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AN APPRAISAL OF SQUARE-PLANAR SUBSTITUTION REACTIONS

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I. Introduction

Ligand substitution at square-planar complexes is one of the most thoroughly investigated reactions in inorganic chemistry. The knowledge and understanding of the subject probably rivals that of octahedral complexes, though the number of compounds with square-planar geometry is only a fraction of the former, being largely confined to the d^8 metal ions near the end of the transition series (Rh^I, Ir^I, Ni^{II}, Pd^{II}, Pt^{II}, and Au^{III}). The reasons for this are instructive. First, the fact that complexes of platinum(II) are kinetically inert should not be overlooked. They provided the vehicle for early work in the way that compounds of Co^{III} and Cr^{III} did for octahedral complexes; and once started, the interest was maintained because the substitution processes appeared to proceed by simple and straightforward associative mechanisms, in contrast to the common dissociatively controlled processes of octahedral materials. More recently, of course, the availability of methods for following faster reactions has opened the area of study to palladium(II) and the other d^8 ions. In addition, the diamagnetism of these complexes (and most of their reaction intermediates) has meant that NMR spectroscopy has also been employed, both to follow reactions in the normal sense and to measure fluxionality on the NMR timescale.

Another impetus to mechanistic studies arose from the recognition that compounds of these d^8 ions were those on the energy borderline between stable 18-electron and 16-electron molecules (*1*) and that the reactions involving transitions between these states are those encountered in catalytic cycles based on these compounds. Nucleophilic ligand substitution, involving association of an entering nucleophile with a square-planar compound, is just one example of the easy 16→18→16

electron transitions often featured in such catalytic processes. The simple but real relationship of this ligand-exchange sequence to the other important reaction types greatly broadens the scope for study (*2*).

Last, perhaps partly from recognition of this electronic relationship but largely from the intensive effort and detailed study that have been applied to them, the range of reaction types known to lead to ligand substitution at square-planar complexes has recently been greatly extended. Although still dominated by associative nucleophilic attack, the operation of dissociative processes at some square-planar molecules now seems beyond dispute, and associative electrophilic attack has also been recognized, bringing the process of oxidative addition to d^8 complexes (which, when followed by reductive elimination, leads to ligand substitution anyway) into view as a comparative reaction. It has been argued by this author (*3*) that these processes are interrelated and should not be viewed in isolation as particular and well-defined reaction types but as points on a continuum of reaction pathways.

Despite the richness of this field of study, however, a number of anomalies and some major uncertainties remain. One curious feature, which is probably no more than an historical accident, is that though most studies of nucleophilic ligand substitution have been carried out on complexes of platinum(II) and palladium(II) and few on complexes of rhodium(I) and iridium(I), the reverse distribution is apparent for studies of oxidative additions. The scope for rectifying this imbalance is vast. On the other hand, a fundamental and persistent uncertainty in this field of study concerns the very nature of square-planar compounds in solution. We address this problem in some detail.

The mechanistic interest in square-planar compounds has meant that the subject has not been short of reviewers, and many excellent articles and chapters have been written. The reader is referred in particular to reviews by Cattalini (*4*), Tobe (*5*), Mureinik (*6*), and Skibsted (*7*). Other articles are cited at appropriate places.

A main objective of this work is to develop the relationship between the many reaction pathways leading to ligand substitution at square-planar molecules. Concentrating on more recent results to illustrate the processes under discussion, we examine in detail the evidence for operation of the less common and sometimes controversial routes such as dissociative ligand exchange (*6*). It cannot be stressed too much, however, that the field is still dominated by associative reactions, so to maintain a balance, as well as to provide the now necessary comparative evidence, we also cover the essential features of nucleophilic ligand replacements.

Emphasis is given to elucidating the intimate mechanisms of the reactions. Recently, many structural studies have complemented ki-

netic experiments in uncovering mechanistic detail, and this aspect is featured. Attempts to derive intimate mechanisms are, of course, fraught with difficulty, and it is all too easy to be misled. Indeed, Swaddle (*8*) has expressed the view that the more important task is to understand the kinetic properties of molecules rather than to depict their reaction details. Nevertheless, it is the opinion of this author that the ability to compare molecular reaction paths is a valuable exercise that leads to a better understanding of the subject as a whole. This approach means, however, that the possibility of "hidden" steps—for example, fast geometry changes during reaction sequences that are not revealed by kinetic measurements—should be kept in mind.

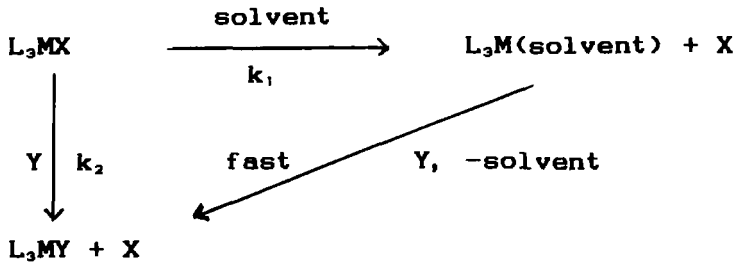
This review, then, is a personal assessment of the mechanisms operating at square-planar molecules. It is not comprehensive, and many important areas are only briefly discussed. (For example, the detailed effects of entering and leaving nucleophiles and the establishment of nucleophilicity series, areas important enough to be reviewed in their own right (*4*), are only superficially covered here.) We begin by examining the evidence for the most central process, that of nucleophilic ligand exchange, taking examples largely from the chemistry of $Pd^{(II)}$ and $Pt^{(II)}$ but making comparisons with the other elements to bring out differences in their likely reaction paths. Next we examine some consequences of nucleophilic attack elsewhere than at the metal atom, with emphasis on conjugate base (CB) formation, since operation of CB pathways at square-planar complexes, though still rare, has recently been more commonly recognized. We then examine the likelihood of geometry changes during reactions, particularly in compounds of nickel, and assess the possible mechanistic consequences of these to the associative reactions discussed. This is followed by an appraisal of dissociatively controlled reactions, leading to reactions that are dependent on electrophilic attack at either ligands or metal ion. Oxidative additions, which can proceed by either nucleophilic or electrophilic interactions, are related to the foregoing. Finally, the mechanistic consequences of partial reductive eliminations, a recently discovered reaction type, are discussed.

