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A Molecular Orbital Study of the Trans Effect

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The trans-effect in Pt^{II} complexes has been studied by a self-consistent molecular orbital method based on the CNDO approach. Systems investigated included the ions $[Pt(X)Cl_3]^-$ *and the neutral species trans-*$[Pt(X)NH_3Cl_2]$ *in which* $X = C_2H_4, PH_3, CO, H_2S, NH_3, H_2O, H^-, CN^-, CH_3^-, Br^-, Cl^-, OH^-, NO_2^-$. *It is concluded that the order of ability of ligands to exert the trans-effect depends on two factors; the trans-influence and the stabilisation of the trigonal bipyramidal transition state. If π-bonding is possible in the transition state this dictates the course of reaction. For a σ-bonding ligand both its trans-influence and its ability to act as a donor in the transition state are important but the trans-influence is more important when the two effects do not reinforce each other.*

Introduction

The *trans*-effect is one of the most intriguing phenomena of transition metal chemistry and has been a subject of increasing interest since its value in synthetic inorganic chemistry was first recognised by Chernyaev.[1] However, in contrast to the considerable amount of experimental work which has been devoted to the study of the *trans*-effect, theoretical investigation of this topic has been rather limited. Since the mechanisms through which the effect manifests itself must ultimately depend on the electronic properties of the systems involved, the problem is well suited to a quantum mechanical approach. It is the purpose of this work, therefore, to attempt a general theoretical description of the nature of the *trans*-effect by means of a molecular orbital treatment.

The *trans*-effect of a group coordinated to a transition metal ion in a complex may be simply defined as the ability of that group to labilise the position *trans* to itself. In any chemical reaction, activation energy is of primary importance and hence any factor influencing the magnitude of this energy barrier, and associated with the ligand *trans* to the labile position, will constitute a *trans*-effect. This means that the *trans*-directing properties of a group may or may not be related to its *trans*-influence, i.e., the effect of the group on the strength of the metal–ligand bond *trans* to itself. This is because the *trans*-effect may operate by stabilisation of the transition state of the reaction rather than by destabilisation of the reactant ground state.

The bulk of the experimental work on the *trans*-effect has been directed towards substitution reactions of square-planar platinum(II) complexes and, consequently, the main features of these reactions are now fairly well established.[2–6] The reactions are known to occur by an associative mechanism and the experimental facts are consistent with a distorted trigonal bipyramidal transition state.

The earlier theories[7,8] considered only bond weakening in the substrate, i.e. the *trans*-influence, and ignored the stabilisation of the transition state. Therefore, although they had some success in predicting the observed *trans*-series, particularly for σ-bonding ligands, they were not comprehensive enough to give a good general account of the *trans*-effect. This deficiency was soon rectified, for π-bonding ligands at least, by the ideas advanced by Chatt *et al.*[9] and Orgel,[10] in which both the *trans*-influence and transition state stabilisation were considered explicitly. These theories have been extended to include σ-bonding effects by Bersuker[11] and Langford and Gray,[4] thus an improved qualitative interpretation of the *trans*-effect was obtained. The role of σ-bonding ligands in the stabilisation of the transition state has been examined theoretically by calculations[12] of the Extended Huckel type. These provided verification of postulated theories and also emphasised the relative importance of the transition-state stabilisation factor compared to the *trans*-influence effect. However, this work considered σ-bonding ligands only and a re-investigation of the *trans*-effect for both σ- and π-bonding ligands seems appropriate. It would also be more interesting to use a calculational procedure which explicitly includes electron interaction, albeit semi-empirically. Therefore, a modified version[13] of the CNDO MO[14] method was employed in all calculations. Our approach was first to investigate the *trans*-influence by a series of calculations on the ground state of various square-planar platinum complexes. This was followed by an examination of the trigonal bipyramidal transition state to ascertain the significance of this intermediate stage in the *trans*-effect.

Results and Discussion

Preliminary Calculations

The parameters input[15] to the computer programme of all the atoms except platinum have been used in previous calculations and have given satisfactory and reliable results. For platinum, in preliminary calculations on $[PtCl_4]^{2-}$ and $[Pt(C_2H_4)Cl_3]^-$, the diagonal elements of the core Hamiltonian matrix were equated to the corresponding valence orbital ionisation potentials,[16] whilst the value of the one-centre, two-electron repulsion integral for *s, p,* and *d* orbitals was 9.8 eV. For $[PtCl_4]^{2-}$ these calculations revealed that the charge on platinum was +0.36, i.e., in reasonable agreement with the value of +0.44 estimated from NQR measurements[17] The excited states of Zeise's anion were also computed (missing out the lowest observed triplet). The agreement with experiment[18] (Table I) can reasonably be taken to indicate the general acceptability of the input parameters for platinum. The geometries of all the complexes studied are set out in Table II.

TABLE I. Calculated and Experimental Electronic Transitions for $[Pt(C_2H_4)Cl_3]^-$.

Experimental transition energies (eV)	Extinction coefficient	Calculated transition energies (eV)	Oscillator strength
2.96	40	–	–
3.76	340	3.96	0.000
4.15	605	4.08	0.001
4.64	3100	4.62	0.001
5.05	3260	4.93	0.000
		5.30	0.012

TABLE II. Geometrical Data (All complexes square planar).

X	Pt–X (nm)
C_2H_4	0.2152[a]
PH_3	0.225[b]
CO	0.200[c]
H_2S	0.230[b]
NH_3	0.217[d]
H_2O	0.210[c]
H^-	0.166[b]
CN^-	0.207[e]
CH_3^-	0.215[b]
Br^-	0.243[c]
Cl^-	0.233[b]
OH^-	0.210[c]
NO_2^-	0.202[d]

[a] Ref. 25. [b] Ref. 12. [c] Value estimated by comparison with similar species. [d] "Interatomic Distances in Molecules and Ions", Chemical Society (Lond.), Special Publication No. 21 (1958). [e] M.L. Moreau–Colin, *Structure and Bonding, 10,* 167 (1972).

