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The *Trans*-Influence of Ligands in Platinum(II) Complexes. The Significance of the Bond Length Data

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Bond lengths in electroneutral, monomeric chloroplatinum(II) complexes containing carbon-donor ligands indicate that there is a correlation between the extent of platinum–carbon multiple bonding and the length of the Pt–Cl (trans to C) bond. A qualitative model is suggested to account for the trans-influence of both σ-donor and π-acceptor ligands on Pt–Cl bonds.

The *trans*-influence of a co-ordinated ligand, *L,* defined as its ability to weaken the metal–*trans* ligand bond,[1] has been observed in many square-planar and octahedral complexes, and also in some square-pyramidal complexes of transition metals.[2,3] Recent theories of *trans*-influence assume that the effect originates principally from σ-bonding in the *L–M* system and that it is transmitted through the molecular σ-bonding framework.[1,4,5] The main success of such theories has been in predicting high *trans*-influence for ligands such as hydride and σ-alkyl, which have strong σ-donor and virtually no π-acceptor properties. Nevertheless, it is now generally accepted that for ligands with π-acceptor properties (*e.g.* isonitriles, carbon monoxide) the *trans*-influence may also depend, at least to some extent, on the metal→ligand π-back bonding.[5,6] The relative importance of the latter effect has been difficult to assess in the absence of adequate experimental evidence.

In view of this, and considering bond lengths as the most straightforward measure of bond strength, and hence of *trans*-influence, we have recently determined by *X*-ray analysis the molecular structures of a number of square-planar platinum(II) complexes, containing carbon-donor ligands expected to display a range of π-acidity. The compounds are all monomeric and electroneutral and they contain four unidentate ligands and a linear C–Pt–Cl system.[7–12] Bond lengths in these, and in related complexes[13] investigated by other workers, are presented in Table I; compounds for which the estimated standard deviation of the Pt–Cl distance is greater then 0.015 Å are not included.

From Table I it is immediately apparent that the Pt–C bond lengths, *l*(Pt–C), depend on the nature of the carbon-donor ligand, and that they decrease in the order σ-carbyl > carbene > isonitrile > carbon monoxide. However, since these bonds involve carbon atoms in different states of hybridisation it is preferable to examine the variation of the effective radius of platinum, *R*(Pt), in the Pt–C bonds. We define *R*(Pt) as *l*(Pt–C)–*R*(C), where *R*(C) is the appropriate covalent radius of the carbon atom; to derive the *R*(Pt) values listed in Table I we have used *R*(C) values of 0.77, 0.74, and 0.69 Å for sp^3, sp^2, and *sp* carbon atoms, respectively.[14] A decrease in *R*(Pt) may be interpreted as a consequence of either (a) re-

TABLE I. Structural Data for Monomeric, Electroneutral Platinum(II) Complexes Containing Linear C–Pt–Cl Systems. All Distances are in Å Units.

Compound	*l*(Pt–Cl)	*l*(Pt–C)	*R*(Pt)[a]	*R'*(Pt)[a]	Ref.
trans-$PtCl(CH_2SiMe_3)(PPhMe_2)_2$	2.415(5)	2.079(14)	1.31	1.30	8
trans-$PtCl(C{\equiv}CPh)(PPhEt_2)_2$	2.407(6)	1.98(2)	1.29	1.29	9
trans-$PtCl(CH{=}CH_2)(PPhEt_2)_2$	2.398(4)	2.03(2)	1.29	1.28	9
cis-$PtCl_2\{C(NPhCH_2)_2\}(PEt_3)$	2.362(3)	2.009(13)	1.27	1.24	10
cis-$PtCl_2\{C(OEt)NHPh\}(PEt_3)$	2.361(5)	1.963(19)	1.22	1.24	13
cis-$PtCl_2(CNPh)(PEt_3)$	2.333(12)	1.87(3)	1.18	1.21	13
cis-$PtCl_2(CNEt)(PEt_2Ph)$	2.314(10)	1.83(4)	1.14	1.18	7
cis-$PtCl_2(CNPh)_2$	2.308(5)	1.896(16)	1.21	1.18	11
cis-$PtCl_2(CO)(PPh_3)$	2.277(3)	1.849(14)	1.16	1.14	12

[a] See text for definition.

