Me groups gave a very low value of ν_{Pt-Me} (476 cm^{-1}) consistent with the very high *trans*-influence of the methide ion.

Iridium(III) complexes. In some Ir^{III} complexes, ν_{Ir-Me} is dependent [141] on the *trans*-ligand, e.g., in the complex XXIIa, ν_{Ir-Me} *trans* to Cl^- occurs at 543 cm^{-1},

XXII

(a) X = Cl, L = PMe_2Ph
(b) X = I, L = PMe_2Ph
(c) X = I, L = $AsMe_2Ph$

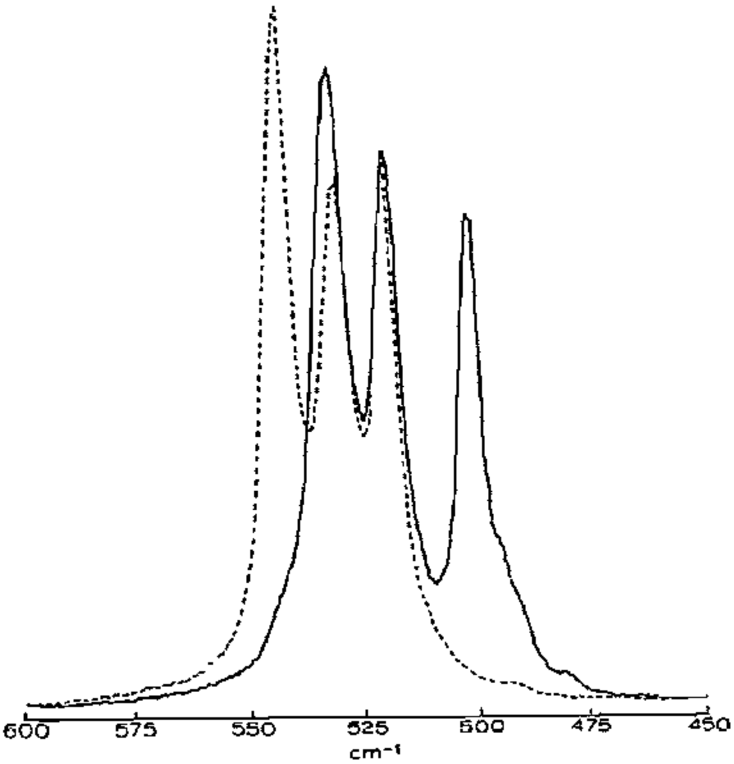


Fig. 5. Pt–CH$_3$ stretching region of (– – –) PtI(CH$_3$)$_3$(PMe$_2$Ph)$_2$ and (——) PtI(CH$_3$)$_2$(CD$_3$)-(PMe$_2$Ph).

but *trans* to PMe$_2$Ph near 495 cm^{-1} (this band is partially obscured by a ligand vibration). In XXIIb $\nu_{\text{Ir-Me}}$ (*trans* to I) occurs at 526 cm^{-1} and *trans* to PMe$_2$Ph at 505 cm^{-1}. In the corresponding arsine complex XXIIc the frequencies are 527 (*trans* to I) and 518 (*trans* to AsMe$_2$Ph). The frequencies *trans* to L may be compared with those for *mer*-IrMe$_3$L$_3$; 510, 495 cm^{-1} for L = PMe$_2$Ph and 517, 510 cm^{-1} for L = AsMe$_2$Ph. These results suggest a *trans*-influence order PMe$_2$Ph > AsMe$_2$Ph > I > Cl.

Gold (III) complexes Tobias and co-workers [191] examined the vibrational spectra of some gold (III) complexes, AuMe$_2$Y(PR$_3$) (Y = Cl, Me, σ-Cp). The Au–Me stretching frequencies were in the range 540–544 cm^{-1} for methyl *trans* to PR$_3$, 514 cm^{-1} for $\nu_{\text{Au-Me}}$ *trans* to σ-Cp, and 504–511 cm^{-1} for the symmetric and asymmetric stretching frequencies for the mutually *trans* methyl groups. The complex *cis*-AuClMe$_2$-(PPh$_3$) gave two bands at 542 and 549 cm^{-1}; the high frequency band corresponding to $\nu_{\text{Au-Me}}$ *trans* to Cl$^-$ The *trans*-influence order is Me > σ-Cp > PR$_3$ > Cl.

(d) Metal–nitrogen stretching frequencies

Powell [192], in one of the earliest infrared investigations of the *trans*-influence examined ν_{Pt-NH_3} in complexes of the type *trans*-$Cl_2PtL(NH_3)$. The order of ν_{Pt-NH_3} was NH_3 (507 cm^{-1}) > Et_2S (493) > C_2H_4 (481).

For *cis*- and *trans*-$PtX_2(NH_3)_2$, Nakamoto et al.[95] observed that ν_{Pt-NH_3} moved to lower frequency as X was changed from Cl to Br to I, this trend being more pronounced for the *cis* isomers. They ascribe this to the different *trans*-influences of the halogens.

Watt and Cuddeback[117] correlated ν_{Pt-N}(*sym*) for a number of ethylenediamine complexes $[Pt(en)L_2]X_2$ with the *trans*-influence of L. The order obtained was $Ph_2AsCH_2CH_2AsPh_2$ (598) < bipy (583) ≃ phen (582) < diphos (558) < $NC{-}\underset{S^-}{C}{=}\underset{S^-}{C}{-}CN^{2-}$ (551) ≃ PPh_3 (551). The position of the diarsine ligand appears to be anomalous.

Clegg and Hall[184] noted that ν_{Pt-NH_3} in the Raman spectrum of aqueous $[PtMe_3(NH_3)_3]Cl$ occurred at 390 cm^{-1} and was considerably lower than ν_{Pt-NH_3} in $[Pt(NH_3)_6]^{4+}$ (569, 545 cm^{-1}), consistent with the high *trans*-influence of the methyl group.

For the complexes[195] *trans*-$PtX_2(NH_2CH_3)_2$, the Pt–N stretching frequency varied only within the range 507–513 cm^{-1}. For the *cis* complexes, the variation was over the wider range 483–517 cm^{-1} in the order Cl^- > NO_2^- > Br^- > SCN^- > I^-. In this series, NO_2 seems to be out of order, perhaps owing to a mis-assignment, or to vibrational coupling since ν_{Pt-NO_2} would be expected to occur near $\nu_{Pt-NH_2CH_3}$.

Lever and Mantovani[193] observed that for the complexes Cu (diamine) X_2, the order of Cu–N force constants decreased in the order NCS > NO_3 > halogens, which corresponded to the reverse order of the spectrochemical series obtained from visible–UV spectra. The results were explained in terms of a variation of effective charge on copper. The situation is complicated since the complexes are probably tetragonal with long axial Cu---X "bonds".

In the complexes *trans*-$RhX_2(cyclam)^+$ (where cyclam = 1, 4, 8, 11-tetraazocyclotetradecane)[194], a single Rh–N stretching band was observed in the infrared ranging in frequency from 482 (X = I) to 501 (X = Cl) cm^{-1}. For the *cis* complexes, two N atoms are *trans* to X and two Rh–N stretching bands were observed. From these frequencies (in parentheses) a *trans*-influence order was obtained: NO_2^- (479, 412) > I^- (470, 423) > Br^- (477, 450) > Cl^- (505, 459) ≃ N_3^- (490, 459) > N (cyclam) > NCS^- (533, 480)

(e) Metal–phosphorus stretching frequencies

Coates and Parkin[106] assigned the Au–P stretching mode to bands of moderate intensity in the frequency range 347–381 cm^{-1} in the infrared spectra of some complexes $Me_3P{-}Au{-}X$. This frequency depends on the *trans* ligand and is inversely related to the *trans*-influence order: Cl^- (381) < Br^- (376) < I^- (371) < $(-C{\equiv}C{-}Bu^t)^-$ (368) < Me^- (357) < $-C{\equiv}C{-}Ph^-$ (347). For the complexes $Me_3P{-}Au{-}X$, where X^- is a halide, Goggin and co-workers[92] made similar assignments of ν_{Au-P}, and also assigned ν_{Au-P} for the cation $Au(PMe_3)_2^+$ at 351 cm^{-1}, consistent with a high *trans*-influence for PMe_3 itself.

Various workers[92, 94, 102, 106, 115, 116, 127, 130] have discussed M–P stretching bands in Ni^{II}, Pd^{II} and Pt^{II} complexes of PMe_3 and PEt_3. The complexes *cis*-MX_2L_2

characteristically give two ν_{M-P} bands, while complexes *trans*-MX_2L_2 give only one[115]. In the *trans* complexes PtX_2L_2 and $PtXYL_2$ (L = PMe_3, PEt_3) ν_{Pt-L} is almost insensitive to X and Y, occurring[115] in the range 409–418 cm^{-1}. For the *cis* complexes[115], with L = PEt_3, the mean of the two Pt–P frequencies varies in the order $X = Cl^-$ (435) > Br^- (434) > $-NCS^-$ (432) > $-C_6F_5^-$ (423) > $-C_6H_5^-$ (417). For the *cis* complexes $PtX_2(PMe_3)_2$, Goggin and co-workers[94] noted that ν_{Pt-P} decreased in the order Cl^- (391) > Br^- (388) > I^- (383), but as usual it is difficult to separate vibrational from mass effects. It was also noted that ν_{Pt-PMe_3} was considerably lower in *trans*-$PtCl_2(PMe_3)_2$ (346 cm^{-1}) than in the *cis* isomer, consistent with a high *trans*-influence of PMe_3 itself. ν_{Pt-PMe_3} was also relatively high in the chloro-bridged dimer $Pt_2Cl_4(PMe_3)_2$ (393 cm^{-1}, *trans* to Cl^-)[115] and $[Pr^n{}_4N]$-$[PtCl_3(PMe_3)]$ (388 cm^{-1})[127]. In the complex $[PtCl(PMe_3)_3]NO_3$ ν_{Pt-PMe_3} (*trans* to Cl^-) occurs at 403 cm^{-1}, while the asymmetric and symmetric stretching frequencies for the mutually *trans* phosphines occur at 365 and 368 cm^{-1} respectively, again consistent with the high *trans*-influence of PMe_3 relative to Cl^-.

Analogous results were obtained for corresponding palladium complexes although trends are sometimes less pronounced. Goggin and co-workers[94] have suggested that this indicates a smaller *trans*-influence for Pd^{II} compared with Pt^{II}.

For Ni^{II}, only *trans* complexes NiX_2L_2, where L = PMe_3, PEt_3, have been examined. For these complexes ν_{Ni-PEt_3} was not very sensitive to X, the range[115] being 412–421 cm^{-1}.

(iii) Internal ligand vibrations

(a) N–H stretching vibrations

An examination of the *trans*-influence in Pt^{II} complexes by Chatt et al.[196], by measuring N–H stretching frequencies in a series of complexes *trans*-$PtCl_2L$(amine), is now of mainly historical interest, and having been discussed in previous reviews[2] will be mentioned only briefly here. The assumption was made that for a given amine (*p*-toluidine or piperidine), increasing negative charge on N (corresponding to a weaker Pt–N bond) increases the N–H force constant. The order of decreasing ν_{N-H} (i.e., decreasing *trans*-influence) was PR_3 > SbR_3 > $P(OR)_3$ > AsR_3 > R_2Te > C_2H_4 > R_2Se > R_2S > piperidine > 4-*n*-pentylpyridine. This sequence is similar to those obtained more recently by examining directly metal–ligand stretching frequencies.

(b) C≡O stretching frequencies in carbonyl complexes

It is well accepted that CO uses synergic σ–π bonding as illustrated schematically in Fig. 4 (a)[197]. Overlap occurs between filled metal d_π orbitals and the vacant carbonyl π^* orbital. This π-back-donation synergistically strengthens the M–CO σ-bond. If ν_{CO} is considered to be dominated by the degree of M→CO π-donation[198], an increase in the occupation of the CO π^* orbitals will decrease ν_{CO}. Because of the σ–π synergism, ν_{CO}, or force constants derived from ν_{CO} values, might be expected to provide a measure of the metal–CO bond strength, a lower C–O force constant indicating a stronger M–C bond. For some series of complexes this appears to be so; for example, in the series $Ni(PMe_3)_n$-

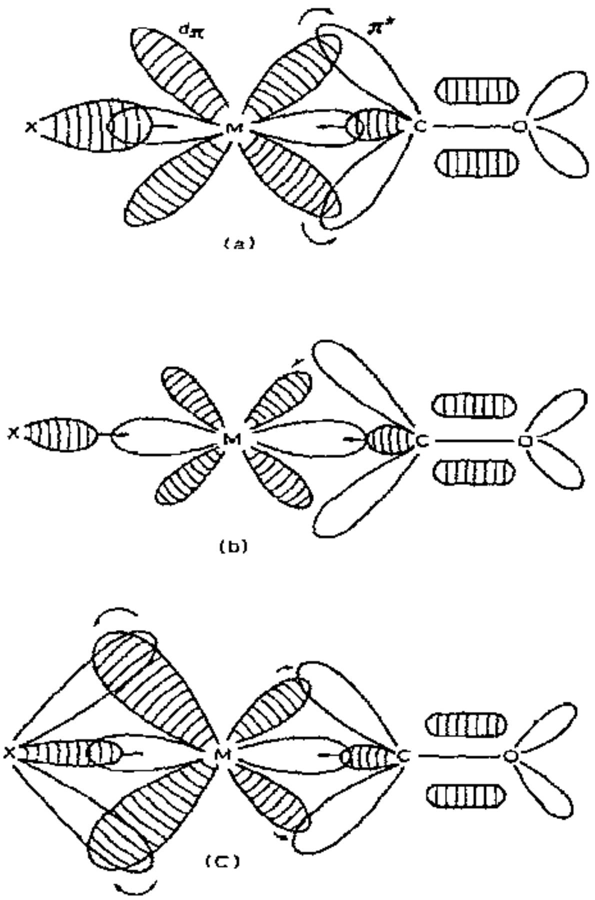


Fig. 4. Effect of the *trans* ligand X on the bonding of coordinated carbonyl (a) X good σ-donor, poor π-acceptor; (b) X poor σ-donor, poor π-acceptor, (c) X good π-acceptor.

$(CO)_{4-n}$ (n = 0–3), the Ni–C force constant increases, and the C–O force constant decreases as n increases[199]. However, in other cases, C–O and M–C force constants appear to decrease together, as for example[200] in (bidentate) $Mo(CO)_4$.

In the complexes *cis*-$PtX_2(CO)L$, Denning and Ware[129] assigned ν_{Pt-CO} to a band in the range 505–540 cm^{-1}, contradicting earlier assignments[201,202]. Where L = PEt_3 and X = Cl, Br, I, it was found that ν_{CO} and ν_{Pt-CO} decreased together as X was changed from Cl to I, so that any change in the Pt–C force constant in the opposite direction to ν_{CO} was outweighed by the mass effect from introducing heavier halogens. Thus, it seems that ν_{CO} cannot always be used as a reliable guide to the strength of the M–CO bond.

There are several ways in which ν_{CO} could be affected by changing the *trans* ligand, X, in a series of complexes such as *trans*-$MX(CO)L_2{}^{n+}$.

(*i*) If X^- is a good σ-donor (i.e., transfers much charge toward the metal) the effective electron density on the metal is increased. Then (*a*) the filled d_π-orbitals would be expected to expand, facilitating π-overlap between the metal and CO, and thus reducing ν_{CO} (Fig. 4(a))[203], and (*b*) the increased M→CO π-bonding will tend to increase the strength of the OC→M σ-bond[203] (Fig. 4b) while the increased negative charge on the metal will tend to reduce OC→M σ-bonding[200]. As the σ-bonding increases, ν_{CO} tends to increase.

(*ii*) If X^- has a high *trans* influence, OC→M σ-bonding would tend to be reduced, and any lengthening of the C—M bond will tend to reduce π-back-bonding. Both effects will cause a decrease in ν_{CO}.

(*iii*) If the X—metal bond requires a significant π-component (*a*) X will compete with CO for the metal π-orbitals, reducing M—CO π-back-bonding (Fig. 4(c)), and (*b*) if substantial negative charge is removed from the metal by M—X π-bonding the effect will be similar to that obtaining if X were a poor σ-donor, i.e., all filled metal d_π-orbitals would tend to contract including d_π-orbitals not involved directly in M—X π-bonding. The effects noted in (*i*) (*b*) will then occur.

The situation is clearly complex, and the various effects are difficult to separate in any but the simplest cases. For the cationic complexes[203] *trans*-$PtMe(CO)(PMe_2Ph)_2^+$ and *trans*-$Pt(CF_3)(CO)(PMe_2Ph)_2^+$, CH_3^- and CF_3^- differ mainly in the charge transferred to the metal (i.e., (*i*) (*a*) and (*b*) should be the most important effects). Effect (*i*) (*a*) causes ν(CO) to be higher for the $-CF_3$ (2140 cm^{-1}) than for the $-CH_3$ (2095 cm^{-1}) complex. In these relatively electron-deficient complexes the net effect[203] of (*i*) (*b*) appears to be a decrease in OC→Pt σ-bonding when $-CH_3$ is replaced by $-CF_3$; that is, the synergic effect of Pt—CO π-bonding on the Pt—CO σ-bond outweighs any increase in σ-bonding from the lower effective negative charge on Pt.

For the relatively electron-rich complexes (e.g., $L_2Mo(CO)_4$), the anomalous variation of ν_{Mo-CO} with ν_{CO} has been explained in terms of increased effective charge on Mo causing a decrease in Mo—CO σ-bonding, in spite of an increase in Mo—CO π-bonding.

Vaska and Peone[205] proposed that for the complexes *trans*-$M(CO)X(PPh_3)_2$ (M = Ir, Rh), ν_{CO} can be used to provide a scale of "total electronegativities"

$$\chi_{X(T)} = \chi_{X(\sigma)} + \chi_{X(\pi)} \tag{1}$$

where $\chi_{X(\sigma)}$ is a "classical" or "σ" electronegativity and $\chi_{X(\pi)}$ a "π-electronegativity" or "π-acidity" of X. Assuming that $\chi_{F(T)} = \chi_{F(\sigma)}$, they used the relation

$$\chi_{X(T)} = \chi_F(\Delta\nu^2_{CO})_F/(\Delta\nu^2_{CO})_X \tag{2}$$

where $(\Delta\nu^2_{CO})_X = [\nu_{CO}(\text{gas})]^2 - [\nu_{CO}(\text{complex in } CHCl_3)]^2$. Comparing $\chi_{X(T)}$ with a theoretical value[206] of $\chi_{X(\sigma)}$ a sequence for $\chi_{X(\pi)}$ was calculated: I > SePh > Br > SPh > CN > Cl > NO_2 > NCS ≃ N_3 > ONO_2 > NCO > OCOMe > OCOPh > OPh > OH ≃ F. However, this series seems suspect for the following reasons.

(*a*) No account is taken of factor (*ii*) above, or the complications involved in (*i*) (*b*).

(*b*) There seems to be no reason for supposing that removal of a given electronic charge from the metal by σ-bonding (which can only have an indirect effect on metal *d*-orbitals) will have the same effect on ν_{CO} as removal of the same charge from metal *d*-orbitals by π-bonding. That is, ν_{CO} more probably correlates with $(\chi_{X(\sigma)} + \lambda\chi_{X(\pi)})$, where λ is a constant.

(*c*) It is not clear that electronegativities such as those obtained by Wilmshurst[206] refer only to σ-effects, rather than the overall tendency of X to gain electrons from any source.

(*d*) The values calculated by Vaska and Peone[205] seem unrealistic for some ligands For example, $\chi_{Cl(\pi)}$ is calculated to be 1.25 (for M = Ir^{III}) compared with $\chi_{Cl(\sigma)} = 2.94$. That is, the π-electronegativity of Cl is 0.43 of its σ-electronegativity This does not fit in with the usual picture of Cl^- as a weak π-donor. A detailed discussion of ν_{CO} in the related series *trans*-$PtX(CO)L_2^+$ is also difficult[204].

For the formally iridium(III) complexes $IrCl(CO)(PPh_3)_2XY$, a linear correlation was observed[207] between ν_{CO} and the Mossbauer center shift for the ^{193}Ir nucleus. Since the latter depends on *s*-electron density at the iridium nucleus (increased by σ-donation, decreased by π-back-bonding), this suggests a correlation between ν_{CO} and the σ-electronegativities of X and Y.