Electronic Structure of Zeise's Anion

The ground state of Zeise's anion has been the subject of previous theoretical investigations[18–21] but, since it plays a significant rôle in subsequent calculations and argument, it is pertinent to re-examine its electronic structure at this point.

The first qualitative description of $[(C_2H_4)PtCl_3]^-$ was given by Chatt[22] and was confirmed by a limited basis set calculation[23] in which synergic σ–π bond formation was shown to be operative. It was suggested that electron density was removed from the platinum by π-bonding and donated to the metal by σ-bonding. The resulting charge on the platinum was +0.036. A later calculation[24] gave the charge on platinum as +0.617 and showed also that the *trans*-Pt–Cl bond is more "ionic" than the *cis*-bonds.

In the present calculations, the crystallographic structure due to Black[25] was employed, in which the ethylene ligand is perpendicular to the plane of the $[PtCl_3]^-$ group (defined as [*xy*]): two Pt–Cl bonds are positioned along the *y* axis. The positions of the ethylene hydrogens are not known and so two calculations were performed to further determine the preferred configuration of the ethylene moiety: a lower energy was obtained when the ethylene was orientated in the *yz* plane rather than in the *xz* plane. Consequently, this former configuration was used in all subsequent calculations which involved ethylene as ligand. Atom charges, bond indices, and valencies for ethylene and Zeise's anion are presented in Table III. The latter two quantities have been recently defined[26,27] in terms of the density matrix elements *P*.

TABLE III. Atomic Charges, Bond Indices, and Valencies for Ethylene and Zeise's Anion.

Atom	Atomic charge $[(C_2H_4)PtCl_3]^-$	Atomic charge C_2H_4[a]	Valencies $[(C_2H_4)PtCl_3]^-$	Valencies C_2H_4[a]
C	−0.05	−0.06	3.99	3.99
H	+0.06	+0.03	1.00	1.00
Pt	+0.44		2.90	
cis-Cl	−0.54		1.14	
trans-Cl	−0.46		1.17	

Bond	Bond indices $[(C_2H_4)PtCl_3]^-$	Bond indices C_2H_4[a]
Pt–Cl *(trans)*	0.72	–
Pt–Cl *(cis)*	0.68	–
Pt–C	0.33	–
C–C	1.65	2.03
C–H	0.93	0.98

[a] Ref. 27.

$$V_A = \sum_{\lambda \text{ on } A} 2 P_{\lambda\lambda} - \sum_{\lambda \text{ on } A} \sum_{\sigma \text{ on } A} P_{\lambda\sigma}^2$$

$$B_{AB} = \sum_{\lambda \text{ on } A} \sum_{\sigma \text{ on } B} P_{\lambda\sigma}^2$$

The valency, V_A, of atom A in a molecule gives, by comparison with the maximum value of V_A, a measure of the reactivity of atom A. The bond index, B_{AB}, is a useful quantity with which to categorise the bonding between atoms A and B, since it signifies the multiplicity of the bond, e.g., bond indices of 1, 2, 3 are calculated for the C–C bonds in C_2H_6, C_2H_4, and C_2H_2, respectively. In the present work we use the Pt–L bond index as a guide to whether *trans* ligands produce a weakening or a strengthening of this bond. The usefulness of this index for such a purpose was investigated by comparing the bond indices calculated for the Pt–H bonds in the series *trans*-$[Pt(PH_3)_2HL]$, where L = I, Cl, CN, H, with published vibrational spectra for related molecules[28] (i.e., $[Pt(PEt_3)_2HL]$). In summary, we found that the decrease of bond index as L = Cl > I > CN > H paralleled exactly the decrease of ν(Pt–H). The relationship is not, of course, linear, since the Pt–H stretch cannot be fully isolated from the mass effects of the rest of the species.

The charge found on platinum is +0.44, intermediate between the values obtained from previous calculations. The total electron density on the ethylene moiety surprisingly remains unaltered by coordination to the $[PtCl_3]^-$ species. However, the carbon–carbon bond indices show clearly that the "double-bond" character of the C–C bond is diminished by complex formation; this occurs with a concomitant increase in the platinum–carbon bond index. Although the most important single contribution to the Pt–C bond involves the d_{xz} orbital, the σ-bonding components incorporating the Pt($d_{x^2-y^2}$) and Pt(s) orbitals are not negligible. The rearrangement of electrons which does occur manifests itself through the presence of 0.31 electrons in the π^* orbital of ethylene whilst the number of electrons in the π orbital of ethylene falls to 1.76. The platinum–chlorine bond indices show that these bonds are weaker than single bonds though, surprisingly, the *trans*-Pt–Cl bond is a trifle stronger than the *cis*-bonds. At the same time, there is a bigger build-up of electronic charge at the *cis*-chlorine atoms than at the *trans*-atom. The carbon, hydrogen and chlorine valencies are near to their maxima, whereas platinum has a valency of 2.90 which, compared with the largest calculated valency for this element (3.62), indicates that platinum is a centre of reactivity.

The trans-Influence

We studied the *trans*-influence in two series of complexes: *trans*-$[Pt(X)(L)Cl_2]$ with L = Cl^- and NH_3. The ligand X was varied and the effect on the *trans*-Pt–L bond was examined. Now, as the *trans*-influence of X increases, then we expect that the strength of the Pt–L bond will decrease and this should be manifest in the Pt–L bond index over the series. Since varying the overall anionic charge on the complex may affect the electronic nature of the bond under scrutiny, we considered it important to keep the charge constant. For this reason, the complexes containing the neutral ligands C_2H_4, PH_3, CO, H_2S, NH_3, H_2O and those including the uninegative ligands H^-, CN^-, CH_3^-, Br^-, Cl^-, OH^-, NO_2^- have been considered as two distinct series.

