

# The Geometries of and Bonding in Certain Transition Metal Complexes

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Two topics in structural transition metal chemistry are discussed. First the Chatt-Dewar theory for the bonding between metals and unsaturated ligands such as carbon disulphide, oxygen and acetylene is developed; it is shown that the molecular orbital wave function contains wave functions belonging to the excited states of the individual fragments and the theory is then correlated with some recent structural results. Secondly, the trans-influence of a number of ligands in several platinum(II) complexes is described and related to their electronegativities and ligand-metal  $p(\sigma)$  overlaps.

The Chatt-Dewar model<sup>1, 2</sup> for the bonding between transition metals and unsaturated ligands has been qualitatively successful for many discussions of the properties of organometallic molecules; during the last few years, semi-empirical theories of varying sophistication and reliability have developed this largely symmetry-based model to predictions of molecular energy levels and related matters. We now examine the implications of a simple molecular orbital theory on recent observations of the geometries of unsaturated ligands co-ordinated to metals in low oxidation states.

The model for the bonding between the metal and ligand is based, as in the Chatt-Dewar model, on the highest occupied orbitals of the metal M and ligand L being respectively  $\pi$  and  $\sigma$  symmetry, the lowest empty orbitals being of opposite symmetry. The molecular orbitals are constructed, as usual, by a linear combination of orbitals of the component systems. The  $\sigma$  orbitals lie close together and interact quite strongly to give the bonding and antibonding orbitals,  $\sigma_{ML}$  and  $\sigma_{ML}^*$ . The  $\pi$  orbitals, initially filled on the metal and unfilled on the ligand, in general interact more weakly to give the  $\pi_{ML}$  and  $\pi_{ML}^*$  orbitals. If we disregard mixture of all other orbitals, we consider only the electron configurations  $ML[\pi^2\sigma^2]$ ,  $M[\pi_M^2]$  and  $L[\sigma_L^2]$  which all correspond to spin singlet ground states (the complexes of interest are all diamagnetic). If we neglect overlap, the molecular orbitals ML have the normalized form,

$$\begin{aligned}\sigma &= \sigma_M \sin \theta + \sigma_L \cos \theta, \\ \sigma^* &= \sigma_M \cos \theta - \sigma_L \sin \theta, \\ \pi &= \pi_M \cos \phi + \pi_L \sin \phi, \\ \pi^* &= \pi_M \sin \phi + \pi_L \cos \phi,\end{aligned}\tag{1}$$

with the ground state of the complex being represented by the wave function

$$\Psi = \frac{1}{2} | \sigma \bar{\sigma} \pi \bar{\pi} | .\tag{2}$$

$\sigma$  and  $\bar{\sigma}$ , for example, represent spin-orbitals with  $\alpha$  and  $\beta$  spin factors respectively;  $\theta$  and  $\phi$  are defined by the equations

$$\begin{aligned}\delta_\sigma &= 2 \sin^2 \theta \text{ (}\sigma \text{ charge donated by the ligand),} \\ \delta_\pi &= 2 \sin^2 \phi \text{ (}\pi \text{ charge back-donated by metal).}\end{aligned}$$

Inserting (1) into (2) and expanding, we obtain the following terms in the wave function:

