The *cis-* and *trans-*Effects of Ligands

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1 Introduction

The co-ordination of one ligand to a metal ion influences the bonding between that metal ion and every other ligand. With square-planar and octahedral complexes it is convenient to consider this influence under two broad headings, namely *cis-* and *trans-*effects, depending on the relative positions of the 'influenced' (hereafter L) and 'influencing' (hereafter A) ligands. *cis-* and *trans-*effects can be observed by their influence on three properties of the *trans* metal–ligand bond: ground-state, thermodynamic, and kinetic.

A. Ground-state Properties.—The co-ordination of a ligand (A) affects the ground-state properties, such as bond length, stretching force constant, and n.m.r. chemical shift and coupling constant, of the *trans* M–L bond. This influence of A on the ground-state properties of other bonds is generally referred to as the *cis-* or *trans-*influence of A,[1,2] although it is only one manifestation of the more general *cis-* or *trans-*effect.

B. Thermodynamic Properties.—The co-ordination of a ligand (A) to a metal ion affects the free-energy change consequent to replacement of another ligand (L) by an outside ligand (E) [reaction (1)] by altering the free energies of the two complexes A–M–L and A–M–E.

$$\text{A–M–L} + \text{E} \rightleftharpoons \text{A–M–E} + \text{L} \qquad (1)$$

C. Kinetic Properties.—The co-ordination of a ligand (A) to a metal ion modifies the rate of substitution of the other ligands (L), through the effect of A on the energy difference between the ground and transition states. This aspect of the subject was first recognized by Chernyaev[3] and for many years was the only way in which the influence of one ligand on the properties of another could be observed experimentally. It is apparent, however, that the number of factors involved and hence the difficulty of interpretation increases in the order: ground-state < thermodynamic < kinetic properties.

Ever since the *trans-*effect was first observed kinetically there have been

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

[2] L. M. Venanzi, *Chem. in Britain*, 1968, **4**, 162.

[3] I. I. Chernyaev, *Ann. Inst. Platine* (*U.S.S.R.*), 1926, **1**, 243 (*Chem. Abs.*, 1927, **21**, 2620).

attempts to produce universal series for the *trans*-effects of ligands. All such attempts have failed for one or more of the following reasons:

(i) The influence of a ligand (A) on the ground-state properties of the *trans* M–L bond might well be expected to be different from its influence on the kinetic properties of that bond since in the latter case not only will the effect of A on the ground state be important, but so also will its influence on the transition state, which will depend on the detailed mechanism of the reaction. This prediction is indeed borne out by experimental results.

(ii) The mechanisms of the substitution reactions of square-planar complexes, which involve associative activation, are very different from those of octahedral complexes, which involve dissociative activation. Accordingly, the influence of the non-labile ligands in the two series of complexes would not be expected to be the same. A comparison of the *trans*-effect series in Sections 5A and 6B (iii) indicates that this expectation is fulfilled.

(iii) No two ground-state properties are dependent on entirely the same property of a bond. Thus metal–ligand bond lengths are dependent on the overall metal–ligand bonding, whereas n.m.r. coupling constants are very dependent on the degree of metal *s*-electron density in the metal–ligand bond. Whilst these two are often closely related they are not always so and, accordingly, n.m.r. and *X*-ray diffraction will not always give identical *cis*- and *trans*-influence series. However, broad similarities between the various series deduced from ground-state properties are found.

(iv) The influence of a ligand (A) on the properties of another metal–ligand bond (M–L) will depend on the nature of the M–L bond. Thus different orders of A ligands will be obtained when L is a pure σ-donor compared with when L is a modest π-acceptor as well.

It is therefore undesirable to search for a universal *trans*-effect series, but worthwhile to exploit the differences between series to obtain further information about specific details of metal–ligand bonds. Unfortunately, partly as a result of attempts to find a universal series, *cis*- and *trans*-effect data have on a number of occasions been used to derive conclusions which they do not actually support. The reader must therefore be wary of this problem, which has not only confused the subject but also occasionally brought derision upon it.

2 Origin of the *trans*-Effect

Two main theories of the *trans*-effect, one based on σ-bonding and the other on π-bonding effects, have been put forward. Both effects contribute to the overall influence of a ligand on the properties of the *trans* M–L bond in square-planar complexes, although the π-*trans*-effect mechanism discussed here is not applicable to octahedral complexes.

A. σ-*trans*-Effect.—The σ-*trans*-effect or polarization theory[4] considers the *trans*-effect to be principally electrostatic in origin and transmitted through

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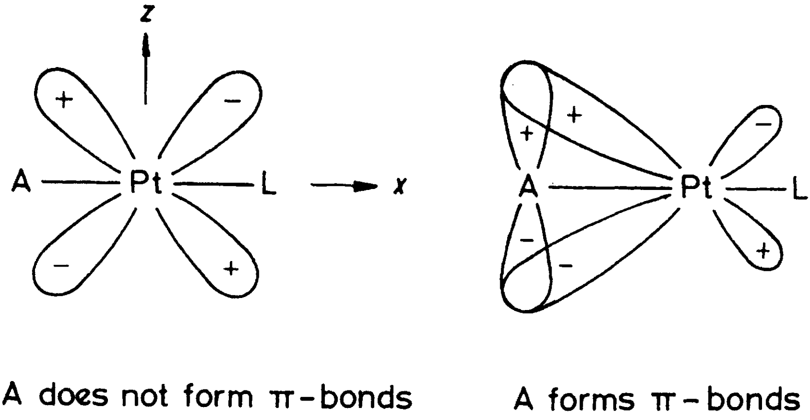
[4] A. A. Grinberg, *Acta Physicochim.* (*U.S.S.R.*), 1935, **3**, 573 (*Chem. Abs.*, 1936, **30**, 4074).