II. Ligand Replacement by Nucleophilic Attack

A. The Simple Rate Law and Nature of the Reactions

The vast majority of ligand-replacement reactions fit into this category. Most conform to a simple two-term rate law of Eq. (1):

$$\text{Rate} = (k_1 + k_2[\text{Y}])[\text{L}_3\text{MX}] \qquad (1)$$



SCHEME 1

This equation relates to the operation of the branched reaction path of Scheme 1, in which incoming nucleophile Y replaces resident ligand X. With weak nucleophiles and polar solvents, it is common to observe total dominance by the k_1 solvation path, whereas examples dominated by the k_2 nucleophile-dependent route are found when these factors are reversed. For this simple rate law to hold, it is necessary, of course, for the second step of the solvento pathway (often called the anation step when Y is an anion), in which Y replaces coordinated solvent, to be fast; and many independent rate determinations of such anation reactions confirm that this is generally so.

We deal with the three reactions of Scheme 1 in turn, as applied to the chemistry of platinum(II) and palladium(II) complexes (most of the evidence relates to these), and noting later where variations may occur with the other elements.

The ligand-dependent pathway, represented by the k_2[Y] term, is readily understood as a nucleophilic attack of Y at the metal ion. Thus, increasing steric hindrance at the metal atom markedly retards the reaction, exemplified by reaction (2), in which bulkier *N*-substituents, R, on the diethylenetriamine (dien) ligand reduce k_2 (*9*).

$$[PdCl(R_5\text{-dien})]^+ + I^- \longrightarrow [PdI(R_5\text{-dien})]^+ + Cl^- \qquad (2)$$

A counterbalancing example of the retarding effects of bulky entering groups is afforded by reaction (3), in which the use of amines (am) of increasing size progressively diminishes the k_2 values (*10*).

$$[PtCl_2(NHEt_2)(PPr_3)] + am \longrightarrow [PtCl_2(am)(PPr_3)] + NHEt_2 \qquad (3)$$

A second classical test for detecting associative or dissociative pathways is the effect of electronic charge on substitution rates. A number of comparative studies have revealed only small changes in rate con-

stants despite charge changes of several units (*11*). This confirms the operation of an associative pathway for the k_2 part and is in sharp contrast to related studies on octahedral molecules, in which dissociative processes operate and the rate constants span several orders of magnitude (*12*).

The activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$ in general also point to associative reactions for the ligand-dependent part of these exchange reactions at platinum and palladium. Many early values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been collected (*13*), and more recent values are in broad agreement. Most striking is that the entropy terms are all similar and negative, ranging from about -60 to -120 J K^{-1} mol^{-1}. Because the values relate to a range of substrates and ligand types, it is unlikely that changes in solvation can be responsible. Indeed, a reasonable conclusion is that solvation effects are unimportant in the k_2 steps of these reactions. The negative $\Delta S^{\ddagger}$ values can thus be interpreted as indicative of associative reactions, the rates for which are largely controlled by $\Delta H^{\ddagger}$, values of which can vary widely.

Last, the increasing numbers of $\Delta V^{\ddagger}$ values obtained from kinetic measurements at various pressures also supply evidence of associative activation. Values usually range from -5 to -20 cm^3 mol^{-1} (*9, 14–17*). Like the entropy values, these parameters require caution in their interpretation but are seen in general as indicative of A or I_a reactions dominated by bond making.

Although, from the kinetic evidence alone, the k_1 term could be assigned either to a dissociative contribution to the exchange process or to the operation of a solvento pathway, it is this latter option that is compellingly supported by a wealth of evidence for most reactions. In the first place, activation parameters assigned to this step are very similar to those associated with the k_2 step. The reactions of Eq. (2) provide good examples (*9*). They also serve to show that steric effects of ligands both cis and trans to the leaving group are similar and affect both k_1 and k_2 in analogous fashion. Increasingly bulky R_5-dien ligands reduce the values of both, indicating that they arise from similar associative steps.

The solvento route has frequently been studied in the absence of the direct pathway, either fortuitously (with poor incoming nucleophiles the k_2 term can be vanishingly small) or by deliberately observing the aquation in the absence of competing nucleophiles. The k_1 values so determined are generally identical to those found in the presence of competing nucleophiles (*18*), and activation parameters derived from them are again in accord with bimolecular associative reactions having 5-coordinate solvento species $ML_3X(S)$ as intermediates or transi-

tion states. Equation (4) (L = CO, C_2H_4, or PMe_3) shows some examples (*19*).

$$trans\text{-}[PtCl_2L(am)] + Cl^- \longrightarrow [PtCl_3L]^- + am \quad (4)$$

Proceeding almost exclusively by the solvento route in 5% aqueous methanol, the k_1 term dominates and is considerably reduced by bulky leaving groups, am (substituted pyridines).