$$\begin{aligned} & \sin^2 \theta \cos^2 \phi |\sigma_M \bar{\sigma}_M \pi_M \bar{\pi}_M| + \cos^2 \theta \sin^2 \phi |\sigma_L \bar{\sigma}_L \pi_L \bar{\pi}_L| + \cos \theta \sin \theta \cos \phi \sin \phi \times \\ & \quad \{ - |\sigma_M \pi_M \bar{\sigma}_L \bar{\pi}_L| + |\sigma_M \bar{\pi}_M \sigma_L \bar{\pi}_L| + |\bar{\sigma}_M \pi_M \bar{\sigma}_L \pi_L| - |\bar{\sigma}_M \bar{\pi}_M \sigma_L \pi_L| \} + \\ & \sin^2 \theta \sin^2 \phi |\sigma_M \bar{\sigma}_M \pi_L \bar{\pi}_L| + \cos^2 \theta \cos^2 \phi |\sigma_L \bar{\sigma}_L \pi_M \bar{\pi}_M| + \\ & \sin^2 \theta \cos \phi \sin \phi \{ |\sigma_M \bar{\sigma}_M \pi_M \bar{\pi}_L| - |\sigma_M \bar{\sigma}_M \bar{\pi}_L \pi_M| + \\ & \cos^2 \phi \sin \theta \cos \theta \{ |\sigma_M \pi_M \bar{\pi}_M \bar{\sigma}_L| - |\bar{\sigma}_M \pi_M \bar{\pi}_M \sigma_L| \} + \\ & \cos^2 \theta \cos \phi \sin \phi \{ |\sigma_L \bar{\sigma}_L \pi_M \bar{\pi}_L| - |\sigma_L \bar{\sigma}_L \bar{\pi}_L \pi_M| \} + \\ & \sin^2 \phi \sin \theta \cos \theta \{ |\sigma_L \pi_L \bar{\pi}_L \bar{\sigma}_M| - |\bar{\sigma}_L \pi_L \bar{\pi}_L \sigma_M| \}. \end{aligned} \quad (3)$$

The various terms are identifiable as antisymmetrised products of wave functions representing the states of the separate systems M and L. For example,

$$\frac{1}{2} |\sigma_L \bar{\sigma}_L \pi_M \bar{\pi}_M| = A \cdot 1/\sqrt{2} |\sigma_L \bar{\sigma}_L| 1/\sqrt{2} |\pi_M \bar{\pi}_M|$$

with  $A$  antisymmetrizing the product of two normalized wave functions representing the singlet ground states of  $[\pi_M^2]$  and  $[\sigma_L^2]$ , performing all possible electron interchanges and summing with appropriate signs.

The first two terms in eqn. (3) arise from the ionic wavefunctions  $M^{2-} \cdot L^{2+}$  and  $M^{2+} \cdot L^{2-}$  while the last four terms describe singlet states belonging to the singly ionized functions,  $M^- \cdot L^+$  and  $M^+ \cdot L^-$  respectively—they are, therefore, relatively unimportant. That is to say, if the coefficients of the various wave functions in (3) were regarded as variational parameters, those of the “ionic states” would decrease in magnitude on optimizing the wave function. (A similar situation occurs in the molecular orbital treatment of the hydrogen molecule where complete neglect of the “ionic states” yields the Heitler-London wave function). The remaining terms may now be written in the form,

$$\begin{aligned} \Psi = & aA(\Phi_{Lg}\Phi_{Me}) + bA(\Phi_{Le}\Phi_{Me}) + \\ & c\{A[{}^3\Phi_{L,0}{}^3\Phi_{M,0} - {}^3\Phi_{L,-1}{}^3\Phi_{M,+1} - {}^3\Phi_{L,+1}{}^3\Phi_{M,-1}] + A({}^1\Phi_L{}^1\Phi_M)\}. \end{aligned}$$

$\Phi_{Lg}$  and  $\Phi_{Me}$  are the ground states of L and M while  $\Phi_{Le}\Phi_{Me}$  are excited singlet states produced by *double* excitations into the lowest empty orbitals. The second term must be expected to have lower weight than the first which represents the “no-bond” situation. We note that in the limit of very small overlap, our function will correspond to the well-known Mulliken charge transfer wave functions. The singly excited wave functions appear only when overlap is large and the molecular orbital method more appropriate. We infer from (3) that the coefficients  $a$  and  $c$  are defined by

$$c/a = \tan \theta \tan \phi$$

showing that the importance of the interaction terms, and hence the excited state components of the wave function, increases with increasing charge transfer from the metal to ligand and vice versa.