For the polycarbonyl complexes, $Z_mM(CO)_n$, the situation is more complex, although many attempts have been made to use ν_{CO} or force constants derived from IR frequencies to provide information about the bonding of Z, and in particular to determine the σ- and π- (if any) components of this bonding. A detailed discussion of this field is beyond the scope of this review, but an outline will be given of some of the approaches that have been made, since these usually involve assumptions about σ-inductive effects that are related to the *trans*-influence.

There is general agreement that as the net (σ and π) electron donation from Z increases (or the net electron acceptance of Z decreases) k_{CO} tends to decrease[89, 198, 208] but there is considerable controversy about the relative importance of σ- and π-bonding of Z, especially when Z is a substituted phosphine. In many of the earlier interpretations[198, 209, 210] of CO stretching frequencies, changes in π-bonding of Z as Z was changed were usually considered to have the dominant effect on ν_{CO}. Thus, Cotton[198b] considered that k_{CO} indicates the C—O bond order and he performed a rough quantitative calculation of the electrons involved in Mo—CO π-bonding in $Mo(PF_3)_3(CO)_3$ compared with $Mo(CO)_6$ and thus estimated that PF_3 is 1 32 times stronger as a π-acceptor than CO itself. More recently, few authors[208] have considered changes in M—Z π-bonding to be dominant. At the other extreme, Bigorgne[199, 211], on the basis of a correlation between k_{CO} and Taft's polar substituent constants σ^* for substituents on phosphorus in L, concludes that any effect of Ni→L π-bonding on ν_{CO} is negligible compared with that of L→Ni σ-bonding. Similarly Angelici[212], noting that ν_{CO} in $LW(CO)_5$ varied with the pK_a of L in a similar way when L represents amines or phosphines considered that changes in L→W σ-bonding alone were sufficient to cause the observed variations in ν_{CO}.

Graham[89] considered that σ- and π-effects can both be important in complexes $ZM(CO)_5$, and that they can be separated using C—O force constants The assumptions are made that:

(*a*) The σ-inductive property of a given ligand operates equally in all five carbonyl groups. That is, there is no *trans*-influence and factor (*ii*) (p. 375) is negligible.

(*b*) The π-acceptor property of a ligand has twice the effect on the *trans* carbonyl that it has on the *cis*, since the *trans* carbonyl shares two metal d_π-orbitals with X, while the *cis* carbonyls share only one.

Assumption (*a*) has been criticized by Church and Mays[97].

Assumption (*b*) ignores any effect of (*i*) (*b*) (p. 375). In the complexes $XMn(CO)_5$ Graham concluded that the π-properties of $-CH_3$, $-C_6H_5$, $-CF_3$, $-C_6F_5$ were negligible (σ-donor strength decreased in the above order), and that halides were π-donors and Y_3M groups (M = Si, Ge, Sn, Pb) and Au—PPh_3 were strong σ-donors and π-acceptors. In the complexes $LMo(CO)_5$ the phosphines, phosphites, $AsPh_3$, and $SbPh_3$ were considered to be strong π-acceptors and σ-donors, with PF_3 and CO being the strongest π-acceptors. SEt_2 was a weak π-acceptor, amines and CH_3CN were moderate π-donors and interacted little with π-orbitals, $Pr^i{}_2O$ was a weaker σ-donor and a moderate π-donor, and methyl formamide and dimethylformamide strong π-donors Stewart and Treichel[213] used Graham's method on the analogous $LW(CO)_5$ compounds with similar results

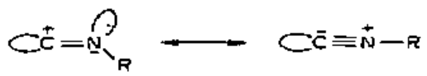
Darensbourg and Brown[214] consider that the intensities of C—O stretching bands give the best indication of the electronic populations of CO π-orbitals. Using intensities in combination with frequencies, they concluded that in the complexes $LMo(CO)_5$ phosphines had appreciable π-acceptor properties.

At present, the relative importance of σ- and π-effects in M—PX_3 C—O stretching frequencies must still be considered an open question. The complexity of the problem is such that an unequivocal answer probably lies some distance in the future.

N—O stretching frequencies in nitrosyl complexes are also sensitive to the nature of other groups coordinated to the metal[210, 215].

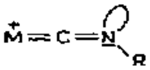
(c) C≡N stretching frequencies

The C≡N stretching frequencies in cyanide, organic nitrile and organic isocyanide complexes depends on the nature of other ligands bound to the metal. Cotton and Zingales[216] showed that ν_{NC} for some organic isocyanides increased when the isocyanide was coordinated to a metal ion which has little tendency to π-back-bond. Such frequency increases on coordination for C≡N groups have been examined by a molecular orbital treatment by Purcell and Drago[217, 218]. In valence bond terms, the increased frequency on coordination (illustrated for RNC, analogous structures may be drawn for CN^- and RCN) results mainly from an increased N—C force constant due to the greater contribution from the canonical form B when the carbon lone pair is donated to a metal ion (i.e , the negative charge on C in B is partially transferred to the metal). Kinematic coupling between



A B

$\nu_{C\equiv N}$ and ν_{M-C} cause only a minor increase in $\nu_{C\equiv N}$. For a series of related complexes, this σ-inductive effect would be expected to increase with increasing positive charge on the metal. Cotton and Zingales[216] also showed that when the metal to which RNC was coordinated was capable of π-back-bonding (e g., zerovalent metals), ν_{NC} was considerably reduced owing to contributions (again in valence bond terms) from the form



Within a series of complexes, π-back-bonding to the ligand would depend on the charge on the metal. When ν_{NC} is influenced by a combination of both σ-inductive and π-bonding effects, it is difficult to separate out these contributions, but in general ν_{NC} will increase with increasing positive charge on the metal. Thus, Halpern and Maher[219] observed that the complexes $[Co(CN)_5X]^-$ gave a single broad ν_{CN} band (presumably composed of the expected three bands), whose frequency tended to decrease with increasing electron donation by X in the order: CN^- (2134 cm^{-1}) > H_2O (2128) > Br^- (2125) > Cl^- (2124) > I^- > (2117) > $-CH_2SO_3^-$ (2113) > $-CH_2CO_2^{2-}$ (2106) ⩾ $-CH_2CO_2Me^-$ (2105) ⩾ $-CH_2CONH_2^-$ (2103) > H^- (2098) > $-CH_2CH_2CO_2^{2-}$ (2097) ⩾ $-CH_2CH_2CO_2Me^-$ (2096) ⩾ $-CH_3^-$ (2094) ≃ $-CH_2CH_3^-$ (2094) ⩾ $-CH_2Ph^-$ (2093). Since cyanide groups *cis* and *trans* to X were affected similarly, the changes in ν_{CN} must be interpreted in terms of metal electron density rather than competition between CN^- and X^- for metal d_π orbitals. A rather similar series was obtained for ν_{CN} *trans* to X^- in some cobalt(III) corrinoid complexes (vitamin B_{12} analogues)[220].

For Pt^{II} complexes, ν_{NC} for nitriles[180] and isocyanides[177] has been interpreted in terms of charge on platinum. For the series of complexes *trans*-$[PtMe(PMe_2Ph)_2(p\text{-}NC\text{-}C_6H_4\text{-}X)]^+$ Clark and Manzer[180] observed a correlation between ν_{NC} and the Hammett substituent constant for the aromatic substituent X^-. For the complexes *trans*-$PtR(CN)(PMe_2Ph)_2$ and *trans*-$PtRL(PMe_2Ph)_2$, where L = RCN, RNC, CO, $\nu_{C\equiv X}$ shows a consistent increase when R is changed from $-CH_3$ to $-CF_3$, owing to the greater electronegativity[203] of $-CF_3$.

(d) $-CH_3$ deformations

Adams et al.[174] noted that the symmetrical $-CH_3$ deformation band (near 1200 cm^{-1}) in their methylplatinum(II) complexes followed the same sequence as ν_{Pt-Me} within a series of complexes. In fact there was a linear relationship between the two frequencies. Subsequent workers have found similar relationships for Pt^{IV} (ref. 186) and Ir^{III} (ref. 141) complexes.

(iv) Nuclear magnetic resonance coupling constants

(a) Theory of coupling between directly bound nuclei

In most discussions of J_{AB}, where atoms A and B are bound by a covalent bond and have nuclei with spin quantum numbers $I = \pm\frac{1}{2}$, the coupling is thought to be dominated by the Fermi contact term[221]. This assumes that contributions to the coupling from interaction of the nuclear spin of the atom A (or B) with the electronic orbital motion are negligible, and that the Fermi contact interaction at the nucleus between the nuclear spin and *s*-electrons (which have a finite density at the nucleus) makes the dominant contribution. Approximate calculations[222, 223] on platinum complexes have supported this assumption. J_{AB} is then given by

$$J_{AB} \propto \gamma_A \gamma_B \alpha_A^2 \alpha_B^2 |\psi_{A(ns)}(0)|^2 |\psi_{B(ns)}(0)|^2 ({}^3\Delta E)^{-1} \qquad (3)$$

where γ_A is the gyromagnetic ratio for the nucleus A, α_A^2 is the *s*-character of the bonding hybrid orbital used by A in the A–B bond, $|\psi_{A(ns)}0|^2$ is the electron density of the *ns* valence orbital at the nucleus, and ${}^3\Delta E$ is a mean singlet–triplet excitation energy.

(b) Platinum–phosphorus coupling constants

For the complexes $PtCl_2(PR_3)_2$, the coupling between ^{195}Pt ($I = \frac{1}{2}$, 33.8% natural abundance) and ^{31}P ($I = \frac{1}{2}$, 100% abundance) is greater[10, 11] for the *cis* isomers than for the *trans* isomers. This was initially explained in terms of competition between phosphines for platinum *d*-orbitals (see earlier discussion). However, Pidcock et al.[1] showed that the results can be explained in terms of the appropriate form of eqn. (3) where A and B are Pt and P. They considered that within a related series of compounds, $(^3\Delta E)^{-1}$ and $\alpha_P^2|\psi_{P(3s)}(0)|^2$ would change relatively little, leaving α_{Pt}^2 and $|\psi_{Pt(6s)}(0)|^2$ as the factors which probably vary most. Since eqn. (3) applies to covalent bonds, any decrease in covalency (i.e., increase in ionic character) of the Pt–P bond will also reduce the coupling. In the complex[224] *cis*-$PtMeCl(PEt_3)_2$, $^1J_{Pt-P}$ (*trans* to $-CH_3^-$, 1719 Hz) was much less than $^1J_{Pt-P}$ (*trans* to Cl^-, 4179 Hz). Since $|\psi_{Pt(6s)}(0)|^2$ (and perhaps $^3\Delta E$) is common to the two coupling constants, the large difference in coupling constants must be related to differences in the two Pt–P bonds, in particular to different values of α_{Pt}^2. Additional support for the dominant role of α_{Pt}^2 has been obtained[1] by comparing coupling constants for Pt^{II} and Pt^{IV} complexes. The low value for α_{Pt}^2 for the Pt^{II}–P bond in the *trans* isomer relative to the *cis* isomer was related to the high *trans*-influence of phosphines relative to chloride, this also being indicated by X-ray crystallography and infrared spectroscopic data. Since $^1J_{Pt-P}$ (*cis*)/$^1J_{Pt-P}$ (*trans*) is similar for $PtCl_2(PBu^n{}_3)_2$ and $PtCl_4(PBu^n{}_3)_2$, the *trans*-influence of phosphines relative to chloride is also high for Pt^{IV}.

The variation in $^1J_{Pt-P}$ according to the ligand *trans* to the phosphine was also explained in the same terms by Allen and Pidcock[224]. For example, the large difference between $^1J_{Pt-P}$ *trans* to Cl^- (3454 Hz) and *trans* to $PBu^n{}_3$ (2270 Hz) in $[ClPt(PBu^n{}_3)_3]^+$ was again consistent with the higher *trans*-influence of $PBu^n{}_3$ relative to Cl^-.

Allen et al.[225] examined $^1J_{Pt-P}$ for some Pt^{II} complexes of triphenylphosphite, $P(OPh)_3$, and phosphonates, $(RO)_2PO^-$ and $(RO)_2POH$ (R = Me, Ph). Coupling to ^{31}P in complexes of $(PhO)_2PO^-$ varies with the other ligands in the same way as for PEt_3 complexes. There is a linear relationship of $^1J_{Pt-P(phosphine)}$ for the complexes *trans*-$[PtX\{(PhO)_2PO\}(PBu^n{}_3)_2]$, with $^2J_{Pt-Me}$ for the complexes *trans*-$PtXMe(PEt_3)_2$ (discussed later).

Combining several sets of results, Allen and Sze[226] obtained a *trans*-influence series (order of increasing coupling constants) $SiMePh_2^-$ (ref. 227) > Ph^- > Me^- ≫ PEt_3, $PBu^n{}_3$ > PMe_2Ph > PPh_3 > $P(OPh)_3$, CN^- > $AsEt_3$ > NO_2^- > *p*-toluidine > $EtNH_2$ > Et_2NH > py, N_3^-, NCO^-, NCS^- > Cl^-, Br^-, I^- > ONO_2^-. This order represents a decreasing tendency for the ligands to concentrate Pt(6s) character into their bonds with Pt^{II}.

It is more difficult to discuss the variation in $^1J_{Pt-P}$ when the ligand *cis* to the phosphine is changed. The changes are small relative to those when the *trans* ligand is varied and changes in any of the variables in eqn. (3) could be equally important. As pointed out by Allen and Sze[226] values of $^1J_{Pt-P}$ in the three series *trans*-$PtHX(PEt_3)_2$ (ref. 149), *trans*-$PtMeX(PEt_3)_2$ (ref. 224) and *trans*-$Pt[(PhO)_2PO]X(PEt_3)_2$ (ref. 225) give a consistent *cis*-influence series (increasing order of $^1J_{Pt-P}$) CN^-, I^- > NCS^-, Br^- > NCO^-, Cl^- > N_3^- > NO_2^- > ONO_2^-. If the variation in $^1J_{Pt-P}$ is compared with that for the ^{195}Pt chemical shifts in *trans*-$PtHX(PEt_3)_2$ (ref. 228) a linear correlation is obtained, except for I^- (Fig. 5). Since the ^{31}P chemical shift also correlates with the ^{195}Pt chemical shift[228], the correlation between $^1J_{Pt-P}$ and δ_P observed by

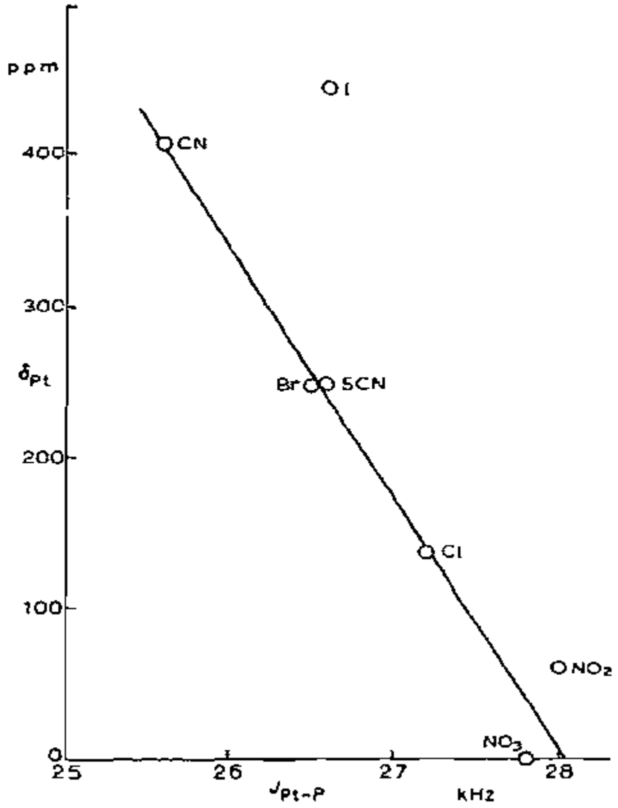


Fig. 5. Plot of J_{Pt-P} vs ^{195}Pt chemical shift in complexes *trans*-$PtX(H)(PEt_3)_2$

Socrates[149] necessarily follows These correlations appear to be too good to be coincident, but it is not clear what they mean in terms of the variables in eqn. (3) for $^1J_{Pt-P}$. If, as suggested by Dean and Green[228], ^{195}Pt chemical shifts in *trans*-$PtHX(PEt_3)_2$ are determined mainly by the covalency of the Pt–X bond (and any Pt–X π-bonding), the implication is that as Pt–X becomes more covalent (or Pt→X π-bonding increases), $^1J_{Pt-P}$ *cis* to X decreases. But Me^- appears to have a low *cis*-influence, since $^1J_{Pt-P}$ *trans* to Me^- in *cis*-$PtMe_2(PEt_3)_2$ (1856 Hz) is greater than in *cis*-$PtMeCl(PEt_3)_2$ (1719 Hz)[224]. Although the Pt–Me bond is usually considered to be very covalent a possible reason for this is that $|\psi_{Pt(6s)}(0)|^2$ is very high in the dimethylplatinum complex owing to the strong σ-donor power * of Me^-.

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* Some disagreement exists between Church and Mays[97] and Allen et al.[225] on the effect of a strong donor ligand on $|\psi_{Pt\,(6s)}(0)|^2$ Allen et al.[225] point out that this represents the square of the amplitude of the atomic wavefunction, and that a decrease in σ-donor strength of L will cause a contraction of the *s*-orbital, which will tend to increase this amplitude. However, ψ_s^2 at any point represents the *s*-electron density at that point and direct donation of electronic charge into the orbital is usually considered to outweigh orbital expansion. Of course, removal of charge from other metal (d_π) orbitals causes an increase in ψ_s^2 at the nucleus. This approach seems to be quite successful in discussing center shifts in Mossbauer spectroscopy, which depend on *s*-electron density at the nucleus[229].

Allen and Sze [226] used $^1J_{Pt-P}$ in the complexes *cis*-$PtCl_2L(PBu^n{}_3)$ to arrange the ligands L in a *cis*-influence order (increasing $^1J_{Pt-P}$): $(PhO)_3P > (MeO)_3P > PPh_3 > PMePh_2 > PBu^n{}_3$, PEt_3.

Although Grim and Wheatland [230] have continued to support their theory that $^1J_{Pt-P}$ is determined mainly by the extent of Pt→P π-bonding, this theory is certainly incorrect. The most convincing argument against it is provided by the essential similarity between the variation of $^1J_{Pt-P}$ with the *trans* ligand and that of $^1J_{Pt-H}$, $^2J_{Pt-Me}$, etc. (see following discussion). No π-bonding can occur in the Pt—H bond.

(c) Platinum—hydride coupling constants

Powell and Shaw [231] measured $^1J_{Pt-H}$ for a series of complexes *trans*-$PtHX(PEt_3)_2$. τ_H was correlated with the *trans*-effect of X^-, but no apparent correlations appeared to exist involving $^1J_{Pt-H}$. Atkins et al. [158] observed that, for the closely related complexes *trans*-$PtH(RCO_2)(PEt_3)_2$, $^1J_{Pt-H}$ (along with τ_H and ν_{Pt-H}) correlated linearly with pK_a of RCO_2H. The results were interpreted in terms of the appropriate form of eqn. (3) (substituting Pt and H for A and B) Increased donation of charge to platinum caused a decrease in $\alpha_{Pt}{}^2$ in the Pt—H bond. The lack of correlation between $^1J_{Pt-H}$ and τ_H, or ν_{Pt-H} when X = Cl^-, Br^-, I^-, NCS^-, SCN^-, $NO_2{}^-$, CN^-, and the observation of a correlation between $^1J_{Pt-H}$ and the position of X^- in the spectrochemical series (determined from the UV spectra of Co^{III} complexes) led to the suggestion that changes in $^3\Delta E$ might be dominant in (3) when "gross" changes were made in X. However, the correlation with the spectrochemical series might equally well be explained in terms of variations in $\alpha_{Pt}{}^2$ being dominant if ligands which tend to concentrate *s*-character into their bonds with platinum are also those which cause a large *d*-orbital splitting

Church and Mays [97] studied $^1J_{Pt-H}$ for a number of cationic complexes *trans*-$[PtHL(PEt_3)_2]^+$. The results were interpreted in terms of variation in $\alpha_{Pt}{}^2$. Changes in $^1J_{Pt-H}$ with the *trans*-ligand parallel those in $^1J_{Pt-P}$ as would be expected if $\alpha_{Pt}{}^2$ is dominant in both cases. When values of $^1J_{Pt-H}$ for complexes *trans*-$PtHX(PEt_3)_2$ are compared with those for *trans*-$PtHX(PMe_2Ph)_2$ (ref. 154), the former are consistently higher than the latter (e.g., with X = NO_3, $^1J_{Pt-H}$ = 1322 Hz for the PEt_3 complex [231] and 1316 Hz for the PMe_2Ph complex). A large difference is observed between corresponding values of $^1J_{Pt-H}$ for *trans*-$[PtHL'L_2]^+$, where L = PEt_3 (ref. 97) and $AsEt_3$ (ref. 156) (e.g., for L′ = PPh_3, $^1J_{Pt-H}$ = 890 Hz when L = PEt_3 and 739 Hz when L = $AsEt_3$). The relative difference is greater than that in ν_{Pt-H} (2069 cm^{-1} for $[PtH(PPh_3)(AsEt_3)_2]^+$ and 2100 cm^{-1} for $[PtH(PPh_3)(PEt_3)_2]^+$). As usual for "NMR *cis*-influences" no definite statement can be made on factors responsible in eqn. (3), although variations in $|\psi_{Pt(6s)}(0)|^2$ might produce the observed differences. It should be mentioned that the *cis*-influence on $^1J_{Pt-H}$ is magnified in these complexes since two *cis* ligands are being changed.