σ-bonds. In a square-planar complex with four identical ligands, the polarization of each of the ligands by the metal ion will be equal and no dipole will result. However, if one ligand (A) is more polarizable than the others, then an induced dipole will result and the distribution of electron density will move through the σ-bonds towards the *trans*-ligand (L). Although this will usually weaken the M–L bond and thus be manifest in the ground-state properties of this bond, it will not always do so since a kinetic *trans*-effect may arise simply from A having a greater share of the empty p_σ orbital of the metal in the transition state than in the ground state, thus reducing the energy difference between these two states.[5,6] This theory has been put on a semi-quantitative basis by calculating the overlap of the valence orbitals of several ligands with the platinum $6p_\sigma$ orbital,[5] giving a σ-*trans*-effect order* of $H^- > PR_3 > \underline{S}CN^- > I^- \sim CH_3^- \sim CO \sim CN^- > Br^- > Cl^- > NH_3 > OH^-$, which is approximately the order of decreasing polarizability of these ligands. Since the polarizability of the metal ion is important, this theory readily accounts for the observation that the *trans*-effect is greatest in the most polarizable or softest metals [*e.g.* *trans*-effects are greater in platinum(II) than palladium(II) complexes].

B. π-*trans*-Effect.—In the π-*trans*-effect theory for square-planar complexes,[7,8] a ligand A (Figure 1) with an empty orbital of π-symmetry can withdraw some



A does not form π-bonds

A forms π-bonds

Figure 1 *Schematic representation of the π-bonding mechanism for the* trans-*effect*

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* Here and throughout the atom underlined in an ambidentate ligand is the donor atom.

[5] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York, 1965, Chapter 2.

[6] S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 1968, **90**, 6669.

[7] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 1955, 4456.

[8] L. E. Orgel, *J. Inorg. Nuclear Chem.*, 1956, **2**, 137.

of the electron density in the metal d_{xz} orbital away from the *trans*-ligand (L). This will have little influence on the ground-state properties of the M–L bond unless that bond also involves π-bonding. In a square-planar complex this will[5,9] firstly direct an incoming nucleophile towards L, which is the region of lowest electron density, and secondly, stabilize the trigonal-bipyramidal transition state since A, L, and the incoming ligand all lie in the trigonal plane where A can be most effective at delocalizing the extra charge from the metal. Calculation of the overlap of the valence orbitals of several ligands with the platinum $6p_\pi$ orbital[5] suggests a π-*trans*-effect order of $H_2C{=}CH_2$, CO > CN^- > $\underline{N}O_2^-$ > $\underline{S}CN^-$ > I^- > Br^- > Cl^- > NH_3 > OH^-, in which the ligands vary between the strongly π-accepting ethylene and the modest π-donating hydroxide ion.

With octahedral complexes π-*trans*-effects are more complex, as is apparent from Table 6, and not so well understood.

3 Origin of the *cis*-Effect

cis-Effects in square-planar complexes are generally very much smaller than *trans*-effects [but see section 6A (iii)] and may be similar to[10] or of opposite sign to[11,12] *trans*-effects. Although their origin is less clearly understood they also appear to operate in two ways. In the first, the π-*cis*-effect mechanism, the ligand alters the ground-state distribution of charge by withdrawing electron density from the metal, so facilitating attack by the reagent.[13] By virtue of the metal orbitals involved in transmitting this effect it would be expected to be smaller in magnitude than the corresponding π-*trans*-effect. Alternatively, a ligand can exert a σ-*cis*-effect which has little influence on the ground-state charge distribution, but by virtue of the micropolarizability of the ligand the extra charge donated to the metal by the incoming ligand is delocalized, so stabilizing the transition state.[14]

4 The *trans*-Effect and the Principle of Hard and Soft Acids and Bases

Pearson[15] has pointed out that very soft ligands co-ordinated to soft metals are not only the most strongly *trans*-influencing but are also the most strongly *trans*-influenced, and thus that two soft ligands in mutually *trans*-positions will have a destabilizing effect on each other when attached to a soft metal atom. This observation, which may be termed 'antisymbiotic behaviour', can account for a number of phenomena, such as the observation that most of the dialkyls of

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[9] L. Oleari, L. Di Sipio, and G. De Michelis, *Ricerca sci., Rend. Sez. A*, 1965, **8**, 413 (*Chem. Abs.*, 1966, **64**, 4567d).

[10] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.

[11] A. A. Grinberg, *Russ. J. Inorg. Chem.*, 1959, **4**, 683.

[12] I. B. Bersuker, *Russ. J. Struct. Chem.*, 1963, **4**, 419.

[13] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Amer. Chem. Soc.*, 1965, **87**, 241.

[14] L. Cattalini and M. Martelli, *Inorg. Chim. Acta*, 1967, **1**, 189.

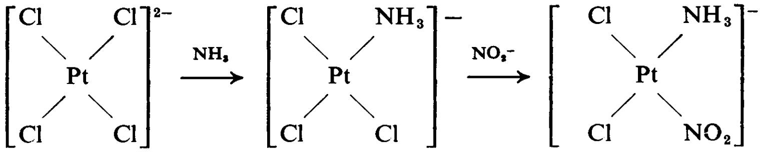
[15] R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712.

Au^{III}, Pt^{II}, and Pt^{IV} are *cis*,[16] and that a very soft ligand such as ethylene in $[Pt(C_2H_4)Cl_3]^-$ makes the *trans*-position susceptible to attack by hard ligands.[17]

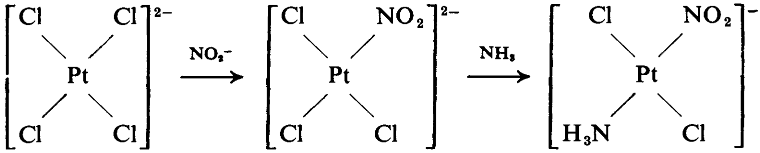
5 Applications

The applications of the *trans*-effect can be divided into two main groups: synthetic and bonding.