As would be expected, changing the nature of the solvent exerts a vast effect on the rates of this ligand-independent reaction, but the effects are complicated because of the dual role of the solvent as nucleophile and reaction medium (*16, 20–24*). An early investigation based on chloride exchange at *trans*-$[PtCl_2py_2]$ [Eq. (5)] found no solvent path in poor solvents such as benzene or CCl_4 but found k_1 values that vary over four orders of magnitude in Me_2SO, $MeNO_2$, EtOH, and water (*20*).

$$[PtCl_2py_2] + {}^{36}Cl^- \longrightarrow [PtCl^{36}Cl(py)_2] + Cl^- \quad (5)$$

Related solvent dependences were found for the reactions of $[PtCl_2(pip)_2]$ and $[Pt(NO_2)_2(pip)_2]$ (pip is piperidine) with several nucleophiles (*21, 22*). That the k_2 terms also vary in magnitude quite markedly with changing solvent reveals that other effects are operating, however, and straightforward comparisons between solvents cannot be made, a point further illustrated by the reaction between 1-pentene and *trans*-$[PtCl_2(PhCH{=}CH_2)(am)]$ (am are substituted anilines) (*23*). In noncoordinating $CHCl_3$ the k_1 term is indistinguishable from zero. As ethanol is added to the solvent, however, not only does the k_1 term become important, but the k_2 value decreases. Presumably solvation of the chloride or substrate slows the direct path.

The k_1 term, then, can be generally regarded as representing an associative solvation step, an important conclusion in view of the mounting evidence that some ligand replacements at square-planar molecules proceed dissociatively. Measures of the true magnitudes of k_1 for comparisons with k_2 are obtained by dividing by the solvent "concentration."

Logic would suggest that the second step of the solvento route, the fast anation reaction, should also be associative because it qualitatively resembles the other two reactions of Scheme 1. This appears to be the case. Several such reactions have been independently examined. Reactions (6) are typical (*24, 25*).

$$[Pt(OH_2)(dien)]^{2+} + Y^- \longrightarrow [PtY(dien)]^+ + H_2O \quad (6)$$

Second-order kinetics were found (there can, of course, be no solvento step), and the rate constants, when compared with those of direct substitution reactions of $[PtX(dien)]^+$ by Y^-, were found to be greater in every case.

Anation reactions of the related palladium complexes, $[Pd(OH_2)(dien)]^{2+}$, have so far proved to be too fast to follow kinetically; but with bulkier ligands, usually R_3-dien, R_4-dien, or R_5-dien, where the R are methyl or ethyl groups substituting the *N*-bonded hydrogens of the dien, successful observations have been made by stopped-flow methods (*26*). Again the reactions were first-order in substrate and in Y^-, and increasing steric bulk at the metal led to increased $\Delta H^\ddagger$ and slower reaction rates, compatible with associative processes. Negative values of $\Delta S^\ddagger$ and $\Delta V^\ddagger$ similarly indicate associative activation, probably I_a, with bond formation between anion and substrate making the dominant contribution to values of $\Delta V^\ddagger$. Thus, all three reactions of Scheme 1 appear to be similarly associative, and their relative rates fit the observed law.

Two special cases of ligand exchange are worthy of additional emphasis. The first, a type that often yields valuable mechanistic information because of its inherent simplicity, is that of solvent exchange at the solvento-ions. Exchange of free and coordinated water at $[Pd(OH_2)_4]^{2+}$ and $[Pt(OH_2)_4]^{2+}$ has been followed at various temperatures and pressures by using ^{17}O NMR spectroscopy with enriched $H_2{}^{17}O$ (*27*). Negative values of $\Delta S^\ddagger$ and $\Delta V^\ddagger$ indicate A or I_a activation processes, quite in line with the other reactions discussed. The data are also suggestive of no or, at best, weak solvation at the metal sites above and below the plane, also in keeping with many other observations.

The second case is the reaction of dimethylsulfoxide (Me_2SO) with $[Pd(OH_2)_4]^{2+}$ to form $[Pd(OH_2)_3(Me_2SO)]^{2+}$. Values of $\Delta V^\ddagger$ have been measured for both the forward and reverse reactions, solvent effects being minimized by the use of uncharged ligands. It is clear that whereas ΔV^0 for the process is far from negligible, the negative $\Delta V^\ddagger$ values support associative activation in both directions (Fig. 1) (*28*). The $\Delta S^\ddagger$ values are also negative. The work clearly emphasizes the need for caution in interpreting the magnitudes of $\Delta V^\ddagger$, particularly in the absence of data for the reverse steps.

B. More Complex Rate Laws

With a greater sophistication of instrumentation and the ability to follow faster reactions, rate laws more complicated than Eq. (1) are

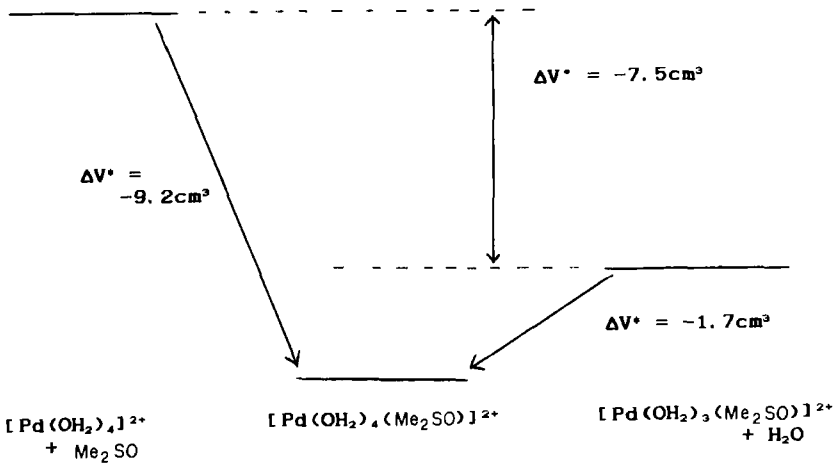
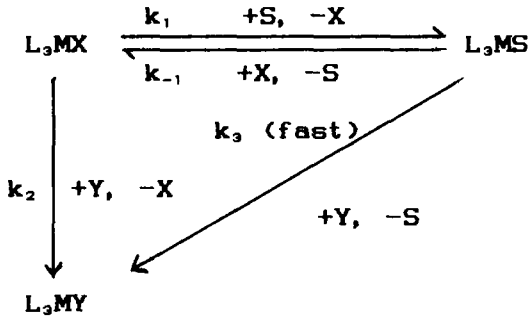


FIG. 1. Volume profile for the reaction of $[Pd(OH_2)_4]^{2+}$ and Me_2SO in water.

being increasingly encountered. In general, this does not indicate the operation of different reaction pathways but arises from competition from reverse reactions. Most often the solvolysis route is involved due to the high reactivity of the solvento intermediate. Two limiting cases are readily envisaged here. In one, the solvolysis step is essentially rate-determining, but a significant reverse reaction (k_{-1}) affects the kinetics. In the other case, the anation step becomes rate-limiting in the solvolysis pathway, and the faster k_1 and k_{-1} produce a pre-equilibrium. Considering the vast range of substrates, entering groups, and solvents that have been employed, it is not surprising that several examples conforming to both situations have been analyzed, and their study has considerably enhanced our knowledge of these ligand-exchange reactions (*6*).



