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Theoretical Studies of Inorganic and Organometallic Reaction Mechanisms. 2. The Trans Effect in Square-Planar Platinum(II) and Rhodium(I) Substitution Reactions

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Ab initio calculations with an effective core potential have been used to study the mechanism of substitution reactions for square-planar transition-metal complexes. Pseudo-trigonal-bipyramidal transition states with rather small entering-ligand to metal to leaving-ligand angles (70–85°) were found for the substitution reactions investigated in this paper. The stability of the transition state is determined by both σ and π effects of the ligands. The analysis of the Laplacian of the total electron density indicated that there are two electron concentrations located in the equatorial plane of the pseudo-trigonal-bipyramidal transition state. These are the same concentrations that one finds above and below the plane of the square-planar d^8 reactant. For a strong π-acceptor as the trans-directing ligand, these two concentrations are stabilized through π-back-donation. A strong σ-donor as the trans-directing ligand weakens the bonds between metal and entering/leaving ligands in the transition state and therefore decreases the electron repulsion between each of the two lone pairs on the central metal and the lone pairs on the entering/leaving ligands. The trans effect is thus rationalized by the σ and π effects on the stability of the transition state.

Introduction

Although it has long been known that ligand substitution reactions in square-planar complexes show distinct preferences for the site trans to one ligand rather than another, the mechanism of this trans effect is still uncertain. From a number of theoretical explanations[1,2] one can extract two simple viewpoints. The first is essentially a static one emphasizing a weakening of the trans bond by a strong σ-donor; the second is the stabilization of the activated complex (or transition state) by a π-acceptor in the trans position. The former is closely related to the trans influence, which may be defined as the influence of one ligand weakening the bonding trans to itself in the equilibrium state, with the order[3]

$$H^- > PR_3 > SCN^- > I^-, CH_3^-, CO, CN^- > Br^- > Cl^- > NH_3 > OH^-$$

In the latter, the expected trigonal-bipyramidal transition state can be stabilized by the trans-directing ligand if the ligand with strong π-accepting ability preferentially occupies the equatorial position. The π-accepting ability of some ligands is summarized in the following order:[3]

$$C_2H_4, CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$$

The combination of the two sequences above can be used to rationalize the trans-effect order[3]

$$C_2H_4, CO, CN^- > PR_3, H^- > CH_3^- > C_6H_5^-, NO_2^-, SCN^-, I^- > Br^-, Cl^- > Py, NH_3, OH^-, H_2O$$

The effects of entering, leaving, and trans-directing ligands in substitution reactions of square-planar complexes have been comprehensively summarized by Atwood.[4] In this paper, ab initio calculations were made to determine geometries of transition states, to search for 5-coordinate intermediates, to clarify the existing theoretical explanations of the trans effect, and to test the level of theory required to predict the experimental observations.

Theoretical Details

Ab initio effective core potentials were employed in all calculations. All geometries were optimized at the restricted Hartree–Fock (RHF) level. The core electrons of Pt (and Rh) were fit to an effective core potential, while the valence electrons were described with a double-ζ basis [(3s3p3d/2s2p2d) for Pt and (3s3p4d/2s2p2d) for Rh] as described by Hay and Wadt.[5] The cores of Pt and Rh are [Xe] and [Kr] configurations, respectively. For ligand atoms, effective core potentials and basis sets of Stevens, Basch, and Krauss were used.[6] [He] and [Ne] configurations were taken as cores for first- and second-row main-group atoms, respectively. The basis set for H consisted of a three Gaussian contractions from which the most diffuse component was split off to form a double-ζ basis.[7] We also have examined the effect of electron correlation on our results through a generalized-valence-bond, perfect-pair (GVB-8/PP)[8] calculation involving eight pairs (five metal–ligand bonds and three CO bonds) in the system of $Pt(CO)Cl_2(NH_3)_2$. The HF molecular orbitals were localized with the Boys criteria[9] to generate bond pairs for starting the GVB calculations. All calculations were performed with the GAMESS package.[10] The Laplacian of the total electron density was plotted with use of the program MOPLOT.[11] All GAMESS calculations were performed at the Cornell National Supercomputer Facility on an IBM 3090-600VF computer and at the Supercomputer Center of Texas A&M University on a Cray Y-MP2/116 computer.

Results

Transition States. The principle of microscopic reversibility requires that in the transition state of an exchange reaction the entering and leaving groups have like geometric relations to the rest of the structure.[12] When the entering and leaving groups are identical, the principle of microscopic reversibility demands that the entering group and the leaving group are equivalent at the transition state as long as there is no intermediate. As an "experimental" test, we performed calculations on the NH_3–BH_3–NH_3 system. We optimized the D_{3h} $NH_3BH_3NH_3$ structure using an energy minimization technique with symmetry constraint, and we did a saddle point calculation on the $NH_3BH_3 + NH_3$ reaction. The resulting geometries derived from the two calculations are identical. Thus, we can find the transition state (or intermediate) for systems with identical entering and leaving ligands by doing geometry optimization with symmetry restriction instead of doing saddle point calculations.