TABLE II. Pt–Cl Bond Lengths (Å) *trans* to Various Ligands in Platinum(II) Complexes.

Compound	l(Pt–Cl)	*trans*-ligand	Ref.
trans-$PtCl(SiMePh_2)(PMe_2Ph)_2$	2.45(1)	$SiMePh_2^-$	5
trans-$PtClH(PPh_2Et)_2$	2.422(9)	H^-	17
a	2.376(5)	PR_3	–
cis-$PtCl_2(NH_3)_2$	2.33(1)	NH_3	18
b	2.303(5)	Cl^-	–
cis-$PtCl_2\{S(C_6H_4Cl)_2\}_2$	2.300(4)	$S(C_6H_4Cl)_2$	19
$K[Pt(acac)_2Cl]$	2.276(5)	O (acac)	20

[a] Average of following: 2.381(3) Å in *cis*-$PtCl_2\{C(NPhCH_2)_2\}(PEt_3)$, ref. 10; 2.367(7) Å in *cis*-$PtCl_2\{C(OEt)NHPh\}(PEt_3)$, ref. 13; 2.390(8) Å in *cis*-$PtCl_2(CNEt)(PPhEt_2)$, ref.7; 2.365(11) Å in *cis*-$PtCl_2(CNPh)(PEt_3)$, ref. 13; 2.364(8) and 2.388(9) Å in *cis*-$PtCl_2(PMe_3)_2$, G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem., 6,* 725 (1967).

[b] Average of following: 2.311(6) Å in *trans*-$PtCl_2\{C(NPhCH_2)\}(PEt_3)$, ref. 10; 2.314(7) and 2.296(7) Å in $K[PtCl_3(C_2H_4)]\cdot H_2O$, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *Acta Cryst., B27,* 366 (1971); 2.293(2) and 2.311(2) Å in $[PtCl_3(C_4H_{12}N_2)]Cl\cdot 0.5H_2O$, R. Spagna and L. Zambonelli, *J. Chem. Soc. (A),* 1971, 2544; 2.291(9) and 2.301(8) in $[Ph_4P][PtCl_3(C_4H_8O_2)]$, M. Colapietro and L. Zambonelli, *Acta Cryst., B27,* 734 (1971); 2.308(2) Å in $K_2[PtCl_4]$, R. H. B. Mais, P. G. Owston, and A. M. Wood, *Acta Cryst., B28,* 393 (1972).

hybridisation of the platinum σ-bonding orbitals, leading to stronger Pt–C σ-bonds, or (b) increase in Pt–C multiple bonding. If (a) were true we would expect, from current theories,[5] that the *trans*-influence of the carbon-donor ligands should increase as R(Pt) decreases; however, the Pt–Cl (*trans* to C) distances in Table I show an opposite trend. We are therefore forced to conclude that the variation of R(Pt) in these compounds represents mainly changes in the extent of Pt–C multiple bonding.

The decrease in the R(Pt) values in Table I is paralleled by a decrease in the Pt–Cl distances. The correlation coefficient, r, between the R(Pt) and l(Pt–Cl) values is +0.91, and the probability that there is no functional relationship between these variables is less than 0.5%.[15] * Since the Pt–Cl bond lengths can be determined more accurately than the Pt–C distances, it may be preferable to derive the effective radius of platinum from the regression equation $R'(Pt) = 1.17\, l(Pt\text{–}Cl) - 1.53$, rather than directly from l(Pt–C). The R'(Pt) values so derived (Table I) may be useful as a measure of π-back donation in the Pt–C bonds. Both R(Pt) and R'(Pt) values lead to the π-acceptor series: σ-carbyl < carbene < isonitrile < carbon monoxide. This series is in agreement with current views on π-acidity of carbon-donor ligands, based on chemical and spectroscopic evidence.[16]

The Pt–Cl bond lengths in Table I give rise to the *trans*-influence series σ-carbyl > carbene > isonitrile > carbon monoxide, and this series is an exact reversal of the π-acidity series discussed above. We therefore suggest that the *trans*-influence of the carbon-donor ligands in the compounds shown in Table I depends mainly on the extent of metal-to-ligand π-back bonding.

