studies indicate that the pK_a of CoH $\gg$ 14). On the other hand, the measured[10] bond dissociation energy of 57 kcal/mole for the CoH bond in $Co(CN)_5H^{3-}$ leads to the conclusion that for most, if not all, of the substrates under consideration the outright transfer of a H atom, according to eq 8, is close to thermoneutral, a conclusion that tends to favor mechanism iii.

$$Co(CN)_5H^{3-} + CH_2{=}C(R)X \longrightarrow Co(CN)_5^{3-} + CH_3\dot{C}(R)X \quad (8)$$

Supporting this conclusion is the kinetic evidence advanced by Simandi and Nagy[11] that the $Co(CN)_5^{3-}$-catalyzed hydrogenation of cinnamate involves the rate-determining H-atom transfer step

$$Co(CN)_5H^{3-} + C_6H_5CH{=}CHCOO^- \longrightarrow Co(CN)_5^{3-} + C_6H_5\dot{C}HCH_2COO^- \quad (9)$$

A similar mechanism has been proposed[12] for the $Co(CN)_5^{3-}$-catalyzed hydrogenation of styrene.

It is significant, and perhaps further indicative of the unimportance of Co···C(R)X bonding in the transition states of these reactions, that the kinetic trends fail to parallel the stabilities of the $CoC(CH_3)(R)X$ adducts which, in contrast to the corresponding rates, are clearly greatest for acrylonitrile and 2-vinylpyridine.

Significance is also attached to the absence of any CN^- dependence of the rates of these reactions. This observation appears to rule out mechanisms involving preequilibria such as

$$Co(CN)_5H^{3-} \rightleftarrows Co(CN)_4H^{2-} + CN^- \quad (10)$$

$$Co(CN)_5H^{3-} + CH{=}C(R)X \rightleftarrows Co(CN)_4(CH_2{=}C(R)X)H^{2-} + CN^- \quad (11)$$

This conclusion is of interest in view of the suggestion frequently encountered[6] that "insertion" of unsaturated molecules into metal–ligand bonds may require prior coordination to the metal, by reaction with a coordinately unsaturated complex.

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A Molecular Orbital Study of the *trans* Influence and Kinetic *trans* Effect in Square-Planar Platinum(II) Complexes[1]

Steven S. Zumdahl and Russell S. Drago

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received June 3, 1968*

Abstract: Extended Hückel molecular orbital calculations were carried out on a series of square-planar platinum(II) complexes of the type *trans*-$PtCl_2(L)(NH_3)$, where L represents a number of different kinds of σ-bonding ligands. These calculations were done to explore the *trans*-influence phenomenon and the kinetic *trans* effect. Calculation of the over lap populations and overlap energies for the above series of molecules gave evidence for a *trans*-influence series very similar to the kinetic *trans*-effect series for σ-bonding ligands. A *cis* influence comparable in magnitude to the *trans* influence was also observed. The molecular orbital calculations were found to support, qualitatively and quantitatively, a mechanism for the kinetic *trans* effect for σ-bonding ligands which is based on stabilization of the activated complex by σ-donor interactions.

The square-planar complexes of Pt(II) have interested chemists for many years. A great many kinetic studies have been conducted on these complexes, and there is much experimental evidence for the phenomenon called the *trans* effect.[2-4] It has been found that ligands can be arranged in a series based upon their ability to labilize the *trans* group in the square-planar complexes of Pt(II). Qualitatively, this labilizing effect decreases in the order[3] $C_2H_4 \sim NO \sim CO \sim CN^- > R_3P \sim H^- \sim SC(NH_2)_2 > CH_3^- > C_6H_5^- > SCN^- > NO_2^- > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O$.

The above series is based upon the relative rates of substitution of the ligand *trans* to the *trans* director, L, as L is varied. Very few of the kinetic studies on these complexes have included measurements of the enthalpies and entropies of activation for the substitution reactions, and many of these studies have been conducted in very polar solvents. These facts make it more difficult to isolate the reason or reasons for the apparent labilizing effect of the *trans* director.

Since the *trans* effect is defined as the influence of the *trans* director on the rate of substitution of the *trans* ligand, to explain the *trans* effect one should consider the effects of L on the activation energy for the reaction. The *trans* director can lower the activation energy for the substitution reaction by destabilizing the ground state of the complex or by stabilizing the activated complex or both. Most early theories of the *trans* effect[5-8] emphasized destabilization of the ground state by weakening of the bond *trans* to L. More recent explanations have emphasized the effects of L on the

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energy of the activated complex for both π-[9,10] and σ-bonding[4] *trans* directors.