Bond indices for the Pt–Cl and Pt–N bonds of the two series are presented in Table IV. Now, the *trans*-effect series from experimental studies is $C_2H_4 \sim CO \sim CN^- > PR_3 \sim SR_2 \sim H^- > CH_3^- > NO_2^- > Br^- > Cl^- > NH_3 > OH^- > H_2O$.[12] If we assume that the *trans*-influence controls the directing properties of a group, the following *trans*-effect series can be derived from Table IV:

$PH_3 \sim C_2H_4 > CO > H_2S > NH_3 > H_2O$ and
$H^- > CN^- > CH_3^- > Br^- > Cl^- > OH^- > NO_2^-$

It is interesting to note that the only significant deviations from the experimental series occur with π-bonding ligands. For the σ-bonding ligands the order is correctly reproduced. It therefore seems likely that the *trans*-influence plays a large part in determining the *trans*-directing properties of σ-bonding ligands but it appears to be only partly responsible for the efficacy of π-bonding ligands.

In the calculations, the planar complex $[Pt(L)(X)Cl_2]$ was taken to lie in the xy plane having the X–Pt–L bonds coincident with the x axis. Now, the high *trans*-influence of a σ-bonding ligand was previously rationalised in terms of its ability to interact with the platinum p_x orbital.[4] If the *trans*-group X uses the platinum p_x orbital in the Pt–X bond, then the corresponding Pt(p_x)–L interaction will be decreased. This will weaken the Pt–L bond and give rise to a high *trans*-influence. It is, however, unrealistic to assume that this will be the only important contribution to the bond and it is now generally recognised that the remainder of the σ-bonding plus π-bonding must be taken into account. The three most important contributions to the overall Pt–L bond index are also listed in Table IV. In both series the dominant interaction is that between the Pt($d_{x^2-y^2}$) and L and, moreover, the order of this contribution within the series reflects that for the order of total bond indices. The Pt(s)–L share is quite significant, especially when L is the chloride ion but the Pt(p_x)–L portion of the total bond order is comparatively small, due presumably to the higher energy of the 6p orbitals.

The valency of platinum in the two series of complexes is also shown in Table IV. When X is a negatively charged ligand, there is no noticeable trend in the valency values. However, for the neutral ligands there is a discernible decrease in the valency of platinum over the following series of ligands: $C_2H_4 > CO > PH_3 >$

TABLE IV. Bond Indices for Pt–Cl and Pt–N, and the Valency of Platinum in the Series of Complexes *trans*-$[Pt(X)Cl_3]^-$ and *trans*-$[Pt(X)NH_3Cl_2]$.

$[Pt(X)Cl_3]^-$

X	Pt(s)–Cl	Pt(p_x)–Cl	Pt($d_{x^2-y^2}$)–Cl	Total Pt–Cl	Valency of platinum
C_2H_4	0.21	0.11	0.28	0.72	2.90
PH_3	0.18	0.11	0.29	0.71	2.66
CO	0.20	0.11	0.29	0.77	2.87
H_2S	0.19	0.10	0.34	0.77	2.66
NH_3	0.20	0.10	0.35	0.81	2.46
H_2O	0.20	0.10	0.37	0.85	2.44
H^-	0.10	0.09	0.16	0.50	2.45
CN^-	0.14	0.09	0.19	0.57	2.56
CH_3^-	0.16	0.10	0.21	0.61	2.49
Br^-	0.15	0.10	0.24	0.63	2.57
Cl^-	0.15	0.09	0.25	0.64	2.56
OH^-	0.15	0.10	0.24	0.65	2.44
NO_2^-	0.17	0.09	0.26	0.68	2.51

$Pt(X)NH_3Cl_2$

X	Pt(s)–N	Pt(p_x)–N	Pt($d_{x^2-y^2}$)–N	Total Pt–N	
C_2H_4	0.05	0.02	0.12	0.23	2.69
PH_3	0.04	0.03	0.13	0.23	2.51
CO	0.05	0.03	0.14	0.25	2.65
H_2S	0.05	0.02	0.16	0.27	2.51
NH_3	0.05	0.02	0.17	0.29	2.30
H_2O	0.06	0.02	0.19	0.32	2.27
H^-	0.01	0.02	0.07	0.13	2.37
CN^-	0.02	0.02	0.07	0.15	2.47
CH_3^-	0.03	0.02	0.08	0.17	2.38
Br^-	0.02	0.02	0.10	0.19	2.46
Cl^-	0.03	0.02	0.11	0.20	2.47
OH^-	0.02	0.02	0.10	0.20	2.35
NO_2	0.03	0.02	0.11	0.21	2.42

$H_2S > NH_3 > H_3 > H_2O$. This order is remarkably similar to that obtained from the *trans*-influence and implies that a ligand may be effective at labilising the position *trans* to itself but, at the same time, it reduces the ability of the Pt to act as a reactive centre.

Although the possibility of predicting the *trans*-effect series solely on the basis of *trans*-influence has been considered, two problems still remain. Firstly, a more comprehensive explanation for the high *trans*-effect of π-bonding ligands must be sought and, secondly, it must be determined whether or not the *trans*-influence is the only important factor for σ-bonding ligands, i.e., we must consider the possible stabilisation of transition states. These points will now be considered in turn.

The Transition-state Complex for π-bonding Ligands

Three main types of potential π-bonding ligands were considered. These were

(a) ethylene,

(b) linear π-bonding ligands; CO and CN^-,

(c) ligands with low-energy *d* orbitals which are formally unoccupied, PH_3, SH_2.