Combining results on *trans*-$PtHXL_2$ and $PtH(L')L_2{}^+$, the order of decreasing NMR *trans*-influence, corresponding to the increasing order of $\alpha_{Pt}{}^2$ in the Pt—H bond, shown in Table 8 is obtained.

There are a few anomalies in this series. Church and Mays [97] commented on the position of PPh_3 relative to PEt_3 and the phosphites, although Pt—H stretching fre-

TABLE 8

Pt–H coupling constants and *trans*-influences for platinum(II) compounds[a]

CN^- (768) (ref 154) > PEt_3 (790*) (ref 97) > $PMePh_2$ (840) (ref 154) $\geq$ $P(OMe)_3$ (846*) (ref 97) > $P(OPh)_3$ (872*) (ref 97) $\simeq$ *p*-Me-C_6H_4NC (872) (ref. 154) > PPh_3 (890*) (ref 97) $\simeq$ *p*-MeO-C_6H_4NC (890*) (ref. 97) $\geq$ *t*-BuNC (895*) (ref. 97) > C_2H_4 (931) (ref. 157) > CO (967*) (ref 97) $\simeq$ S-$C_6H_5^-$ (PPh_3 complex, 969) (ref. 231a) > NO_2^- (1003*) (ref 231) > –NCO^- (1080*) (ref. 231) $\simeq$ –NCS^- (1072 (ref 154), 1086* (ref. 231)) $\simeq$ 2-Me-py (1080) (ref. 154) $\simeq$ 2,4,6-trimethylpyridine (1073) (ref. 154) $\geq$ py (1106) (ref 97) > *p*-$MeC_6H_4CO_2^-$ (1195*) (ref 158) > –SCN^- (1204 (ref 154), 1233* (ref. 231)) > Cl^- (1260) (ref. 154) $\geq$ $CF_3CO_2^-$ (1286*) (ref. 158) > Br^- (1302) (ref 154) > NO_3^- (1316) (ref. 154) > I^- (1332) (ref. 154) > Me_2CO (1458) (ref. 154) > ClO_4^- (PPh_3 complex, 1466) (ref. 163)

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[a] $^1J_{Pt-H}$ (Hz) for *trans*-$PtHXL_2$ or *trans*-$PtHL'L_2$, where L = $PMePh_2$ except where otherwise noted, or when indicated by an asterisk, in which case L = PEt_3. The order is that of increasing *J*, and decreasing *trans*-influence

quencies show the same order. By comparison with the ν_{Pt-H} series of Br^-, I^- and SCN^- are out of order This is a general feature of *trans*-influence series derived from coupling constants (see discussion later).

(d) Coupling constants to the platinum–methyl group platinum(II).
Platinum(II) Coupling between ^{195}Pt and ^{13}C in $Pt-CH_3$ would be expected to be defined by eqn (3) where A and B are Pt and C respectively. The platinum–proton coupling over two bonds, $^2J_{Pt-Me}$, is more complicated[232]. However, Smith[233] showed that the coupling $^2J_{X-C-H}$ could be treated in an analogous way to $^2J_{HCH}$, which is fairly well understood. These considerations suggested[203] that $^2J_{Pt-Me}$ would be given by

$$|^2J_{Pt-Me}| \propto \frac{\gamma_{Pt}\gamma_H \alpha_{Pt}^2 \alpha_H^2 \, f(C) |\psi_{Pt(6s)}(0)|^2 |\psi_{H(1s)}(0)|^2}{^3\Delta E} \tag{4}$$

f(C) represents the various factors that affect the transmission of the xoupling through the carbon atom. Within a series of complexes *trans*-$PtMeXL_2$, provided changes in f(C) are relatively small, variation in $^2J_{Pt-Me}$ with X would depend mainly on variations in α_{Pt}^2, as for $^1J_{Pt-P}$ and $^1J_{Pt-H}$. A linear correlation[203] between $^2J_{Pt-Me}$ for these complexes with $^1J_{Pt-H}$ for corresponding complexes *trans*-$PtHXL_2$ indicates that changes in f(C) are not important. This conclusion is confirmed by the observed linear correlation between $^1J_{^{195}Pt-^{13}C}$ and $^2J_{^{195}Pt-C-^1H}$ for a series of platinum–methyl complexes[234].

Allen and Pidcock[224] noted that $^2J_{Pt-Me}$ in the complexes *trans*-$PtMeX(PEt_3)_2$ was dependent on X^- and varied in much the same way as $^1J_{Pt-H}$ in the hydrides. Clark and Ruddick[235] examined $^2J_{Pt-Me}$ in the cationic complexes *trans*-$[PtMeL(PMe_2Ph)_2]^+$ and pointed out that the dependence of $^2J_{Pt-Me}$ on L was similar to that of $^1J_{Pt-H}$ in corresponding hydrides. More recent work[176–180, 236, 237] has extended the range of methylplatinum(II) complexes. Combining results for $^2J_{Pt-Me}$ in PEt_3 and PMe_2Ph complexes (the change of phosphine has little effect[203] on $^2J_{Pt-CH_3}$) the NMR *trans*-influence order shown in Table 9A is obtained.

For complexes *cis*-$PtMe_2L_2$, $^2J_{Pt-Me}$ also shows a dependence on L, to give the *trans*-

TABLE 9

Coupling constants and *trans*-influences for methyl–platinum(II) compounds

A. $^2J_{Pt-C-H}$ *values for* trans-$PtMeXL_2$ *and* trans-$[PtMeL'L_2]^+$ *complexes* [a]
X or L = p-F-$C_6H_4^-$ (49.5) (ref. 251) $\geq$ m-F-$C_6H_4^-$ (50.0) (ref. 251) > carbenes (e.g., .C(OMe)-Me) (51) (ref. 176) > $SbPh_3$ (55) (ref. 235) > PMe_2Ph (57) (ref. 235) $\geq$ $-C{\equiv}CCF_3$ (57.8) (ref. 236) $\simeq$ $P(OPh)_3$ (58) (ref. 235) > PPh_3 (60) (ref. 235) $\geq$ CN^- (61) (ref. 203) > CO (63) (ref. 235) $\geq$ RNC (63) (ref. 177) > $AsPh_3$ (67) (ref. 235) > NO_2^- (71.3) (ref. 203) $\geq$ $CH_2{=}C{=}CH_2$ (72.0) (ref. 178) > $Me{-}CH{=}CH_2$ (73.5) (ref. 179) $\geq$ py (74) (ref. 235) $\simeq$ C_2H_4 (74.2) (ref. 179) $\geq$ $CH_2{=}CHCH{=}CH_2$ (75) (ref. 178) $\geq$ $NH{=}C(OMe)C_6F_5$ (76.4) (ref. 180) $\simeq$ $MeC{\equiv}CMe$ (77) (ref. 179) $\geq$ NCO^- (78) (ref. 203) $\simeq$ NCS^- (78.5) (ref. 203) $\simeq$ N_3^- (78.6) (ref. 224) > RCN (80) (ref. 180) $\geq$ I^- (81) (ref. 108) $\simeq$ Cl^- (82) (ref. 108) $\simeq$ Br^- (83) (ref. 108) > NO_3^- (86) (ref. 203) > Me_2CO (88) (ref. 237)

B $^2J_{Pt-C-H}$ *values for* cis-$PtMe_2L_2$ [a]
$SbMe_3$ [b] (54) (ref. 239) > PMe_2Ph (67) (ref. 108) > PPh_3 (69) (ref. 240) $\simeq$ $P(p\text{-}C_6H_4Me)_3$ (69) (ref. 241) > p-CN-C_6H_4Me (74.6) (ref. 241) $\simeq$ CNEt (75) (ref. 240) > $AsMe_3$ [b] (77.5) (refs. 239, 242) $\geq$ $AsMe_2Ph$ (79) (ref. 109) > COD (83.4) (ref. 241)

[a] The order is that of decreasing *trans*-influence with J values (Hz) in parentheses.
[b] The $^2J_{Pt-CH_3}$ coupling constants in ref. 239 appear to be half the true values

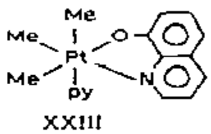
influence order shown in Table 9B. For the limited number of complexes of this type for which ^{13}C NMR data are available[234, 243] changes in $^1J_{Pt-C}$ parallel those for $^2J_{Pt-C-H}$. The results suggest rather large differences between the *trans*-influences of phosphine, arsine and stibine ligands, which are not apparent when NMR spectra of a series of *trans*-complexes $PtMeL(PMe_2Ph)_2^+$ are examined[235]. Platinum–methyl coupling constants in the *cis*-dimethyl complexes probably provide a less reliable guide to *trans*-influence because.

(*i*) Results will reflect a *cis*-influence as well as a *trans*-influence

(*ii*) Two ligands are being varied from compound to compound so that "perturbations" from changes in $^3\Delta E$, $|\psi_{Pt(6s)}(0)|^2$ will be more pronounced.

A series[244] of complexes *cis*-$Pt(CH_2SiMe_3)_2L_2$ shows an analogous variation in $^2J_{Pt-CH}$ with L although the coupling constants are consistently higher than corresponding values of $^2J_{Pt-Me}$ for the analogous platinum–methyl compounds.

Platinum(IV) In trimethylplatinum(IV) complexes, $^2J_{Pt-Me}$ depends[245] on the *trans* donor atom, e.g., complex XXIII

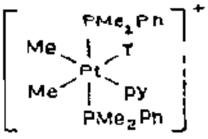


XXIII

shows three Pt–Me resonances with $^2J_{Pt-Me}$ = 73.6 (*trans* to O), 71 (*trans* to py) and 69.7

(*trans* to N) Hz. The complexes $[PtMe_3X]_4$ gave[188] $^2J_{Pt-Me}$ = 81.7 (X = Cl), 80.1 (Br), 80 1 (OH), 78.4 (I) and 73.4 (SH) Hz. The range of coupling constants obtained by Kite et al.[245] was not very large (69–82) since no ligands of very high *trans*-influence were included Ruddick and Shaw[108, 109] examined the NMR spectra of some Pt^{IV} non-electrolytes containing ligands such as tertiary phosphines and arsines with high *trans*-influence. For example, for the complex *fac*-$PtMe_3(PMe_2Ph)_2I$ (XX), $^2J_{Pt-Me}$ (*trans* to I^-) is 70 Hz and 56 Hz *trans* to PMe_2Ph. For the corresponding complex with $AsMe_2Ph$ the coupling constants are 72 and 64 Hz *trans* to I^- and arsine respectively. The lowest value of $^2J_{Pt-Me}$ occurred for the complex *cis*-$PtMe_4(PMe_2Ph)_2$ for which the platinum–methyl coupling constant for the mutually *trans* methyl groups was 44 Hz (57 Hz *trans* to PMe_2Ph).

Clegg and Hall[185] measured $^2J_{Pt-Me}$ for some trimethylplatinum(IV) complexes, $PtMe_3X_3{}^{2-}$ and $PtMe_3L_3{}^+$. The coupling constant was dependent on the *trans* ligand and correlated with ν_{Pt-Me} from Raman spectral data For the anionic complexes, the order of $^2J_{Pt-Me}$ was NCS^- (73.4 Hz) > $NO_2{}^-$ (70.9) > CN^- (60 8), suggesting a reverse *trans*-influence order For the series $Pt(CH_3)_3(bipy)X$ and $Pt(CH_3)_3(bipy)L^+$ it was found[185a] that $^2J_{Pt-CH_3}$ *trans* to X or L was very sensitive to change in X or L and $^2J_{Pt-CH_3}$ *trans* to bipy almost insensitive to X or L The *trans*-influence order obtained is given in Table 10A. This order showed some correlation with ν_{Pt-CH_3} (*trans* to X). For cationic trimethylplatinum(IV) complexes containing three neutral ligands, $^2J_{Pt-Me}$ is very dependent on the nature of the ligand *trans* to the methyl group in question, but almost independent of the *cis* ligands For example, $^2J_{Pt-Me}$ *trans* to pyridine is virtually constant at 67–68 Hz in the complexes $PtMe_3(py)_n(OH_2)_{3-n}{}^+$ (n = 1–3) (ref. 185), $PtMe_3(py)_2(PMe_2Ph)^+$ (ref. 189), $PtMe_3(py)(PMe_2Ph)_2$ (ref. 189). However, the value changes for different classes of compounds, e.g., 61 6 Hz (ref. 190) for $PtMe_2I(PMe_2Ph)_2(py)^+$, XXIV,



XXIV

60.8 Hz for $PtMe_2(py)_2(PMe_2Ph)_2{}^{2+}$, XIV (ref 190) and 71 Hz in XXIII (ref. 245). Consequently it is important, when making detailed comparisons, to confine considerations to complexes of a particular class. For the complexes $PtMe_3L_3{}^+$ (refs. 185, 189) and $PtMe_3(L')L_2{}^+$ (ref. 189) the *trans*-influence order is given in Table 10B, and for the dimethylplatinum(IV) cations $[PtMe_2(PMe_2Ph)_2L_2]^+$ and $[PtMe_2(PMe_2Ph)_2IL]^+$ in Table 10C. The *trans*-influence order in Table 10C correlates well with that obtained from ν_{Pt-Me} in the Raman spectra. A linear correlation was also found between these coupling constants and those obtained for *trans*-$[PtMeL(PMe_2Ph)_2]^+$.

The trifluoromethyl group also exhibits a high NMR *trans*-influence in platinum(IV) compounds. For example, in the complex XXVa, $^2J_{Pt-Me}$ has the low value[246] 44.6 Hz *trans* to $-CF_3{}^-$ (66.4 Hz *trans* to I^-) and in XXVI both Pt–Me coupling constants are low (44 and 46 Hz)[237].

In the dimeric complex $[Pt(CH_3)_3(acac)]_2$, the $Pt-CH_3$ coupling *trans* to the σ-C of acac (73.3 Hz) is similar[235] to that for the methyl groups *trans* to O (75.1 Hz), indicating

TABLE 10

Coupling constants and *trans*-influences for methyl–platinum(IV) complexes[a, b]

A. ${}^2J_{Pt-CH_3}$ *values for* $PtMe_3X(bipy)$ *and* $PtMe_3L(bipy)^+$ (trans *to X or L) in nitrobenzene*[185a]
CH_3^- (44 2) > CN^- (55 5) > PPh_3 (58.5) > acac$^-$ (C-bound) (63 8) > NO_2^- (67.2) > piperidine (68.8) > $MeNH_2$ (69.6) ≃ $EtNH_2$ (69.9) > $-SCN^-$ (70 5) > py (70 9) > NH_3 (71 7) > NCO^- (72.3) ≃ I^- (72 4) > $-NCS^-$ (73 0) > $CH_3CO_2^-$ (74.0) > Br^- (74 6) ≃ Cl^- (74 7) > NO_3^- (79.5) > H_2O (82)

B ${}^2J_{Pt-C-H}$ *values*[185, 189] *for* $[PtMe_3L_3]^+$ *and* $[PtMe_3L'_2L]^+$ [c]
L = $\cdot CCH_2CH_2CH_2O$ (49 Hz in $PtMe_3(AsMe_3)_2L^+$) > PMe_2Ph (54 5) > $SbMe_3$ (60) ~ p-CNC_6H_4-Me (60) ≥ CNMe (60 8) ≃ p-CNC_6H_4OMe (61.2) ≃ CNC_2H_5 (61 2) > py (68) ≥ NH_2Me ($PtMe_3L_3^+$, 68 4) > NH_3($PtMe_3L_3^+$, 71) > NCC_6F_5 ($PtMe_3(AsMe_3)_2L^+$, 77.4) > H_2O ($PtMe_3L_3^+$, 79.7)

C ${}^2J_{Pt-C-H}$ *values*[2] *for* $[PtMe_2(PMe_2Ph)_2L_2]^{2+}$ *and* $[PtMe_2(PMe_2Ph)_2IL]^+$ (ref. 190)
L = $CCH_2CH_2CH_2O$ (47) > PMe_2Ph (50 5) > diars (56.0) > CNC_6H_4OMe (57.8) ≥ CNC_6H_4Me (58 0) ≥ CNMe (58.2) ≃ CNEt (58 2) > $P(OMe)_3$ (60.0) > diphos (60 6) > py (60.8) > tetrapyrazolylborate, Bpz_4^- (64 2) > bipy (64.4) ≥ terpy (64 6) > $S_2CNEt_2^-$ (64 8) > NH=C(OMe)-C_6F_5 (65.2) > phen (65 5) > p-$NCC_6H_4OCH_3$ (70 2)

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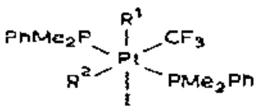
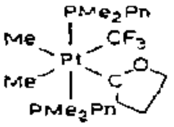
[a] The order is that of decreasing *trans*-influence (increasing *J*) values (Hz).
[b] Values in Hz are given in parentheses for each ligand
[c] L′ = PMe_2Ph unless otherwise noted



XXV

(a) $R^1 = R^2 = Me$
(b) $R^1 = I, R^2 = CF_3$
(c) $R^1 = R^2 = C_6H_5$



XXVI

that the σ-C bonded acetylacetonate group is exceptional among σ-alkyl groups in having a low NMR *trans*-influence. This supports a similar conclusion from Pt–CH_3 bond lengths in related complexes[44b,c]. In the complex $Pt(CH_3)_3(bipy)[\text{-}CH(COCH_3)_2]$ the Pt–CH_3 coupling *trans* to the carbon-bonded acetylacetonate[185a] (63.8 Hz) is smaller, indicating that the *trans*-influence of this group is a little higher than that of bipy (*trans*-coupling 68.8 Hz), but still much less than that of CH_3^- (*trans*-coupling 44.2 Hz). The crystal structure of this complex[44a] supports the conclusion that there is little difference between the *trans*-influences of bipy and C–acetylacetonate.

King[246a] has reported the preparation of the dinitrogen complex $Pt(CH_3)_3$(dipyrazolylborate)(N_2). A comparison of the Pt–CH_3 coupling constants *cis* and *trans* to the dinitrogen ligand (78 and 64 Hz respectively) implies a moderately high *trans*-influence for N_2.

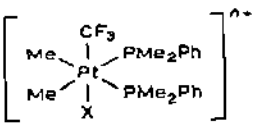
(e) Pt–CF_3 coupling

It has been suggested[203] that ${}^2J_{^{195}Pt-C-^{19}F}$ in trifluoromethylplatinum complexes is given by an equation analogous to (3) A linear correlation[203] between ${}^2J_{Pt-Me}$ and

$^2J_{Pt-CF_3}$ for corresponding complexes *trans*-Pt(R)X(PMe$_2$Ph)$_2$ and *trans*-Pt(R)L·(PMe$_2$Ph)$_2^+$ supports this conclusion. The deviation from the line of points representing L = SbPh$_3$ and CO was explained in terms of these ligands requiring back-bonding from filled metal d_π-orbitals which were contracted in the trifluoromethyl complex owing to a greater effective positive charge on platinum.

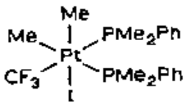
A dependence of $^2J_{Pt-CF_3}$ on L was also observed for the complexes *cis*-Pt(CF$_3$)$_2$L$_2$ (ref. 241) analogous to that for *cis*-PtMe$_2$L$_2$. The decreasing order of coupling constant, $^2J_{Pt-CF_3}$, and hence the order of increasing *trans*-influence, is 4Me-py (793 Hz) $\leqslant$ SbPh$_3$ (791) < COD (736) < AsPh$_3$ (731) < CNEt (713) < AsMe$_3$ (713) $\ll$ PMe$_2$Ph (627) Triphenylstibine again has a low *trans*-influence in a metal complex where the effective positive charge on platinum is high; but, surprisingly, the *trans*-influence of COD appears to be similar to that in the dimethylplatinum complexes.