A. Synthetic Applications.—The most important application of the *trans*-effect is undoubtedly its use in the preparation of specific isomeric forms of square-planar complexes of platinum(II). An approximate order of the decreasing *trans*-labilizing ability of ligands in square-planar complexes is:[18,19] $C_2H_4 \sim Me_2(HO)CC{\equiv}CC(OH)Me_2 \sim NO \sim CO \sim CN^- > R_3Sb > R_3P > R_3As \sim H^- \sim SC(NH_2)_2 > CH_3^- > C_6H_5^- > \underline{S}CN^- > \underline{N}O_2^- > I^- > Br^- > Cl^- > py >$ amines $\sim NH_3 > OH^- > H_2O$. An example of the application of this series which exploits a *trans*-effect order of $\underline{N}O_2^- > Cl^- > NH_3$ is the synthesis of *cis*- and *trans*-$[PtCl_2(NO_2)NH_3]$ {equations (2) and (3)}. Many further examples from platinum(II) chemistry could be cited, the most elegant undoubtedly being the syntheses of all three possible geometric isomers of [PtABCD] such as $[PtBr(NO_2)NH_3(py)]$[20] and $[PtBrCl(NH_3)py]$.[21] The *trans*-effect is far less useful for the synthesis of isomeric palladium(II) complexes, because of the much greater rates of isomerization of these complexes compared with their platinum (II) analogues.[22a]



(2)



(3)

The *trans*-effect is also much less useful in the synthesis of octahedral com-

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[16] R. S. Tobias, *Inorg. Chem.*, 1970, 9, 1296.

[17] J. Chatt and B. T. Heaton, *J. Chem. Soc.* (*A*), 1968, 2745.

[18] F. Basolo, *Adv. Chem. Ser.*, 1965, no. 49, 81.

[19] T. P. Cheeseman, A. L. Odell, and H. A. Raethel, *Chem. Comm.*, 1968, 1496.

[20] A. D. Gelman and L. N. Essen, 'Proceedings of the 10th International Conference on Coordination Chemistry', ed. K. Yamasaki, The Chemical Society of Japan, Tokyo, 1967, p. 385.

[21] A. D. Gelman, E. F. Karandashova, and L. N. Essen, *Doklady Akad. Nauk S.S.S.R.*, 1948, **63**, 37 (*Chem. Abs.*, 1949, **43**, 1678).

[22] F. R. Hartley, 'The Chemistry of Platinum and Palladium', Applied Science, London. 1973 (*a*) p. 313, (*b*) pp. 240—244, and references therein.

plexes, partly because many of these rearrange during the course of reaction and partly because their mechanisms depend not only on the nature of the *trans*-ligands but also on the *cis*-ligands (see Table 6), thus making predictions more difficult and their synthetic utility consequently less. However, an exception to this is the exploitation of the high *trans*-effect of carbon monoxide in the synthesis of a range of *cis*-$[MnBrL(CO)_4]$ and *fac*-$[MnBrL_2(CO)_3]$ complexes by treating $[MnBr(CO)_5]$ with neutral[23] and negatively charged ligands.[24,25]

B. Bonding Applications.—A second, and far more controversial, application of *cis*- and *trans*-effect studies involves their use in obtaining information about metal–ligand bonding. Thus if, in a square-planar complex, a ligand shows a very high kinetic *trans*-effect but has little or no *trans*-influence on ground-state properties such as bond lengths, then it is reasonable to ascribe the kinetic *trans*-effect to a π-mechanism, which will not be manifest in a ground-state effect, and thus to suggest that the M–A bond involves π-character. Whilst such results are valid for clear-cut cases such as olefins and carbon monoxide, attempts to extend the use of this approach to less strongly π-bonding ligands, and in particular to attempt to construct series of π-bonding abilities, have generally met with disaster. This is because such an approach inevitably assumes that the *trans*-influence and *trans*-effect series reflect solely the electronic influence of ligand A. However, both series are the consequence not only of electronic but also of steric effects, together with effects that are peculiar to the physical technique being used [for example, in vibrational spectroscopy, the interaction of vibrational modes of the same symmetry – see section 6A (i)]. As a result no two *trans*-influence series agree in detail with one another and thus no two π-bonding ability series can be expected to agree.

6 Experimental Observation of *cis*- and *trans*-Effects

A. Square-planar Complexes.—(i) *Ground-state Properties.* There are three principal experimental techniques for observing the *cis*- and *trans*-effects of ligands on ground-state properties, namely *X*-ray diffraction, vibrational spectroscopy, and n.m.r., and all three indicate that the *trans*-influence of a ligand increases as its σ-donor ability increases. The precision with which metal–ligand bond lengths can be measured by *X*-ray diffraction relative to the magnitude of the effect being looked for is not very great, so that it is generally impossible to derive a detailed series of ligands from *X*-ray diffraction, but rather possible to divide ligands into broad groups. Thus the influence of ligands on *trans* Pt–Cl bond lengths (Table 1) suggests that ligands fall into three groups. In the first, which give rise to *trans* Pt–Cl bond lengths of less than 2.33 Å, are modest σ-donor ligands such as oxygen-containing ligands, N- and

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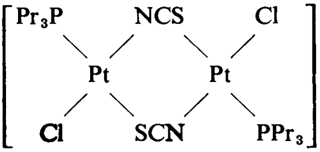
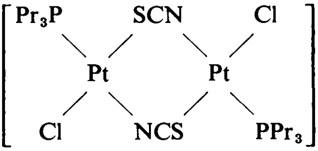
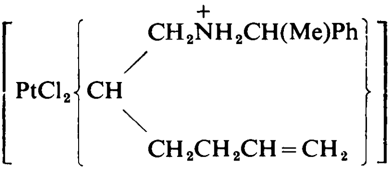
[23] R. J. Angelici, F. Basolo, and A. J. Pöe, *J. Amer. Chem. Soc.*, 1963, **85**, 2215, and references therein.
[24] E. W. Abel and I. S. Butler, *J. Chem. Soc.*, 1964, 434.
[25] R. J. Angelici, *Inorg. Chem.*, 1964, **3**, 1099.