Initially, the two following processes, previously studied by Leden and Chatt,[29] were considered,

$[Pt(C_2H_4)Cl_3]^- + Cl^- \rightarrow [Pt(C_2H_4)Cl_3]^- + Cl^-$

$[Pt(C_2H_4)Cl_3]^- + NH_3 \rightarrow [Pt(C_2H_4)Cl_2NH_3] + Cl^-$

Calculations were performed on the transition state in the reaction and the two possible trigonal bipyramidal transition states are shown in Fig. 1. For both processes the calculations showed that the transition state (A) had the lower total energy. The source of the differential stability is readily uncovered by comparing the bonding in the two systems through the results in Table V. In transition state (A) there is less electron density on the platinum atom and more electronic charge associated with the ethylene. A lower carbon–carbon bond index and stronger bonding to the entering

TABLE V. Atomic Charges, Bond Indices and Valencies for Transition States A and B for $[Pt(C_2H_4)Cl_4]^{2-}$ and $[Pt(C_2H_4)Cl_3NH_3]^-$.

Atom	Atomic charge				Valency			
	$[Pt(C_2H_4)Cl_4]^{2-}$		$[Pt(C_2H_4)NH_3Cl_3]^-$		$[Pt(C_2H_4)Cl_4]^{2-}$		$[Pt(C_2H_4)NH_3Cl_3]^-$	
	A	B	A	B	A	B	A	B
Pt	+0.59	+0.46	+0.48	+0.41	3.62	3.37	3.31	3.10
N	–	–	−0.20	−0.22	–	–	3.13	3.10
H(5)	–	–	+0.11	+0.10	–	–	0.99	1.00
H(6)	–	–	+0.14	+0.13	–	–	0.98	0.93
H(7)	–	–	+0.14	+0.14	–	–	0.98	0.98
C(1)	−0.16	−0.11	−0.13	−0.10	3.92	3.97	3.96	3.98
H(1)	+0.01	+0.08	+0.04	+0.04	1.00	0.99	1.00	1.00
H(2)	+0.01	+0.03	+0.04	+0.05	1.00	1.00	1.00	1.00
C(2)	−0.16	−0.11	+0.09	−0.07	3.92	3.97	3.98	3.98
H(3)	+0.01	+0.08	+0.05	+0.10	1.00	0.99	1.00	0.99
H(4)	+0.01	+0.03	+0.05	+0.07	1.00	1.00	1.00	1.00
Cl(1)	−0.61	−0.53	−0.58	−0.49	1.16	1.26	1.16	1.26
Cl(2)	−0.56	−0.65	−0.53	−0.60	1.25	1.07	1.24	1.19
Cl(3)	−0.56	−0.65	−0.53	−0.56	1.25	1.07	1.24	1.17
Cl(4)	−0.61	−0.64	–	–	1.16	1.19	–	–

Bond	Bond indices			
	$[Pt(C_2H_4)Cl_4]^{2-}$		$[Pt(C_2H_4)NH_3Cl_3]^-$	
	A	B	A	B
Pt–C	0.47	0.39	0.42	0.37
$Pt–Cl_1$	0.58	0.69	0.64	0.73
$Pt–Cl_2$	0.67	0.63	0.71	0.62
$Pt–Cl_3$	0.67	0.63	0.71	0.71
$Pt–Cl_4$	0.58	0.56	–	–
Pt–N	–	–	0.12	0.11
$N–H_5$	–	–	0.95	0.96
$N–H_6$	–	–	0.93	0.93
$N–H_7$	–	–	0.93	0.92
$C_1–C_2$	1.35	1.44	1.49	1.55
$C_1–H_1$	0.92	0.91	0.92	0.93
$C_1–H_2$	0.92	0.92	0.92	0.93
$C_2–H_3$	0.92	0.91	0.92	0.90
$C_2–H_4$	0.92	0.92	0.92	0.92

ligand are also features of the preferred transition state. These elements are, of course, interrelated and can be satisfactorily explained by the arguments of Chatt and Orgel.[9,10] The ethylene accommodates some of the excess electron density placed on the platinum by the incoming ligand and the consequent delocalisation increases the bonding in the trigonal plane. This, in turn, lowers the energy of the system.

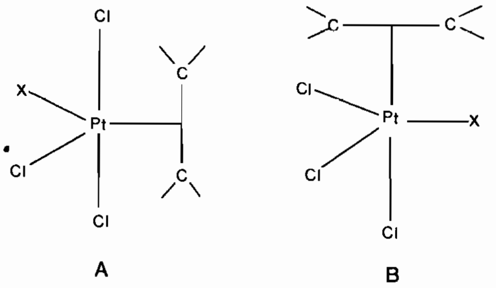


Figure 1. The two trigonal bipyramidal conformations of $[Pt(C_2H_4)XCl_3]^-$.