SCHEME 2

Scheme 2, which represents a simple extension of Scheme 1, includes the reverse hydrolysis (a competing anation reaction). Application of the steady-state approximation to the solvento intermediate $[ML_3S]$ leads to rate law (7) (assuming a contribution from the ligand pathway also), which is adhered to when $k_{-1}[X]$ is significant.

$$k_{obs} = \frac{k_1 k_3[Y]}{k_{-1}[X] + k_3[Y]} + k_2[Y] \tag{7}$$

A dominant $k_3[Y]$ reduces Eq. (7) to the familiar Eq. (1).

Complications of this type were apparent as early as 1962 in the reaction of $[PtBr(dien)]NO_2$ with pyridine (*29*). The reaction, which proceeds mainly by the solvolysis route, slows as $[Br^-]$ builds up, due to the competing back-reaction. $[PtBr(dien)]^+$ reacts with the nucleobase inosine (Ino) mainly by the solvolysis pathway and is likewise inhibited by bromide (*30*). The observed rate law fits Eq. (7) with X = Br^- and Y = Ino. By means of stopped-flow methods, reactions between the palladium analog $[PdBr(dien)]^+$ and Ino have also been followed (*31*). Due to the low reactivity of Ino, its affinity for the solvento intermediate is similar to that of Br^-, and in this case a third complicating feature, the rare operation of a reverse reaction to the ligand-dependent route, is also apparent. Equations (8–10) show the reactions from which rate law 11 is derived.

$$[PdBr(dien)]^+ + H_2O \rightleftharpoons [Pd(OH_2)(dien)]^{2+} + Br^- \tag{8}$$

$$[Pd(OH_2)(dien)]^{2+} + Ino \rightleftharpoons [PdIno(dien)]^{2+} + H_2O \tag{9}$$

$$[PdBr(dien)]^+ + Ino \rightleftharpoons [PdIno(dien)]^{2+} + Br^- \tag{10}$$

$$k_{obs} = \frac{k_1 k_3[Ino] + k_{-1}k_{-3}[Br^-]}{k_{-1}[Br^-] + k_3[Ino]} + k_2[Ino] + k_{-2}[Br^-] \tag{11}$$

Similar kinetic rate laws have recently been found for the reaction between $[PdCl(dien)]^+$ and inosine, k_1, k_{-1}, and k_3 all being of similar magnitude (*32*). With adenosine instead of Ino, k_3 is diminished to the extent that k_1 and k_{-1} can be treated as a pre-equilibrium, and with the unreactive nucleobase uridine, even the reverse anation step, k_{-3}, can again make a contribution. This type of complication has been found in reactions of palladium–dien complexes with the common buffering agent tris(hydroxymethyl)aminomethane (*33*), which acts as a poor nucleophile.

Operation of reverse solvento steps have been detected also in reactions of a number of triethylphosphine complexes of platinum. Under pseudo-first-order conditions, the rate of replacement of Cl^- from *trans*-$[PtCl_2(PEt_3)_2]$ by NO_2^- in MeOH deviates markedly from linearity due to the operation of reaction (12) (*34*).

$$trans\text{-}[PtCl(MeOH)(PEt_3)_2]^+ + Cl^- \longrightarrow [PtCl_2(PEt_3)_2] + MeOH \qquad (12)$$

Again, application of the steady-state approximation allowed derivation of the value of k_1, which agreed with those found from other reactions. Replacement of chloride by pyridine in methanolic *trans*-$[PtClR(PEt_3)_2]$ also produced k_1 values different from those found using other nucleophiles (*35*), a result of importance since early studies of this reaction provided evidence for the operation of associative mechanisms through the effects of steric hindrance. The more-recent data indicate that only for R = phenyl (Ph) did a significant direct pathway operate; for the rest (R = *o*-tolyl or mesityl), reversible reactions along the solvento route fitted the observations. Although the detail is different, the interpretation of the effects of crowding at the metal center remain indicative of associative activation.

It is worth noting that when a solvolytic pre-equilibrium is established, an apparent first-order dependence on Y usually results. In consequence, the operation of the solvento path is not directly obvious and must be deduced, for example, from comparisons with other reactions. Thus, when reverse steps of any of the three reactions of Scheme 1 become important, rate laws that are more complex than Eq. (1) naturally result. The important point, however, is that the experimental rate laws have all been accommodated by this interpretation and provide no reason in themselves to believe that reaction types other than those involving associative activation are involved in any of these processes.

C. The Intimate Mechanism

With strong evidence from an overwhelming number of reactions that the processes are associative (or at least I_a), intermediates or transition states with coordination numbers greater than four are clearly indicated. The general lack of evidence for solvation of the metal above and below the square planes points to the involvement of 5-coordinate rather than 6-coordinate species: any occupation of the sixth-coordination site would usually have to be by a solvent molecule; and with little compelling reasons, so far, to believe that even solvents

of considerable donor ability coordinate to the metal ions of square-planar molecules, there seems no reason to expect them to do so at 5-coordinate intermediates. (Nickel complexes are exceptional here; they are discussed later, along with the possible complications of geometry changes to tetrahedral.)