$^2J_{Pt-CF_3}$ also shows a dependence on the *trans* ligand in platinum(IV) complexes The coupling constant order is: Me$_2$CO (612 Hz in XXVIIb)[246] > I$^-$ (505 in XXVIIa)[247] > CNEt (452 Hz in XXIX)[241] > PMe$_2$Ph (419 in XXVIII)[246] > CF$_3^-$ (289 in XXVb)[246] > Me$^-$ (280 Hz in XXVa)[246] > $-C_6H_5^-$ (235.5 Hz in XXVc)[246].

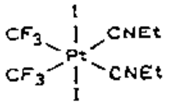


XXVII

(a) X = I, n = 0
(b) X = Me$_2$CO, n = 1



XXVIII



XXIX

(f) ^{195}Pt–^{15}N coupling

Very recently, Venanzi[247a] has reported the observation of coupling between ^{195}Pt and ^{15}N in ^{15}N-enriched complexes *cis*- and *trans*-PtX$_2$L$_2$ (X = Cl, Br; L = n-C$_{12}$H$_{25}$NH$_2$) of $^1J_{Pt-N}$ in *cis*-PtCl$_2$L$_2$ (351 Hz). The higher value compared with that in the *trans*-isomer (290 Hz) implies that the amine has a higher *trans*-influence than chloride. The difference in coupling between *cis* and *trans* isomers is less pronounced than that for $^1J_{Pt-P}$ in the analogous PBu$^n_3$ complexes[1] These data are consistent with the *trans*-influence series R$_3$P > RNH$_2$ > Cl$^-$, Br$^-$ obtained from Pt–P, Pt–H and Pt–CH$_3$ coupling constants.

(g) Couplings involving ^{195}Pt over more than two bonds

Theoretically, the treatment of $^nJ_{Pt-X}$ becomes extremely complicated as n increases. However, experimental results have indicated that the behavior of the coupling constants involving ^{195}Pt is often analogous to that of coupling constants involving ^{1}H For example, $^3J_{Pt-N-C-H}$ shows a dependence[248,249] on the dihedral angle between the planes Pt–N–C and N–C–H similar to the Karplus relation for $^3J_{H-C-C-H}$ in the fragment H–C–C–H Likewise, $^4J_{PtNCCH}$ shows an angular dependence[249], similar to that for $^4J_{HCCCH}$. Consequently, in considering a coupling $^nJ_{Pt-A-B\ ..M-X}$ which is transmitted through bonding electrons, it is reasonable to use the relation

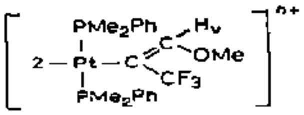
$$|{}^nJ_{\text{Pt-A-B...M-X}}| \propto \frac{\gamma_{\text{Pt}}\gamma_{\text{X}}\alpha_{\text{Pt}}^2\alpha_{\text{X}}^2\ \text{F(A-B....M)}|\psi_{\text{Pt}(6s)}(0)|^2|\psi_{\text{X}(ns)}(0)|^2}{{}^3\Delta E} \tag{5}$$

In this extension of eqn. (3), F(A—B....M) represents all the electronic and stereochemical factors in the A—B....M fragment which can affect the coupling. If, within a series of complexes, changes in $\alpha_X{}^2$ F(AB. ..M)$|\psi_{X(ns)}(0)|^2$ are relatively small the coupling will depend on $\alpha_{Pt}{}^2|\psi_{Pt(6s)}(0)|^2/{}^3\Delta E$, just as for ${}^1J_{Pt-X}$.

Thus for the complexes $Pt(en)L_2{}^{2+}$, ${}^3J_{Pt-N-CH_2}$ varies with L in a similar way to ${}^2J_{Pt-CH_3}$, varying[249] from 32 Hz (*trans* to PPh_3) to 52.5 Hz (*trans* to H_2O). ${}^3J_{Pt-P-CH_3}$ for the phosphine *trans* to X in the complexes $PtX(PMe_2Ph)_3{}^+$ depends on the *trans*-influence of X, as illustrated in Table 11. The difference between the coupling constants ${}^3J_{Pt-P-CH_3}$ *cis* and *trans* to Cl^- may be compared with that between ${}^1J_{Pt-P}$ in related complexes $PtX(PR_3)_3{}^+$ (see earlier discussion)[11, 224].

${}^3J_{Pt-P-CH_3}$ *trans* to all the σ-C bonded organic groups is low, indicating a high *trans*-influence. The significant variation in ${}^3J_{Pt-P-CH_3}$ (*cis* to R) suggests that these coupling constants cannot be used as a precise indication of *trans*-influence differences between —R groups

Within the series of complexes XXX



XXX

(a) Z = X⁻, n = 0
(b) Z = L, n = 1

${}^3J_{Pt-C-CF_3}$ and ${}^3J_{Pt-C-C-H_v}$ both vary linearly with ${}^2J_{Pt-CH_3}$ for the corresponding methylplatinum complexes $PtMeZ(PMe_2Ph)_2{}^{n+}$ (except for the points representing L = $SbPh_3$), although the lines do not pass through the origin[250]. This suggests that over the observable range of coupling constants (77—144 Hz for ${}^3J_{Pt-C-CF_3}$) the dominant factor in eqn. (4) is $\alpha_{Pt}{}^2$.

Glockling and Hooton[111] studied the variation of ${}^3J_{Pt-Ge-CH_3}$ with X in the complexes *trans*-$PtX(GeMe_3)(PEt_3)_2$. The coupling ranges from 11.8 Hz for X = CN^- to 20 Hz for X = Cl^-, varying in an analogous way to ${}^2J_{Pt-CH_3}$ in the methylplatinum complexes.

(h) Coupling constants involving ^{103}Rh

Some typical data on coupling between ^{31}P and ^{103}Rh ($I = \frac{1}{2}$, 100% abundance) are given in Table 12.

In the complexes $RhX(PPh_3)_3$, ${}^1J_{Rh-P}$ is always larger *trans* to X than *trans* to PPh_3. Grim and Ference[252] have given an explanation in terms of the mutually *trans* phosphine ligands competing for M d_π electrons. The fact that values of ${}^1J_{Rh-P}$ for the Rh^{III} complexes are smaller than for Rh^I complexes with the same *trans* ligands is then explained in terms of less π-bonding for Rh^{III}. However, just as ${}^1J_{Pt-P}$ (*trans* to P)/${}^1J_{Pt-P}$ (*trans* to Cl) was the same[1] for Pt^{II} and Pt^{IV}, ${}^1J_{Rh-P}$ (*trans* to P)/${}^1J_{Rh-P}$ (*trans* to Cl) is 0.75

TABLE 11

$^3J_{Pt-P-CH_3}$ for complexes $[PtX(PMe_2Ph)_3]^+$

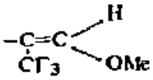
R	^3J (*cis* to R)	^3J (*trans* to R)	Ref.
$-Cl$	23.5	40.0	235
 $-C(CF_3)=C(H)(OMe)$	30.0	20.6	
	29.2		250
$-C_6H_5$	32.6	17.6	250
$-CF_3$	28.0	19.0	203
$-CH_3$	30.0	18.5	235
$-H$	39.5	20.5	154

TABLE 12

$^{103}Rh-^{31}P$ coupling constants in CH_2Cl_2

Compound	$\|^1J_{Rh-P}\|$ *trans* to halogen or COD	$\|^1J_{Rh-P}\|$ *trans* to P	Ref
trans- $RhCl(CO)(PPh_3)_2$		129	252
		124[a]	253
$RhCl(PPh_3)_3$	189	142	253
$RhBr(PPh_3)_3$	192	141	253
$RhI(PPh_3)_3$	194	139	253
mer- $RhCl_3(PBu^n{}_3)_3$	114	84	252
	112.5	83.6	254
mer- $RhBr_3(PBu^n{}_3)_3$	108	84	253
mer- $RhCl_3(PMe_3)_3$	103	82	253
mer- $RhCl_3(PMe_2Ph)_3$	112.3	84.6	254
mer- $RhCl_3(PMePh_2)_3$	114.5	86.0	254
$Rh(COD)(PPh_3)Cl$	152		252
mer- $RhCl_3(PEt_2Ph)_3$	108	84	252
	111.1	84	254

[a] Spectrum run in $CHCl_3$

for $RhCl(PPh_3)_3$ and for $RhCl_3(PMePh_2)_3$ *, which could not be expected if $^1J_{Rh-P}$ depended mainly on Rh–P π-bonding, and such π-bonding was reduced for Rh^{III} relative to Rh^I. It should also be noted* that $^1J_{Rh^{III}-P}/^1J_{Rh^I-P}$ for this pair of complexes is 0.6 for phosphine *trans* to Cl and *trans* to phosphine, almost identical[1] to corresponding values of $^1J_{Pt^{IV}-P}/^1J_{Pt^{II}-P}$, and comparable with the "theoretical" value[203] of 0.67. Consequently we prefer to discuss variations in $^1J_{Rh-P}$ in terms of the appropriate form of eqn. (3), with changes in $\alpha_{Rh}{}^2$ being predominant. At least, it is clear that the mechanism of coupling for $^1J_{Rh-P}$ is similar to that for $^1J_{Pt-P}$.

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* This discussion ignores the probable small differences between $^1J_{Rh-P}$ for PPh_3 and $PMePh_2$ complexes

The ratio $^1J_{Rh-P}$(*trans* to PPh_3)/$^1J_{Rh-P}$(*trans* to Cl) for $RhCl(PPh_3)_3$, 0.75, is significantly larger than for $^1J_{Pt-P}$(*trans* to $PPhPr^n{}_2$)/$^1J_{Pt-P}$(*trans* to Cl) in the complex $PtCl(PPhPr^n{}_2)_3{}^+$, 0.66. This suggest that the *trans*-influence of phosphines relative to Cl^- is less for Rh^I than for Pt^{II}. A significant *cis*-influence on $^1J_{Rh-P}$(*trans* to PPh_3) is demonstrated by the coupling constants in *trans*-$RhCl(CO)(PPh_3)_2$ (129) and $RhCl(PPh_3)_3$ (142). The *trans*-influence of COD appears to be slightly lower than that of Cl^-.

(i) Coupling constants involving ^{199}Hg

Hatton et al.[255] examined the variation in $^2J_{Hg-CH_3}$ (^{199}Hg, $I = \frac{1}{2}$, 16.9% natural abundance) with X in the series Me—Hg—X. The series has been extended by Schaaf and Oliver[256], and Goggin et al.[257] have studied some cationic complexes Me—Hg—L^+. Hatton et al.[255] interpret the results in terms of variation in the *s*-character of the Hg—CH_3 bond. The *trans*-influence series thus obtained is given in Table 13. Trends analogous to those in Table 12 are observed[255] for $^2J_{Hg-CH_2}$ and $^3J_{Hg-CH_2-CH_3}$ in complexes EtHgX.

Schaaf and Oliver[256] found that $^3J_{Hg-SiCH_3}$ in the complexes Me_3SiHgX varied linearly with $^2J_{Hg-CH_3}$ in the corresponding complexes Me—Hg—X (although the plot does not pass through the origin) indicating that changes in Hg hybridization are dominant in both series. The situation is similar to that in the complexes[111] *trans*-$PtX(GeMe_3)(PEt_3)_2$ mentioned above.

Pidcock and co-workers[86] measured $^1J_{Hg-P}$ in some complexes $HgX[PO(OEt)_2]$ in benzene. The complexes are dimeric in solution with Hg—P—O····Hg bridges, but from the crystal structure of the solid complex $HgCl[PO(OEt)_2]$ it was concluded that the P—Hg—Cl unit was not greatly perturbed by these interactions and remained almost linear. $^1J_{Hg-P}$ varies with X in the order: $MeCO_2{}^-$ (12.97 kHz) > Cl^- (12.67) > Br^- (12.24) > I^- (11.18) ≫ $(EtO)_2PO^-$ (7.50). The similarity of this behavior to that[225] in *trans*-$PtX[PO(OEt)_2]$ $(PEt_3)_2$ was noted. Since Hg^{II} has a closed *d*-shell, effects involving metal *d*-electrons are not expected to be important. This provides additional evidence that Pt—P d_π bonding does not control $^1J_{Pt-P}$ in Pt^{II} complexes. Since Hg^{II} is formally *sp*-hybridized but appears to show an NMR *trans*-influence similar to that in formally dsp^2 Pt^{II}, the results suggest (if the Fermi contact explanation is correct) that changes in *s*- and *p*-orbitals are dominant in giving rise to the *trans*-influence in Pt^{II} complexes.

Goggin et al.[257] measured $^3J_{Hg-P-CH_3}$ in the series $[HgX(PMe_3)]^+$ and $[HgL(PMe_3)]^{2+}$ in D_2O. The NMR *trans*-influence order thus obtained was: Me^- (43.9 Hz) > Ph^- (50.8) > PMe_3 (84.3) > $AsMe_3$ (~ 92) > CN^- (99.6) > I^- (106.4) > Br^- (117.0) > Cl^- (121.9). It was noted that this trend is similar to that observed for $^2J_{Hg-CH_3}$. Correlations with ν_{Hg-CH_3} and ν_{Hg-P} were noted.

McFarlane[259] noted that in the complexes $(CF_3-C_6H_4)HgX$, J_{Hg-F} increased by a factor of approximately two as X was changed from $-C_6H_4-CF_3$ to Br when the trifluoromethyl group was *meta* or *para*. This could be explained in the usual way in terms of variations in $\alpha_{Hg}{}^2$. However, when the CF_3 group was *ortho* no such change with X occurred. It was therefore suggested that the mercury *o*-CF_3 coupling contained a large "through space" component. The corollary of this finding is that coupling constants can only be expected to provide data about the *trans*-influence when such "through space" coupling is absent.

TABLE 13

Coupling constants [a] and *trans*-influences in MeHgX and $[MeHgL]^+$

X^- or L = $SiMe_3^-$ (96.8, cyclopentane) (ref. 256) > Me^- (102 (ref. 258), 100.6 cyclohexane (ref. 255); 102.5, $CFCl_3$ (ref. 256), 104.3 pyridine (ref. 255)) > $-\overline{CHCH_2CH_2}^-$ (103.5, $CFCl_3$) (ref. 256) $\gg$ $-CH{=}CH_2^-$ (107, $CFCl_3$) (ref. 256) $\simeq$ $-CH_2Ph^-$ (107.2, 1,2-dimethoxyethane) (ref. 256) $\geq$ $-C_6H_5^-$ (108.5, $CFCl_3$) (ref. 256) > $-\underset{\overset{\|}{O}}{C}-Et$ (148, 1,2-dimethoxyethane) (ref. 256) $\geq$ $-C{\equiv}CH^-$ (150.6, pyridine) (ref. 255) > $S-Hg-Me^-$ (156.6, pyridine) (ref. 255) $\simeq$ $-N(SiMe_3)_2^-$ (157.2, 1,2-dimethoxyethane) (ref. 256) > PMe_3 (167.3, D_2O) (ref. 257) > CN^- (176) (ref. 255) > $AsMe_3$ (~ 180, D_2O) (ref. 257) > I^- (200, pyridine) (ref. 255) > SCN^- (208, pyridine) (ref. 255) > Br^- (212, pyridine) (ref. 255) $\simeq$ OH^- (204, 214.2, pyridine) (ref. 255) $\geq$ $C_2O_4(HgMe)^-$ (205; 215.2, pyridine) (ref. 255) $\simeq$ $SO_4(HgMe)^-$ (205, 216, pyridine) (ref. 255) > $PO_4(HgMe)_2^-$ (220.5, pyridine) (ref. 255) $\simeq$ $OCOMe^-$ (214.3; 220.8, pyridine) (ref. 255) $\simeq$ SMe_2 (220.7, D_2O) (ref. 257) > py [227 for $MeHgpy(NO_3)$, 233.2 for $MeHgpy(ClO_4)$] (ref. 255) > NO_3^- (240.6) (ref. 255) > D_2O (259.2 for $[MeHg(D_2O)]NO_3$ and $[MeHg(D_2O)]ClO_4$)

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[a] The order is that of decreasing *trans*-influence. Values of $^2J_{Hg-C-H}$ (Hz) are given in parentheses, and were measured in benzene unless otherwise noted.

(j) Coupling involving ^{183}W

Grim et al.[208, 230, 260–262] have examined the coupling between ^{183}W ($I = \frac{1}{2}$, 14.3% natural abundance) and ^{31}P in the complexes $LW(CO)_5$ and $L_2W(CO)_4$ where L is a phosphine or phosphite. Two main conclusions were reached:

(*i*) In the complexes $LW(CO)_5$, $^1J_{W-P}$ tended to increase[208, 262] with increasing substitution of electron-withdrawing groups on P, varying linearly with ν_{CO} (*E* mode)

(*ii*) In the complexes $(PR_3)_2W(CO)_4$, $^1J_{W-P}$ in the *trans* isomer was appreciably greater than in the *cis* isomer[230, 261].

The results are explained in terms of W–P π-bonding. Point (*i*) was taken to indicate that $^1J_{W-P}$ was a measure of W→P π-bonding, since if spin–spin coupling is transmitted mainly through σ-bonds, one might expect the best σ-bond to have the largest $^1J_{W-P}$. Either coupling was transmitted via π-bonds, or, in the Fermi Contact Theory (appropriate form of eqn. (3)) π-bonding enhanced $|\psi_{W(6s)}(0)|^2$, with a synergic increase in P→W σ-bonding also affecting the coupling. Point (*ii*) was explained as arising from greater competition by CO for π-electrons than by PR_3.

Mather and Pidcock[263] have challenged these conclusions. They point out that when the groups on phosphorus are varied, the factors in the appropriate form of eqn. (3) which would be expected to be most affected are $\alpha_P^2|\psi_{P(3s)}(0)|^2$, rather than $\alpha_W^2|\psi_{W(6s)}(0)|^2$. Over a wider series of complexes than that examined by Grim et al. little correlation was observed between $^1J_{W-P}$ and the expected strength of W–P π-bonding.

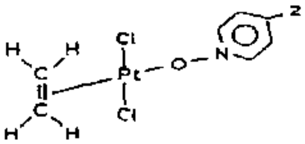
It has previously been shown that ν_{CO} in metal carbonyls $LM(CO)_5$ correlated with the net electronegativity of L, whether the electron flow involved is σ, π or a combination (see earlier discussions on ν_{CO}), so that the linear plot[208, 262] of $^1J_{W-P}$ against ν_{CO} indicates that phosphorus hybridization and net L→M charge transfer both change regularly as electron-withdrawing substituents are introduced on the phosphorus atom.

The lower value of J_{W-P} *trans* to CO than *trans* to PR_3 can be explained in terms of higher α_W^2 in the former case if CO has a higher NMR *trans*-influence than PR_3 in these complexes. In the relatively electron-deficient complexes *trans*-$PtMeL(PMePh)_2^+$, the *trans*-influence of CO ($^2J_{Pt-CH_3}$ for L = CO, 63 Hz)[235] is only slightly less than that of phosphines ($^2J_{Pt-CH_3}$, for L = PPh_3, 60 Hz). It would be expected that the *trans*-influence of CO would be greater in the "electron-rich" tungsten(0) complexes. If this explanation is correct, it directly contradicts the assumption that there is no *trans*-influence in complexes such as these[89].

(k) Metal–olefin coupling constants

X-ray data[42] suggest that the Pt–olefin bond is weakened when *trans* to a ligand of high *trans*-influence. Coupling constants to olefins also depend on the *trans*-ligand. Since the bonding of olefins to metals is considerably more complicated than that of a methide or hydride ion, or phosphine, such coupling constants should not be used alone as an indicator of *trans*-influence. However, it is of interest to examine the effect of *trans*-ligands on metal–olefin bonding as revealed by these coupling constants.

Kaplan and Orchin[264] found that, in the complexes XXXI, electron withdrawing groups, Z, increased the coupling between ^{195}Pt and the olefin protons, although chemical shifts were consistent with the expected decrease in Pt–olefin π-bonding



XXXI

Braterman[265] explained these results in terms of the *s*-character of the Pt σ-orbital varying with the nature of the *trans* group X in an analogous way to that discussed above to account for variations in $^1J_{Pt-P}$, $^1J_{Pt-H}$, etc. In platinum(II) complexes (Fig. 6) a mirror plane passing through X, Pt and the center of the C=C bond prevents *s*-character in the Pt orbitals used for the π-back-bonding from contributing to the coupling. Since there is no mirror plane containing the C=C bond, symmetry does not prevent mixing of C 2*s* character into the olefin π-orbital which is used to form the olefin→metal σ-bond. The *s*-character of this π-orbital will presumably depend on such factors as changes in Pt–olefin π-bonding caused by changing X, but by Braterman's model such changes are outweighed by those in the Pt σ-orbital.