The appearance of triplet states in the term describing the interaction is of most interest to us.  ${}^3\Phi_{L,m}$ , for example, is the spin-triplet state of the ligand arising from a single excitation into the empty  $\pi$  orbital, with spins coupled to unity and with “ $z$ ” component  $m = 0, \pm 1$ . The functions in the square brackets arise by vector coupling the triplet states of the fragments to a resultant spin  $S = 0$ . The term

$A(^1\Phi_L ^1\Phi_M)$  arises from the same single excitations but with spins coupled to give a singlet state of each fragment. Since each term is individually normalized, the triplet terms occur with three times the weight of the singlet term. A variational calculation would allow the ratio of these coefficients to vary but the general picture will remain unchanged.

In the complex the charge density is a weighted sum of densities associated with fragments in their various individual states. The terms in which the fragments are in their first excited triplet states appear with large weighting and all lead to a ligand charge distribution virtually identical with that possessed by an isolated ligand molecule in its first excited triplet state. The geometry of a ligand will therefore spontaneously change on co-ordination, the forces acting on the nuclei being more nearly those of the triplet state rather than those of the ground state.

Recent X-ray structural analyses show that (i) the carbon disulphide ligand in  $(\text{Ph}_3\text{P})_2\text{PtCS}_2$  has a geometry remarkably similar to that of its  $^3A_2$  excited state.<sup>3, 4</sup> (ii) The electron distribution in  $\pi$ -bonded oxygen complexes approximates that of the  $^3\Sigma_u^-$  excited state in a way which varies according to the electronic nature of the remaining ligands in the complex.<sup>5, 6</sup> The  $^3\Sigma_u^-$  state is, in valence bond terms, predominantly  $\text{O}^+ - \text{O}^-$  and the reactivity of  $(\text{Ph}_3\text{P})_2\text{PtO}_2$  towards carbon dioxide, sulphur dioxide, aldehydes and ketones may be rationalized along these lines.<sup>7</sup> (iii) The geometries of acetylene, ethylene and butadiene co-ordinated to metals in low valence states often approaches that of their excited states.<sup>6</sup> For acetylene, Blizzard and Santry have recently discussed its co-ordinated geometry.<sup>8</sup> Substituted acetylenes are cis-bent on co-ordination in contrast to the excited state of the unco-ordinated molecule which is trans-bent. It is obvious qualitatively that non-bonded interactions of the substituent groups with the metal will stabilize the cis-bent ligand on co-ordination. However, Blizzard and Santry<sup>8</sup> point out that the cis-bent structure can be explained solely in terms of the symmetry of the various orbitals of the metal and ligand—it is largely a question of the contribution of the carbon  $2s$  orbitals to the various metal-ligand molecular orbitals. CNDO—MO calculations indicate that the observed angles of bonding in co-ordinated acetylene can be accounted for by the transfer of approximately 0.5 electron from the ligand  $\pi_u$  orbitals to its  $\pi^*$  counterpart; this estimate is not inconsistent with other estimates of the extent of charge transfer in metal to ligand interactions.<sup>9</sup>

#### THE TRANS-INFLUENCE OF LIGANDS

The classification of ligands according to their “trans-directing” properties, i.e., their relative tendency to direct an incoming ligand into a trans-position to themselves, for substitution reactions in planar platinum (II) complexes, has been established for some time.<sup>10</sup> The extension of this classification to a series based on the effectiveness of a ligand to influence the rate of displacement of trans-ligands was made by Basolo and Pearson<sup>11</sup> and forms the definition of the “trans-effect”.