Therefore, for the theoretical simplicity, we only investigated substitution reactions with same entering and leaving ligands. Furthermore, so that our gas-phase result would give a simple relationship to the liquid-phase experiments, we chose only neutral

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(1) (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; John Wiley: New York, 1968. (b) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1965.

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(9) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300.

(10) M. F. Guest, Daresbury Laboratory, Warrington WA4 4AD, U.K.

(11) Interactive MOPLOT: a package for the interative display and analysis of molecular wave functions incorporating the programs MOPLOT (D. Lichtenburger), PLOTDEN (R. F. W. Bader, D. J. Kenworthy, P. M. Beddal, G. R. Runtz, and S. G. Anderson), SCHUSS (R. F. W. Bader, G. R. Runtz, S. G. Anderson, and F. W. Biegler-Koenig), and EXTREM (R. F. W. Bader and F. W. Biegler-Koenig, P. Sherwood, and P. J. MacDougall, 1989).

(12) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*; John Wiley: New York, 1953.

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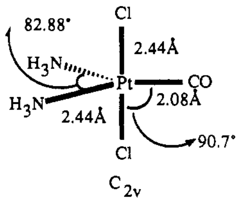
systems with neutral entering and leaving groups. For example, in the reaction of *trans*-$Pt(CO)Cl_2NH_3 + NH_3$, where the NH_3 ligands are the entering and leaving ligands, the transition state can be taken as the optimized structure of $Pt(CO)Cl_2(NH_3)_2$ with at least one mirror operation relating the entering and leaving NH_3's. We optimized all bond lengths and bond angles with C_{2v} symmetry except within the two NH_3 units, where we used the standard bond lengths and angles[13] (N–H = 1.01 Å and H–N–H = 109.47°). The optimized structure shown in **1** is taken as the transition state of the reaction above. To examine the nature of the proposed transition state, we calculated the Hessian for the optimized structure **1**. Three eigenvalues of the Hessian have negative curvatures, where the most negative one is associated with a transition vector involving the leaving of one NH_3 and the entering of the other. The other two negative curvatures are associated with the bending motions within the two NH_3 ligands, which were not optimized in this calculation.



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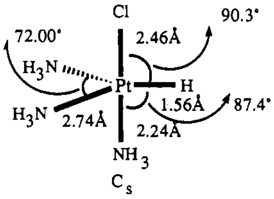

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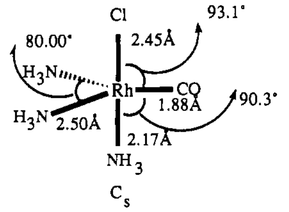

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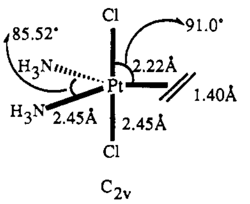

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By the same procedure, we also found the transition state for the reaction *cis*-$PtHCl(NH_3)_2 + NH_3$ (**2**). Initially, the Hessian had four negative eigenvalues. After optimizing the NH_3 ligand trans to Cl, we found only three negative curvatures. Again, the most negative value was associated with the transition vector and the other two were associated with the bending motions of the two unoptimized NH_3 ligands. These two examples convinced us that the transition states obtained from the procedure above are true transition states except for some small adjustments within each NH_3 ligand.

Many substitution reactions of square-planar metal (d^8) complexes do not involve identical entering and leaving ligands. However, a number of actual exchange reactions of square-planar metal (d^8) complexes have been studied and the results parallel the nonexchange reactions closely.[14-16] Thus, although our results are strictly correct only for actual exchange reactions, they should be good models even in cases where the entering and leaving ligands are not identical.

Reaction Coordinate. After obtaining the transition state, we let one of the two NH_3 ligands, which are related by the mirror operation, dissociate by fixing the Pt–N bond length of the leaving NH_3 and optimizing the remaining geometric parameters. We repeatedly increased this Pt–N bond length and optimized the geometry until this bond length was larger than 3.0 Å. Thus, we obtained the energy vs reaction coordinate relationship from transition state to products. Since there is a mirror relationship between the reactants and the products, from the principle of microscopic reversibility,[12] the remaining half-reaction coordinate from reactants to transition state can be easily defined from the mirror operation. Transition-state structures for the following four substitution reactions are designated as follows:

reaction system	transition state
trans-$Pt(CO)Cl_2NH_3 + NH_3$	1
cis-$PtHCl(NH_3)_2 + NH_3$	2
cis-$Rh(CO)Cl(NH_3)_2 + NH_3$	3
trans-$Pt(C_2H_4)Cl_2NH_3 + NH_3$	4