Table 1 *The* trans-*influence of ligands on platinum*(II)*-chlorine bond lengths*

Complex	trans *Atom* (*or ligand*)	Pt–Cl/Å	*Ref.*
	-NCS	2.277(4)	26
$\mathrm{K[Pt(acac)_2Cl]}$	O	2.28(1)	27
trans-$\mathrm{[(PEt_3)_2PtCl_2]}$	Cl	2.30(1)	28
cis-$\mathrm{[(}p\mathrm{\text{-}ClC_6H_4S)_2PtCl_2]}$	S (of $\mathrm{RS^-}$)	2.30	29
trans-$\mathrm{[(PEt_3)_2Pt(CO)Cl]}$	CO	2.30	30
$\mathrm{(PPh_4)[PtCl_3(HOCH_2CH{=}CHCH_2OH)]}$	C=C	2.301(8)	31
	-SCN	2.304(4)	26
cis-$\mathrm{[(PEt_2Ph)Pt(CNEt)Cl_2]}$	RNC	2.314(10)	32
$\mathrm{K_2[PtCl_4]}$	Cl	2.316	33
$\mathrm{[Pt(}$L$\mathrm{\text{-}methionineH)Cl_2]}$	S (of $\mathrm{R_2S}$)	2.32	34
$\mathrm{K[Pt(NH_3)Cl_3],H_2O}$	N	2.321(7)	35
$\mathrm{K[Pt(C_2H_4)Cl_3],H_2O}$	C=C	2.327(7)	36
$\mathrm{[Pt(H_3NCH_2CH{=}CHCH_2NH_3)Cl_3]Cl}$	C=C	2.342(2)	37
cis-$\mathrm{[(PEt_3)Pt\{C(OEt)NHPh\}Cl_2]}$	C (of carbene)	2.365(5)	38
cis-$\mathrm{[(PMe_3)_2PtCl_2]}$	P	2.37(1)	39
cis-$\mathrm{[(PEt_2Ph)Pt(CNEt)Cl_2]}$	P	2.390(8)	32
trans-$\mathrm{[(PMe_2Ph)_2Pt(CH_2SiMe_3)Cl]}$	C (of alkyl)	2.415(5)	40
trans-$\mathrm{[(PPh_2Et)_2PtHCl]}$	H	2.42(1)	41
cis- 	C (of alkyl)	2.430	42
trans-$\mathrm{[(PMe_2Ph)_2Pt(SiMePh_2)Cl]}$	Si	2.45(1)	43

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[26] U. A. Gregory, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc.* (*A*), 1970, 2770.

[27] R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc.* (*A*), 1969, 485.

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

[29] W. A. Spofford, E. L. Amma, and C. V. Senoff, *Inorg. Chem.*, 1971, **10**, 2309.

[30] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1967, **89**, 3360.

[31] M. Colapietro and L. Zambonelli, *Acta Cryst.*, 1971, **B27**, 734.

[32] B. Jovanović and Lj. Manojlović-Muir, *J.C.S. Dalton*, 1972, 1176.