Two theories have some success in rationalizing the trans-effect in terms of electronic effects transmitted by the trans-directing ligand across the metal to the leaving group; they are based respectively on the inductive and mesomeric effects of the trans-directing ligand.<sup>12, 13</sup> A generalization of the relative importance of inductive and mesomeric effects is difficult for little is still known of the detailed mechanisms of substitution in  $d^6$  and  $d^8$  planar complexes while the variations of reaction rate with solvent, metal oxidation state, incoming group participation and steric effects are not understood in any general way. These difficulties have led to an increasing interest in observable ground state effects of a ligand L on a trans-ligand

X and infra-red and nuclear magnetic resonance spectroscopy has been used to study the trans-bond weakening effect of a ligand <sup>14, 15</sup> (differentiating an equilibrium property (trans-influence) from the kinetic trans-effect). We prefer to examine bond lengths in this connection since again it is not clear that interpretation of infra-red and nuclear magnetic resonance data is at all straightforward—for example, few data are available for bond force constants in the complexes of interest. Structural data, from X-ray analyses, of some planar platinum(II) complexes are collected in table 1.

TABLE 1.—PLATINUM-CHLORINE BONDLNGTHS IN SOME PLATINUM(II) COMPLEXES

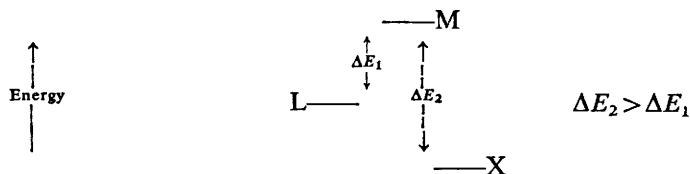
molecule	trans-ligand	Pt—Cl bond length (Å)
(Pr(acac) <sub>2</sub> Cl) <sup>−</sup>	O	2.28 ± 0.01 <sup>16</sup>
trans-(PEt <sub>3</sub> ) <sub>2</sub> PtCl <sub>2</sub>	Cl	2.30 ± 0.01 <sup>17</sup>
(C <sub>12</sub> H <sub>17</sub> ) <sub>2</sub> Pt <sub>2</sub> Cl <sub>2</sub>	C=C	2.31 ± 0.01 <sup>18</sup>
cis-(PMe <sub>3</sub> ) <sub>2</sub> PtCl <sub>2</sub>	P	2.37 ± 0.01 <sup>19</sup>
trans-(PPh <sub>2</sub> Et) <sub>2</sub> PtHCl	H	2.42 ± 0.01 <sup>20</sup>
trans-(PPhMe <sub>2</sub> ) <sub>2</sub> (SiPh <sub>2</sub> Me)PtCl	Si	2.45 ± 0.01 <sup>21</sup>

The order of trans-influence is seen to be : Si > H > P > C=C, Cl > O.

Although less data are available, a similar series may be provided for other  $d^8$  (Ni(II) and Pd(II)) planar complexes and for octahedral  $d^6$  (Co(III), Rh(III), Ir(III), Pt(IV)).<sup>22</sup>

Grinberg's original discussion <sup>12</sup> of the trans-effect was based on purely electrostatic grounds, relating polarizability to the trans-directing ability of a ligand. Syrkin and Yashkin related polarizability of a ligand to the covalent character of the metal-ligand bond and, using valence bond methods, showed that in  $d^8$  planar complexes an increase in the degree of covalence in the M—L  $\sigma$  bond decreased the covalence of the trans M—X  $\sigma$  bond and hence increased the lability of X.<sup>23</sup>

Fig. 1 shows that for the data of table 1, the trans-influence of L increases smoothly with decreasing electronegativity (the effective electronegativity of C=C is that of trigonal carbon).<sup>24</sup> Chatt *et al.*<sup>25</sup> reached a similar conclusion from infra-red data. This result is related to those of Syrkin and Yashkin; if we consider relative energies of L, M and X  $\sigma$ -bonding orbitals, then if the ligand X is more electronegative than L, the following qualitative scheme is obvious.



The  $\sigma$ -molecular orbital electron density will be principally within the M—L bond (high covalence) and on the ligand X (high ionic character of M—X).