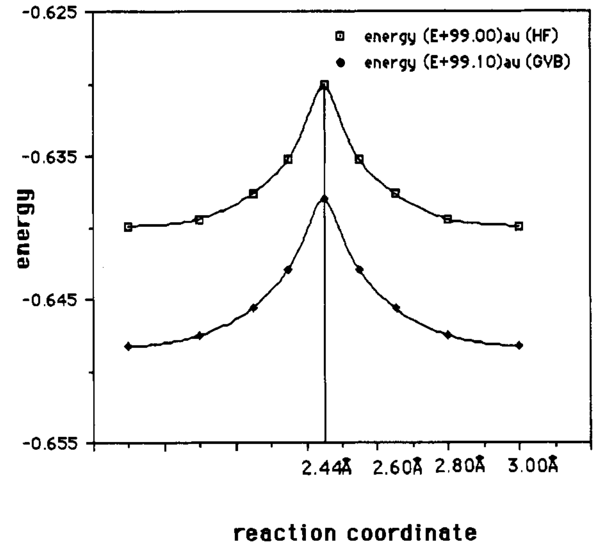

Figure 1. Potential energy curve along the reaction coordinate for the reaction trans-$Pt(CO)Cl_2NH_3 + NH_3$ (HF and GVB results).

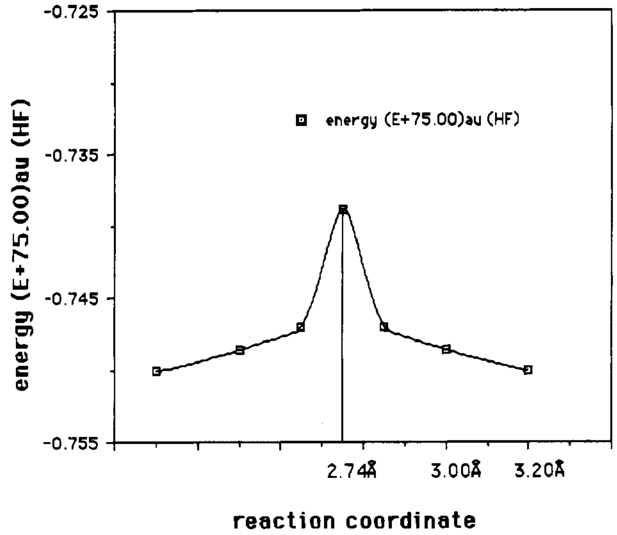

Figure 2. Potential energy curve along the reaction coordinate for the reaction *cis*-$PtHCl(NH_3)_2 + NH_3$ (HF result).

The total energies as a function of reaction coordinates are shown in Figures 1–4. Figure 1 also shows the result of GVB-8/PP calculations. We can see that the principal effect of electron correlation is simply lowering the whole energy surface and is not important for the relative energies, since the bond breaking does not involve the separation of electrons in the bond pair, as does the dissociation of the H_2 molecule.[8] Therefore, the RHF results should be reasonably reliable for the systems investigated in this paper.

The activation energies for the four reactions above are as follows:

reaction system	activation energy, kcal/mol
trans-$Pt(CO)Cl_2NH_3 + NH_3$ (**1**)	6.15, kcal/mol
cis-$PtHCl(NH_3)_2 + NH_3$ (**2**)	7.15, kcal/mol
cis-$Rh(CO)Cl(NH_3)_2 + NH_3$ (**3**)	3.55, kcal/mol
trans-$Pt(C_2H_4)Cl_2NH_3 + NH_3$ (**4**)	2.51, kcal/mol

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(13) Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769.
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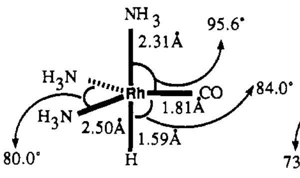
The GVB calculations on the first reaction give 6.46 kcal/mol for the activation energy, which is very close to the RHF result.

Trans Effect. Having established a method to find the transition state of a reaction by optimizing a structure with a mirror symmetry restriction, we investigated the following reactions to compare the effect of the trans-directing ligands through the total energies of different isomers of the activated complexes:

reaction system		transition states
cis-$Rh(CO)H(NH_3)_2 + NH_3$	comparing CO and H^-	**5** and **6**
cis-$PtH(Cl)(NH_3)_2 + NH_3$	comparing H^- and Cl^-	**2** and **7**
cis-$Pt(CH_3)Cl(NH_3)_2 + NH_3$	comparing CH_3^- and Cl^-	**8** and **9**
cis-$Rh(Cl)NH_3(H_2O)_2 + H_2O$	comparing Cl^- and NH_3	**10** and **11**

Each reaction has two transition states (see **5**–**11** for the structures of the additional transition states) depending on which trans-directing ligand is in effect. For example, in the first reaction, if CO is the trans-directing ligand, the transition state is the one with the mirror operation relating the entering NH_3 and the NH_3 trans to CO (i.e. the leaving ligand). If H^- is the trans-directing ligand, the transition state is the one with the mirror operation relating the entering NH_3 and the NH_3 trans to H^-. By comparing the energies of these two isomers (two transition states) for each reaction, we can determine which ligand has stronger trans effect.