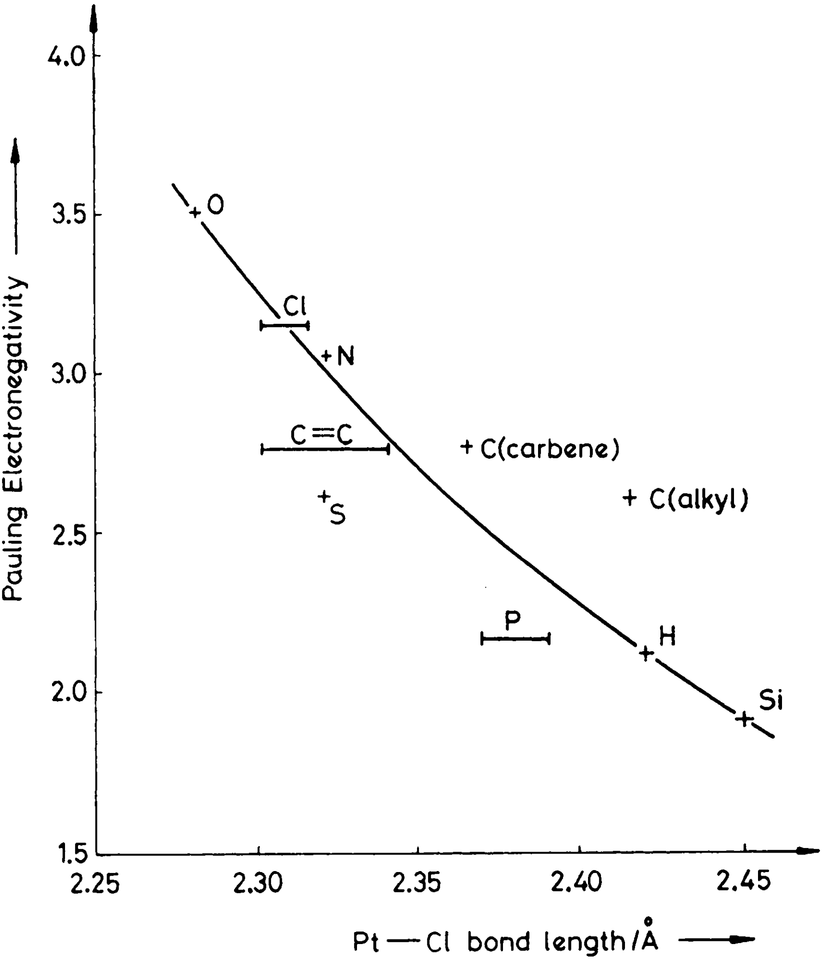

Figure 2 *Variation of the* Pt–Cl *bond length with the Pauling electronegativity of the ligand* trans *to* Cl

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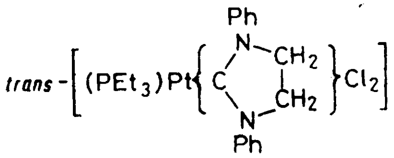
[33] R. H. B. Mais, P. G. Owston, and A. M. Wood, *Acta Cryst.*, 1972, **B28**, 393.
[34] H. C. Freeman and M. L. Golomb, *Chem. Comm.*, 1970, 1523.
[35] Y. P. Jeannin and D. R. Russell, *Inorg. Chem.*, 1970, 9, 778.
[36] J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *Acta Cryst.*, 1971, **B27**, 366.
[37] R. Spagna and L. Zambonelli, *J. Chem. Soc.* (*A*), 1971, 2544.
[38] E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Comm.*, 1969, 1322.
[39] G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 725.
[40] M. R. Collier, C. Eaborn, B. Jovanović, M. F. Lappert, Lj. Manojlović-Muir, K. W. Muir, and M. M. Truelock, *J.C.S. Chem. Comm.*, 1972, 613.
[41] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 773.
[42] C. Pedone and E. Benedetti, *J. Organometallic Chem.*, 1971, **31**, 403.
[43] R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, no. 47, 20.

S-bonded thiocyanate, amines, thiols, aryl sulphides, and chlorine, as well as modest σ-donors that are also π-acceptors such as olefins, carbon monoxide, and isocyanides; in the second, which give rise to *trans* Pt–Cl bond lengths between 2.36 and 2.39 Å, are carbene and tertiary phosphine ligands, which are strong σ-donors and also modest π-acceptors; in the third group, which give rise to *trans* Pt–Cl bond lengths greater than 2.40 Å, are alkyl, hydride, and silyl ligands, all of which are powerful σ-donors with virtually no π-acceptor ability. The Pt–Cl bond lengths in Table 1 increase steadily with decreasing electronegativity of the influencing ligand (A) (Figure 2), a result which has been expressed semi-quantitatively by observing that the *trans*-influence of A is related to $S^2/\Delta E$, where S is the overlap integral and ΔE the energy difference between the metal and A orbitals being mixed.[43] Although the co-ordination of one ligand to a metal ion affects the co-ordination of all the other ligands, *cis* Pt–Cl bond lengths show very little dependence on the other ligands present (Table 2); furthermore, what influence there is appears to be opposite to that for *trans*-ligands, with tertiary phosphines and carbenes giving rise to the shorter Pt–Cl bonds, and amines and chloride ligands giving rise to the longer *cis* Pt–Cl bonds.

Table 2 *The* cis-*influence of ligands on platinum*(II)*–chlorine bond lengths*

Molecule	cis *Atom* (*or ligand*)	Pt–Cl/Å	*Ref.*
trans-$[(PEt_3)_2PtCl_2]$	P	2.29	28
$[Pt(\mathit{cis}\text{-}MeCH{=}CHCH_2NH_3)Cl_3]$	C=C	2.297(6)	44
	P and C (of carbene)	2.30	45, 46
$K[Pt(C_2H_4)Cl_3],H_2O$	C=C	2.305	36
$K[Pt(NH_3)Cl_3],H_2O$	N	2.315	35
$K_2[PtCl_4]$	Cl	2.316	33
trans-$[Pt(NH_3)_2Cl_2]$	N	2.32(1)	47

Force constants are required to determine the influence of one ligand on the vibrational properties of the *trans* M–L bond and very few force constants have been determined because a detailed force-field analysis is complex, usually

[44] R. Spagna, L. M. Venanzi, and L. Zambonelli, *Inorg. Chim. Acta*, 1970, **4**, 475.
[45] D. J. Cardin, B. Cetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400.
[46] Lj. Manojlović-Muir and K. W. Muir, personal communication.
[47] G. H. W. Milburn and M. R. Truter, *J. Chem. Soc.* (*A*), 1966, 1609.

requires data from many isotopically substituted species, and often involves the introduction of a number of questionable assumptions. Many workers have accordingly used frequencies, particularly of M–H (which are the best because they are generally well removed from other vibrational modes within the complex),[48,49] M–Cl,[22b] or M–CH_3[50] vibrations. Whilst in broad agreement with the *X*-ray diffraction series, *trans*-influence series derived from vibrational frequencies never agree in detail, either with each other or with series obtained by other methods, because of the considerable interaction of the vibration being studied with others within the complex.[22b]