The theory was used by Fritz and Sellmann[266] in discussing $J_{Pt-C_2H_4}$ in the complexes *trans*-$PtCl_2(C_2H_4)L$, where L was an amine ligand (mainly substituted pyridines). Over the narrow range of coupling constants observed (59.5–63 Hz) the coupling did increase with increased electron-withdrawing power of the pyridine substituent.

In propene complexes steric interaction of the propene methyl group with other ligands can give rise to two distortions in the Pt–olefin geometry.

(*i*) The C=C axis can bend back[268] as in XXXIIb

(a) (b)

XXXII

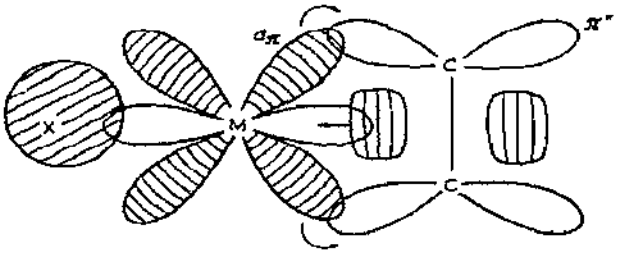


Fig. 6 The Dewar–Chatt–Duncanson model of metal–olefin bonding.

If this occurs, it has little effect on platinum–proton coupling constants since J_{Pt-H_A} is similar to J_{Pt-H_C}.

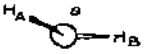
(*ii*) Twisting can occur about the C=C axis, XXXIIIb.

(a) (b)

XXXIII

This does have a significant effect on coupling constants[267–269], causing J_{Pt-H_B} to be smaller than J_{Pt-H_A} (67.2 and 77 Hz respectively in *trans*-$PtCl_2(MeCH{=}CH_2)$-$(O{-}NC_5H_4{-}Me)$.

Holloway et al [269] showed that in the complex PtCl(acac) (Me–CH=CH_2), the platinum coupling constants to the vinyl protons were negative, so that "the effect of moving (vinyl) protons nearer to the platinum atom involves an increase in the negative character of the ^{195}Pt–H coupling"[269]. It was implied that "the ^{195}Pt–H coupling constants of the olefin ligand are more complex in origin than would be expected from consideration of only the Fermi Contact term"[269]. The situation does not appear to be markedly different from that in the "simple" H_A–C–C–H_B fragment, although it is more difficult to analyze in detail. Karplus[270] showed that $J_{H_ACCH_B}$ depended markedly on the dihedral angle between the planes H_A–C–C and C–C–H_B, XXXIV



XXXIV

A similar angular dependence is found[248, 249] for $^3J_{Pt-N-C-H}$. When propene is twisted, the dihedral angles ϕ_A and ϕ_B (XXXIIIb) differ from the dihedral angle, ϕ, before twisting by the torsional angle α such that $\phi_A = \phi - \alpha$; $\phi_B = \phi + \alpha$. Dependence of J_{Pt-H} on ϕ would be expected on the Braterman model Holloway et al.[269] also found that platinum coupling to the propene methyl group was opposite in sign (positive) to that to the vinyl protons (negative), just as in $[PtEt_3Cl]_4$, where $^2J_{Pt-CH_2}$ is opposite in sign[271] to $^3J_{Pt-CH_3}$. This represents a typical reversal of sign of coupling constants $^{n+1}J_{A-C_n-X}$ as n changes from odd to even[272], although there are exceptions. It should be remembered that when a coupling $^nJ_{A-B\ .M-X}$ is said to originate in Fermi Contact, this refers to the mechanism by which the electrons in the bonding orbitals of A and X are perturbed by the nuclear spin. It does *not* refer to the way in which this perturbation is transmitted through B ..M (which does not necessarily involve *s*-electrons at all). These results do suggest that the Pt—H (olefin) coupling constants should only be used as an indication of the *trans*-influence of the ligand *trans* to the olefin when such steric factors are constant.

The direct couplings $^1J_{^{195}Pt-^{13}C}$ to the olefin carbon atoms are not subject to these configurational complications. The Pt—C coupling constants in the complexes $PtX_2(COD)$ where X = I, CF_3 and CH_3 are 124 ± 4, 56 ± 3 and 55 ± 3 Hz respectively[273]. The virtually identical coupling constants *trans* to $-CH_3^-$ and $-CF_3^-$ are consistent with the high NMR *trans*-influence of both these ligands[203] and make it clear that the Pt—C (COD) couplings are not dominated by the effective charge on platinum since the trifluoromethyl complex would be closer to the iodo than the methyl complex in this respect. This is reflected in the ^{13}C chemical shifts of the vinyl carbons[273] (111 p.p.m. downfield from TMS for $Pt(CF_3)_2(COD)$ and 98 8 p.p.m. for $PtMe_2(COD)$). Coupling between platinum and the vinyl protons (70, 40 and 42 Hz for X = I, CH_3 and CF_3 respectively) is also sensitive[274] to the *trans*-influence of X^-.

In the platinum(0) complexes, PtL_2(olefin), the olefin lies approximately in the plane of PtL_2 so that the symmetry restriction noted by Braterman for Pt^{II} complexes preventing participation of Pt—S orbitals in the Pt—olefin π-bonding is no longer present. Thus there are two possible mechanisms for coupling between platinum and nuclei on the coordinated olefin. One is essentially the same as that proposed by Braterman[265] for Pt^{II} with the platinum considered to be trigonally hybridized, XXXVa (largely sp^2) The other corresponds to a dsp^2 square planar hybridization, and to a "metallocyclic" structure. The situation[275] is not necessarily either (a) or (b). Clark et al.[273] consider, on the basis of a comparison of platinum—carbon couplings in Pt^{II} and Pt^0 complexes of C_2H_4 and Me—C≡C—Me, that the coupling mechanism in Pt^0 complexes is essentially similar to that in Pt^{II} complexes, the formal oxidation state only contributing to the magnitude of this coupling.

XXXV

The results of Kemmitt and Moore[276] suggest that the *s*-character in the platinum

σ-orbitals depends on the nature of L in the complexes $PtL_2(C_2F_4)$. J_{Pt-F} is sensitive to L, decreasing in the order en > bipy ≃ phen > $AsPh_3$ > diphos > $PEt_2Ph \geq PMe_2Ph \geq PMePh_2 \geq PBu^n{}_3 \geq PPh_3$. The overall *trans*-influence N-donors < As-donors < phosphines is comparable to a "normal" *trans*-influence series from platinum rehybridization.

(e) Summary

Most of the above coupling constant data can be explained in terms of variation of the factors contained in eqn (3), or the extensions (4) and (5). The variations in coupling between M and a nucleus in the "indicator" group A as L is changed in the linear fragment A—M—L can be consistently explained in terms of variation in the *s*-character of the hybrid orbitals used by M in the M—A bond This is clearly related to the *trans*-influence, defined as the weakening of the M—A bond, and it is found by comparison with other measures of M—A bond strength (see discussion on correlations later) that those ligands with high *trans*-influence are also those which tend to reduce the *s*-character of the M—A bond. To a first approximation, the M—A coupling constant is sensitive only to the hybridization, not to changes in electronegativity of L (as when L is $-CH_3{}^-$ or $CF_3{}^-$). Since the *trans*-influence of L, as defined, appears to depend on both metal hybridization and electronegativity L, the series obtained from M—A coupling constants is slightly different from the *trans*-influence series obtained by other experimental techniques, and thus should be referred to as the "NMR *trans*-influence series"[1]. Correlations between coupling constant data and results from other experimental techniques will be considered later.

(v) NMR chemical shifts

(a) ^{195}*Pt chemical shifts*

Strictly speaking, the chemical shift of the ^{195}Pt nucleus in Pt^{II} complexes does not constitute an experimental observation of the *trans*-influence[1] However, it does indicate the effect of ligands on platinum itself, and since it is clearly related to the hydride chemical shift[228] in the complexes *trans*-$PtHX(PEt_3)_2$ (which has been used as an indication of *trans*-influence) it will be discussed briefly.

The shielding constant for a nucleus is

$$\sigma = \sigma_d + \sigma_p \tag{6}$$

where σ_d and σ_p are the diamagnetic and paramagnetic contributions to the shielding, respectively. According to Ramsey's theory for chemical shifts[277] the paramagnetic contribution to the chemical shift is

$$\sigma_p = \frac{1}{3}\left(\sigma_{p_{xx}} + \sigma_{p_{yy}} + \sigma_{p_{zz}}\right) \tag{7}$$

$$\begin{aligned}\sigma_{p_{xx}} = \frac{-e^2}{2m^2c^2} \sum_{n\neq 0} (E_n - E_0)^{-1} \{ &< 0|\sum_j l_{xj}|n >< n|\sum_k r^{-3} l_{xk}|0 > \\ &+ < 0|\sum_k r_k{}^{-3} l_{xk}\, n >< n|\sum_j l_{xj}|\, 0 > \}\end{aligned} \tag{8}$$

where $|0>$ and $|n>$ are ground and excited molecular wave functions of energies E_0 and E_n, l_{ix} is the x-component of the one-electron angular momentum operator for the electron, i, and r_i is its distance from the nucleus concerned..

When large chemical shifts are involved, σ_d is usually considered negligible compared with σ_p. In classic NMR experiments[278], the chemical shift of the ^{59}Co nucleus in octahedral Co^{III} complexes was shown to be inversely proportional to the wavelength of the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition in the electronic spectra of the complexes. However, in spite of a qualitative correlation[279] between ^{195}Pt chemical shifts and color in some complexes $PtCl_2(PR_3)_2$, detailed attempts to correlate the chemical shift with excitation energies alone were unsuccessful[280].

Dean and Green[228], in considering ^{195}Pt chemical shifts in complexes *trans*-PtHX·$(PEt_3)_2$, derived the expression

$$\sigma_p = \frac{-e^2h^2}{3m^2c^2} < r^{-3} > C_{a_{1g}}{}^2 [8C_{a_{2g}} \{E(^1A_{2g}) - E(^1A_{1g})\}^{-1}$$

$$+ 4\, C_{eg}{}^2\ \{E(^1E_g) - E(^1A_{1g}))\}] \tag{9}$$

where $< r^{-3} >$ is an average over the radial $5d$ functions used as a basis set and $C_{a_{1g}}$, C_{eg} are the coefficients of the corresponding d-orbitals in molecular orbitals used on platinum.

If X forms a covalent bond with platinum, $C_{a_{1g}}{}^2$ is reduced (since this orbital corresponds to $d_{x^2-y^2}$ used in these bonds). If X π-bonds with Pt, the coefficients of the orbitals involved also decrease ($C_{a_{2g}}^2$, $C_{eg}{}^2$). Thus, if X either forms very covalent bonds, or π-bonds appreciably with platinum, the chemical shift moves upfield. The equilibrium constant for the reaction

$$Me{-}Hg^+ + X^- \rightleftharpoons Me{-}Hg{-}X$$

and the nephelauxetic series were used as an indicator of covalency of the Pt—X bond and a good correlation was found between these and the ^{195}Pt chemical shift, except for CN^-, which could be due either to its exceptionally high ligand field strength or high π-bonding.

If one factor influencing the *trans*-influence of X^- is the covalency of the M—X bond some relationship might be expected between the order of ^{195}Pt chemical shifts, $RCO_2^- < NO_3^- < NO_2^- < Cl^- < -SCN^- \simeq Pn^- < CN^- < I^-$ and the *trans*-influence series determined, for example from ν_{Pt-H} ($RCO_2^- \simeq NO_3^- < Cl^- \leq Br^- < I^- < NO_2^- < SCN^- < CN^-$). Halides occur higher in the chemical shift series and are more differentiated. Otherwise the order is similar.

When R was changed in the RCO_2^- complexes, small chemical shift changes were observed.

(*i*) The ortho, para and meta series all varied independently with pK_a of the corresponding acid.

(*ii*) In each series there was an increase in shielding with decreasing pK_a.

(*iii*) Meta derivatives were less sensitive to changes in pK_a.

Those trends were interpreted in terms of variation in π-acceptor properties of the carboxylate ligands. However the chemical shift variation is small (< 8 p.p.m.) and the trends are not clearly defined.

(b) Hydride chemical shifts

Buckingham and Stephens[281, 282] considered that the large high-field shifts characteristic of transition metal hydrides arose chiefly from paramagnetic shielding by the incomplete *d*-electron subshell. They calculated, from Ramsey's equation, the following expressions for σ_d and σ_p for a proton H, at a distance R along the x axis from a metal atom.

$$\sigma_d = \frac{e^2}{3mc^2} < 0 \mid \frac{\sum_j r_{H_j}^2 + R x_{H_j}}{r_{H_j}^3} \mid 0 > \tag{10}$$

$$\sigma_{p_{xx}} = \frac{-e^2}{2m^2c^2} \sum_{n \neq 0} (E_n - E_0)^- \{ < 0 \mid \sum_j l_{m_{xj}} \mid n > < n \mid \sum_k r_{H_k}^{-3} \, l_{H_{xk}} \mid 0 >$$

$$+ < 0 \mid \sum_k r_{H_k}^{-3} \, l_{H_{xk}} \, n > < n \mid \sum_j l_{m_{xj}} \mid 0 > \} \tag{11}$$

(Analogous expressions were developed for $\sigma_{p_{yy}}$ and $\sigma_{p_{zz}}$.)
Most symbols have the same significance as in eqn. (8). l_{m_i} and l_{H_i} are one-electron angular momentum operators corresponding to motion about the metal and the hydride respectively. r_{H_i} is the distance of the electron i from the hydride.

The main contributions to σ_p arise from the influence of the metal *d*-electrons on the hydride. This clearly depends on the distance, R, between the hydride and the metal (σ_p decreases as R increases), the properties (especially optical extension) of the metal *d*-orbitals, defined by k where kr is the exponent in the Slater *d*-orbital functions, and excitation energies, ΔE. Buckingham and Stephens[281] showed that as $R \to 0$, eqns. (10) and (11) reduce to the expression for the *d*-electron contribution to the shielding metal nucleus.

Platinum(II) complexes. Powell and Shaw[231] observed that τ_H in the complexes *trans*-PtHX(PEt$_3$) correlated with the *trans*-effect series for X$^-$ (except for X = NO$_2^-$ which was out of order; their explanation for this in terms of an oxygen-bound nitrito group is not correct[203, 225]). Although it was suggested[158] that little correlation existed between τ_H and a parameter which varied with the *trans*-influence of X$^-$ (e.g., ν_{M-H}), if a sufficient number of complexes is taken, some correlation is clearly present (ref. 154 and discussions later). Buckingham and Stephens[281] suggested that variations in the platinum—hydrogen bond length, R , might be the main cause of the variations in τ_H. However the nearly linear correlation found by Dean and Green[228] between hydride and ^{195}Pt chemical shifts suggest that variations in R are of subsidiary importance, and that the effect on Pt *d*-orbitals of variations in covalency and π-bonding have a very similar effect on the hydride and ^{195}Pt chemical shifts. Because of the "perturbing" effect of variations in R, the hydride chemical shift presumably provides a less reliable guide to the nature of the Pt—X bond than the chemical shift of the ^{195}Pt nucleus itself. The hydride chemical shift is, however, very much easier to measure than that of ^{195}Pt and is available for a wider range of complexes. Unlike ν_{Pt-H}, and, to some extent, J_{Pt-H}, τ_H does not really indicate primarily variations in the Pt—H bond itself but rather variations at the platinum atom. Consequently, we suggest that if the *trans*-influence of a ligand as indicated by τ_H is at variance with that indicated by $\nu_{\text{Pt-H}}$ and $J_{\text{Pt-H}}$ (as for NO_2^-), the latter parameters should usually be considered to provide a better indication. When small variations in τ_H are being considered, it should also be remembered that anisotropic effects from ligands containing unsaturated groups (such as $-C{\equiv}N^-$, $C{\equiv}O$) or aromatic rings appear to have some effect on the chemical shift. For complexes such as *trans*-$PtHX(PMePh_2)_2$, any preferred orientation of the phosphine ligands could allow the anisotropic effects of the aromatic rings attached to phosphorus to influence τ_H.

Atkins et al.[158] found that for the complexes *trans*-$PtH(O_2CR)(PEt_3)_2$ linear correlations existed between τ_H and pK_a of the acids RCO_2H, a better fit being obtained if three different lines were drawn corresponding to acetato-, *o*-benzoato, and *m*-, *p*-benzoato derivatives. When τ_H was plotted against the parameters $\nu_{\text{Pt-H}}$ and $J_{\text{Pt-H}}$, separate linear correlations were usually observed for benzoato and acetato derivatives. Keskinen and Senoff[231a], however, observed no such correlations involving τ_H for the series *trans*-$PtH(SC_6H_4X)(PPh_3)_2$.

Dependence of τ_H on X and correlations between τ_H and other parameters for complexes *trans*-$PtHXL_2$ are illustrated in Figs. 10—12.

Nickel(II) and palladium(II). The hydride chemical shifts for the complexes *trans*-$NiHX(PCy_3)_2$ and *trans*-$PdHX(PCy_3)_2$ clearly vary in an analogous way with X to τ_{PtH} in *trans*-$PtHX(PEt_3)_2$ (Fig. 7). Presumably similar factors affect the chemical shifts in the three series of complexes. This is interesting in view of the apparently anomalous order of $\nu_{\text{Ni-H}}$ for halide complexes (see earlier discussion).

Octahedral complexes. Buckingham and Stevens[282] considered in detail the variation of τ_H in octahedral hydrido complexes with R, k and ΔE and found it difficult to separate out the dominant factors in any particular case. They observed that the order of increasing τ when H was *trans* to a halogen ($I < Br < Cl$) was best explained in terms of variations in k corresponding to the nephelauxetic series and covalency of the M—X bond since an explanation in terms of ΔE would predict the reverse order. However, when the *trans* ligand was constant and the *cis* ligand was varied, the order of τ_H is $Cl < Br < I$, suggesting that variations in ΔE are perhaps in this case predominant. These orders have been shown to hold for a wide variety of complexes[170]. Ligands which have a high *trans*-influence, are high in the spectrochemical series and form more covalent bonds, such as H^-, CH_3^- and $-C_6H_5^-$ (ref. 283), cause low-field shifts for hydrides *trans* to them. R, k, and ΔE all produce effects in the same direction for these ligands.

τ_H is usually more sensitive to the nature of the *trans* ligand than the *cis* dihydrido complexes. τ_H is usually lower for a hydride *trans* to the ligand of greater *trans*-influence. For example, τ_H in XXXVIa is 30.2 p.p.m. (*trans* to Cl^-) and 21.1 p.p.m. (*trans* to PPh_3).

When Cl^- is replaced by $SnCl_3^-$, XXXVIb (higher *trans*-influence than Cl^-), τ_H (*trans* to $SnCl_3^-$) is 24.7 p.p.m., a substantial decrease from that *trans* to Cl^-, while τ_H (*trans* to PPh_3) increases slightly[173] to 22.15. However, it should be remembered that τ_H is complex in origin and does not provide a direct measure of the *trans*-influence, as does, presumably, the M—H force constant.

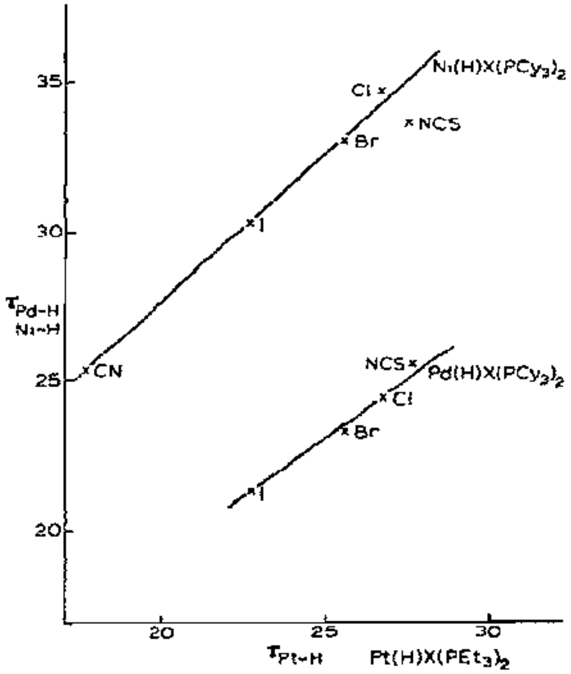
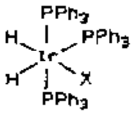


Fig. 7. Plots of τ_H in *trans*-M(H)X(PCy$_3$)$_2$ (M = Ni, Pd) vs τ_H in corresponding complexes *trans*-Pt(H)X(PEt$_3$)$_2$.