Another phenomenon characteristic of square-planar Pt(II) complexes, which deals specifically with the effect of a ligand on the strength of the metal–ligand bond *trans* to itself in the ground state of the complex, has been called the "*trans* influence."[11] This effect is distinct from the kinetic *trans* effect since it focuses attention on the strength of the *trans* bond rather than on the kinetic labilization of the *trans* ligand. These two phenomena may or may not be related.

The *trans*-influence series for ligands in Pt(II) complexes has been studied by infrared,[12–19] nuclear magnetic resonance,[11,20,21] and X-ray[22] methods, and a qualitative *trans*-influence series has been established. The resulting series has been found to be quite similar to the kinetic *trans*-effect series given above.

Our purpose in doing this work was to explore, theoretically, the *trans*-influence phenomenon and the kinetic *trans* effect. Particularly, we were interested in determining whether a relationship exists between these two phenomena. To this end we have done extended Hückel molecular orbital calculations on a series of square-planar Pt(II) complexes of the type *trans*-$PtCl_2(L)(NH_3)$ where L represents a series of σ-bonding ligands.

Method of Calculation

The LCAO–MO procedure employed in this study is a modification of the extended Hückel molecular orbital theory used by Hoffmann.[23] Specifically, the method used here follows very closely the procedure developed by Cotton and Harris[24] for their molecular orbital study of tetrachloroplatinate(II).

Hamiltonian Matrix Elements. As is usually done in the extended Hückel method, the diagonal Hamiltonian matrix elements (H_{ii}) used in these calculations have been approximated by valence-state ionization potentials (VSIP's). Cotton and Harris[24] found that they were able to obtain very reasonable results for tetrachloroplatinate(II) by using VSIP's to estimate the H_{ii} values. However, these VSIP's were charge-corrected by only 1 eV per unit atomic charge instead of the approximately 10 eV per charge necessary for free ions. In this way these authors were able to qualitatively account for point charge and penetration effects. In view of the good results obtained by Cotton and Harris,[24] this procedure has been followed for the calculations presented here.

The VSIP's used for the orbitals of platinum and chlorine in this study were obtained from Cotton and Harris.[24] All other VSIP's were obtained from the tabulations by Cusachs.[25,26]

All off-diagonal Hamiltonian matrix elements were approximated by use of the Mulliken–Wolfsberg–Helmholz approximation[27,28] with K set equal to 1.8.

Atomic Orbitals. In this study SCF extended-basis-set atomic orbitals (linear combinations of Slater-type orbitals) were used for all atoms except hydrogen and chlorine.

In matrix notation the SCF atomic orbitals can be expressed in terms of Slater-type orbitals as

$$\Phi^{\mathrm{SCF}} = \chi^{\mathrm{STO}}\mathbf{C} \tag{1}$$

where **C** is the coefficient matrix relating the two basis sets. For the overlap matrix of the SCF basis set one has

$$\mathbf{S}^{\mathrm{SCF}} = \tilde{\mathbf{C}}\mathbf{S}^{\mathrm{STO}}\mathbf{C} \tag{2}$$

where

$$S_{ij}^{\mathrm{STO}} = \int \chi_i \chi_j \mathrm{d}\tau$$

$$S_{ij}^{\mathrm{SCF}} = \int \phi_i \phi_j \mathrm{d}\tau$$

In this study $\mathbf{S}^{\mathrm{SCF}}$ was obtained by first calculating the overlap matrix in the Slater-type orbital basis set in the usual manner. This overlap matrix was then transformed into the SCF basis set according to eq 2 by matrix techniques. This process was accomplished by use of a computer program ILCO5 which was obtained by extensively modifying the Hoffmann MO program.[23] In present form ILCO5 is a four-core-load program. In the first core load the overlap matrix in the Slater basis set is calculated. The matrix transformation into the SCF basis set is done in the second and third core loads, and in the fourth core load the MO calculation is completed.

The overlap matrix was calculated only once for each molecule and, therefore, was not adjusted for changes in molecular charge distribution as the molecule was iterated to self-consistent charge. However, Cotton and Harris[24] have estimated that this produces an average error of only ~5% in the calculated overlap integrals.

The atomic orbitals used in this study are as follows. The platinum 5d, 6s, and 6p orbitals are those derived by Basch and Gray[29] for Pt^+ by fitting numerical SCF functions.[30] The orbitals used for chlorine are single exponential Slater-type orbitals with exponents determined by Cotton and Harris[24] by fitting the overlaps of Hartree–Fock wave functions. An exponent of 1.0 was used for the hydrogen 1s Slater-type orbital. Clem-

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Table I. Overlap Populations for the *trans*-$PtCl_2(L)(NH_3)$ Series of Complexes