N.m.r. yields two parameters that are influenced by the *trans*-ligand, namely coupling constants and chemical shifts. Only coupling constants between directly bound nuclei can be said to be well understood and these appear to be dominated by the Fermi contact contribution[50–52] and in particular by the amount of metal *s*-electron density in the hybrid orbital. Consequently, direct coupling constants such as *J*(Pt–P) in phosphine complexes,[50,53,54] *J*(Pt–H) in hybrides,[55] and *J*(Pt–C) in methyl complexes[56] decrease as the σ-donor ability of the *trans*-influencing ligand increases and thus give broadly similar *trans*-influence series to those obtained from *X*-ray diffraction and vibrational spectroscopy. Ligands co-ordinated *cis* to hydride appear to have the opposite influence on *J*(Pt–H) to when they are *trans*.[55] The origin of indirect coupling constants such as *J*(Pt–C–H) in methyl complexes and *J*(Pt–P–C–H) in methylphosphine complexes is far from clear,[55,57–59] although from empirical correlations with other properties the former appear to reflect the σ-donor ability of the *trans*-ligand[53,60] whereas the latter appear to reflect the total electron density on the platinum atom.[61] If this is correct, then by comparing *J*(Pt–C–H) and *J*(Pt–P–C–H) it would be possible to construct a π-acceptor ability series of ligands.[60]

The origins of even simple n.m.r. chemical shifts, such as those of protons in hydride complexes, are insufficiently understood[62–65] for them to be used in

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[48] A. E. Keskinen and C. V. Senoff, *J. Organometallic Chem.*, 1972, 37, 201.
[49] J. Chatt, L. A. Duncanson, and B. L. Shaw, *Chem. and Ind.*, 1958, 859.
[50] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.
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studying the *trans*-influences of ligands. A suggestion that the ^{19}F chemical shift in a *m*-fluorophenyl ligand bound to a metal arises solely from the inductive effect of the *trans*-ligand whereas in a *p*-fluorophenyl ligand the ^{19}F chemical shift arises from a combination of the σ-inductive and π-mesomeric effects of the *trans*-ligand, and that therefore the difference between the *para*- and *meta*-chemical shifts should reflect the π-acceptor ability of the *trans*-ligand,[66] has been criticized[52] because the *trans*-ligand will affect the π-electron density in the aromatic ring in two ways: (*a*) an increase in the π-acceptor ability of the 'influencing' ligand will reduce the π-electron density available to the aryl group; (*b*) a change in the σ-donor strength of the 'influencing' ligand will alter the ability of the aryl group to accept electron density [thus interfering with (*a*)] by two mechanisms. First, an increase in the σ-donor strength of the 'influencing' ligand will decrease the effective nuclear charge in the metal and thus cause an expansion of the *d*-orbitals, thereby changing the degree of π-overlap of these orbitals with the aryl group. Secondly, an increase in the σ-donor ability of the 'influencing' ligand will weaken and lengthen the platinum(II)–aryl bond, thus altering the platinum(II)–aryl interaction. The influence of these σ-effects on the difference between the *para* and *meta* chemical shifts is not clear since the optimum conditions for good π-overlap between the metal and the aryl groups are unknown and therefore any π-acceptor series obtained in this way must be regarded with suspicion. This is supported by the anomalous results of a number of workers obtained using this technique.[67,68]

(ii) *Thermodynamic Properties.* The ideal thermodynamic data for studying the *trans*-influence of a ligand (A) would be the gas-phase enthalpy data for reaction (4).

$$trans\text{-}[MX_2AL] \rightleftharpoons [MX_2A]^+ + L^- \qquad (4)$$

Unfortunately, no such data are available. The closest available data are for the hydrolysis of $[PtACl_3]^-$ (see Table 3), and this indicates that ligand A has little influence on the extent of hydrolysis probably because its influence on the co-ordination of chloro- and aquo-ligands is very similar.

(iii) *Kinetic Properties.* The kinetic effect of a *trans*-ligand was first observed in preparative studies, where it was found that ligands could be arranged in order of their *trans*-labilizing ability as given in Section 5A, above. Later quantitative kinetic data confirmed this, but also showed that just as the influence of the *trans*-ligand (A) on ground-state properties depends on the nature of the probe ligand, so the kinetic *trans*-effect of ligand A depends on the nature of the attacking nucleophile (Table 4). The reactivity of the complexes towards weak nucleophiles is determined principally by the intrinsic reactivity of the sub-

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Table 3 *Thermodynamic data for the equilibrium* trans-$[PtACl_3]^- \overset{K}{\rightleftharpoons}$ trans-$[PtACl_2(H_2O)] + Cl^-$

$[PtACl_3]^-$	K/mol l^{-1}	ΔH/kcal mol^{-1}	ΔS/e.u.	*Ref.*
$[PtCl_4]^{2-}$	18.0×10^{-3}	—	—	69
$[Pt(H_2O)Cl_3]^-$	1.0×10^{-3}	—	—	70
$[Pt(NH_3)Cl_3]^-$	14.4×10^{-3}	2.1	−1	71
$[Pt(C_2H_4)Cl_3]^-$	2.5×10^{-3}	—	—	72
$[Pt\{Me_2C(OH)C{\equiv}CC(OH)Me_2\}Cl_3]^-$	2.0×10^{-3}	3.4	−1	72

Table 4 *Second-order rate constants*/l mol^{-1} s^{-1} *for the reaction of nucleophiles with* trans-$[(PEt_3)_2PtACl]$ *in methanol at* 30 °C

Nucleophile	A = Me[a]	A = Ph[b]	A = *o*-tolyl[b]	A = Cl[c]
py	0.067[d]	0.016[d]	0.0017[d]	0.0004[d]
NO_2^-	1.6	0.45	0[e]	0.0027
N_3^-	7.0	0.8	0[e]	0.02
Br^-	11.6	1.8	0[e]	0.093
I^-	40	6.0	0[e]	23.6
thiourea	15000	630	65.2	very fast
CN^-	—	3610	23.4	—