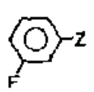


(a) X = Cl$^-$
(b) X = SnCl$_3^-$

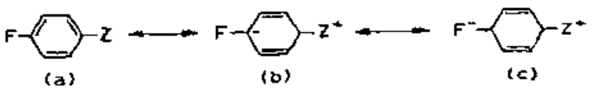
XXXVI

(c) ^{19}F chemical shifts in fluorophenyl derivatives

Parshall^{251} used the method of Taft et al.^{284} in an attempt to separate out σ and π effects in platinum substituents. The technique assumes that in a *meta*-substituted fluorobenzene XXXVII, the ^{19}F chemical shift is dependent on the σ-inductive power of Z,



XXXVII



XXXVIII

while in a *para*-substituted fluorobenzene XXXVIIIa a mesomeric effect is imposed on the σ-inductive effect from contributions due to resonance structures XXXVIIIb, c. Thus $(\delta_{F(para)} - \delta_{F(meta)})$ is considered to give a measure of the π-donation to the aromatic ring.

Parshall[251] examined the systems where Z = *trans*-Pt(PEt$_3$)$_2$X. The difference ($\delta_{F(para)}-\delta_{F(meta)})_X$ was subtracted from that for X = Me$^-$ (for which π-effects were considered to be absent) to give a π-acceptor parameter. $\delta_{F(meta)}$ was used as a measure of σ-inductive effect.

Taft's method has been the center of some controversy amongst organic chemists in recent years and some authors[285] have claimed that $\delta_{F(para)}-\delta_{F(meta)}$ cannot be used to give a simple measure of mesomeric effects, especially if Z is more electropositive than H$^-$ or Me$^-$ (footnote 12 in ref. 251(b)). However, if it is assumed that the technique is substantially correct in giving the π-donation from Z (Pt(PEt$_3$)$_2$X) into the aromatic ring, these results cannot be reliably used to give a measure of the π-properties of the platinum substituent X. Parshall considered that X could only affect Pt → C_6H_4F π bonding by competing with the fluorophenyl group for the same metal d_π orbitals. However, Church and Mays[97] pointed out that X could also decrease the Pt—aryl π-bonding if

(*i*) X was a poorer σ-donor, increasing the effective positive charge on the metal, causing the metal d_π orbitals to contract and have lower energy.

(*ii*) X has a higher *trans*-influence, causing an increase in the Pt—C (C_6H_4F) bond length, which could tend to reduce overlap between the aryl π^* orbitals and Pt d_π-orbitals.

Conversely, changes in the π-acceptor properties of X will cause variations in the σ-inductive power of —Pt(PEt$_3$)$_2$X, since, as d_π electrons are withdrawn by X, the group as a whole will become more electron-withdrawing via σ-orbitals (these considerations are analogous to those used earlier in the discussion of C≡O stretching frequencies).

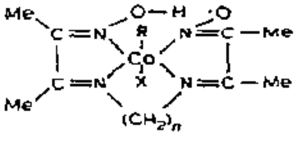
The "σ-inductive series" from $\delta_{F(meta)}$ found by Parshall[251] was $CH_3 > C_6H_5 > PEt_3 >$ *p*-F—C_6H_4— > Ph—C≡C— > *m*-F—C_6H_4 > NCO > CN > Cl > Br > NCS (or SCN) > I ≫ $SnCl_3$. The "π-acceptor series" from ($\delta_{F(para)}-\delta_{F(meta)}$) was CN > $SnCl_3$ > —C≡CPh > Ph ≃ C_6H_4F > NCS(SCN). The methyl group by definition had no π-acceptor capacity and the "π-acceptor parameter" for NCO was zero. The halogens were found to be "π-donors". The order for neutral ligands found by Church and Mays[97] was: "σ-inductive", Me_3CNC > *p*-MeO—C_6H_4—NC > PEt_3 > $P(OMe)_3$ > $P(OPh)_3$ > CO, "π-acceptor", CO > $P(OPh)_3$ ≃ PEt_3 > $P(OMe)_3$ > ArNC > RNC.

While many aspects of these series are "reasonable" they should not be considered to be completely valid for the reasons above. Church and Mays[97] noted the anomalous position of PEt$_3$ relative to the phosphites in their "π-acceptor series". The conclusion that halides are π-donors from Parshall's[251] and Graham's[89] treatments cannot, by any objective criterion, be considered to be firmly established.

^{19}F chemical shifts in *m*- and *p*-FC$_6$H$_4$Z, FC$_6$H$_4$CH$_2$Z and related systems, have been used to study fluoroaryl complexes of mercury[285, 286], main Group IV metals[285, 287], copper[288], iron[289, 290], manganese, nickel, molybdenum and cobalt carbonyl complexes[290] and cobalt(III) Schiff-base (vitamin B$_{12}$ analogues) complexes[291].

Interpretation of results depends on the theoretical standpoint of the authors (for example, whether they accept Taft's basic premise that $\delta_{F(meta)}$ is sensitive only to inductive effects and $\delta_{F(para)}$ to both inductive and mesomeric effects). Stewart and Treichel[290] studied a wide range of carbonyl complexes and concluded that, since their results (and others in the literature) showed a very small range in metal—aryl π-interaction over a wide range of transition metals and their substituents, metal—aryl π-bonding was very small relative to σ-bonding. They showed that a clear relationship existed between the ^{19}F chemical shifts in the complexes m-$FC_6H_4CH_2Z$ and hence they assigned to each of the various ML_n groups a group electronegativity which is appreciably dependent on the metal substituents.

The results of Hill et al.[291] on the complexes XXXIX, with $R = C_6H_4F$, $n = 3$,

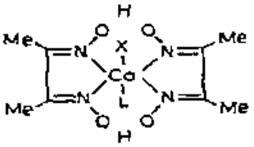


XXXIX

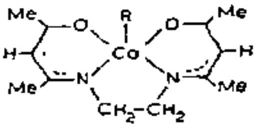
provide an interesting comparison with those of Parshall on platinum(II) compounds. Quite good linear correlations were found for both the *meta* and *para* fluorines between δ_F $(-PtX(PEt_3)_2)$ and $\delta_F(-CoLX)$ Significant deviations were observed only for points representing X = I, NCO The effect of varying X on the electronegativity of the groups (metal and ligands) is clearly similar in the two series. The conclusion was reached from the $\delta_{F(meta)}$ values that the Co^{III} complexes consistently transferred less charge by a σ-inductive mechanism into the aryl ring than the Pt^{II} complexes. From the values of $(\delta_{F(para)} - \delta_{F(meta)})$ it was concluded that the Co^{III} complexes were better π-donors into the aryl ring than Pt^{II} and that this π-donation was more dependent on X.

(d) Proton chemical shifts in cobalt(III) vitamin B_{12} analogues

The best illustration of the use of proton chemical shifts in the study of the effect on a given ligand by varying other ligands attached to the central metal is provided by the results obtained largely by Hill et al. on vitamin B_{12} analogues such as dimethylglyoximates, XL[292, 293], Schiff-base complexes, XLI[294, 295] and corrinoids[296]



XL



XLI

Typical results are provided by the dimethylglyoximate complexes, XL. When L is PPh_3 and X is changed[292] the chemical shift of the dimethylglyoximate methyl groups changes over the range $\tau = 7.70$–8.20 in the order (increasing high-field shift): $-NO_2 < CN < Cl < Br < I < -ONO \ll CH_2CF_3 < CH_3 \leq C_2H_5, n\text{-}C_3H_7$. A similar order is found when L = pyridine. The chemical shift was considered to be a measure of the electron density on the protons and correlated well with Hammett σ-functions. In the pyridine series, the chemical shifts of the protons, especially α-protons, were found to be sensitive to X, though the variation was in the opposite direction to that expected from changes in electron density. It was considered that variation in shielding by the equatorial ligands, arising mainly from variation in the Co–N bond length was responsible. In the complexes where $X = -C_2H_5$, and L was changed (mainly nitrogen donors), the chemical shift difference between the methylene and methyl protons of the ethyl group was considered to be a measure of the electronegativity of the attached $Co(DMG)_2L$ group. Separate linear correlations were observed between pK_a of the bases L for substituted pyridines and for other amines. The authors suggested that anisotropic effects from the aromatic pyridine rings cannot account for the separate correlations, and attributed them to Co—py π-bonding. However, this conclusion is doubtful since it assumes that σ-coordination behavior of a base towards Co^{III} must be identical to that towards H^+.

For the five-coordinate Schiff-base complexes XLI (CoR(BAE)) analogous variations were observed in the chemical shift of the methine protons as R was changed[294, 295]. When R was a *para*-substituted phenyl group, $-C_6H_4-X$, the methine chemical shifts increased to high field in the order $X = NO_2 < CN < Br < I < H < Me \simeq OMe$, i.e., the order of Hammett σ-*para* function[294]. A correlation was observed between these chemical shifts and the thermodynamic *trans*-effect as measured by the equilibrium constants for the reactions.

$$[CoR(BAE)] + L \rightleftharpoons [CoR(BAE)L]$$

In the complexes [CoMe(BAE)L] a dependence of the Me—Co chemical shift upon the basicity of L was noted[295].

Chemical shift data, such as those discussed above, represent the effect of variation in σ-electron transfer by one ligand on electron densities at another ligand. *Cis* and *trans* ligands appear to be affected similarly. The electron density variations do not in themselves represent a *trans*-influence defined in terms of metal—ligand bond weakening, although correlations with thermodynamic *trans*-effects such as that mentioned above imply that the *trans*-influence is related to such electron density variations.

(e) N—H chemical shifts

Brief mention should be made of the different chemical shift behavior for the N—H protons *cis* and *trans* to X in the complexes $[CoX(NH_3)_5]^{2+}$ and in related complexes. Available data have been summarized by Pratt and Thorp[20], who concluded that the chemical shift orders obtained did not provide any single and simple *trans*- or *cis*-influence order, since several different effects probably operated.

Watt and Cuddeback[117] attempted to correlate the $-NH_2$ chemical shifts for the ethylenediamine ligand in the complexes $Pt(en)X_2$ and $Pt(en)L_2^{2+}$ in d_6-DMSO with the *trans*-influence of L (as measured by Pt—Cl stretching frequencies in the complexes PtL_2Cl_2). Some correspondence was found but it is very likely that anisotropic effects (in, for example, $[Pt(en)(phen)]^{2+}$) and changes in solvation have important effects on the $-NH_2$ chemical shift.

(vi) Chlorine nuclear quadrupole resonance spectroscopy

Fryer and Smith[297, 298] have studied a wide range of platinum(II) and palladium(II) chloro complexes by NQR. The most interesting results are provided by the correlations between ^{35}Cl resonance frequencies $^{35}\nu$, and the Pt—Cl bond lengths, r, obtained from X-ray structure determinations. The plots are reproduced in Fig. 8. Fryer and Smith noted that:

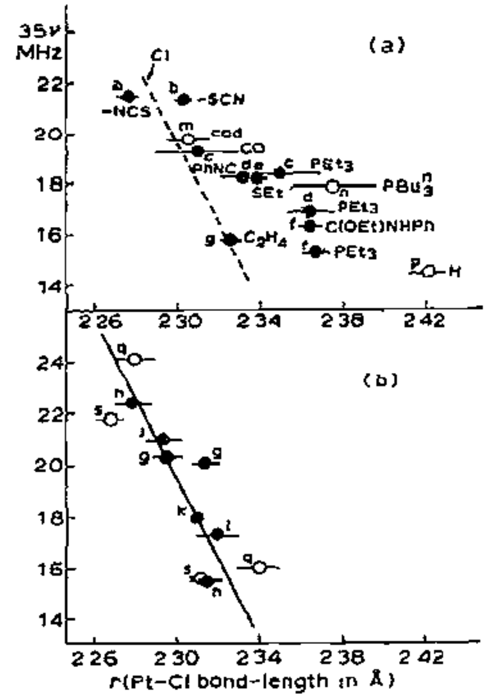


Fig. 8 Variation of chlorine-35 NQR frequency $^{35}\nu$ at 0°C with Pt–Cl bond length r in Pt$^{\mathrm{II}}$ complexes. (a) Chlorines *trans* to the ligand specified; (b) chlorines *trans* to another chlorine ligand. Reproduced, with permission, from ref. 298

Key to Fig 8*

Section I

a	β-$Pt_2Cl_2(SCN)_2(PPr^n_3)_2$	g	$K[PtCl_3(C_2H_4)]H_2O$
b	α-$Pt_2Cl_2(SCN)_2(PPr^n_3)_2$	h	*trans*-$Pt_2Cl_4(PPr^n_3)_2$
c	*cis*-$PtCl_2(CO)(PEt_3)$	j	*trans*-$PtCl_2(PEt_3)_2$
d	*cis*-$PtCl_2(PhNC)(PEt_3)$	k	K_2PtCl_4
e	*cis*-$Pt_2Cl_2(SEt)_2(PPr^n_3)_2$	l	*trans*-$PtCl_2(NH_3)_2$
f	*cis*-$PtCl_2\{C(OEt)NHPh\}(PEt_3)$		

Section II

m	Pt(cyclo-octadiene)Cl_2; $C_{10}H_{14}O_3PtCl_2$
n	*cis*-$PtCl_2(PBu^n_3)_2$; *cis*-$PtCl_2(PMe_3)_2$
p	*trans*-$PtHCl(PMe_2Ph)_2$, *trans*-$PtHCl(PEtPh_2)_2$
q	$Pt_2Cl_4(CH_3CH{=}CH_2)_2$; $Pt_2Cl_4(Me_2C{=}C{=}CMe_2)_2$
s	$Pt_2Cl_4(AsEt_3)_2$; $Pt_2Cl_4(AsMe_3)_2$

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* The full circles apply to the compounds in Section I for which both $^{35}\nu$ and r values are available The open circles represent less reliable correlations for which $^{35}\nu$ applies to the compound given first in Section II, and r to the structurally similar compound given second.

(*i*) There is a general tendency for $^{35}\nu$ to decrease as r increases.

(*ii*) The bond length $r_{\text{Pt-Cl}}$ is more sensitive to variation of the ligand *trans* to Cl than to variation of the *cis* ligand, but $^{35}\nu$ is sensitive to variation in both *cis* and *trans* ligands.

(*iii*) If the *trans* ligand is kept constant and the *cis* ligand is changed, $^{35}\nu$ decreases linearly as r increases

The results were explained in terms of the Townes—Dailey approximation[299]

$$\frac{e^2Qq_{\text{mol}}}{e^2Qq_{\text{at}}} = (1-s)\,\sigma - \tfrac{1}{2}\,\pi \tag{12}$$

where $(e^2Qq_{\text{mol}})/h$ and $(e^2Qq_{\text{at}})/h$ are the quadrupole coupling constants for the Cl atom in the molecule and in the free chlorine atom, s is the degree of s-hybridization in the chlorine bonding orbital, σ is the σ-covalent character of the Pt—Cl bond and π is the π-character of the Pt—Cl bond.

Point (*i*) was taken to indicate that variations in σ were the main cause of the variations in $^{35}\nu$. If s and π are considered to be constant then changes in σ will imply inverse changes in the negative charge on chlorine. Point (*ii*) indicates that a greater increase in r is obtained by altering the *trans* ligand than the *cis* ligand even when the same reduction in σ for the Pt—Cl bond occurs. This can be explained if the weakening of a Pt—Cl bond by a ligand L *trans* to it is the result of two effects:

(1) as L transfers more charge to Pt, the Pt—Cl bond *trans* to it is weakened. A Pt—Cl bond *cis* to L will also be weakened although electrostatic arguments such as Grinberg's, and that given in ref. 298, predict that the *trans* ligand will be affected more.

(2) The Pt atom hybridizes according to Syrkin's theory, i.e., the Pt—Cl bond *trans* to L gains p-character at the expense of s- and d- and is weakened while a Pt—Cl bond *cis* to L gains s-character and is strengthened.

Thus for the Pt—Cl bond *trans* to L, points (1) and (2) tend to reinforce one another, and for the bond *cis* to L they tend to counteract. Observation (*ii*) implies that the X-ray bond length is more sensitive to effect (1) relative to (2) than the NQR frequency.

A *cis*-influence order is readily obtained from the results on complexes *trans*-MCl_2L_2. For M = Pd the increasing order of $^{35}\nu$ (0°C) (increasing Pd—Cl covalency, decreasing Cl negative charge and decreasing *cis*-influence) is piperidine (16.11, 16.31 MHz) $<$ pyridine (17.72) $<$ $AsBu^n_3$ (18.23, 18.59) $<$ PBu^n_3 (18.37, 18.50, 18.58, 18.63) $<$ DMSO (19.75) $<$ EtCN (20.30) $<$ PhCN (20.58). For M = Pt the series is NH_3 (17.30) $<$ Me_2NH (18.16) $<$ py (19.62) $<$ PEt_3 (20.99) $<$ PBu^n_3 (20.90, 21.04, 21.08) $<$ PBu^n_2Ph (21.32, 21.64).

There is no comparable series that illustrates the *trans*-influence series without *cis*-influence also being present. Two other series where further study should prove to be profitable are *trans*-$Pt(X)Cl(PR_3)_2$ and $PtCl_3L^-$. The first series would enable the change in $^{35}\nu$ with the *trans* ligand X to be studied. The results could be correlated with X-ray, NMR and IR results. The only available results on this series would appear to be those for X = H and X = Cl, where $^{35}\nu$ occurs at 14.4 and 21.0 MHz respectively. The series $PtCl_3L^-$ has been studied only for L = C_2H_4, *cis*-2-butene and styrene[300] and L = pyridine[297]. This series, in principle, would allow the *cis*- and *trans*-influences of L to be studied together and the results could be compared with those from infrared studies. Three frequencies were observed for $[NMe_4][PtCl_3(py)]$ at 16.88, 17.89 and 20.68 MHz but no attempt was made to assign them[297]. For Zeise's salt, Yesinowski and Brown[300] found frequencies (13°C) of 16.001, 20.137, and 20.370 MHz. The two higher frequencies were assigned to the two crystallographically distinct Cl atoms *cis* to ethylene, the lower frequency to the Cl atom *trans* to ethylene. This was interpreted in terms of ethylene having a higher *trans*-influence than chlorine, because of its σ-π synergic bonding.

In the complexes[297] *cis* $PtCl_2L_2$, both *cis*- and *trans*-influences of L operate on each chloride atom. The increasing order of $^{35}\nu$ in these complexes at 0°C is Me_2NH (17.21) < py (17.70) < $PBu^n{}_3$ (17.73, 17.79, 17.89, 17.96) < PEt_2Ph (17.82, 17.99) < $PBu^n{}_2Ph$ (18.33) < norbornadiene (30°C, 18.573, 18.799) ≃ bipy (18.98) < COD (19.772, 30°C) < EtCN (21.05, 21.33)

A consistent finding from the NQR data is that, as expected, covalency in Pd—Cl bonds is considerably less than in Pt—Cl bonds[297]

(vii) Photoelectron spectroscopy

As with NQR, the application of photoelectron spectroscopy to the *trans*-influence is in its infancy. In principle, the method has the advantage over most other forms of spectroscopy that some aspects of the electronic structures of several of the atoms in a complex can be examined at the same time.

In an X-ray photoelectron study, Clark et al.[301] examined some complexes *cis*- and *trans*-MX_2PR_3 (M = Pt and Pd). Results relevant to the *trans*-influence are listed in Table 14.

The results were interpreted in terms of variations in the binding energies of the core electrons qualitatively reflecting variations in the charge on the atom concerned, a lower binding energy indicating greater negative charge. With this hypothesis the following deductions can be made from the data in Table 14.

(*i*) Replacement of Cl by Me in diphos-PtX_2 causes a substantial increase in negative charge on Pt and phosphorus.

(*ii*) In the complexes *cis*- and *trans*-$PtCl_2(PR_3)_2$ the charge on Pt is similar for the two isomers, but in the *cis* complexes chlorine is more negative and phosphorus more positive than in the *trans* complexes. This is consistent with the high *trans*-influence of phosphines. The variations of charge on phosphorus are less marked than on Cl presumably because the charge is also distributed over the R groups attached to P.