In Table II we have presented bond length data for square-planar platinum(II) complexes[5,17–20] in which the ligands, L, *trans* to chloride, have negligible π-acidity.** McWeeny, Mason, and Towl[5] have shown that in such complexes the *trans*-influence of L, measured by the length of the Pt–Cl (*trans* to L) bond, is related to the strength of the Pt–L σ-bond. As a measure of σ-bond strength they have used the quantity $S^2/\Delta E$, where S is the overlap integral and ΔE the energy separation between the σ-orbital of L and the platinum $6p$ σ-orbital; ΔE is related to the Pauling electronegativity of the donor atom of L.

The range of Pt–Cl bond lengths in Table I is very nearly co-extensive with that in Table II. We therefore conclude that in chloro–platinum(II) complexes the π-acceptor properties of ligands L may have as profound an effect on the strength of the metal–*trans*-ligand bond as the σ-donor properties of L. It thus becomes obvious that any rationalisation of a *trans*-influence series of ligands with both σ-donor and π-acceptor properties should take into account both the σ- and π-components in the L–M bond. This view implies involvement of the metal d_π orbital and, hence, the interaction of this orbital with both the influencing and influenced ligands should be considered.

In the compounds we have discussed (Tables I and II) the ligand *trans* to L, chloride, forms a highly ionic bond with platinum. If the ligand L forms a strongly covalent bond with platinum and has negligible

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* Exact positive correlation, r = +1.0, would not be expected since (i) the data are subject, to some extent, to random and systematic errors, (ii) a linear relationship between R(Pt) and l(Pt–Cl) need not apply; in the complexes considered (iii) the σ-Pt–C bond strength and hence the inductive *trans*-influence need not be uniform, and (iv) the *cis* ligands are not the same.

** The extent of back-donation from platinum to monotertiary phosphine still appears controversial.

π-acidity, then the electron density in the L–Pt–Cl bonding molecular orbitals will be distributed mainly on the ligand Cl^- and along the L–Pt bond. The asymmetry of the charge distribution in the L–Pt–Cl system will induce, by electrostatic repulsion, a flow of metal d_π electron density towards the chloride ligand, which will in turn be repelled by the metal atom, and thus a lengthening of the Pt–Cl bond will occur. For a series of ligands with virtually no π-acidity the *trans*-influence will decrease as the electronegativity of the L-donor atom increases and the covalency of the L–Pt bond decreases (*i.e.* as the σ-electron density along the L–Pt bond gradually shifts towards L); for ligands capable of accepting charge from the metal d_π orbital the *trans*-influence will decrease as the π-acidity increases. In summary, the *trans*-influence on Pt–Cl bonds is largely electrostatic, and it is transmitted mainly through the metal d_π orbital.

An advantage of this simple, qualitative explanation of *trans*-influence is that it allows for the effects of both the σ- and π-components in the L–M bond. It brings together, and relates to *trans*-influence, elements of the two main theories of the kinetic *trans*-effect: Grinberg's original theory,[21] based on purely electrostatic effects in the ground state, and Chatt *et al.*[22] and Orgel's[23] theory, which considers the effects of L–M π-bonding on stabilisation of transition states.

So far we have discussed only the influence of ligands on *trans* Pt–Cl bonds, since accurate structural data for extensive series of related complexes are available. At present there is insufficient bond length data to warrant a similar discussion of the *trans*-influence on orher types of bond. We would, however, expect that both the character of the metal atom (hard–soft) and the nature of its bonding with the influenced ligand may have to be considered separately for each type of metal–*trans* ligand bond.

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