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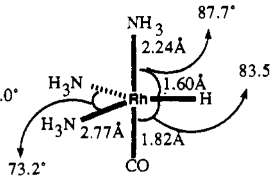

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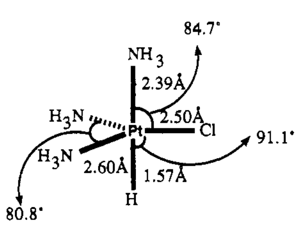

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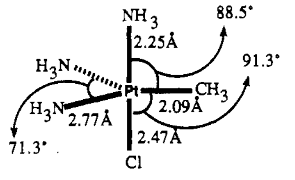

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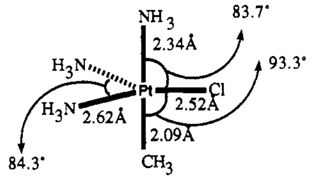

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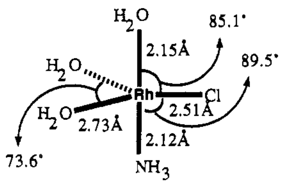

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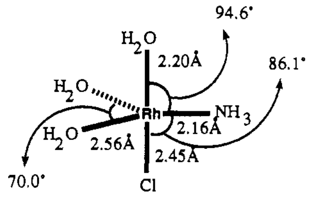

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The results show that all transition states have a pseudo-trigonal-bipyramidal geometry, with the entering, leaving, and trans-directing ligands occupying the equatorial positions. The total energies and Mulliken populations of transition states for the four reaction systems above are listed in Table I. The trans-effect order (CO > H^- > CH_3^- > Cl^- > NH_3) predicted by these results agrees with the experimental order.

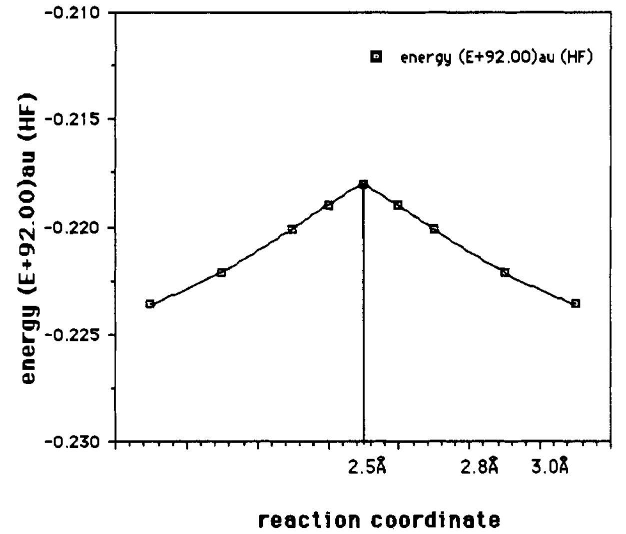


Figure 3. Potential energy curve along the reaction coordinate for reaction *cis*-$RhCOCl(NH_3)_2 + NH_3$ (HF result).

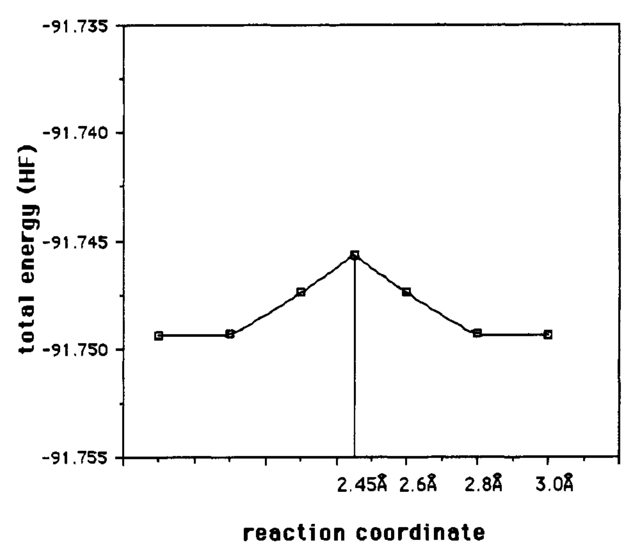
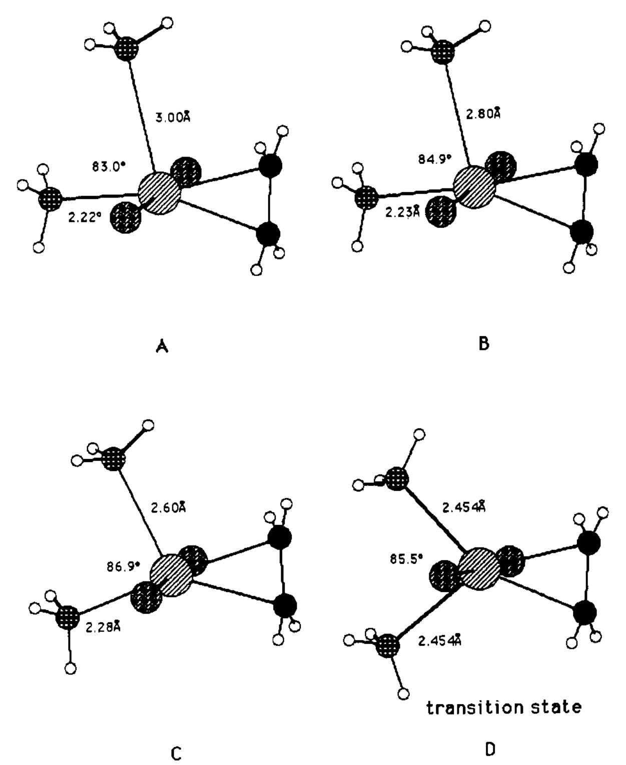


Figure 4. Potential energy curve along the reaction coordinate for reaction *trans*-$Pt(C_2H_4)Cl_2NH_3 + NH_3$ (HF result).