TABLE 14

X-ray photoelectron binding energies[301] (eV)

Complex	$Pt(4f_{7/2})$ or $Pd(3d_{5/2})$	$Cl(2p_{3/2})$ or $I(3d_{5/2})$	$P(2p_{3/2})$	$C(1s)$
$Pt(diphos)Cl_2$	72.1		130.9	284.7
$Pt(diphos)Me_2$	71.1		130.5	284.7
cis-$PtCl_2(PBu^n{}_3)_2$	72.0	198.1	131.1	284.7
trans-$PtCl_2(PBu^n{}_3)_2$	72.0	199.3	130.7	284.7
cis-$PtI_2(PMe_3)_2$	72.9	621.4	132.6	285.1
trans-$PtI_2(PMe_3)_2$	72.9	622.1	132.1	285.0
Pt metal	71.1			
cis-$PdCl_2(PEt_2Ph)_2$	338.0	197.4	130.9	284.7
trans-$PdCl_2(PEt_2Ph)_2$	338.0	198.2	130.6	284.7

(*iii*) Palladium complexes show similar effects although the Cl atoms are more negative than in the platinum complexes.

(*iv*) It was suggested from a comparison of Pt and P binding energies for $PtCl_2(PBu^n{}_3)_2$ and $PtI_2(PMe_3)_2$ that iodine transferred less charge to platinum than chlorine (as Parshall suggested)[251]. This is probably valid, though it is unfortunate that the phosphines differ in the two sets of complexes

Correlations with NQR results were pointed out. As with NQR, a detailed photoelectron study could profitably be carried out with extended series such as *trans*-$PtClX(PR_3)_2$ and $PtCl_3L^-$.

D. CORRELATIONS BETWEEN RESULTS OBTAINED BY DIFFERENT EXPERIMENTAL METHODS

(*i*) *An empirical approach to the* trans-*influence*

Most correlations between different experimental techniques pertaining to the *trans*-influence, such as those above, can be explained by the following assumptions:

(*i*) The *trans*-influence of a given ligand, L, depends on (*a*) the effect of L on the hybrid orbital used by the metal in its bond to the *trans* ligand A, and (*b*) the net charge transfer ($\sigma_{\text{covalent}}-\pi$) from ligand to the metal

(*ii*) Different experimental techniques have different sensitivities to (*i*) (*a*) and (*b*).

However, (*i*) (*a*) and (*b*) are not altogether unrelated. Metal hybridization will be such as to maximize the energy over all ligand bonds Each metal ligand bond will have an optimum metal *s*, *p* and *d* orbital population which could maximize a quantity[14, 15] such as $S^2/\Delta E$, where S is the overlap integral between metal and ligand orbitals and ΔE is the absolute energy separation between them This optimum metal hybridization for a given metal—ligand bond will seldom be achieved because of the demands of the other M—L bonds. However, the ligand which is capable of strongest covalent bonding (i.e., for which $S^2/\Delta E$ is potentially largest) will come closest to having optimum metal hybridization in its M—L bond, at the expense of the *trans*-M—A bond. If the optimum metal hybrid for the M—L bond contains a high degree of *s*-character, the *trans*-M—A bond is then deprived of *s*-character Many ligands which form strong covalent bonds do have large metal *s*-participation in their M—L bonds (e.g., PR_3, $-CH_3{}^-$, $-CN^-$) and thus the M—A bond *trans* to these ligands is weakened both through low *s*-character in the M—A metal hybrid, (*i*) (*a*), and through the "electrostatic" effect of the covalent charge transfer, (*i*) (*b*). But for some ligands (e.g , N-donors, I^-, Br^-) optimum metal hybridization in the M—L bond does not appear to contain much *s*-character. Then, although for example the M—N bond is quite strong in terms of bond energy[302], the M—A bond *trans* to it is not greatly depleted in metal *s*-character. The *trans*-influence of nitrogen donors then depends only on the degree of covalent charge transfer, (*i*) (*b*). Nitrogen donors thus have a lower overall *trans*-influence ((*i*) (*a*) + (*i*) (*b*) as measured by ν_{M-Cl}) than, for example, phosphines which form strong covalent bonds (*i*) (*b*) and deplete *s*-character of the *trans*-bond (*i*) (*a*). N-donors even have an IR *trans*-influence lower than or comparable with those of olefins in platinum(II) complexes, in spite of the facts that (*a*) the Pt—N bond is thermodynamically more stable than the Pt—olefin bond[302], and (*b*) that Pt—olefin π-bonding tends to strengthen the *trans*-

Pt—Cl bond by withdrawing charge from Pt, (*i*) (*b*). This must be because the Pt—olefin bond requires more *s*-character than the optimum Pt—N bond and hence (*i*) (*a*) outweighs (*i*) (*b*).

The tendency to deplete metal *s*-character in the *trans*-M—A bond appears to depend primarily on the nature of the donor atom, and secondly on the orbital hybridization of the donor atom, and the electronegativity of its substituents From NMR coupling constants this tendency decreases in the order: C-donors ($sp^3 \simeq sp^2 > sp$) > P-donors ≥ As-donors > S-donors > N-donors > halides ≥ O-donors.

At this time, a detailed discussion of the way in which maximization of $S^2/\Delta E$ affects the metal hybridization in the optimum M—L bond is probably not justified. However, the following speculative suggestions can be made. The degree of orbital overlap, S^2, is certainly an important factor in determining the covalency of the M—L bond[14, 15]. However, the effect of the metal rehybridization appears to be mainly a lowering of the energy of the metal orbitals (decreased ΔE) by increasing *s*- and *d*-participation (as suggested by Syrkin) rather than to increase orbital overlap (S^2) by increasing *p*-participation. On this model, a ligand X whose orbital energy closely matches that of a metal hybrid with relatively low *s*-character will have a lower *s*-demand than a ligand Y whose orbital energy more closely matches that of a metal hybrid with high *s*-character (Fig 9). Typically, pyridine might represent a ligand such as X, a phosphine a ligand such as Y.

The experimental results can be explained in terms of the differing sensitivities of different experimental techniques. Again the approach is empirical, based on the results, and only secondly on the theoretical concepts.

NMR coupling constants depend primarily on the metal hybridization, (*i*) (*a*).

Chemical shifts of nuclei well removed from direct contact with metal *d*-orbitals (e.g., ^{19}F chemical shifts in *m*- and *p*-fluoroaryl derivatives — not M—H chemical shifts) depend almost entirely on effective metal charge, (*i*) (*b*)

Hydride chemical shifts are very complex in origin but probably correlate best with $\sigma + \pi$ covalency of the *trans* ligand

NQR frequencies, photoelectron spectroscopic binding energies, vibrational stretching frequencies and bond lengths would all be expected to depend on both (*i*) (*a*) and (*i*) (*b*). NQR and photoelectron spectroscopy results appear to depend mainly on electrostatic effects (*i*) (*b*) (see above).

The relative effects of (*i*) (*a*) and (*i*) (*b*) on an M—A stretching frequency depend on

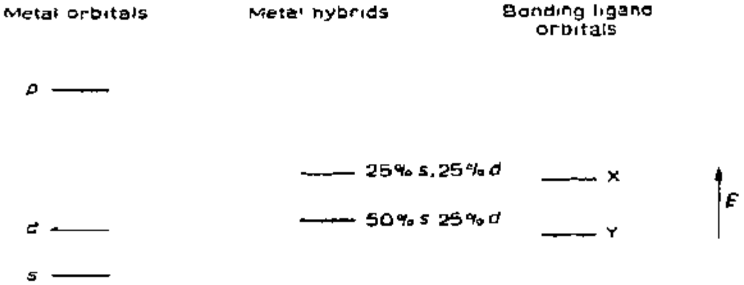


Fig. 9. Hypothetical energy level diagram. Y has a higher *s*-demand than X.

the nature of A. From the correlations which follow, it is clear that Pt—H and Pt—CH_3 stretching frequencies can distinguish between different *trans*-ligands with moderate or weak *trans*-influence, e.g., between RNC, CO, C_2H_4, py, Cl^-, while ν_{Pt-Cl} is almost constant *trans* to these ligands (Table 3). At the other end of the *trans*-influence series, however, Pt—Cl stretching frequencies are very sensitive to the *trans* ligand and can distinguish, for example, between different aryl-substituted silyl groups (Table 3). Pt—Cl bond lengths appear to show similar behavior, since there is little difference between Pt—Cl bond lengths *trans* to different ligands with weak to moderate *trans*-influence (Tables 1, 2), but appreciable differences[15] between Pt—Cl bond lengths *trans* to PR_3, H^-, $SiR_3{}^-$. These results can be explained as follows: Pt—Cl bonds have a low optimum Pt(6*s*) character. If the demand on the *trans* ligand, L, for Pt(6*s*) character in the Pt—L bond is not high, the Pt-hybridization in the Pt—Cl bond is near optimum and the Pt—Cl bond is not greatly weakened by an increase in the *s*-demand of L, and will be affected mainly by electrostatic factors, (*i*) (*b*) (especially since the Pt—Cl bond contains appreciable ionic character). When L has a high *s*-demand, however, the Pt—Cl bond is depleted of Pt(6*s*) character below optimum, and is consequently progressively weakened as the *s*-demand of L increases. Bonds such as Pt—H and Pt—CH_3 which have very high optimum Pt(6*s*) character are sensitive to small variations in the *s*-demand of the *trans*-ligand, L, even when the *s*-demand of L is very low.

In the following sections graphs in which one spectroscopic parameter is plotted against another are used to determine the degree of correlation between *trans*-influence series derived from different spectroscopic measurements It should be emphasized that perfect linear correlations between various parameters used as a measure of the *trans*-influence would not be expected, since as pointed out above different techniques have different sensitivities to the hybridization and electrostatic aspects of the *trans*-influence, and since the interpretation of any spectroscopic result in terms of the properties of a bond is subject to approximations and simplifications (mentioned in the appropriate sections above). The plots which follow are intended to show general trends only, and minor deviations of individual points from lines drawn to illustrate these have little physical significance.

(ii) Correlations in hydrido-platinum(II) complexes

Atkins et al.[158] found that within the closely related series of complexes *trans*-PtH(O_2CR)$(PEt_3)_2$ very good straight lines were obtained when each of the parameters J_{Pt-H}, ν_{Pt-H} or τ_{Pt-H} was plotted against each of the other parameters Each of the parameters varied linearly with pK_a of RCO_2H as well.

As pointed out by Keskinen and Senoff[231a], the various hydride parameters when R is substituted aryl group $-C_6H_4X$ can equally well be plotted against σ_p, the Hammett substituent parameter, for X. These authors found that both J_{Pt-H} and ν_{Pt-H} in the series *trans*-Pt(H)(S-C_6H_4X)$(PPh_3)_2$ varied linearly with σ_p for X, and that a rough linear correlation existed between ${}^1J_{Pt-H}$ and ν_{Pt-H} over this series of complexes. Somewhat surprisingly, τ_H was insensitive to X.

Plots between the three hydride parameters over a wide range of ligands are given in Figs. 10–12. It would be preferable to have values of all parameters in the same solvent but in some cases these are not available, as indicated. From the plots it is clear that there

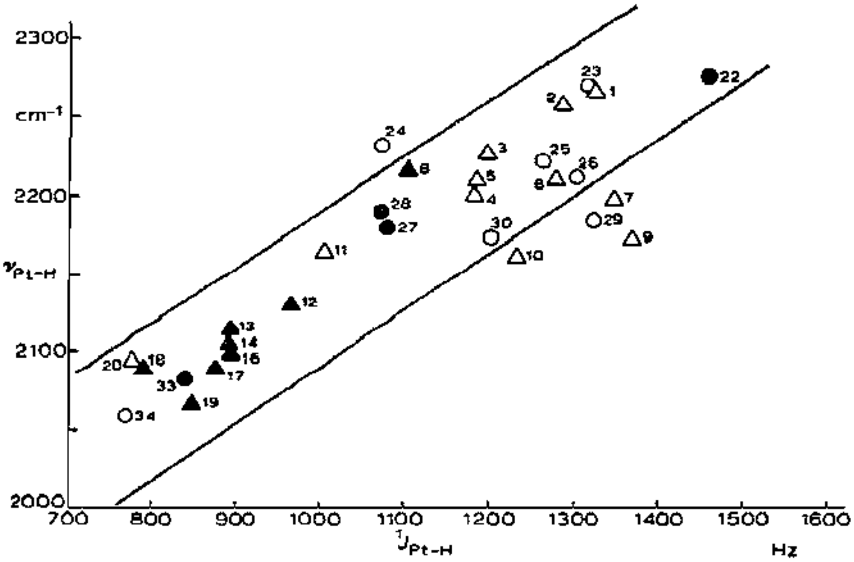


Fig. 10. Plot of ν_{Pt-H} vs. $^1J_{Pt-H}$ in complexes *trans*-Pt(H)X$(PR_3)_2$ and *trans*-Pt(H)L$(PR_3)_2^+$ (PR_3 = PEt_3, $PMePh_2$)

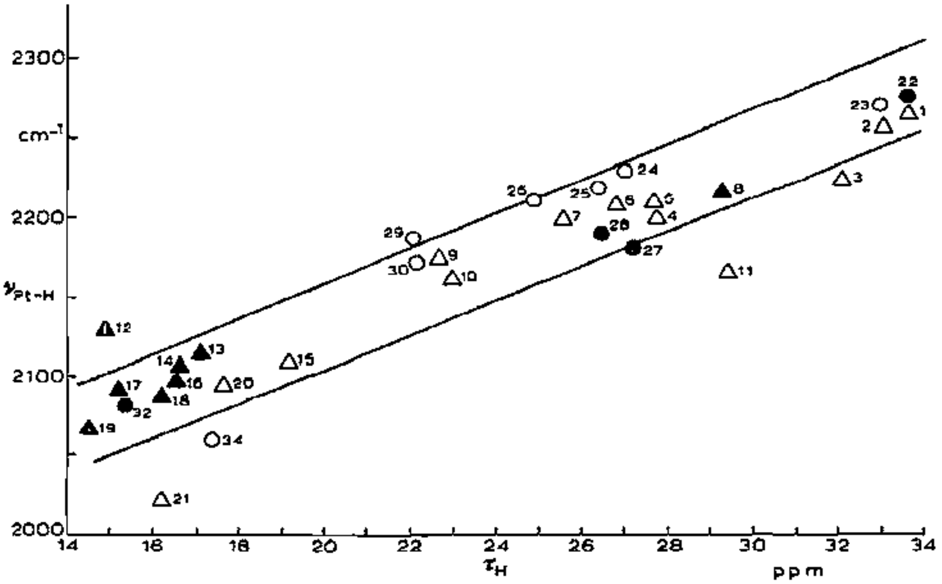


Fig. 11. Plot of ν_{Pt-H} vs τ_H in complexes *trans*-Pt(H)X$(PR_3)_2$ and *trans*-Pt(H)L$(PR_3)_2^+$.

is an overall trend for ν_{Pt-H}, $^1J_{Pt-H}$ and ν_{Pt-H} to decrease together. As discussed above, $^1J_{Pt-H}$ depends predominantly on the *s*-character of the platinum hybrid orbital used in the Pt—H bond, α_{Pt}^2; τ_{Pt-H} (see above) probably depends mainly on Pt—X or Pt—L covalency. ν_{Pt-H} would be expected to depend on both α_{Pt}^2 and the net charge transferred to Pt by X or L (which in the absence of Pt—X, Pt—L π-back-donation is directly related

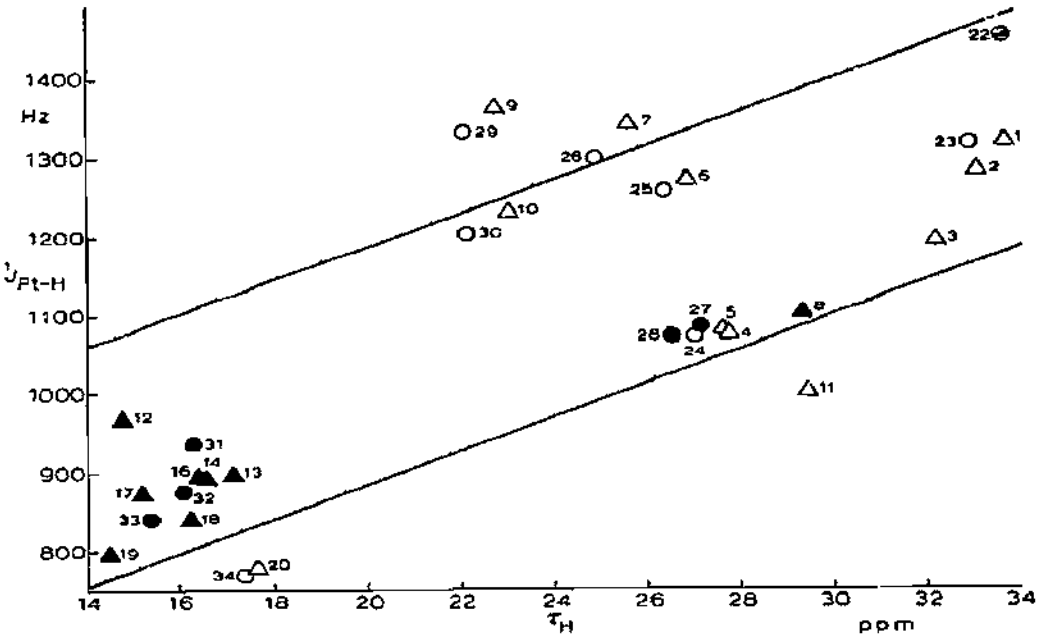


Fig 12 Plot of $^1J_{Pt-H}$ vs τ_H in complexes *trans*-$Pt(H)X(PR_3)_2$ and *trans*-$Pt(H)L(PR_3)_2^+$

Key to Figs. 10, 11, 12

Parameters in $CHCl_3$ or CH_2Cl_2 unless otherwise stated

No.	Complex	Notes
1	$Pt(H)(NO_3)(PEt_3)_2$	τ and J in benzene
2	$Pt(H)(CF_3CO_2)(PEt_3)_2$	All in acetone
3	$Pt(H)(p\text{-}MeC_6H_4CO_2)(PEt_3)_2$	
4	$Pt(H)(NCO)(PEt_3)_2$	τ and J in benzene
5	$Pt(H)(NCS)(PEt_3)_2$	τ and J in benzene
6	$Pt(H)Cl(PEt_3)_2$	τ and J in benzene
7	$Pt(H)Br(PEt_3)_2$	τ and J in benzene
8	$[Pt(H)py(PEt_3)_2]ClO_4$	
9	$Pt(H)I(PEt_3)_2$	τ and J in benzene
10	$Pt(H)(SCN)(PEt_3)_2$	τ and J in benzene
11	$Pt(H)(NO_2)(PEt_3)_2$	τ and J in benzene
12	$[Pt(H)(CO)(PEt_3)_2]ClO_4$	ν "corrected"
13	$[Pt(H)(t\text{-}BuNC)(PEt_3)_2]ClO_4$	ν "corrected"
14	$[Pt(H)(p\text{-}MeOC_6H_4NC)(PEt_3)_2]ClO_4$	ν "corrected"
15	$Pt(H)(SnCl_3)(PEt_3)_2$	In hexane? J not available
16	$[Pt(H)(PPh_3)(PEt_3)_2]ClO_4$	
17	$[Pt(H)\{P(OPh)_3\}(PEt_3)_2]ClO_4$	
18	$[Pt(H)(PEt_3)_3]ClO_4$	
19	$[Pt(H)\{P(OMe)_3\}(PEt_3)_2]ClO_4$	
20	$Pt(H)(CN)(PEt_3)_2$	ν "corrected"

Key to Figs. 10, 11, 12 (continued)

No	Complex	Notes
21	$Pt(H)(-C{\equiv}C-Ph)(PEt_3)_2$	ν not "corrected" J not available
22	$[Pt(H)(acetone)(PMePh_2)_2]PF_6$	ν in Nujol
23	$Pt(H)(NO_3)(PMePh_2)_2$	
24	$Pt(H)(NCS)(PMePh_2)_2$	
25	$Pt(H)Cl(PMePh_2)_2$	
26	$Pt(H)Br(PMePh_2)_2$	
27	$[Pt(H)(2\text{-}Mepy)(PMePh_2)_2]PF_6$	ν in Nujol
28	$[Pt(H)(2,4,6\text{-}Mepy)(PMePh_2)_2]PF_6$	ν in Nujol
29	$Pt(H)I(PMePh_2)_2$	
30	$Pt(H)(SCN)(PMePh_2)_2$	
31	$[Pt(H)(C_2H_4)(PMePh_2)_2]PF_6$	ν not known
32	$[Pt(H)(p\text{-}MeC_6H_4NC)(PMePh_2)_2]PF_6$	ν not accurately known
33	$[Pt(H)(PMePh_2)_3]PF_6$	ν in Nujol
34	$Pt(H)(CN)(PMePh_2)_2]PF_6$	

to Pt—X(L) σ-covalency; π-bonding would make Pt more positive and strengthen the Pt—H bond) Thus, the general trends illustrated by the graphs are to be expected, but the worst overall correlation is between τ_H and ${}^1J_{Pt-H}$.