The large number of structurally characterized 5-coordinate compounds of Pd(II) and Pt(II) also points toward this configuration being involved along the ligand exchange reaction coordinate. Whether these species are to be regarded as transition states or intermediates, or can even be isolated, depends on the presence and depth of any potential wells along the reaction profile. This is subtly dependent on a variety of factors and cannot easily be predicted. For example, there is good evidence that all the reactions of tertiary phosphines with bis-β-diketonato complexes of palladium(II) and platinum(II) proceed by 5-coordinate species. Though some can be isolated, others can only be detected spectroscopically, and many cannot be observed at all (*36*).

Strong support for the operation of square-planar to 5-coordinate to square-planar reaction pathways comes from an unusual source: negative ion mass spectrometry (*37*). Several reactions replacing X^- by Y^- in *trans*-$[PtX_2L_2]$ (X^- and Y^- are halides; L is PEt_3) were examined in the gas phase. Equation (13) is an example.

$$[PtCl_2L_2] \xrightarrow{I^-} [PtClIL_2] \xrightarrow{I^-} [PtI_2L_2] \qquad (13)$$

I^- was generated from MeI. Not only were the products of mono- and di-substitution readily observed in the mass spectrometer, but also a variety of adducts corresponding to probable 5-coordinate intermediates, $[Pt(X, Y)_3L_2]$, could also be identified. These have lifetimes between 10^{-3} and 10^{-6} sec and included the addition of X^-, liberated during the reaction sequences, to unreacted *trans*-$[PtX_2L_2]$. Other gas-phase studies using electron-impact mass spectrometry on reactions between *trans*-$[PtHClL_2]$ (L = PPh_3) and $SnCl_2$, and *trans*-$[PtH(SnCl_3)L_2]$ and CO or ethene, reveal production of cationic 5-coordinate species (*38*).

Although caution is necessary in relating gas-phase reactions to solution chemistry, there does seem to be grounds for believing that, in at least some of these cases, the processes are similar. The mass spectrometric studies have most probably detected the reaction intermediates in these associative substitution processes.

A necessary consequence of assigning these 5-coordinate species as intermediates or transition states in the square-planar ligand ex-

change profile is that those 5-coordinate d^8 molecules that have been fully characterized should show a tendency to lose a ligand. This appears to be the case. For example, NMR spectroscopic measurements show that 5-coordinate $[PdBr_2(PMe_3)_3]$ and $[PdBr(PMe_3)_4]^+$ readily lose Br^- and PMe_3, respectively, in CD_2Cl_2 solution (*39*); most of the 5-coordinate olefin complexes $[PtX_2(olefin)(biL)]$ (biL are bidentate nitrogen donors) reversibly eliminate an equatorial nitrogen in solution (*40*); in the square-pyramidal complexes $[MX(biL)_2]^+$ (M is Ni, Pd, or Pt; X is halide; biL are meso or racemic diphosphine or diarsine ligands), the apical halide changes sites from one side of the $[M(biL)_2]^{2+}$ plane to the other by an intermolecular route (*41*). Several examples of 4- to 5-coordination equilibria of type (14) have been detected by vt-NMR spectroscopy (vt is variable temperature) (*42*).

$$[PtX_2(PR_3)_2] + PR_3 \rightleftharpoons [PtX_2(PR_3)_3] \tag{14}$$

Clearly, then, having formed a 5-coordinate species, we find that loss of a ligand, the necessary next step, is indeed a general and facile process, even when the 5-coordinate complexes are stable enough to be examined and isolated. The processes of Scheme 1 can thus be typically represented as in Eq. (15).

$$[ML_3X] + Y \longrightarrow [ML_3XY] \longrightarrow [ML_3Y] + X \tag{15}$$

1. The Reaction Profile: Structures of the 5-Coordinate Intermediates

Consideration of the shapes of the reaction profiles for these associative ligand-exchange reactions have been dominated by one factor: nearly all the reactions examined appear to be stereoretentive, that is, the geometrical arrangement of the "nonparticipating" ligands, L_3 of Schemes 1 and 2, remains unchanged. Perhaps mainly because of this, and because it helps to account for the frequently observed behavior parallel between entering and leaving nucleophiles (*4, 5, 12*), as well as assigning a special significance to the trans ligand (observed as the trans effect) (*43*), a reaction coordinate with a single minimum corresponding to a trigonal-bipyramidal intermediate was for a long time favored (Fig. 2). Square-pyramidal structures could then make up transition states for the bond-making and bond-breaking steps (*4*). Such a profile has been supported by calculations (*44*), though the possibility of square-pyramidal complexes occupying (minor) energy minima has long been recognized (*5*). Nevertheless, as recently as 1988, the stereoretentive nature of substitution reactions and the very