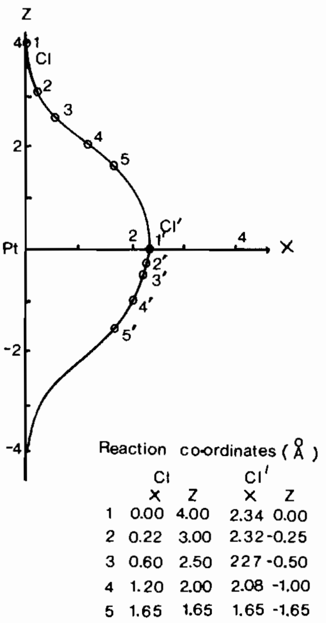
Comparison of the electronic situation in both preferred transition states with that in Zeise's anion reveals that, in the two reactions, electrons are withdrawn from the platinum atom. The entering chloride ion loses 0.4 electrons whilst the ammonia in the second reaction gains 0.2 electrons. In spite of the differing electronegativities of these groups, both cause negative charge to accumulate on the ethylene, thus stabilising the Pt–C and destabilising the C–C bond. The strength of the new Pt–Cl bond is of the same order as the other Pt–Cl bonds, whilst the Pt–N bond has a value typical of a donor-acceptor bond.[30]

The contributions to the new Pt–Cl bond show that the platinum d_{xz} orbital plays an important rôle, as it is conveniently situated to bond with all the groups in the trigonal plane and is responsible for increased Pt–Cl bonding in transition state A as compared with B. Because of the revelations of these calculations, we next considered it to be of some importance to investigate the reaction path

$$[Pt(C_2H_4)Cl_3]^- + Cl^- \rightarrow [Pt(C_2H_4)Cl_3]^- + Cl^-$$

The Reaction Path

Square-planar platinum(II) complexes will normally be solvated under the envisaged reaction conditions and it is reasonable to assume that the first step in the reaction will be solvent displacement. Reaction paths in which the entering nucleophile is initially placed in the solvation positions above and below the molecular plane (xy plane) were therefore considered. Assuming that the reaction path involves a trigonal bipyramidal transition state, our total energy calculations show that the entering ligand should deviate from a straightforward attack perpendicular to the plane of the substrate at ~0.4 nm distant from the platinum. The entering ligand, because of its greater distance from the platinum, will initially move further than the leaving ligand, since the latter is more strongly bonded in the complex. Hence, we believe that the reaction coordinate in Fig. 2 is a reasonable approximation to the actual reaction path.



Reaction co-ordinates (Å)

	Cl		Cl'	
	X	Z	X	Z
1	0.00	4.00	2.34	0.00
2	0.22	3.00	2.32	-0.25
3	0.60	2.50	227	-0.50
4	1.20	2.00	2.08	-1.00
5	1.65	1.65	1.65	-1.65

Figure 2. The reaction path and coordinates for the reaction $[Pt(C_2H_4)Cl_2Cl']^- + Cl^- \rightarrow [Pt(C_2H_4)Cl_2Cl]^- + Cl'^-$.

Variations of atom charges and bond orders as the systems pass along the reaction coordinate are presented in Table VI. Taking the ethylene complex as example, as the reaction proceeds, the electron density donated by the entering chloride ion is delocalised over the ethylene. The occupation of the ethylene π^* orbital increases dramatically as the system approaches the trigonal bipyramidal transition state and the corresponding increase in Pt–C bonding demonstrates the importance of synergic σ–π reinforcement in the transition state. Stabilisation of this transition state is due to electron delocalisation *via* the platinum d_{xz} orbital and this, in turn, depends critically on the ability of the ethylene carbon atoms to accept electron density.

The low symmetry of the reaction path unfortunately precludes the usefulness of symmetry rules[31] but it is instructive, nevertheless, to examine the changes which occur in eigenvalues and eigenvectors along the reaction coordinate. In Fig. 3 this is examined: only half the reaction coordinate is required, since it is symmetrical about the trigonal bipyramidal configuration. The reaction is seen to be symmetry allowed, since there is no crossing of the highest filled and lowest virtual molecular orbitals. The energy gap separating these two particular orbitals remains large at all points, so the involvement of excited states in the reaction is limited. The most significant energy changes occur for the highest bonding level and these parallel the behaviour of the total energies of the systems. It seems likely, therefore, that modifications of the energy of the highest-filled molecular orbital will dictate the course of the reaction. Examination of the eigenvectors of this orbital indicates increasing contributions from both the ethylene π^* and the platinum d_{xz} orbitals as the reaction proceeds

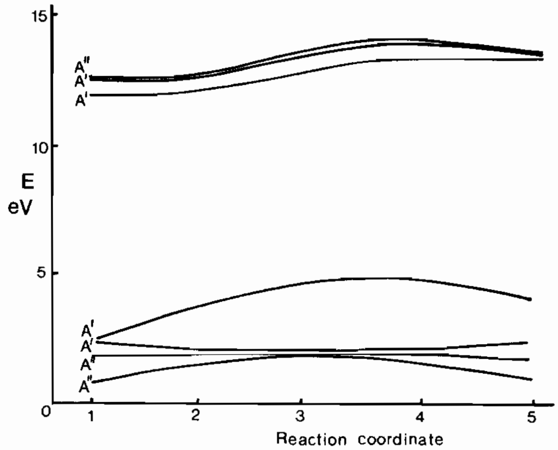
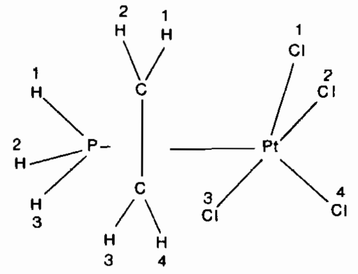


Figure 3. Variation of the four highest filled and three lowest unfilled orbitals along the reaction path for $[Pt(C_2H_4)Cl_3]^- + Cl^- \rightarrow [Pt(C_2H_4)Cl_3]^- + Cl^-$.

TABLE VI. Atomic Charges and Bond Indices at Positions Along the Reaction Path of $[Pt(L)Cl_3]^- + Cl^- \rightarrow [Pt(L)Cl_3]^- + Cl^-$.