Gray and Langford <sup>26</sup> base a theory of the trans-effect on the magnitude of the M—L and M—X  $\sigma$ -overlap integrals. The suggestion here is that if the  $\sigma$ -donor orbital of the ligand L has a greater overlap with the metal  $p\sigma$  orbital than does the ligand X  $\sigma$ -orbital, then the M—L bond is strengthened at the expense of the M—X bond. The overlap calculations of Gray and Langford have now been extended comprehensively to a number of ligands and metals and are given in table 2.

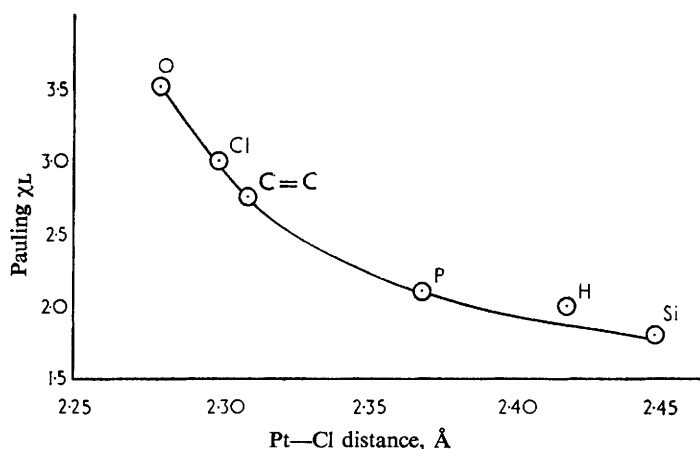


FIG. 1.—Variation of the Pt—Cl bond length in L—Pt—Cl as a function of the Pauling electronegativity,  $\chi_L$ , of the trans-ligand L.

TABLE 2.—METAL ( $p\sigma$ )—LIGAND HYBRID ( $\sigma$ ) OVERLAP INTEGRALS

ligand atom and hybridization	Co(III)	Ni(II)	Rh(III)	Pd(II)	Ir(III)	Pt(II)	Au(III)
C ( $sp^3$ )	0.45	0.49	0.49	0.48	0.48	0.48	0.48
C ( $sp^2$ )	0.47	0.52	0.52	0.52	0.51	0.51	0.51
C (sp)	0.51	0.55	0.55	0.55	0.54	0.54	0.54
N ( $sp^3$ )	0.40	0.45	0.45	0.45	0.44	0.44	0.45
N ( $sp^2$ )	0.43	0.47	0.47	0.48	0.47	0.47	0.48
O ( $sp^3$ )	0.36	0.40	0.40	0.41	0.40	0.41	0.41
O ( $sp^2$ )	0.38	0.43	0.42	0.42	0.41	0.42	0.42
F ( $sp^3$ )	0.31	0.36	0.37	0.37	0.36	0.37	0.37
F ( $sp^2$ )	0.34	0.38	0.38	0.38	0.37	0.38	0.38
F (sp)	0.37	0.41	0.38	0.39	0.38	0.39	0.39
Si ( $sp^3$ )	0.56	0.55	0.51	0.50	0.49	0.49	0.49
P ( $sp^3$ )	0.51	0.53	0.50	0.49	0.49	0.49	0.48
S ( $sp^3$ )	0.48	0.50	0.47	0.47	0.46	0.46	0.45
S ( $sp^2$ )	0.51	0.52	0.47	0.47	0.46	0.46	0.46
Cl ( $sp^3$ )	0.45	0.47	0.44	0.43	0.42	0.43	0.42
Cl ( $sp^2$ )	0.47	0.49	0.44	0.44	0.43	0.43	0.43
Cl (sp)	0.50	0.50	0.44	0.44	0.43	0.43	0.42
As ( $sp^3$ )	0.52	0.53	0.48	0.48	0.47	0.46	0.46
Br ( $sp^3$ )	0.48	0.48	0.43	0.43	0.42	0.42	0.41
Br ( $sp^2$ )	0.50	0.49	0.44	0.43	0.42	0.42	0.41
Br (sp)	0.51	0.50	0.43	0.43	0.41	0.41	0.41
H (s)	0.54	0.56	0.51	0.51	0.50	0.50	0.50