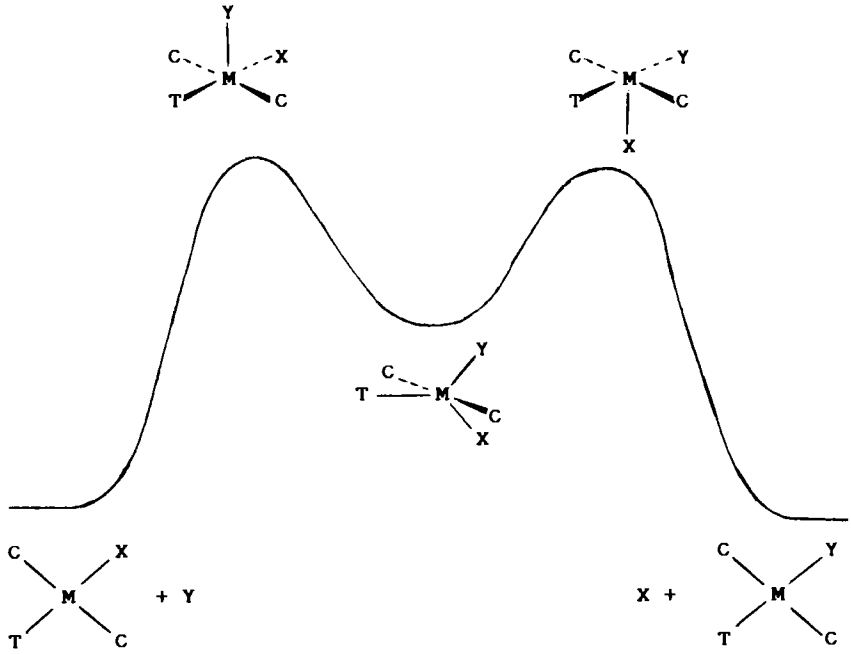


FIG. 2. Reaction coordinate showing a single minimum for a trigonal-bipyramidal intermediate. Ligand replacements at Rh(I) and Ir(I) are most likely to conform to this profile. C and T are ligands cis and trans, respectively, to the ligand being replaced.

existence of the trans effect has been cited as evidence for adherence to such a reaction profile (*45*).

Over the years, however, information has emerged that indicates that the shape of Fig. 2 may be a simplification or may be restricted to special circumstances. Of great importance has been the structural elucidation of large numbers of 5-coordinate complexes. The isolation of these compounds means that any closely related species encountered on the reaction coordinate could reasonably be regarded as intermediates and not transition states. The geometry of these compounds is therefore of great interest, and a structural survey of these types is worthwhile. At this stage we widen the scope to cover all the d^8 ion complexes in order to make comparisons and contrasts with the reactions of palladium(II) and platinum(II) on which we have concentrated thus far.

A useful starting point is a molecular orbital treatment of transition metal 5-coordination by Rossi and Hoffmann (*46*). Figure 3 shows the *d*-orbital energies for both D_{3h} and C_{4v} molecules derived from consid-

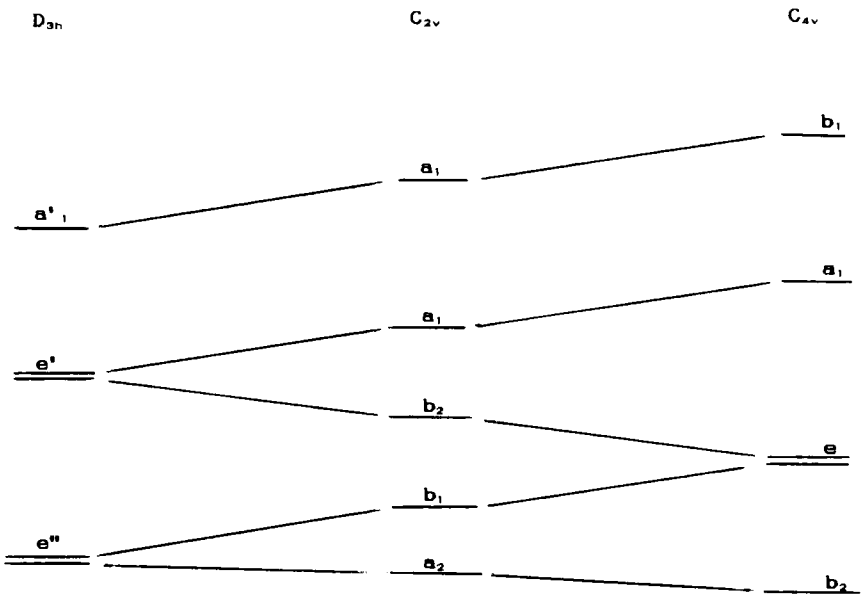


FIG. 3. *d*-Orbital energies for trigonal-bipyramidal (D_{3h}) and square-pyramidal (C_{4v}) molecules, showing correlations by a C_{2v} intermediate.

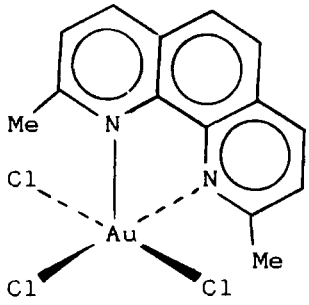
eration of the σ-orbital framework only. The energy levels for the square pyramidal molecules are for an angle of 98° between the apical and basal ligands, the calculated optimum for d^8 complexes. (Correlations for interconverting the two structures by a C_{2v} intermediate (the Berry pseudorotation) are also shown. This is symmetry-allowed for d^8–d^{10} species, an important conclusion that is discussed later). The two structures are of similar overall stability. The equatorial bonds of D_{3h} and the apical bond of C_{4v} are calculated to be weaker than the others. More powerful σ-donor ligands should show a preference for the axial sites of the trigonal bipyramid and the base sites of the square pyramid.

When the effects of π-bonding are taken into account, it transpires that π-accepting ligands have a preference for the equatorial sites of the trigonal-bipyramidal molecules and that a single-faced π-acceptor such as an olefin should lie parallel to the equator; π-donor ligands, on the other hand, favor the axial sites. In square-pyramidal molecules, the preferences do not appear to be so clear-cut, especially with variations possible in the bond angles.

It is interesting to compare these predictions with the patterns found. A survey of the d^8 metal complexes quickly reveals that there are few well-authenticated 5-coordinate compounds of gold(III), a rea-

sonable number for palladium(II) and platinum(II), and a substantial number for nickel(II), rhodium(I), and iridium(I). It is always dangerous to draw conclusions from such observations: future work might yet reveal enough new examples to change the balance. In this case, however, the trend is probably real. It reflects the tendency away from 16-electron molecules toward 18-electron species on moving to the left in the periodic table from gold through platinum to iridium, and also as each group is ascended (*2*). Indeed, if we extend our observations further left to the iron-group elements or up the iridium group to cobalt, we note that d^8 compounds of Co(I), Fe(O), Ru(O), or Os(O) are hardly ever found as 16-electron square-planar molecules (though such species may well be accessible as reaction intermediates); instead they are found as 18-electron compounds with higher coordination numbers.