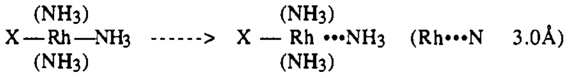
Table I. Comparison of the Total Energies and Mulliken Populations of Those Transition States with Different Trans-Directing Ligands

System	$Rh(CO)H(NH_3)_3$		$PtHCl(NH_3)_3$	
trans-directing ligand	CO	H^-	H^-	Cl^-
optimised geometry	(**5**)	(**6**)	(**2**)	(**7**)
total energy (a.u.)	-78.0154	-78.0239	-75.7388	-75.7363
energy difference	10.92 kcal/mol		1.57 kcal/mol	
Mulliken population on atoms	Rh(9.30) CO(9.80) H(0.98)	Rh(9.33) CO(9.76) H(0.98)	Pt(9.90) H(0.87) Cl(7.44)	Pt(9.78) H(0.88) Cl(7.50)
System	$Pt(CH_3)Cl(NH_3)_3$		$RhCl(NH_3)(H_2O)_3$	
trans-directing ligand	CH_3^-	Cl^-	Cl^-	NH_3
optimised geometry	(**8**)	(**9**)	(**10**)	(**11**)
total energy (a.u.)	-82.3640	-82.3634	-97.8882	-97.8766
energy difference	0.38 kcal/mol		7.28 kcal/mol	
Mulliken population on atoms	Pt(9.81) CH_3(6.93) Cl(7.45)	Pt(9.70) CH_3(6.93) Cl(7.51)	Rh(8.78) Cl(7.59) NH_3(7.79)	Rh(8.81) Cl(7.53) NH_3(7.83)

Scheme I

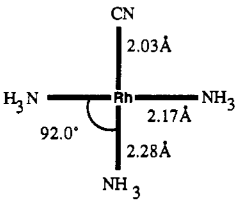


Dissociation. The ligand dissociation process was investigated for the following reaction:



$$X\text{—}\underset{(NH_3)}{\overset{(NH_3)}{Rh}}\text{—}NH_3 \text{ ------> } X\text{ — }\underset{(NH_3)}{\overset{(NH_3)}{Rh}}\text{ •••}NH_3 \quad (Rh\text{•••}N \quad 3.0Å)$$

where X = CN^-, H^-, CH_3^-, and Cl^- ligands. We optimized the structural parameters of both reactant and product above. The optimized structures for reactants are shown in **12–15**. The results



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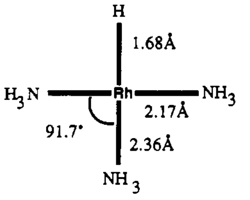

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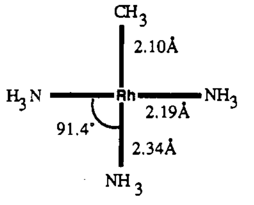

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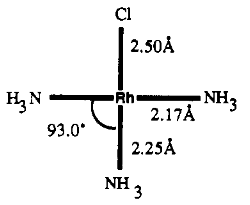

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show the NH_3 dissociation energies follow in the order:

$$H^- \text{ (9.6 kcal/mol)} < CN^- \text{ (9.9 kcal/mol)} < CH_3^- \text{ (10.4 kcal/mol)} < Cl^- \text{ (14.8 kcal/mol)}$$

This order reflects the trans influence (a thermodynamic effect) rather than the trans effect (a kinetic effect). As expected, the dissociation energies are much higher than the activation energies of the associative mechanism. Therefore, it is unlikely that a dissociative reaction mechanism can contribute much to the substitution reactions of these square-planar complexes.

Discussion

Reaction Mechanism. The associative reactions for the four systems presented in the reaction cordinate section above follow a similar path from the reactants to transition state. Here we discuss in detail the two reactions

$$trans\text{-}Pt(C_2H_4)Cl_2(NH_3) + NH_3 \quad \text{(Scheme I)}$$

$$cis\text{-}PtHCl(NH_3)_2 + NH_3 \quad \text{(Scheme II)}$$

For a 16-electron square-planar transition-metal complex, a simple MO scheme is presented in Figure 5. The vacant pure p_z orbital, which is perpendicular to the molecular plane and nonbonding, can accept an electron pair from the entering ligand. At the early stage of the reaction, the entering ligand attacks the vacancy to form a square-pyramidal structure. It can be seen from Figure 5 that there are also three occupied nonbonding d orbitals (d_{z^2}, d_{xz}, and d_{yz}) with their lobes directed above and below the xy plane