Reaction	Atomic charges								Bond indices							
Coordinate	Pt	Cl(1)	Cl(2, 3)	Cl(4)	C(1)	C(2)	H(1, 2)	H(3, 4)	$Pt–C_1$	$Pt–C_2$	$Pt–Cl_1$	$Pt–Cl_2$	$Pt–Cl_4$	C–C	$C_1–H_1$	$C_2–H_3$
$[Pt(C_2H_4)Cl_3]^- + Cl^- \rightarrow [Pt(C_2H_4)Cl_3]^- + Cl^-$																
1	+0.41	−0.85	−0.57	−0.53	−0.04	−0.09	+0.08	+0.04	0.34	0.33	0.27	0.65	0.68	1.63	0.93	0.93
2	+0.45	−0.79	−0.58	−0.55	−0.05	−0.10	+0.07	+0.03	0.36	0.34	0.35	0.65	0.66	1.59	0.92	0.93
3	+0.51	−0.70	−0.58	−0.57	−0.08	−0.14	+0.05	+0.02	0.42	0.38	0.43	0.66	0.65	1.47	0.92	0.93
4	+0.58	−0.61	−0.57	−0.58	−0.14	−0.17	+0.02	+0.01	0.48	0.45	0.54	0.67	0.62	1.34	0.92	0.92
5	+0.59	−0.61	−0.56	−0.61	−0.16	−0.16	+0.01	+0.01	0.47	0.47	0.58	0.67	0.58	1.35	0.92	0.92
$[Pt(PH_3)Cl_3]^- + Cl^- \rightarrow [Pt(PH_3)Cl_3]^- + Cl^-$																
	Pt	Cl(1)	Cl(2, 3)	Cl(4)	P(1)	H(1)	H(2)	H(3)	Pt–P	$Pt–Cl_1$	$Pt–Cl_2$	$Pt–Cl_4$	$P–H_1$	$P–H_2$	$P–H_3$	
1	+0.33	−0.82	−0.50	−0.52	−0.15	+0.08	+0.04	+0.04	0.46	0.26	0.62	0.68	0.93	0.92	0.92	
2	+0.36	−0.76	−0.51	−0.54	−0.16	+0.06	+0.03	+0.03	0.47	0.31	0.62	0.66	0.92	0.92	0.92	
3	+0.39	−0.72	−0.51	−0.56	−0.17	+0.04	+0.02	+0.02	0.50	0.36	0.62	0.65	0.91	0.92	0.92	
4	+0.39	−0.66	−0.51	−0.59	−0.19	+0.02	+0.02	+0.02	0.54	0.46	0.63	0.62	0.89	0.92	0.92	
5	+0.40	−0.64	−0.50	−0.64	−0.19	+0.01	+0.02	+0.02	0.53	0.53	0.64	0.54	0.90	0.92	0.92	
$[Pt(CO)Cl_3]^- + Cl^- \rightarrow [Pt(CO)Cl_3]^- + Cl^-$																
	Pt	Cl(1)	Cl(2, 3)	Cl(4)	C	O			Pt–C	$Pt–Cl_1$	$Pt–Cl_2$	$Pt–Cl_4$	C–O			
1	+0.41	−0.83	−0.54	−0.50	+0.19	−0.18			0.53	0.30	0.68	0.72	2.31			
2	+0.44	−0.79	−0.56	−0.52	+0.18	−0.20			0.54	0.38	0.67	0.69	2.28			
3	+0.47	−0.74	−0.56	−0.54	+0.15	−0.22			0.58	0.41	0.67	0.69	2.24			
4	+0.52	−0.67	−0.55	−0.57	+0.07	−0.25			0.68	0.47	0.69	0.65	2.16			
5	+0.55	−0.64	−0.54	−0.64	+0.06	−0.25			0.67	0.54	0.69	0.54	2.15			



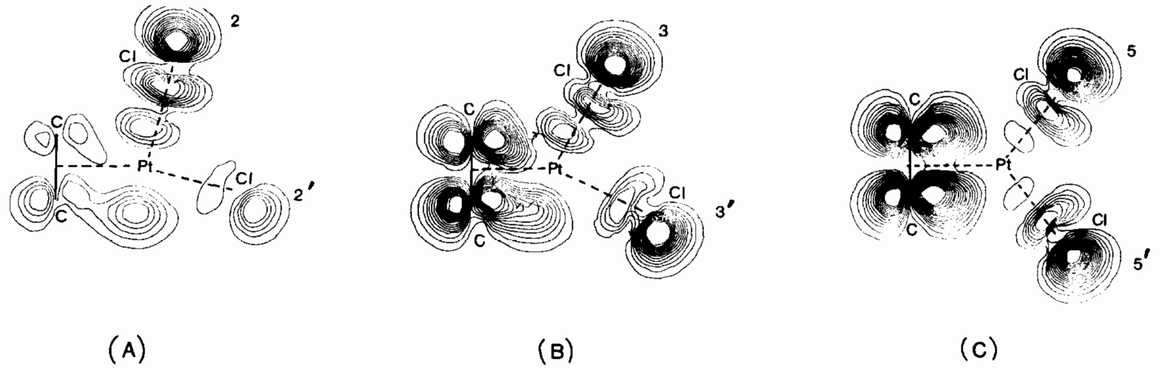


Figure 4. Electron-density contours of the highest filled molecular orbital for three stages in the reaction coordinate of $[Pt(C_2H_4)Cl_3]^- + Cl^- \rightarrow [Pt(C_2H_4)Cl_3]^- + Cl^-$.

to the intermediate trigonal pyramidal state. This is clearly shown by electron density maps of this orbital. In Fig. 4 (A, B, C) are shown contour maps for three points on the reaction coordinate. These can be identified by reference to the numbers given in Fig. 2. The electron population of the ethylene π^* orbital reaches a maximum at the trigonal bipyramidal transition state (Fig. 4 [C]).