Compound	Pt–L bond length, Å	Pt–N	Pt–Cl	Pt–L	Pt($6p_y$)–L	Pt($6p_y$)–N	Pt(6s)–N	Pt($5d_{x^2-y^2}$)–N
$PtCl_2(H_2O)(NH_3)$	2.00	0.3370	0.3909	0.2406	0.1114	0.1235	0.1205	0.1275
$PtCl_2(NH_3)_2$ (a)	2.00	0.3221	0.3832	0.3221	0.1313	0.1313	0.1139	0.1145
$PtCl_2(NH_3)_2$ (b)	2.17	0.3235	0.3882	0.3246	0.1428	0.1215	0.1185	0.1202
$PtCl_3(NH_3)^-$	2.33	0.3240	0.3843	0.3822	0.1759	0.1212	0.1181	0.1225
$PtCl_2(H_2S)(NH_3)$ (a)	2.30	0.3244	0.3745	0.4295	0.2070	0.1320	0.1158	0.1154
$PtCl_2(H_2S)(NH_3)$ (b)	2.44	0.3260	0.3815	0.3892	0.1904	0.1221	0.1213	0.1207
$PtCl_2(CH_3)(NH_3)^-$	2.15	0.3009	0.3724	0.4637	0.1945	0.1431	0.1036	0.0949
$PtCl_2(PH_3)(NH_3)$	2.25	0.3092	0.3569	0.5685	0.2435	0.1490	0.1054	0.0966
$PtCl_2(H)(NH_3)^-$	1.66	0.3074	0.3641	0.6069	0.2603	0.1415	0.1046	0.1009

enti double-ζ functions[31] were used for the atomic orbitals of all other atoms in the complexes.

Structural Parameters. The coordinate system used for the calculations is shown in Figure 1. The Pt–L bond distances were obtained from X-ray data[32] when possible and were estimated from covalent radii when X-ray data were unavailable. (Calculations on complexes where the Pt–L distance was varied indicate that the results (see Table I) are relatively insensitive to small errors in estimating Pt–L.) The Pt–N bond length was held constant at 2.00 Å in all of the complexes studied in order to simplify the interpretation of the effects of the various L groups. The Pt–Cl distance was held constant at 2.33 Å in all of the complexes.

Results and Discussion

Molecular orbital calculations of the type described above have been carried out on a series of *trans*-$PtCl_2(L)(NH_3)$ complexes in order to study the kinetic *trans* effect and the *trans* influence of various σ-bonding ligands. The L groups chosen for study are H_2O, NH_3, Cl^-, H_2S, CH_3^-, H^-, and PH_3. Some of the resulting complexes are hypothetical, because to save computer time, protons were sometimes placed on the coordinating atom of L instead of the larger substituents present in known complexes. However, this should not affect our results, since we are most interested in the effects due to the coordinating atom, and substitution of hydrogen for alkyl or aryl groups should not influence the conclusions drawn.

***trans* Influence.** In studying the *trans* influence for a series of ligands in the *trans*-$PtCl_2(L)(NH_3)$ complexes, one is primarily interested in the relative bond strengths in these complexes. Particularly, one is interested in the changes in the bond strengths in the complex as the ligand L is varied. Information of this type is best obtained from a Mulliken population analysis[33] of the calculated molecular orbitals.

The population analysis provides two criteria for measuring relative bond strengths in molecules: overlap populations and overlap energies. The overlap population is a measure of the electron density in the bonding region between two atomic orbitals. Summation of the overlap populations for all atomic orbitals on a given pair of atoms over all occupied molecular orbitals gives the reduced overlap population between those atoms. Reduced overlap populations can be used as indications of relative bond orders. Similarly, overlap energies can be used as indications of the energies of interaction between orbitals and atoms.[33]

A Mulliken population analysis was performed on each of the *trans*-$PtCl_2(L)(NH_3)$ complexes, and the resulting overlap populations are given in Table I. The corresponding overlap energies were also calculated. However, since the trends in these values were found to be identical with those in the overlap populations shown in Table I, the overlap energies are not presented here.

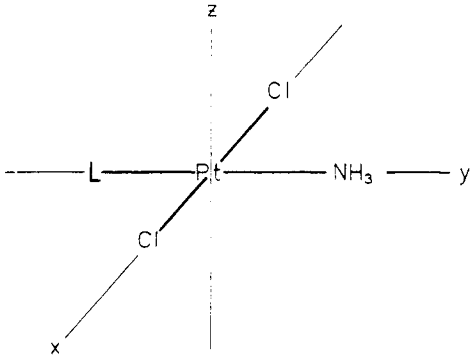

Figure 1. The coordinate system used for the molecular orbital calculations on the *trans*-$PtCl_2(L)(NH_3)$ complexes.