Determined by X-ray crystallography in the solid phase, many structures fall between the two extremes of square pyramidal and trigonal bipyramidal, but most can be identified as lying much nearer to one than the other. Most of the few gold(III) complexes have structures closer to square pyramidal. Compounds **1–3** are typical (*47*). In every



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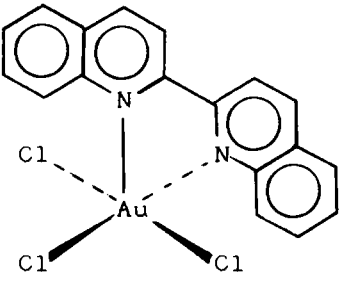

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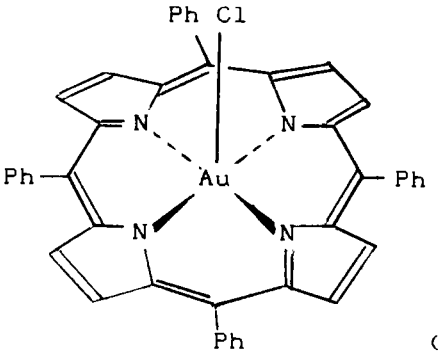
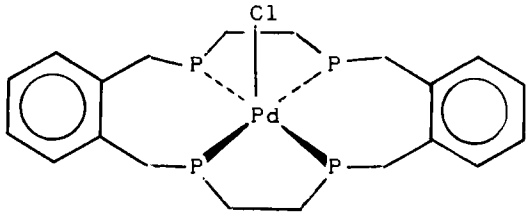


(3)

case the axial bond is considerably lengthened compared with the basal bonds. The substituted bpy and phen complexes, **1** and **2**, are especially interesting since related molecules without the substituents can be 4-coordinate {e.g., $[AuCl_2(bpy)]^+$} (*48*). A plausible explanation, in view of the scarcity of 5-coordinate complexes of this element, is that only when bulky ligand substituents force chelating ligands out of the molecular plane does coordination at the fifth site occur. Compound **3** is evidence that this is not always the case.

The majority of the 5-coordinate complexes of Pd(II) and Pt(II) also appear to have structures closer to square pyramidal than trigonal bipyramidal. Examples include compounds **4–6** (*49*), and references (*3*)



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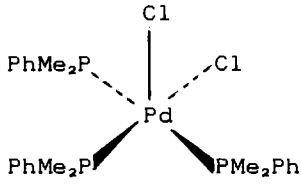

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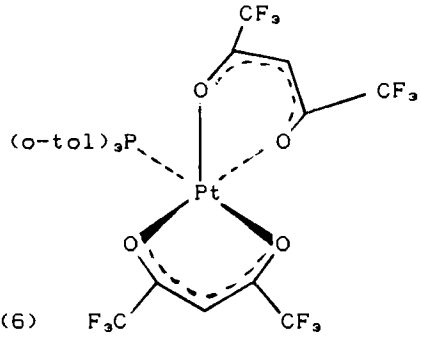
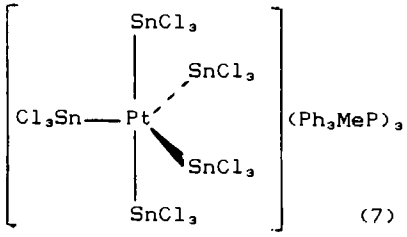


(6)

and (*50*) list many others. The metal atoms generally lie slightly above the basal plane, expected from calculations (*46*), and the apical bond lengths are long compared with those in the base. Structures best described as trigonal bipyramids are known, however (*3, 50*), and compounds **7** and **8** are representative (*51*). Both contain π-accepting li-



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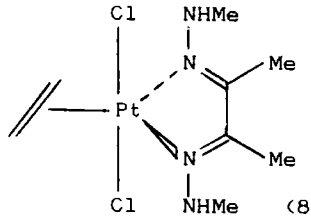


(8)

gands. Particularly significant is structure **8,** which is one of a family of structures of this type (*52*), many of which are known to retain their structural integrity in solution. The observed arrangements of axial π-donors, equatorial π-acceptors, and in-plane olefin orientation neatly fit the molecular orbital calculations (*46*). X-ray photoelectron studies on these molecules add further support and suggest that an important factor in expanding coordination from 4 to 5 in these d^8 Pt(II) compounds is the use of π-accepting ligands (*53*).

The 5-coordinate complexes of d^8 nickel(II) are more numerous than those of Pd(II) or Pt(II) and are more evenly represented by both trigonal-bipyramidal and square-pyramidal structures (though most structures are slightly distorted away from the ideal angles) (*54, 55*). Many of the earliest 5-coordinate species to be discovered were of nickel(II), and often tridentate or tetradentate ("tripod") ligands were employed to help ensure this geometry. It is now realized that this is not essential. Representative is the anion $[Ni(CN)_5]^{3-}$, which crystalizes in two distinct forms, one close to C_{4v}, the other to D_{3h} (*56*). In the former, the axial metal—carbon bond is longer than those in the basal plane, and in the latter the axial bonds are shorter than the equatorial ones. Interestingly, both high-spin and low-spin 5-coordinate complexes of both geometries are known for these nickel complexes (*54*), a consequence of the smaller energy separations of the *d* orbitals in complexes of the first-row elements.

Moving on to 5-coordinate compounds of rhodium(I) and iridium(I), one can see at once that, as well as being more numerous, the trigonal-bipyramidal form dominates (*57*). Examples include $[RhH(CO)(PPh_3)_3]$ with axial H and CO, $[Rh(CO)(dppm)_2]^+$ in which CO lies in the equatorial plane, and $[IrCl(CO)(O_2)(PEtPh_2)_2]$ with equatorial Cl, CO, and O_2 (which lies in the plane).