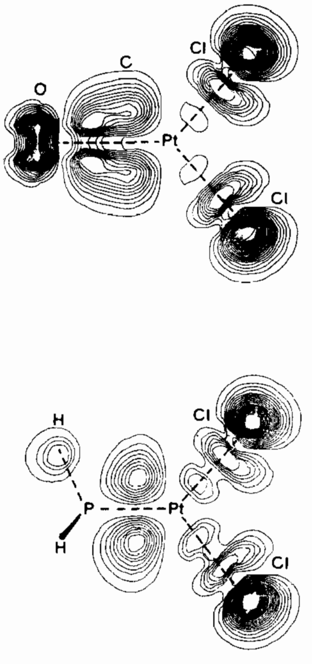


Figure 5. Electron-density contours of the highest filled molecular orbital for the trigonal bipyramidal conformation of $[(CO)PtCl_4]^{2-}$ and $[(PH_3)PtCl_4]^{2-}$.

The calculations were repeated, first with carbon monoxide and then phosphine in place of ethylene in the above reaction. The variation of the atomic charges and bond indices, presented in Table VI, show that the gross effects are similar to those in the reaction involving ethylene but there is an increase in the occupation of the π^* and d_{xz} orbital of carbon monoxide and phosphine, respectively. Electron density maps of the highest filled molecular orbital for the two trigonal bipyramidal transition states are shown in Fig. 5. The electron distribution demonstrates the importance of the π^* and the d_{xz} orbitals on carbon monoxide and phosphorus, respectively. The plots of the eigenvalues for both processes are analogous to those of the first reaction involving ethylene and it turns out that variation of the highest filled molecular orbital decreases in the order $C_2H_4 > CO > PH_3$.

It is clear that ligands of this type owe their high *trans*-directing abilities largely to the electron delocalisation which occurs in the transition states and to occupation of the appropriate vacant orbital on the ligand by interactions with the platinum d_{xz} orbital. The energy of the transition state is thereby lowered.

The Transition-state Complex for σ-bonding Ligands

Before the present work, the *trans*-effect of σ-bonding ligands was correlated[4,32] with the extent of the ligand–metal p_x overlap. It was supposed that, in the reactant, the *trans*-group X and the leaving group L shared the same p_x orbital of platinum whilst in the transition state, the p_z orbital of platinum helped to bond to the entering and leaving groups. If X is a good σ-donor it can take advantage of the now partially vacated p_x orbital in the transition state and strengthen the bonding in the trigonal plane, hence decreasing the activation energy. Presently, we believe that it is the $Pt(d_{x^2-y^2})$ orbital that is important rather than p_x.

In order to investigate these points further, calculations were carried out on the square planar reactant and the trigonal bipyramidal transition states for the reactions $[Pt(X)Cl_3]^- + Cl^- \rightarrow [Pt(X)Cl_3]^- + Cl^-$ and *trans*-$[Pt(X)(NH_3)Cl_2] + Cl^- \rightarrow [Pt(X)Cl_3]^- + NH_3$ with X = H^-, CH_3^-, Br^-, Cl^- and OH^-.

The calculated Pt–X bond indices, as expected, are reduced by assumption of the transition state, since there are now five groups bonded to platinum instead of four. As the entering group is the same in each case, the weakening of the Pt–X bond due to the presence of the additional ligand should be the same in each case. If this is accepted, then the changes in the Pt–X bond index for a particular X on going from square planar to bipyramidal geometry should reflect the σ-electron donor capacity of X. The best σ donor will be associated with the smallest decrease in the Pt–X bond index. We can thus compare the relative bond index changes for the series of ligands X.

From the results (Table VII) it can be seen that the controlling factor in the reduction of the Pt–X bond index on the formation of the trigonal bipyramidal transition is the interaction of the Pt($d_{x^2-y^2}$) orbital. The calculated order of the ligands based on the reduced bond index shows the anomalous position of CH_3^- and the *inversion* of the order for the halide ions as compared with experiment. Now, in the earlier part of our study, the *trans*-influence of σ-bonded ligands was shown to agree well with the experimental observations and so, together with the above results, would seem to indicate that, for σ-bonding ligands, the *trans*-influence is more important than any energy lowering of the trigonal bipyramidal transition state. Of confirmatory interest are the Pt–X bond indices for π-bonded ligands (Table VI). As expected, these show an increase on *trans*-formation to the trigonal bipyramidal transition state.

As a parallel to the study of the reaction path for π-bonding ligands, it is pertinent to carry out the same procedure for a σ-bonding ligand and hence calculations were performed at various points on the reaction path for the reaction

$$[Pt(CH_3)Cl_3]^{2-} + Cl^- \rightarrow [Pt(CH_3)Cl_3]^{2-} + Cl^-$$

TABLE VII. Bond Indices Pt–X for the Reactant and Transition State for the Reactions:
$[Pt(X)Cl_3]^- + Cl^- \rightarrow [Pt(X)Cl_3]^- + Cl^-$
$[Pt(X)(NH_3)Cl_2] + Cl^- \rightarrow [Pt(X)Cl_3]^- + NH_3$.