These overlap integrals have been calculated as follows :

(i) Atom radii (Å) ; C( $sp^3$ ) 0.77, C( $sp^2$ ) 0.74, C(sp) 0.71 ; N( $sp^3$ ) 0.70, N( $sp^2$ ) 0.63 ; H, 0.27 ; O, 0.66 ; F, 0.62 ; Si, 1.00 ; P, 1.00 ; S, 1.00 ; Cl, 0.99 ; As, 1.12 ; Br, 1.14 ; Co(III), 1.26 ; Ni(II), 1.24 ; Rh(IV), 1.33 ; Pd(II), 1.31 ; Ir(III), 1.36 ; Pt(II), 1.33 ; Au(III), 1.31.

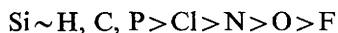
(ii) S.C.F. wavefunctions were used for all atoms. For the first row transition metals they are those of Richardson *et al.*<sup>27</sup> ; for the second and third row metals they are the functions of Basch and Gray.<sup>28</sup>

(iii) All metal wavefunctions are those of the +1 oxidation state. Whilst this assumption will undoubtedly introduce some error, it will probably be a systematic one and with little variation from metal to metal. Cotton and Harris conclude<sup>29</sup> that failure to correct the metal wavefunction for varying metal charge in  $(\text{PtCl}_4)^{2-}$  leads to an error of less than 4 % in the M—L overlap integrals for charge variations between 0 and +1.

(iv) All ligand wavefunctions are those of Clementi<sup>30</sup> for neutral atoms, double zeta functions being used where available.

(v) The calculated values are based on the method of Demuyneck and Kaufmann<sup>31</sup> and Mulliken's rules.

For platinum(II), the  $\sigma$ -overlap integrals have the order :



in general qualitative agreement with trends in the bondlengths noted in table 1 and confirming, for the trans-influence of ligands, the suggestions of Gray and Langford relating to the trans-effect. We emphasize that the agreement is only qualitative—we cannot sensibly deal, for example, with the relative trans-influence of tri-alkyl and triaryl phosphine ligands.

Perturbation theory indicates that bond strength may be related to  $S^2/\Delta E$  ( $S$  the overlap integral and  $\Delta E$ , the energy separation between the orbitals being mixed). The above discussion now shows that both relative ligand  $\sigma$ -orbital energies and relative ligand-metal  $\sigma$  overlap integrals reproduces the trend of the trans-influence ability of a ligand.

The bond length data additionally illustrate a mesomeric contribution to the trans-influence which would, in principle, be exerted in one of two ways,

(i) A  $\pi$ -acceptor ligand L is able, through the usual synergic effect, to effectively increase its donor capacity which in turn increases the inductive contribution to the trans-influence, and

(ii) As has been pointed out previously, a  $\pi$ -acceptor ligand will directly compete with the ligand X for excess charge in the metal. The fact that ethylene and carbon monoxide have little or no trans-influence and that, experimentally, the trans-influence of a  $\sigma$ -bonded alkyl is greater than that of a formally  $\sigma$ -bonded phosphine clearly indicate that the second process is dominant. In short, therefore, a strong trans-influence follows from the ligands with large inductive,  $\sigma$ -donor and weak  $\pi$ -acceptor properties. (In all of this discussion we assume that the ligand X has negligible  $\pi$ -bonding capacity.) By contrast, the large trans-effect of ethylene and carbon monoxide can be accounted for, as Chatt *et al.* and Orgel<sup>32</sup> pointed out, in terms of the stabilization of transition states and not from any initial ground state labilization of the trans-ligand.

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