One advantage of comparing the three hydride parameters in this way is that it is very easy to see if any one of these quantities is "anomalous" for a particular X or L. For example, in both plots involving τ_H, the point representing NO_2^- lies well away from the "line" while for the plot ${}^1J_{Pt-H}$ vs. ν_{Pt-H} it lies very close to the "line". Thus, of the three parameters only τ_H is "anomalous" for $X = NO_2^-$. Similarly, the point representing L = CO lies well off the "line" in plots involving τ_H It is tempting to ascribe these deviations, in part at least, to the magnetic anisotropy of these groups. In plots involving ${}^1J_{Pt-H}$, consistent deviations are observed for points representing $X = Br^-, I^-, -SCN^-$, while these points lie near the "line" in the plot of τ_H against ν_{Pt-H}. The best explanation for these deviations would appear to be that the differences in the effect on ν_{Pt-H} for these ligands is more controlled by Pt—X covalency and X→Pt charge transfer, to which ${}^1J_{Pt-H}$ is not directly sensitive, than by the Pt hybridization, to which ${}^1J_{Pt-H}$ is sensitive.

(iii) Other correlations

In this section the correlations observed in the literature between various parameters related to the *trans*-influence will be listed and discussed, together with a few correlations that have not previously been noted.

(a) Correlations between coupling constants

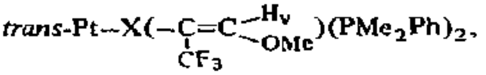
(*i*) ${}^2J_{Pt-CH_3}$ for complexes *trans*-$[PtCH_3L(PMe_2Ph)_2]^+$ varies linearly[234] with ${}^1J_{^{195}Pt-^{13}C}$.

(*ii*) ${}^2J_{Pt-CH_3}$ for complexes *trans*-$PtCH_3X(PMe_2Ph)_2$ varies linearly[203] with ${}^2J_{Pt-H}$ for complexes *trans*-$PtHX(PEt_3)_2$.

(*iii*) $^1J_{Pt-P}$ in the complexes *trans*-$Pt(PO(OPh)_2)X(PEt_3)_2$ varies linearly[225] with $^2J_{Pt-CH_3}$ for the complexes $PtCH_3X(PEt_3)_2$.

(*iv*) $^2J_{Pt-CF_3}$ in the complexes *trans*-$PtX(CF_3)(PMe_2Ph)$ and $[PtL(CF_3)(PMe_2Ph)_2]^+$ varies linearly with $^2J_{Pt-CH_3}$ in the corresponding methylplatinum complexes, except for L = CO, $SbPh_3$ which use synergic σ—π bonding[203].

(*v*) $^3J_{Pt-CCF_3}$ and $^3J_{Pt-C-C-H}$ in the complexes



$$trans\text{-}Pt{-}X(-\underset{\displaystyle CF_3}{\underset{|}{C}}{=}C\begin{smallmatrix}\nearrow H_v\\ \searrow OMe\end{smallmatrix})(PMe_2Ph)_2,\ \mathrm{XXX}$$

vary linearly with J_{Pt-Me} in corresponding methylplatinum complexes[250] except for L = $SbPh_3$.

(*vi*) $^3J_{Pt-Ge-Me}$ in the complexes *trans*-$PtX(GeMe_3)(PEt_3)_2$ correlate[111] with $^2J_{Pt-CH_3}$ in *trans*-$PtX(CH_3)(PEt_3)_2$.

(*vii*) $^2J_{Pt-CH_3}$ in the Pt^{IV} complexes $[Pt(CH_3)_2(PMe_2Ph)_2L_2]^+$, XIX, varies linearly[190] with $^2J_{Pt-CH_3}$ in the Pt^{II} complexes *trans*-$Pt(CH_3)L(PMe_2Ph_2)_2{}^+$.

(*viii*) $^3J_{Hg-P-CH_3}$ in the complexes PMe_3—Hg—X^+ varies[257] in a similar way to $^2J_{Hg-CH_3}$ in the complexes Me—Hg—X.

(*ix*) $^1J_{Pt-CH_3}$ varies[224] with X in *trans*-$PtX(CH_3)(PEt_3)_2$ in a similar way to $^2J_{Hg-CH_3}$ in CH_3HgX.

(*x*) $^1J_{Hg-P}$ in the complexes X—Hg—$P(O)(OPh)_2$ varies with X in a similar way to $^1J_{Hg-P}$ in the series *trans*-$PtX(P(O)(OPh)_2(PEt_3)_2)$.

(*xi*) $^3J_{Hg-Si-CH_3}$ in the series X—$HgOSiMe_3$ varies linearly[256] with $^2J_{Hg-CH_3}$ in the series CH_3—Hg—X

The above correlations are consistent with variations in $\alpha_M{}^2$ dominating the coupling, and being similar for M = Pt, Hg.

(b) Correlations between metal—ligand stretching frequencies

(*i*) ν_{Pt-Cl} *trans* to L in *trans*-$Pt(L)Cl(PEt_3)_2{}^+$, *cis*-$PtCl_2L_2$, $PtCl_3L^-$, $Pt_2Cl_4L_2$ all show rough correlations (see Table 3).

(*ii*) Over the range of complexes available for comparison, ν_{Pt-Cl} in the complexes *trans*-$PtCl(Z)(PEt_3)_2{}^{n+}$ does not correlate very well with ν_{Pt-H} in *trans*-$Pt(H)(Z)(PEt_3)_2{}^{n+}$ (Fig 13(a)) or ν_{Pt-CH_3} in *trans*-$Pt(CH_3)(Z)(PR_3)_2{}^{n+}$ (Fig 13(b)). ν_{Pt-Cl} becomes relatively insensitive to Z as the *trans*-influence of Z becomes weaker.

(*iii*) Quite a good linear correlation is obtained between ν_{Pt-CH_3} in *trans*-$Pt(CH_3)(Z)(PR_3)_2{}^{n+}$ and ν_{Pt-H} in *trans*-$PtCH_3(Z)(PR_3)_2{}^{n+}$ (Fig. 14). ν_{Pt-H} values have been "corrected" for vibrational coupling for Z = CO, *p*-$MeOC_6H_4NC$, CN^-. No attempt has been made to correct for vibrational coupling involving ν_{Pt-CH_3}, which could be significant where ν_{Pt-Z} occurs in a similar region to ν_{Pt-CH_3}, viz. Z = CO, *p*-$MeOC_6H_4NC$, CN^-, $NO_2{}^-$. Clearly ν_{Pt-H} and ν_{Pt-CH_3} depend in a similar way on platinum hybridization and effective metal charge.

(*iv*) Rough correlations exist between *trans*-influence orders as found by ν_{M-Cl}, ν_{M-H}, ν_{M-CH_3} and those obtained from ν_{M-H} and ν_{M-P} (see appropriate sections).

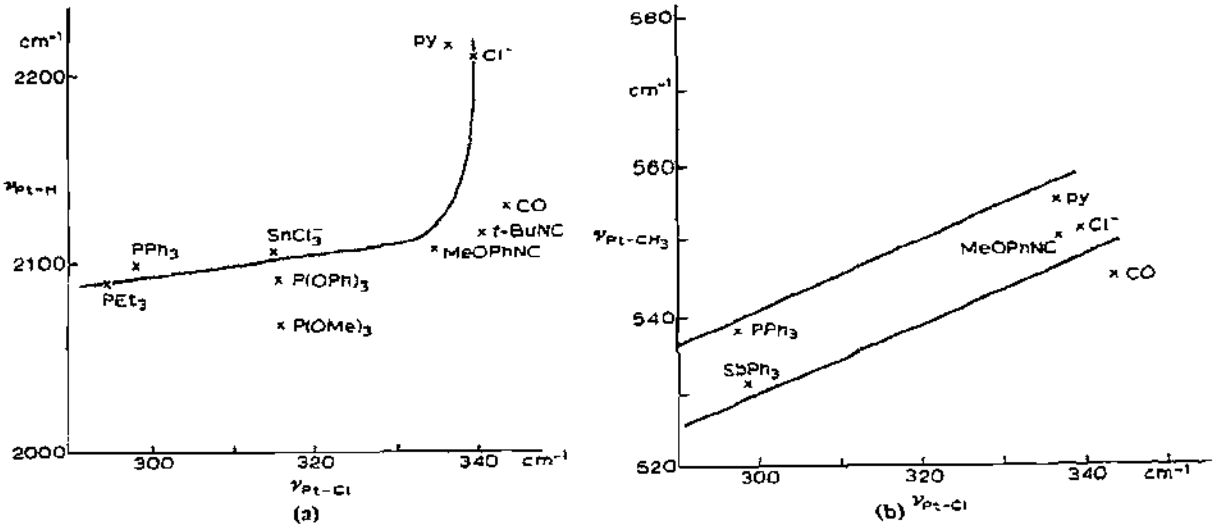


Fig. 13. (a) Plot of ν_{Pt-H} in complexes *trans*-Pt(H)X(PR$_3$)$_2$, Pt(H)L(PR$_3$)$_2^+$ vs. ν_{Pt-Cl} in corresponding complexes *trans*-PtClX(PR$_3$)$_2$, PtClL(PR$_3$)$_2^+$. (b) Plot of ν_{Pt-CH_3} in complexes *trans*-Pt(CH$_3$)X-(PR$_3$)$_2$, Pt(CH$_3$)X(PR$_3$)$_2^+$ vs ν_{Pt-Cl} in corresponding complexes *trans*-PtClX(PR$_3$)$_2$, PtClL(PR$_3$)$_2^+$

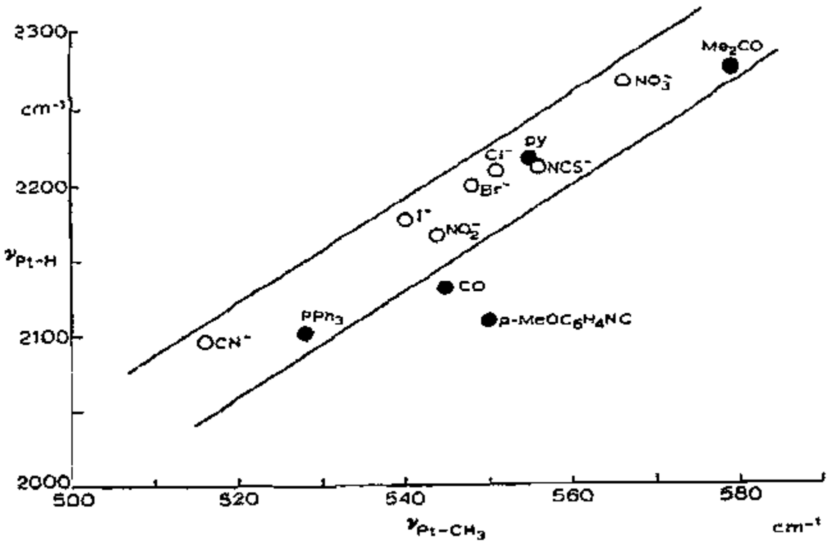


Fig. 14. Plot of ν_{Pt-H} in complexes *trans*-Pt(H)X(PR$_3$)$_2$, Pt(H)L(PR$_3$)$_2^+$ vs ν_{Pt-CH_3} in corresponding complexes *trans*-Pt(CH$_3$)X(PR$_3$)$_2$, Pt(CH$_3$)L(PR$_3$)$_2^+$.

(c) Correlations between metal–ligand stretching frequencies and coupling constants

(*i*) ${}^2J_{Pt-CH_3}$ shows quite a good correlation with ν_{Pt-CH_3} in the complexes *trans*-$Pt(CH_3)(Z)(PR_3)_2{}^{n+}$ (Fig. 15). As usual when a coupling constant is plotted against a stretching frequency, the halides show considerable deviation (see discussion on hydride correlations). No obvious explanation presents itself for the apparently anomalous values of ν_{Pt-CH_3} for the complexes with Ar–CN and Ar_F–CN. Vibrational coupling may be partly responsible for the deviations when Z = CN^-, CO.

(*ii*) Some correlations have been noted between ${}^2J_{Pt-CH_3}$ and ν_{Pt-CH_3} in some series of methylplatinum(IV) complexes, viz. $Pt(CH_3)_3L_3{}^+$ and $Pt(CH_3)_3X_3{}^{2-}$ (ref. 185), and $Pt(CH_3)_2(P(CH_3)_2(C_6H_5))_2L_2{}^{2+}$ (ref. 190).

(*iii*) Church and Mays[97] found a linear correlation between ${}^1J_{Pt-H}$ in the series *trans*-$Pt(H)L(PEt_3)_2{}^+$ and ν_{Pt-Cl} in the series *trans*-$PtClL(PEt_3)_2{}^+$ over a small range of L. When the range is extended to include L = py, the correlation is less remarkable (Fig. 16). Similar results are obtained when ν_{Pt-Cl} in this series is plotted against ${}^2J_{Pt-CH_3}$ in the series *trans*-$Pt(CH_3)L(PR_3)_2{}^+$

(d) Miscellaneous correlations

(*i*) The *trans*-influence based on Pt–Cl bond lengths[15] is similar to that obtained from Pt–Cl stretching frequencies. Like ν_{Pt-Cl}, r_{Pt-Cl} appears to become relatively insensitive at the weak end of the *trans*-influence series.

(*ii*) Correlations between position of a ligand in the *trans*-influence series (from X-ray bond lengths) and calculated overlap between ligand and metal orbitals have been made[14,15].

(*iii*) Correlations have been made between the Pauling electronegativity of the donor atom and the *trans*-influence of the ligand, as measured by X-ray bond lengths[14,15] and stretching frequencies Various authors have noted, however, that the *trans*-influence and electronegativity series are by no means coincident[110,203,273].

(*iv*) In the series $PdCl_2L_2$, the heat of formation of the Pd–L bond correlates well with the *trans*-influence of L as measured by Pd–Cl stretching frequencies[302] for L = olefin, PR_3, AsR_3, but the low *trans*-influence of N-donors was apparently inconsistent with the high Pd–N bond energies. This is discussed in detail above.

(*v*) The correlation between ${}^{35}Cl$ NQR frequencies and bond lengths has been discussed above.

E. THE *trans*-INFLUENCE AND THE *trans*-EFFECT

The relationship between the *trans*-influence and the *trans*-effect was long clouded by a near-exclusive concentration on square-planar platinum(II) complexes, for which the *trans*-effect order is: $H_2O \simeq NO_3{}^- < OH^- < NH_3 < Cl^- < Br^- < I^- \simeq -SCN^- \simeq NO_2{}^- \simeq PR_3 \ll CO \simeq C_2H_4 \simeq CN^- \simeq CH_3{}^- \simeq H^-$. By 1962 it was becoming clear[2] that two types of ligands had a very high *trans*-effect in Pt^{II} complexes, viz. those with (what we now call) high *trans*-influence, and those with π-bonding capacity (and low *trans*-influence). The high *trans*-effects of both types of ligand have been adequately explained on the basis of a trigonal bipyramidal transition state. The stabilizing effect of such a transition state of π-bonding ligands was discussed by Chatt et al.[6] and Orgel[7].

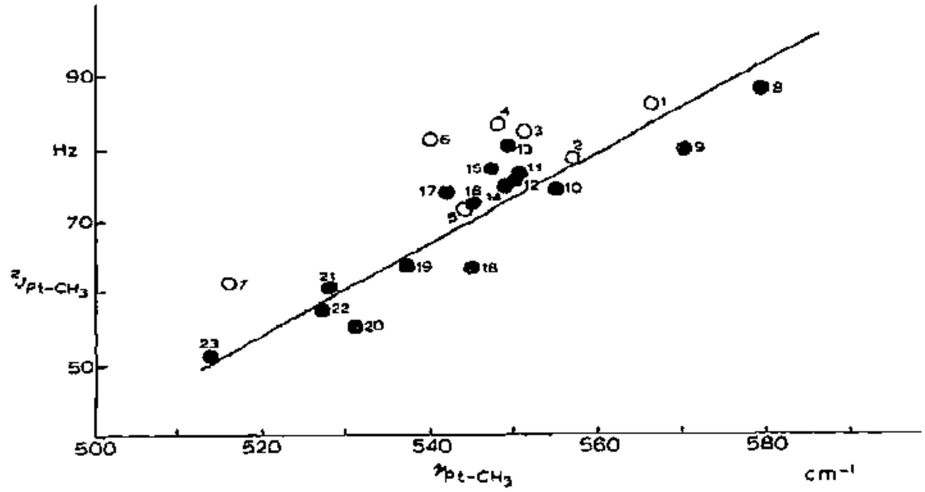


Fig 15. Plot of $^2J_{Pt-CH_3}$ vs. ν_{Pt-CH_3} in complexes *trans*-$Pt(CH_3)X(PR_3)_2$ and $Pt(CH_3)L(PR_3)_2^+$ (PR_3 = PEt_3, PMe_2Ph).

Key to Fig. 15

trans-$PtX(CH_3)(PR_3)_2$			
1	X = NO_3^-	11	←$NH{=}C(OMe){-}C_6F_5$
2	$-NCS^-$	12	$CH_2{=}CH{-}CH{=}CH_2$
3	Cl^-	13	C_6F_5CN
4	Br^-	14	C_2H_4
5	NO_2^-	15	$MeC{\equiv}CMe$
6	I^-	16	$CH_2{=}C{=}CH_2$
7	CN^-	17	$CH_3CH{=}CH_2$
trans-$Pt(CH_3)L(PR_3)_2$		18	CO
		19	EtNC
8	L = Me_2CO	20	$SbPh_3$
9	ArCN	21	PPh_3
10	py	22	PMe_2Ph
		23	$-C(OMe)Me$

In recent theoretical treatments of the five-coordinate transition state[13, 16] it has been suggested that a non-π-bonding ligand of high *trans*-effect weakens the *trans*-bond in the transition state by depriving it of Pt($6p_\sigma$) character. It seems more likely to us that a ligand of high *trans*-influence weakens the *trans*-bond in the transition state by a mechanism essentially similar to that by which it weakens the *trans*-bond in the ground state, i.e., by depriving the Pt orbital to the *trans*-bond of Pt($6s$) character, and making the *trans*-bond more ionic by electrostatic repulsion.

In octahedral complexes the transition state in a substitution reaction is quite different

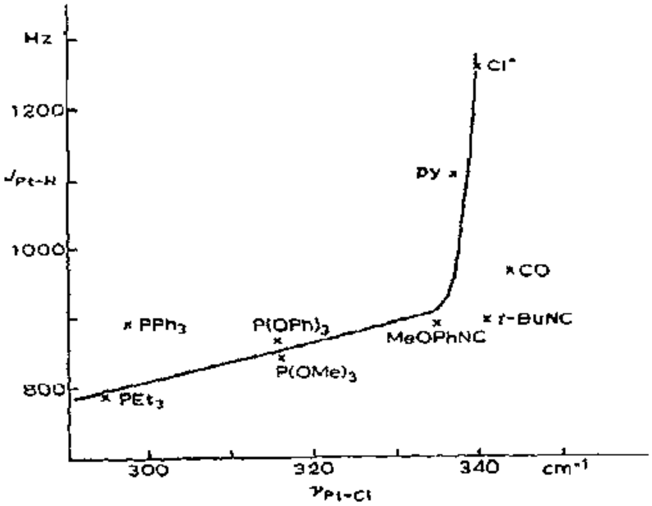


Fig. 16. Plot of $^1J_{Pt-H}$ in complexes *trans*-$PtH(L)(PR_3)_2{}^+$ vs. ν_{Pt-Cl} in corresponding complexes *trans*-$PtCl(L)(PR_3)_2{}^+$.

from that in square planar reactions, and the arguments of Chatt et al. and Orgel do not readily apply. Consequently it is not surprising that for octahedral complexes the *trans*-effect order (so far as it is known) appears to parallel the *trans*-influence order, and ligands with π-bonding capacity (e.g., CO) do not have high *trans*-effects[101, 145, 171].

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