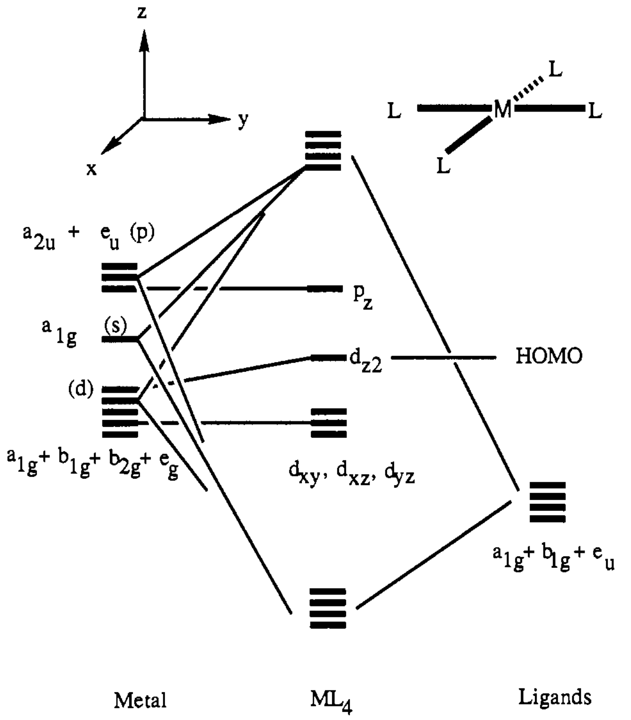
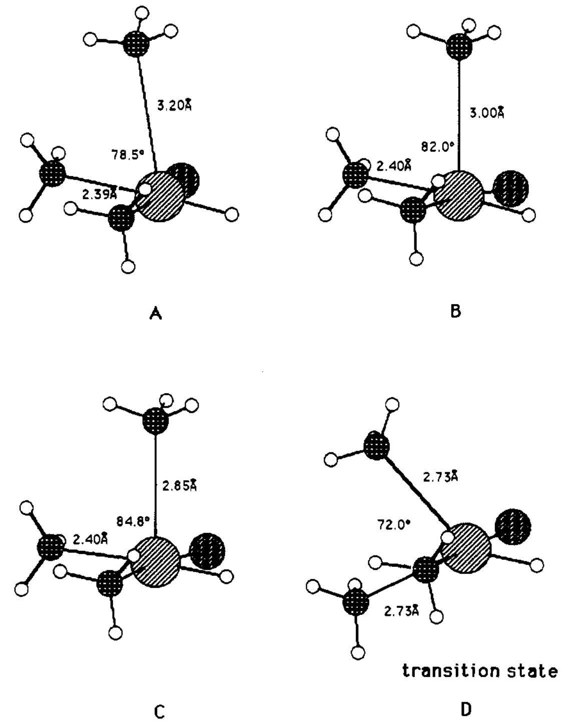


Figure 5. Molecular orbital interaction diagram for a square-planar ML_4 transition-metal complex.

Scheme II



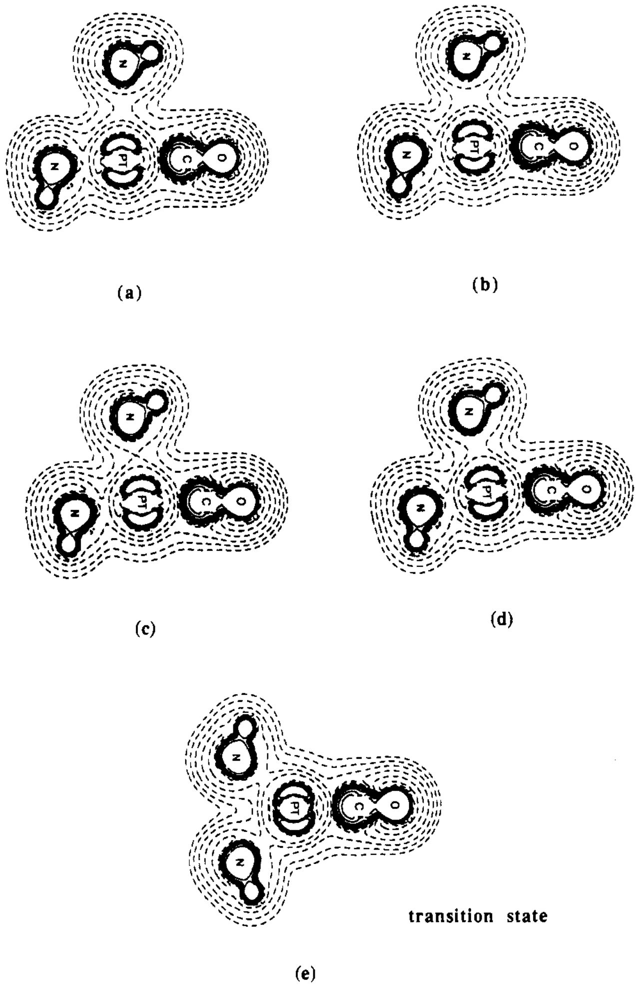
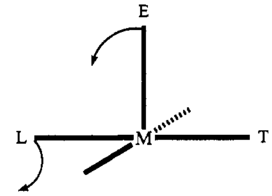


Figure 6. Plots of $-\nabla^2\rho$ on the plane of N–Pt–N for the reaction *trans*-Pt(CO)Cl_2NH_3 + NH_3. Pt–N(entering ligand): (a) 3.00 Å; (b) 2.80 Å; (c) 2.65 Å; (d) 2.55 Å; (e) 2.44 Å (transition state).