The complexes in Table I are listed in order of the increasing kinetic *trans* effect of L in going from the top to the bottom of the table. That is, H_2O is a poor *trans* director, and H^- is a very effective *trans* director (where the effectiveness of L as a *trans* director refers to its ability to labilize the *trans* ligand). Examination of the data in Table I shows that, in general, as L becomes a better *trans* director, it also becomes more effective in weakening the *trans* Pt–N bond. Thus, there appears to be a definite parallel between the ability of L to act as a *trans* director and its effectiveness in causing the *trans*-influence phenomenon.

These results agree, in the main, with the results of several infrared studies of square-planar Pt(II) complexes[12–19] which indicate, at least for σ-bonding ligands, that, in general, if a ligand is a good *trans* director, it also is effective in weakening the *trans* bond. However, since the conclusions reached in these infrared studies are based almost entirely on relative frequencies rather than on force constants, one should proceed cautiously in using these results as evidence for bond weakening. The vibrational problem in these systems

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is very complex and coupling effects could well be important. However, the facts that in almost all of these infrared studies a series of very similar complexes has been studied so that coupling effects should be fairly constant, and that a number of studies using different series of complexes have produced the same ordering of the ligands in the *trans*-influence series, lend credibility to the infrared results. Also, Nakamoto, *et al.*,[18] have recently done a normal coordinate analysis on the complex *trans*-$Pt(NH_3)_2Cl_2$ and have found that "almost no coupling exists between various vibrational modes." Thus, the evidence taken as a whole supports use of the infrared results as a measure of the relative bond strengths. Therefore, the conclusion from our calculations, which is supported by the infrared evidence, that a good σ-bonding *trans* director also has a high *trans* influence appears to be a valid one.

Another interesting observation which can be made about the results shown in Table I is that the Pt–Cl bond *cis* to L also shows weakening as L becomes a better *trans* director. Interestingly, this *cis* weakening appears to be only slightly less in magnitude than the weakening of the Pt–N bond, and the order of effectiveness of L in causing the weakening is very similar for both the Pt–Cl and Pt–N bonds. Contrary to the earlier theories[5–8] these results would seem to indicate that the bond-weakening ability of a σ-bonding ligand in a square-planar complex is not directed specifically toward the *trans* positions.

Relatively little experimental evidence is available regarding the influence of ligands on bonds *cis* to themselves in square-planar complexes; however, this phenomenon has been observed in some recent infrared studies. Nakamoto and his coworkers[18] have carried out a detailed infrared study of the *cis*- and *trans*-$PtX_2(NH_3)_2$ complexes, where $X^- = I^-, Br^-$, and Cl^-. Their results show that the Pt–N bond strength decreases in the order $Cl^- > Br^- > I^-$ for both the *cis* and *trans* complexes although the effect is slightly larger in the former case. Perry, *et al.*,[19b] have found a similar situation to exist for the *cis*- and *trans*-$PdX_2(NH_3)_2$ complexes, where $X^- = Cl^-, Br^-$, and I^-. Also, Rosevear and Stone[34] have observed *cis* and *trans* influences of similar magnitudes in the *cis*- and *trans*-$Pt(Et_3P)_2(C_6H_5)X$ complexes, where $X^- = Cl^-, Br^-$, and I^-. Chatt and his coworkers[15] have noted rather large effects on the Pt–H stretching frequencies due to the *cis* groups, in a series of *trans*-$Pt(L')_2(L)(H)$ complexes, where L′ represents a series of substituted phosphines and arsines. However, in a later study on a series of *cis*- and *trans*-PtX_2L_2 complexes[17] Chatt found only minor effects on the Pt–X stretching frequencies due to the L groups *cis* to X. Taken as a whole, these results seem to suggest that σ-bonding ligands might be expected to influence both *cis* and *trans* bonds with the *trans* weakening expected to be slightly greater. This is also what we would predict on the basis of our calculations.

In a recent study Pidcock, Richards, and Venanzi[11] reported the $^{195}Pt-^{31}P$ coupling constants for a series of square-planar Pt(II) complexes. They found that, as the ligand *trans* to the phosphine becomes a better *trans* director, the $^{195}Pt-^{31}P$ coupling constant decreases. Based on some rather severe assumptions about the nature of $J(^{195}Pt-^{31}P)$ (the constancy of ΔE and the constancy of the contribution of the phosphorus 3s orbital in the series), these authors related the magnitude of the coupling constant to the s character and strength of the Pt–P bond and concluded that, as the ligand *trans* to the phosphine becomes a more effective *trans* director, the s character and the strength of the Pt–P bond decrease. In view of the possible ambiguities in this approach it was decided to compare the conclusions of the nmr study with the results of the molecular orbital calculations. As can be seen by examination of the results in Table I, our calculations provide confirmation for the interpretations of Pidcock, *et al.*[11] As mentioned previously, our results predict parallel *trans*-influence and *trans*-effect series for σ donors in agreement with the nmr results. Also, examination of the trend in the Pt(6s)–N interactions in Table I shows that, in general, as L becomes a better *trans* director, the participation of the Pt(6s) orbital in the Pt–N bond decreases as was predicted on the basis of the $^{195}Pt-^{31}P$ coupling constant data.