Transition state	X	Pt(*s*)–X	Pt(p_x)–X	Pt($d_{x^2-y^2}$)–X	Total	% Change
$[Pt(X)Cl_3]^-$	H^-	0.31	0.03	0.29	0.67	
	CH_3^-	0.07	0.06	0.31	0.50	
	Br^-	0.15	0.09	0.29	0.65	
	Cl^-	0.15	0.10	0.25	0.64	
	OH^-	0.08	0.04	0.32	0.48	
$[Pt(X)Cl_4]^{2-}$	H^-	0.34	0.04	0.26	0.64	–5.2
	CH_3^-	0.08	0.05	0.21	0.40	–21.1
	Br^-	0.17	0.09	0.20	0.56	–14.3
	Cl^-	0.17	0.09	0.18	0.58	–10.0
	OH^-	0.08	0.04	0.23	0.36	–24.6
$[Pt(X)NH_3Cl_2]$	H^-	0.36	0.03	0.33	0.78	
	CH_3^-	0.12	0.07	0.41	0.67	
	Br^-	0.21	0.09	0.39	0.83	
	Cl^-	0.20	0.10	0.34	0.81	
	OH^-	0.13	0.04	0.44	0.67	
$[Pt(X)NH_3Cl_3]^-$	H^-	0.37	0.04	0.27	0.70	–11.2
	CH_3^-	0.08	0.07	0.27	0.47	–29.4
	Br^-	0.18	0.11	0.24	0.64	–22.7
	Cl^-	0.19	0.10	0.21	0.64	–20.3
	OH^-	0.08	0.05	0.28	0.44	–34.4

	Total 'Pt–X'		
	$[Pt(X)Cl_3]^-$	$[Pt(X)Cl_4]^{2-}$	% Change
C_2H_4	0.33	0.47	+42.4
CO	0.53	0.67	+27.5
PH_3	0.46	0.53	+15.2
H_2S	0.45	0.52	+15.6

Inspection of the contributions to the Pt–C bond index reveals that the decreasing bond index is due to smaller interactions between the carbon orbitals and the $d_{x^2-y^2}$ orbital of the platinum. This is similar to the changes observed for the π-bonding ligands but, in the latter cases, the energy loss from the decreasing Pt($d_{x^2-y^2}$) interactions is compensated by increasing interactions with the Pt(d_{xz}) orbital. Variation of eigenvalues over the coordinate is greatest for the highest filled orbital and careful examination of the eigenvectors of this particular orbital shows that progress to the transition state involves removal of electron density from the CH_3^- group. This is in contrast to the calculations on the π-bonding ligands, which all showed increasing electron density on the *trans*-group as the system passed along the reaction coordinate.

In conclusion, we assert that the order of ligands in the *trans*-effect series depends on two factors: the *trans*-influence and the stabilisation of the trigonal bipyramidal transition state. If π-bonding is possible in the transition state, this will dictate the course of the reaction. For a σ-bonding ligand, both its *trans*-influence and its ability to act as a donor in the transition state are important but the *trans*-influence is more important when the two effects do not reinforce each other.

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References

1 I.I. Chernyaev, *Ann. inst. platine* (U.S.S.R), *4*, 243 (1926).
2 F. Basolo and R.G. Pearson, *Prog. Inorg. Chem., 4*, 381 (1962).
3 L. Cattalini, *Prog. Inorg. Chem., 13*, 263 (1970).
4 C.M. Langford and H.B. Gray, "Ligand Substitution Processes", Benjamin, New York, 1965.
5 D. Benson, "Mechanisms of Inorganic Reactions in Solution", McGraw-Hill, London, 1968.
6 F. Basolo and R.G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York (1958).
7 A.A. Grinberg, *Acta Physicochim.* (U.S.S.R), *3*, 573 (1935).
8 Y.K. Syrkin, *Bull. Acad. Sci.* (U.S.S.R), *Classe Sci. Chim.*, 69 (1948).
9 J. Chatt, L.A. Duncanson, and L.M. Venanzi, *J. Chem. Soc., 4*, 4456 (1955).
10 L.E. Orgel, *J. Inorg. Nucl. Chem., 2*, 137 (1956).
11 I.B. Bersuker, *Russ. J. Inorg. Chem., 9*, 18 (1964).
12 S.S. Zumdahl and R.S. Drago, *J. Am. Chem. Soc., 90*, 6669 (1968).
13 D.R. Armstrong, P.G. Perkins, and J.J.P. Stewart, *J. Chem. Soc. (A)*, 3654 (1971).
14 J.A. Pople, D.P. Santry, and G.A. Segal, *J. Chem. Phys., 43*, 5129 (1965).
15 K.A. Levison and P.G. Perkins, *Theoret. chim. Acta, 14*, 206 (1969).
16 C.E. Moore, "Atomic Energy Levels", Natl. Bur. Std. (U.S.), Circ. No. 467.
17 E.P. Marran, E.J. McNiff, and J.L. Ragle, *J. Phys. Chem., 67*, 1719 (1963).
18 H.B. Gray and C.J. Ballhausen, *J. Am. Chem. Soc., 85*, 260 (1963).
19 F.A. Cotton and C.B. Harris, *Inorg. Chem., 6*, 369 (1967).
20 H. Basch and H.B. Gray, *Inorg. Chem., 6*, 365 (1967).
21 R.F. Fenske, D.S. Martin, and K. Ruedenberg, *Inorg. Chem. 1*, 441 (1962).
22 J. Chatt, *J. Chem. Soc.*, 2939 (1953).
23 J.W. Moore, *Acta Chem. Scand., 20*, 1154 (1966).
24 A.F. Schreiner and T.B. Brill, *Theoret. Chim. Acta, 17*, 323 (1970).
25 M. Black, R.H.B. Mais, and P.G. Owston, *Acta Cryst., B25*, 1753 (1969).
26 K. Wiberg, *Tetrahedron, 24*, 1083 (1968).
27 D.R. Armstrong, P.G. Perkins, and J.J.P. Stewart, *J. Chem. Soc., Dalton*, 838 (1973).
28 R.J. Cross, *Organometallic Chem. Revs., 2*, 97, (1967).
29 I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).
30 D.R. Armstrong, P.G. Perkins, and J.J.P. Stewart, *J. Chem. Soc., Dalton, in the press.*
31 R.G. Pearson, *Theoret. Chim. Acta, 16*, 107 (1970).
32 R. McWeeny, R. Mason, and A.D.C. Towl, *Disc. Faraday Soc., 47*, 20 (1969).