Scheme III



of Figure 5. These lone pairs provide a repulsive interaction with the incoming ligand. Therefore, as the reaction proceeds, the entering ligand shifts away from the trans-directing ligand (see Schemes I and II) reducing the electron repulsions between the entering ligand and the lone pairs on the central atom. At the same time, the entering ligand pushes the leaving ligand away from the square plane and weakens the metal–leaving ligand bond. The mechanism is summarized in Scheme III.

To illustrate the importance of these electron repulsions, we plot the Laplacian of the total valence electron density,[17-19] i.e. $-\nabla^2\rho$, from the ab initio results for the reaction *trans*-Pt(CO)-$Cl_2(NH_3)$ + NH_3. Figure 6 shows $-\nabla^2\rho$ on the N–Pt–N plane (the plane of entering ligand, metal, and leaving ligand, which corresponds to the *yz* plane of Figure 5) of the *trans*-Pt(CO)-$Cl_2(NH_3)_2$ system from reactant to transition state. In the contour plots, solid lines denote $-\nabla^2\rho > 0$, where the electron charge is locally concentrated, and dashed lines denote $-\nabla^2\rho < 0$, where the electron charge is locally depleted. Two charge concentrations on the central atom can be seen in Figure 6 for all structures along the reaction path. These two concentrations correspond to the lone pairs discussed qualitatively above. It is the lone pairs (concentrations) on the central atom that exert a repulsion force on the entering ligand. As the transition state is approached, the entering ligand moves away from this concentration toward the leaving ligand. Finally, when the transition state is reached, the entering ligand competes equally with the leaving ligand to coordinate to the same electron depletion region ($-\nabla^2\rho < 0$, the dashed lines in the contour plots), where the total concentration of the charge density is a minimum in the valence shell of the metal atom. As discussed below, this electron repulsion results in the small angle between the leaving ligand and the entering ligand observed for all the transition states investigated in this paper.

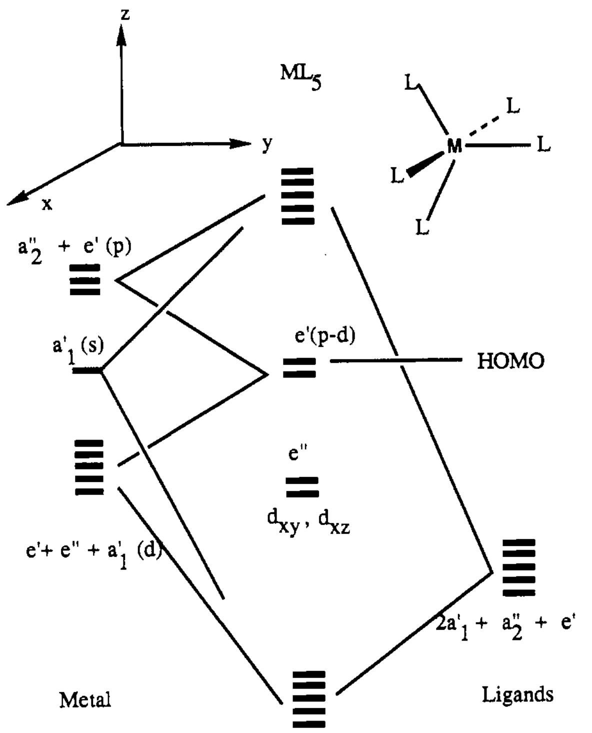


Figure 7. Molecular orbital interaction scheme for a trigonal-bipyramidal ML_5 transition-metal complex.

Transition State and Trans Effect. Since all of the transition states that we found in the substitution reactions of the square-planar complexes have a pseudo-trigonal-bipyramidal geometry with a small angle (less than 90°) between the entering ligand and the leaving ligand, a simple picture of the molecular orbital interaction in a ML_5 transition-metal complex is helpful in illustrating these systems. Figure 7 illustrates the interaction between the central metal atom and five ligand σ-donor orbitals. For an 18-electron ML_5 transition-metal complex, the HOMO's (e′ nonbonding orbitals) are a mixture of *n*d and (*n* + 1)p atomic orbitals of the metal atom. They are high in energy and are potentially strong π-back-donors. Therefore, those ligands having π-accepting abilities preferentially occupy the equatorial positions since the e′(d–p) orbitals have maximum density in the equatorial plane (*yz* plane in Figure 7).