Pidcock *et al.*,[11] also concluded that phosphine has a very high *trans* influence which is due entirely to σ-bonding effects. It was suggested that the effectiveness of a phosphine in weakening the *trans* bond may be due to its ability to interact strongly with the $Pt(p_\sigma)$ orbital thus reducing its availability to the *trans* ligand. Further, it was concluded from this study[11] that anionic ligands, such as the halides, have about equal *cis* and *trans* influences, whereas the phosphines have a *cis* influence which is smaller than their *trans* influence.

Our calculations show that phosphine is a very strong σ donor and that it has a very large *trans* influence. However, our results indicate that the weakening of the *trans* bond is not due to decreased availability of the $Pt(p_\sigma)$ orbital but is due to weakening of the Pt(6s)–N and $Pt(d_{x^2-y^2})$–N interactions. Also, our results indicate that phosphine has a *cis* influence which is comparable in magnitude to its *trans* influence in apparent disagreement with the interpretation of the nmr results.

The conclusion by Pidcock, *et al.*,[11] that π bonding is not important in the phosphine complexes which they studied is mainly based on the fact that the ratio of the $^{195}Pt-^{31}P$ coupling constant in the *cis* complex to that in the *trans* complex is the same for both Pt(II) and Pt(IV) complexes. It was suggested that since π bonding is expected to be much less in Pt(IV) than in Pt(II) complexes, the similar coupling constant ratios for the two types of complexes indicate that π bonding is unimportant in both the Pt(II) and Pt(IV) complexes. In view of the previously mentioned difficulties in interpreting J and in the absence of any other quantitative information, the assumption that there is less π bonding in the Pt(IV) than in the Pt(II) complexes seems far from certain. Consequently, calculations were carried out to attempt to investigate the π bonding in Pt(II) complexes. The extent of $d\pi-d\pi$ interactions between the Pt and P atoms in these complexes is rather hard to estimate because the energy and the Slater exponent for the phosphorus set of 3d orbitals are very uncertain. We performed a calculation on *trans*-$PtCl_2(PH_3)(NH_3)$ in which we included a set of phosphorus 3d orbitals with a Slater exponent of 0.7 and an energy of −5.0 eV. We felt that these parameters would overemphasize any Pt–P $d\pi-d\pi$ bonding.

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The results show that under these conditions the Pt–P π bond order is ~15% of the σ bond order. The Pt–Cl bond order is not much affected by the presence of the phosphorus 3d orbitals. However, inclusion of the 3d orbitals causes a rather large strengthening of the Pt–N bond as indicated by its reduced overlap population of 0.33. This gives phosphine a *trans* influence equal to that of H_2O (see Table I) which is clearly not the case according to all of the experimental evidence. This suggests that we have indeed caused overemphasis of the $d\pi$–$d\pi$ bonding which results in the strengthening of the Pt–N bond causing phosphine to be out of order in the *trans*-influence series. Therefore, we expect Pt–P $d\pi$–$d\pi$ bonding in the actual complexes to be very small.

Kinetic *trans* Effect. In considering what mechanism might be responsible for the kinetic *trans* effect for σ-bonding ligands, two observations should be made about the results of the molecular orbital calculations. First, the weakening observed in the Pt–N bond *trans* to L is not very great in going from a poor *trans* director, H_2O, to a very good *trans* director, H^-. The resulting change in the Pt–N bond strength is only about 10% of the total bond strength. Also, our calculations indicate that the weakening of the *cis* Pt–Cl bonds is comparable in magnitude to the Pt–N weakening.