[a] Reference 73.
[b] Reference 74.
[c] Reference 13.
[d] Reference 10.
[e] Rate independent of nucleophile concentration.

strate,[75] which for *trans*-$[(PEt_3)_2PtACl]$ decreases across the series A = Me > Ph > Cl, and follows the classical *trans*-effect sequence which is based on pyridine as the entering ligand (*i.e.* Me > Ph > Cl). By contrast, the reactivity towards strong nucleophiles, such as thiourea, reflects the ability of the substrate to discriminate between nucleophiles,[75] which increases across the series A = Me < Ph < Cl, and thus gives a different *trans*-effect series (Cl > Me > Ph > *o*-tolyl). Relatively little work has been done to determine to what extent the ease of replacement of the group L depends on the nature of L itself, although the relative rates of replacement of L in *trans*-$[(PEt_3)_2PtAL]$ by thiourea were found to be independent of L.[76] This suggests that there is significant bond formation between platinum(II) and the entering thiourea ligand in the transition

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state, and that in reactions in which there is significant bond-breaking between platinum(II) and the leaving group in the transition state, we may expect to find the *trans*-effect series depending on the nature of the leaving group.

Although ligands *trans* to the leaving group have a profound effect on its rate of substitution, ligands *cis* to it generally have only a minor effect. Thus the rate of replacement of the chloride in *cis*-$[(PEt_3)_2PtACl]$ by pyridine is $3\frac{1}{2}$ times faster when A = Me than when A = Cl,[10] whereas there is a factor of 170 difference in rates when these groups are in the *trans*-position.[10] However, the relative unimportance of the *cis*-effect should not be overstressed, since it can be far more important than the *trans*-effect when groups of nearly equal *trans*-effects are present. This is illustrated in Table 5, where the *cis*-effects of the non-halide ligand on the rates of formation of a series of consecutive complexes are between 5 and 20000 times greater than the *trans*-effects.

Table 5 *Coefficients for the* cis- *and* trans-*effects of ligands* (L) *on the rate of replacement of halide ligands* (X) *by* L *ligands according to the equation* $MX_{4-n}L_n + L \rightarrow MX_{3-n}L_{n+1} + X$, *analysed according to the formula*

$$\frac{Rate}{no.\ of\ equivalent\ X\ in\ complex} = A \times (T)^t \times (C)^c$$

where t = *no. of ligands* trans *and* c = *no. of ligands* cis *to the halide to be replaced*

M	L	X	*T*	*C*	*Ref.*
Pt	H_2O	Cl	3×10^{-3}	3	77
Pt	H_2O	Br	3×10^{-4}	6	77
Pt	NH_3	Cl	0.5	2.4	78
Pd	NH_3	Cl	0.1	10	79

Although some studies[12,80] show that *cis*-effects are of opposite sign to *trans*-effects, others indicate the reverse.[10] Like the *trans*-effect the *cis*-effect depends on the nature of the entering ligand, owing to a combination of the different abilities of two substrates to discriminate between nucleophiles,[75] and the absolute rate constants. Thus the rate of replacement of Cl in *trans*-$[PtA_2Cl_2]$ by the weak nucleophile NO_2^- is A = PEt_3 < py but is PEt_3 > py for the stronger nucleophile I^-.[13]

B. Octahedral Complexes.—(i) *Ground-state Properties. X*-Ray diffraction has been used to investigate *trans*-effects in octahedral complexes of Ru^{III}, Co^{III}, Rh^{III}, Ir^{III}, and Pt^{IV} with a wide range of probe ligands, including σ-donor ligands (H^-, NH_3, H_2O, NCS^-), σ-donor–π-donor ligands (Cl^-, OH^-), and

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σ-donor–π-acceptor ligands (CO, CN^-).[81–83] In all cases the principal factor responsible for lengthening the *trans* metal–ligand bond appears to be the σ-donor ability of the influencing ligand, with a high σ-donor ability giving a long bond.[82] Any π-acceptor ability of the influencing ligand reduces its σ-donor *trans*-influence by reducing the charge density on the metal. Similarly, π-acceptor *cis*-ligands reduce the *trans*-influence of a given *trans*-ligand. An approximate *trans* bond-lengthening series is $Cl^- \sim CO < H_2O \sim CO_3^{2-} \sim NH_3 \sim NO_2^- \sim CN^- \sim SO_3^{2-} < PR_3 <$ alkyls with electronegative substituents < alkyls $\ll NO^-$.

Since too few stretching force constants have been determined, *trans*-effect series from vibrational spectra have been based on frequencies alone [see Section 6A (i) for objections]. In general, such series reflect the σ-donor ability of the influencing ligand; ν(M–Cl) in chloro-complexes[84,85] and ν(C–N) in cyano-complexes[82] both decrease with increasing σ-donor ability of the *trans*-ligand.

ν(C–O) in carbonyl complexes reflects the σ-donor–π-acceptor ability of the *trans*-ligand: strong σ-donors give low C–O stretching frequencies owing to the strong π back-donation of electron density from the metal to the π^* (antibonding) orbital of CO;[86] strong π-acceptors, by reducing this back donation, give higher C–O stretching frequencies.[86] An attempt to use this to construct a π-acceptor ability series for ligands[87] has been criticized[52] since, although it is true that an increase in the π-acceptor ability of A reduces the π-electron density available to the carbonyl group, it is also true that a change in the σ-donor ability of A affects the ability of CO to accept electrons as follows: (i) an increase in the σ-donor ability of A decreases the effective nuclear charge on the metal, so expanding the *d*-orbitals and altering the degree of π-overlap between these orbitals and the π^* (antibonding) orbital of CO; (ii) an increase in the σ-donor ability of A weakens the *trans* M–CO bond, which alters the interaction between the metal and carbon monoxide.