In fact, these two nonbonding orbitals are closely related to two of the lone pairs discussed in the previous section. Since the structural changes from reactants to transition state are almost entirely restricted to the equatorial plane of the pseudo-trigonal-bipyramidal transition state, these two nonbonding orbitals play a significant role in the reaction process. Figure 6c shows the $-\nabla^2\rho$ plot on the equatorial plane for the reaction *trans*-$PtCOCl_2(NH_3)$ + NH_3 (see **1**) for the transition-state geometry.

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(19) Laplacians of the valence electron density that were calculated with effective core potential (ECP) have not been reported previously. For several second-row complexes we compared the results of all-electron calculations with those of an ECP calculation and found that the ECP calculation faithfully reproduced the regions of electron concentration and depletion in the valence shell.

The two concentrations on the central atom derive from the lone pairs discussed above. Two of these lone pairs, which are derived from e′ nonbonding orbitals and have some p character in addition to the d character, strongly donate their electrons to the ligands in the equatorial plane.

For a strong π-acceptor as the trans-directing ligand, these two lone pairs can be stabilized through π-back-donation. A strong σ-donor as the trans-directing ligand substantially weakens the metal–entering ligand and metal–leaving ligand bonds. This is clearly indicated from the structural parameters shown in **1–11**. This weakening effect decreases the electron repulsion between entering–leaving ligands and the lone pairs on the central atom, discussed in the previous section (see Figure 6). It is this repulsion that prevents further entering of the attacking NH_3 ligand before the retreating ligand leaves. Therefore, we can conclude that the transition state can be stabilized either directly by π-acceptors or indirectly by the decrease of electron repulsion through σ weakening. Those ligands with large σ effect, e.g. H^- and CH_3^- etc., are high in the trans-directing series even though they are incapable of π-back-bonding. *This analysis indicates that the mechanism of the trans effect involves both σ and π effects in the transition state.*

Usually, the σ effect is described as a weakening of the trans bond in the ground state of a square-planar complex. Comparing the structural parameters in **12–15** and **1–11**, we can see that the σ effect is much greater in the transition state than in the ground state. For example, ground states **12** and **13** have a small difference (0.08 Å) between their trans bond lengths although one has a strong π trans-directing ligand and the other a strong σ trans-directing ligand, but in their transition states, **5** and **6**, the difference in the trans bond lengths is significant (0.27 Å). Since in a square-planar complex the trans ligand is on the nodal plane of the two concentrations (see Figure 6), the weakening of the trans bond is small. When two ligands compete for the depletion in the nodal plane, the σ-weakening effect is significant. Therefore, we conclude that the σ trans effect is a transition-state effect rather than a ground-state effect, as is often discussed.

The Small Leaving-Ligand to Metal to Entering-Ligand Angle in the Transition State. All transition states that we found have a small leaving-ligand to metal to entering-ligand angle (L–M–E less than 90°). Thus, from the metal point of view, the transition state is a pseudo-square-planar structure, although we referred to it as a pseudo-trigonal-bipyramidal structure in the preceding sections. Figure 6e illustrates that a small angle minimizes the repulsion between the electron concentrations on the central atom and the electron concentrations on the entering and leaving ligands.

The small L–M–E angle in the transition state leads one to predict a high steric effect in those reactions involving bulky entering or leaving ligands. Odell and Raethel[20] have shown the dramatic effect of the size of the entering ligand in amine substitution reactions of *trans*-$(Pr_3P)PtCl_2(NHEt_2)$ in methanol. It also has been observed[1,21] that the size of the trans-directing ligand has less steric effect on the rate of substitution than that of the cis ligands. At an early stage of the reaction, the trans-directing and cis ligands have the same steric effect since they all have an angle of 90° with respect to the entering ligand. However, at the transition state, the trans-directing ligand is away from the entering and leaving ligands by an angle larger than 135°. The cis ligands interact with the entering and leaving ligands at a 90° angle.

Conclusion

The ab initio results on the substitution reactions of the square-planar transition-metal complexes indicate a pseudo-trigonal-bipyramidal transition state with a very small leaving-ligand to metal to entering-ligand (L–M–E) angle. The two "lone pairs" located in the equatorial plane of the pseudo-trigonal-bipyramidal transition state play a significant role in determining the structure and stability of the transition state. As a result of the small L–M–E angle, the transition state minimizes the repulsion between these metal "lone pairs" and electron pairs of the leaving and entering ligands. These ligands must compete for the same region of depletion (coordinate site). The trans effect is best rationalized by σ and π effects on the stabilization of the transition state. The σ effect arises from the weakening of the trans bonds between metal and entering/leaving ligands in the transition state and, consequently, from the decrease of the electron repulsion between the "lone pairs" in the central metal atom and electron pairs from the entering/leaving ligands. The π effect is predominant through π-back-donation in the transition state. The results provide a more unified picture of the trans effect than the usual text book descriptions. We find no indication of a stable intermediate in our "gas-phase" calculations. Thus, the existence of an intermediate may be strongly influenced by solvent effects or by different ligands.

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