These facts suggest to us that bond weakening is probably not the primary cause of the kinetic *trans* effect, at least for σ-bonding ligands. Rather, we believe that our results support a mechanism which is based on the stabilization of the transition state for the substitution reaction. In an earlier study from our laboratory[35] involving the effect of various R groups on the rate of chloride exchange with a series of compounds of the type $RPOCl_2$, the results were interpreted on the basis of the ability of R to stabilize the five-coordinate activated complex by both σ and π interactions in the equatorial positions. Gray[3,4] has proposed that similar effects are operative in the five-coordinate intermediate involved in the substitution reactions of square-planar Pt(II) complexes containing a σ-bonding ligand as the *trans* director. The *trans* effect for σ-bonding *trans* directors can be explained as follows. In the ground state of the square-planar platinum complex the *trans* director L and the leaving group (in the event of a substitution reaction) must share the same $Pt(p_\sigma)$ orbital. Thus, in the series of complexes which we have studied, the ligand, L, and the leaving group, NH_3, are competing for the $Pt(6p_y)$ orbital. Assuming a chloride ion to be the entering group in a substitution reaction on a *trans*-$PtCl_2(L)(NH_3)$ complex, one can postulate the idealized trigonal-bipyramidal activated complex[4] shown in Figure 2. Note that in this structure the entering and leaving groups (Cl^- and NH_3) now lie on either side of the $Pt(6p_y)$ orbital and use both the p_y and p_z orbitals for bonding. Thus, the *trans* director L is left with more than half of the $6p_y$ orbital. This means that if L is a good σ donor and can therefore take advantage of the partially vacated p_y orbital, the activated complex will be stabilized. Thus, the difference in energy between the ground and transition states would be relatively small for a ligand which can effectively interact with the p_y orbital, and this type of ligand would be expected to be a good *trans* director.

Calculations of $Pt(6p_\sigma)$–$L(p_\sigma)$ overlap integrals[4] have shown this approach to be promising. Therefore, in order to explore this postulate further, the $Pt(6p_y)$–L overlap populations were calculated and are listed in Table I. Note that in going down the table there is a rather dramatic increase in the $Pt(6p_y)$–L interaction. Indeed, there is an almost exact correspondence between the ability of L to interact with the $Pt(6p_y)$ orbital and its position in the experimentally determined kinetic *trans*-effect series. The only exception to this appears to be the methide ion. However, note that the methide ion is the most effective of the ligands studied in weakening the *trans* bond. Therefore, the position of the methide ion in the *trans*-effect series may be a combination of its *trans* influence and its ability to interact with the $6p_y$ orbital. Both of these effects would tend to lower the activation energy for a substitution reaction and would thus make methide a better *trans* director than would either effect by itself.

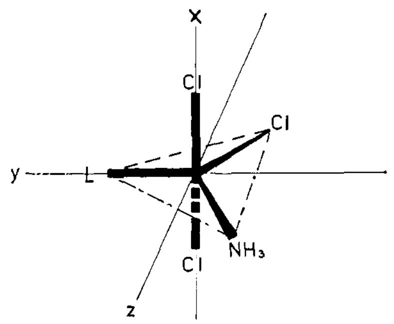

Figure 2. The coordinate system used for the molecular orbital calculations on the trigonal-bipyramidal complexes.

Thus, qualitatively our results support the mechanism for the *trans* effect based on transition-state stabilization. In order to learn whether the effect on which this mechanism is based has the proper magnitude to cause the observed differences in the rates of the substitution reactions, we have done calculations to attempt to estimate the difference in the activation energies of the substitution reactions for complexes containing a poor *trans* director, H_2O, and an effective *trans* director, H^-. Of course, it is impossible to actually calculate activation energies for these complexes, since the true structure of the activated complex is unknown and since it is impossible to estimate accurately enough the total energy of the entering ligand (in this case a chloride ion), etc. However, it does seem possible that a reasonable value can be obtained for the activation energy difference for the complexes with $L = H_2O$ and H^-, since many sources of error, including the two mentioned above, would be expected to cancel out of this difference.

Therefore, we have performed extended Hückel molecular orbital calculations on five-coordinate complexes of the type shown in Figure 2 for $L = H^-$ and H_2O. For these calculations all bond lengths were kept the same as in the square-planar complexes. Table II shows the reduced overlap populations for the bonds in the five-coordinate complexes for $L = H_2O$ and H^-. Table III shows the changes in overlap populations in going from the four- to five-coordinate complexes (keeping all bond lengths the same).

These results show that all bonds weaken in going from the square-planar to the trigonal-bipyrimidal structure. Note that the weakenings of the Pt–N bond

Table II. Overlap Populations for the Trigonal-Bypyramidal Complexes $PtCl_3(H_2O)(NH_3)^-$ and $PtCl_3(H)(NH_3)^{2-}$

Compound	$Pt(6p_y)$-L	Pt-L	Pt-Cl (x-axis)	Pt-Cl (plane)	Pt-N
$PtCl_3(H_2O)(NH_3)^-$	0.1602	0.1895	0.3441	0.3117	0.2920
$PtCl_3(H)(NH_3)^{2-}$	0.3356	0.5868	0.3198	0.2859	0.2674

Table III. Overlap Population Differences[a]

L	$Pt(6p_y)$-L	Pt(6s)-L	$Pt(5d_{x^2-y^2})$-L	Pt-L	Pt-Cl (x-axis)	Pt-Cl (plane)	Pt-N
H_2O	0.0488	−0.0071	−0.0447	−0.0511	−0.0468	0.3117	−0.0450
H^-	0.0753	−0.0142	−0.0382	−0.0213	−0.0443	0.2859	−0.0400