An attempt to overcome this difficulty has been made[88] by evaluating the C–O stretching force constants in $[AM(CO)_5]$ and assuming that the changes in these force constants arise from two effects: (*a*) σ-effects, which were assumed to act isotropically on all five CO groups; (*b*) π-effects, in which it was assumed that the force constant of the *trans*-CO ligand was affected twice as much as that of a *cis*-CO ligand (Cotton–Kraihanzel approximation[89]). Assumption (*a*) is un-

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reasonable, since many examples of properties where ligands exert an extra influence on the *trans* M–L bond are known.

Changes in the electronic spectra resulting from π–π^* transitions in the corrin rings of cobalamin complexes consequent to changing the axial ligands show that the *cis*-influence of ligands increases in accordance with their position in the nephelauxetic series, which in turn reflects the effective residual charge on the metal.[90]

Mössbauer spectroscopy yields two parameters, the chemical shift (c.s.) and the quadrupole splitting (q.s.), both of which can be subdivided into contributions (p.c.s. and p.q.s.; p = partial) from each ligand. Whilst the p.c.s. reflects the total σ-donor + π-acceptor ability of a given ligand [p.c.s. $= -k(\pi + \sigma)$] the p.q.s. reflects the difference in these two [p.q.s. $= -q_{\text{lattice}} + c(\pi' - \sigma')$].[91] Furthermore, the difference in the c.s. values of a pair of *cis*- and *trans*-isomers reflects only the π-bonding components of the ligands present.[91] Although only applicable to complexes which exhibit Mössbauer spectra, this technique is likely to receive considerable attention in the future as a method for separating σ- and π-effects.[92,93]

(ii) *Thermodynamic Properties.* There is a lot of free-energy data which indicates that cobalt(III) shows very little class consciousness,[94] being class 'a' in $[Co(NH_3)_5X]^{2+}$ and class 'b' in $[Co(CN)_5X]^{3-}$. Only for a few systems such as $[CoX_4A(H_2O)]^{n+}$ (where X_4 is corrin, for example) is it possible to find reactions which vary in a systematic way independent of X_4. In such cases the effectiveness of A in increasing the stability constant K $\{K = [CoX_4A(H_2O)][L]/[CoX_4AL]\}$[95] and in increasing the stability of the five-co-ordinate Co^{III} complexes $[CoX_4A]$[81] increases as the σ-donor ability of A increases.

(iii) *Kinetic Properties.* In the substitution reactions of octahedral Co^{III} the nature of the *cis*- and *trans*-ligands not only influences the rate, but also the reaction mechanism, and the factor responsible for a high labilizing ability depends on this mechanism (Table 6). Rh^{III} and Ir^{III} substitution reactions are virtually all of the first type listed in Table 6 and, accordingly, the lability of L in *trans*-$[M(en)_2AL]^{n+}$ depends on the σ-donor ability of A.[99–102]

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Table 6 *The influence of ligands on the mechanism of the substitution reactions of octahedral cobalt*(III)[a]

Type of ligand (A)	*Examples of ligand* (A)	*Examples of complex*	*Stereochemistry of reaction*	*Reaction intermediate*	*Dependence of reaction rate on position of* A	*Order of increasing labilizing ability of* A
Strong σ-donor	H, Me, PR_3	*trans*-$[CoX_4AL]$ (X_4 = partially conjugated system such as corrin)	Retention of configuration (*cis* → *cis*; *trans* → *trans*)	Square pyramid (A at apex)	These ligands are only found *trans* to the leaving group	Ph < Me < Et < Pr[b,c] (increasing σ-donor ability)
σ-Donor that is also π-donor	NR_2^-, OH^-, Cl^-	*cis*- and *trans*-$[Co(en)_2AL]$	May occur with stereochemical change (in general *cis* → *cis*; *trans* → *cis* + *trans*)	Trigonal bipyramidal (A in trigonal plane)	Slightly faster when A is *cis* to the leaving group	$-NCS^- < CH_3CO_2^- < Br^- < Cl^- < OH^- < NR_2^-$ (increasing π-donor ability)[d]
σ-Donor or σ-donor–π-acceptor	NH_3, H_2O, NO_2^-, CN^-	*cis*- and *trans*-$[Co(en)_2AL]$	Retention of configuration (*cis* → *cis*; *trans* → *trans*)	Square pyramid (A at apex)	Slightly faster when A is *trans* to the leaving group	$NH_3 < H_2O < CN^- < NO_2^-$ (increasing π-acceptor ability)[d]

[a] Compiled from data in references 96 and 97. [b] From reference 98. [c] The order of labilizing ability of X_4 is approximately $\{(py)_4 \sim \beta/\gamma\text{-}(pic)_4 \sim (en)_2 \sim (DMG)_2 \sim (CN)_4\} < (NH_3)_4 \leqslant (H_2O)_4 \ll$ corrin ~ porphyrin. [d] From reference 96.

7 Conclusion

From a study of the influence of a ligand (A) on the properties of other metal–ligand (M–L) bonds it is possible to obtain information about both the M–A and M–L bonds. Although many properties reflect a common ligand order, not all can reflect a common order since they are sensitive to different aspects of the metal–ligand bond. Accordingly it is undesirable to search for a universal *trans*-effect series. Hitherto the most important application of *trans*-effect series has been the synthesis of specific isomers of platinum(II) complexes. However, as more data become available it may be possible in the future to use *cis*- and *trans*-effect series to gain greater insight into the nature of the bonding in a given metal–ligand bond. The high sensitivity of n.m.r. coupling constants together with the relative ease with which they can be obtained suggests that these are likely to become the most valuable single source of *cis*- and *trans*-influence data.

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