[a] The overlap populations in the trigonal-bipyramidal activated complex minus the corresponding overlap populations in the square-planar complex for L = H^- and L = H_2O.

and Pt-Cl bonds (originally *cis* to L) are almost exactly equal for both types of complexes. However, the corresponding weakening of the Pt-L bond is much less for L = H^- than for L = H_2O and, significantly, this difference can be traced back almost entirely to the $Pt(6p_y)$-L interactions. The over-all weakening of the Pt-L bond in going to the transition state is due to decreased Pt(6s)-L and $Pt(d_{x^2-y^2})$-L interactions, and note that the sum of the weakenings due to these interactions is almost identical for the two types of complexes. These effects are opposed by the increasing $Pt(6p_y)$-L interactions, the increase being 0.0753 for L = H^- and 0.0488 for L = H_2O. Thus, the $Pt(6p_y)$-L interaction increases in going from the ground to transition state with the increase being greater for the stronger σ donor. Therefore, the different interactions of H_2O and H^- with the $Pt(6p_y)$ orbital account almost entirely for the different Pt-L bond weakenings in going from the ground state to the activated complex. A striking resemblance exists between the mechanisms of substitution on platinum and phosphorus,[35] both involving stabilization of the five-coordinate intermediate.

In order to estimate the magnitude of the above effect, total energies were obtained for the square-planar and trigonal-bipyramidal complexes for L = H_2O and H^- and the quantity ΔE_a was calculated. ΔE_a is defined by the expression

$$\Delta E_a = E_{H^-} - E_{H_2O} \tag{3}$$

where E_L is the total energy for the trigonal-bipyramidal complex minus that for the square-planar complex for ligand L. It was found that $\Delta E_a = -8$ kcal/mole. Thus about 8 kcal/mole less energy is required in going from the square-planar to the trigonal-bipyramidal complex for L = H^- than for L = H_2O.

In order to interpret ΔE_a it is necessary to consider what energy terms it contains. As mentioned above, the weakenings of *cis* Pt-Cl and *trans* Pt-N bonds in going from the square-planar to the trigonal-bipyramidal complex are almost identical for L = H^- and H_2O and, thus, should cancel out of ΔE_a. Therefore, ΔE_a should consist almost entirely of the difference in the Pt-L bond weakenings in going from the ground state to the excited state and the difference in the strengths of the bonds formed by the entering chloride ion (see Table II). Since the Pt-Cl bond formed by the entering chloride ion is slightly stronger for L = H_2O than for L = H^-, this would stabilize the transition state for L = H_2O relative to that for L = H^-. Therefore, the value of 8 kcal/mole can be regarded as a lower limit of the magnitude of the effect on ΔE_a due to the different Pt-L bond weakenings. Since the different Pt-L bond weakenings for the two ligands can be traced back almost entirely to the different $Pt(6p_y)$-L interactions of H^- and H_2O, one can say that the effect of the different donor strengths of H^- and H_2O toward the $Pt(6p_y)$ orbital would be expected to produce an activation energy difference greater than 8 kcal/mole for the complexes containing these two ligands.

It has been estimated[4] that the ratio of the rates of substitution for a ligand *trans* to H^- and H_2O probably is on the order of 10^6. Thus, according to the Arrhenius expression, one can write

$$\frac{k_{H^-}}{k_{H_2O}} = \frac{A_{H^-}e^{-E_{H^-}/RT}}{A_{H_2O}e^{-E_{H_2O}/RT}} = 10^6 \tag{4}$$

By using eq 4 and assuming that $A_{H^-} = A_{H_2O}$ and $T = 300°K$, one can calculate the value of ΔE_a which is expected from the experimental results. The value of ΔE_a obtained in this way is −8.3 kcal/mole, which is in remarkable agreement with the value which we have calculated from the molecular orbital results.

Thus, these calculations show that there is a close correspondence between the effectiveness of L as a *trans* director and its ability to interact with the $Pt(p_\sigma)$ orbital which is shared with the potential leaving group. Also, the calculations show that the $Pt(p_\sigma)$-L interaction increases on going from the square-planar complex to the trigonal-bipyramidal activated complex and that this increase is much greater for a strong σ donor (H^-) than for a relatively weak σ donor (H_2O). Further, the greater increase in the $Pt(p_\sigma)$-L interaction for L = H^- than for L = H_2O in going from the square-planar to the trigonal-bipyramidal complex appears to account for almost all of the observed difference in the activation energies of the substitution reactions for complexes containing these two ligands. Thus, these results are consistent, qualitatively and quantitatively, with the explanation for the *trans* effect of σ-bonding ligands which is based on the stabilization of the transition state.

Summary

In summary, our calculations have shown that σ-bonding ligands do have a definite *trans* influence and that the *trans*-influence series very closely parallels the

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kinetic *trans*-effect series. We have also observed a "*cis* influence" which is comparable in magnitude to the *trans* influence.

It appears that a mechanism based on the stabilization of the five-coordinate activated complex is the most reasonable to explain the kinetic *trans* effect for σ-bonding ligands. Our calculations strongly support this mechanism both qualitatively and quantitatively. However, it is possible that bond-weakening effects may also be important in some cases (for example, the methide ion).

Acknowledgment. The authors acknowledge the support of the National Science Foundation through Grant 5498.

A Reinvestigation of the Crystal and Molecular Structure of Pentaphenylantimony[1]

A. L. Beauchamp,[2] M. J. Bennett, and F. A. Cotton

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received July 5, 1968

Abstract: The structure of pentaphenylantimony has been redetermined from three-dimensional X-ray diffraction data (2337 independent reflections) measured on a counter diffractometer. The results confirm the general structural features found earlier by Wheatley in a two-dimensional study. The improved accuracy obtained with three-dimensional data allows the following conclusions. (1) While the molecule as a whole has C_1 point symmetry, the five carbon atoms bound to the antimony atom are arranged with virtual C_{2v} symmetry. (2) The set of Sb–C bond lengths is consistent with a square-pyramidal geometry, *viz.*, Sb–C(axial) = 2.115 (5) Å; four Sb–C(basal) bonds with an average length of 2.216 (7) Å. (3) The C(axial)–Sb–C(basal) angles deviate alternately by about +4 and −4° from their mean, thus spoiling the ideal C_{4v} symmetry which would exist if all were equal. The principal crystallographic data are as follows: space group, $P\bar{1}$; unit cell dimensions: $a = 10.286 \pm 0.007$ Å; $b = 10.600 \pm 0.007$ Å; $c = 13.594 \pm 0.009$ Å; $\alpha = 79°\,12' \pm 3'$; $\beta = 70°\,28' \pm 3'$; $\gamma = 119°\,31' \pm 3'$; measured density, 1.42 ± 0.01 g cm^{-3}; calculated density (for $Z = 2$), 1.41 g cm^{-3}.

There has been only one reported exception to the generalization that five-connected group V (*i.e.*, P, As, Sb, Bi) elements in compounds with formally 10-electron valence shells have bonds directed to the vertices of a trigonal bipyramid,[3,4] and in fact this generalization seems to apply even more broadly,[4] covering EX_n compounds of group VI (*e.g.*, SF_4) and group VII (*e.g.*, ClF_3) provided "incomplete" trigonal bipyramids are recognized. The lone reported exception is pentaphenylantimony, which has been characterized as having a "distorted square-pyramidal" structure[5] although pentaphenylphosphorus,[6] pentaphenylarsenic,[6] and several $(C_6H_5)_4SbOR$ (R = CH_3,[7] H[8]) compounds are all trigonal bipyramidal.

In view of the exceptional nature of the reported structure of $(C_6H_5)_5Sb$, as well as the importance of the question of the relative stabilities of trigonal-bipyramidal and square-pyramidal structures in understanding the fluxional nature of many molecules with the former as their ground-state geometry,[9] it seemed to us to be of unusual importance to seek confirmation of the reported structure of $(C_6H_5)_5Sb$ and to obtain more accurate structural parameters.

The reported study[5] is based on only two-dimensional data and does not provide meaningful results concerning the relative lengths of the Sb–C bonds. Moreover, it does not appear that the possibility of a water molecule or some other small ligand molecule occupying a sixth coordination site about the antimony atom and thus forcing a square-pyramidal disposition of the phenyl groups is excluded by the reported study.

A redetermination of the structure of pentaphenylantimony, using three-dimensional counter-diffractometer data was therefore undertaken and is described here.

Experimental Section

Preparation. Pentaphenylantimony was prepared by reaction of C_6H_5Li with $(C_6H_5)_3SbCl_2$ (Eastman), as described by Wittig and Clauss.[10] It was recrystallized from isooctane as colorless crystals (mp 167–168°, lit.[10] 169–170°). Part of the crude product was first recrystallized from *n*-hexane to yield yellowish plates which melt at 167–169° with a definite change of phase about 130–135°. The former is probably a solvate similar to $(C_6H_5)_5Sb \cdot 0.5$cyclohexane, isolated by Wittig and Clauss.[10] This solvate was heated at 115° under vacuum for 6 hr (during which some decomposition occurred), and after recrystallization from isooctane the pure, unsolvated, colorless compound was recovered.

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(1) Supported by the National Science Foundation under Grant No. GP 7034X.

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