This distribution of molecular shapes gives the impression that trigonal-bipyramidal molecules become more favorable compared with square-pyramidal as 5-coordinate structures become more common (i.e., up or to the left in the periodic table). For the d^8 complexes under discussion, however, the translation to the left involves a change to lower oxidation number; in consequence, more π-accepting ligands are usually employed. It is possible that this factor could contribute significantly to the trend observed. There is also much to be learned about the trans influence in 5-coordinate structures (*58*), and this, too, could be an important factor in determining the geometry adopted. At present we note the trend but offer no firm explanation.

The first consequence of relating these structures to possible intermediates for nucleophilic ligand replacements at square-planar complexes is that the simple reaction profile of Fig. 2 is inadequate. A

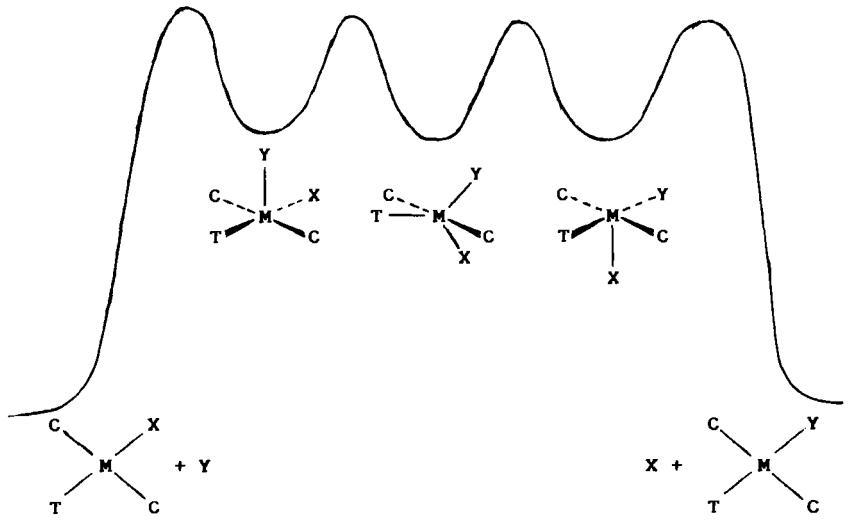
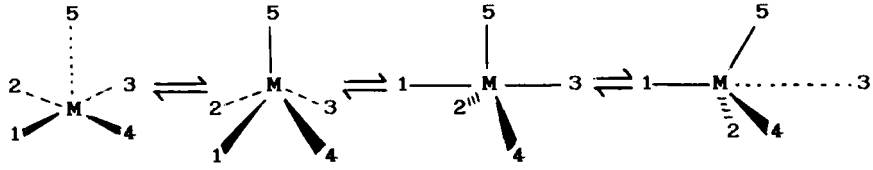


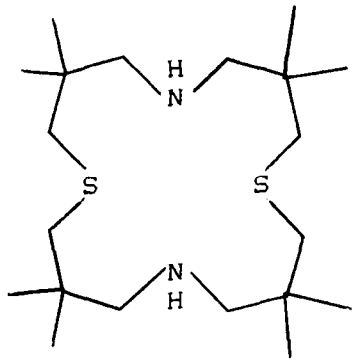
FIG. 4. Reaction profile with energy minima for trigonal-bipyramidal and square-pyramidal intermediates.

profile as complicated as Fig. 4, with energy minima at each of three 5-coordinate structures, is feasible (*3*), though the relative depths of the potential wells of each configuration vary from case to case. That such structures are indeed represented along the reaction coordinate is supported by structure correlation studies on 5-coordinate nickel(II) complexes, in which the structure variations can be placed on such a sequence (Scheme 3) (*55*). This method, of course, provides no indication of relative energies along the profile.



SCHEME 3

Further structural evidence for the dynamics of this process (though again without giving any information about the stabilities of intermediates) emerges from a study of the 5-coordinate palladium complex $[PdCl(tetraL)]Cl \cdot 2H_2O$ (tetraL is the N_2S_2 macrocycle, **9**) (*59*). The



(9)

crystal structure reveals two independent molecules, both similar to square-planar [Pd(tetraL)](PF$_6$), but each with additional apical Pd—Cl bonds of different length. As the Pd—Cl bond contracts, the molecule folds about the N–Pd–N axis. In solutions in nonpolar solvents, moreover, NMR evidence suggests a trigonal-bipyramidal structure for the cation [PdCl(tetraL)]$^+$. Hence, in this system the approach of a nucleophile is seen to be accompanied by a structural change in stages from planar to trigonal bipyramidal.

It is a matter of great interest whether the observed trends in the structures of 5-coordinate d^8 molecules reflect significant changes in the reaction profiles. For gold(III) complexes, attempts to define common ligand nucleophilicity sequences have generally met with failure, unlike for Pd(II) and Pt(II) (*4*, *7*). In comparison with Pd(II) and Pt(II), the importance of both the bond-making and the bond-breaking steps appears to be enhanced, and it has been pointed out that this would fit a reaction profile with just a single maximum, corresponding to a trigonal-bipyramidal transition state. This is entirely in keeping with the general scarcity of 5-coordinate complexes of gold(III); although, keeping in mind the few square-pyramidal compounds that have been characterized, a reaction profile like Fig. 5 might be appropriate. It has been observed that structure deformations of the square-planar gold(III) substrates toward the ligand arrangement adopted in trigonal bipyramids appear to be accompanied by enhanced reactivity (*7*).

If we apply the same type of arguments to complexes of platinum and palladium, in which distinct bond-making and bond-breaking maxima apply and square-pyramidal structures are quite common, a reaction profile like Fig. 6 may well be appropriate. The trigonal-bipyramidal structure is certainly not always a transition state, however, particularly when π-accepting ligands can adopt equatorial sites, so some reactions might well conform to the complicated profile shown in Fig.

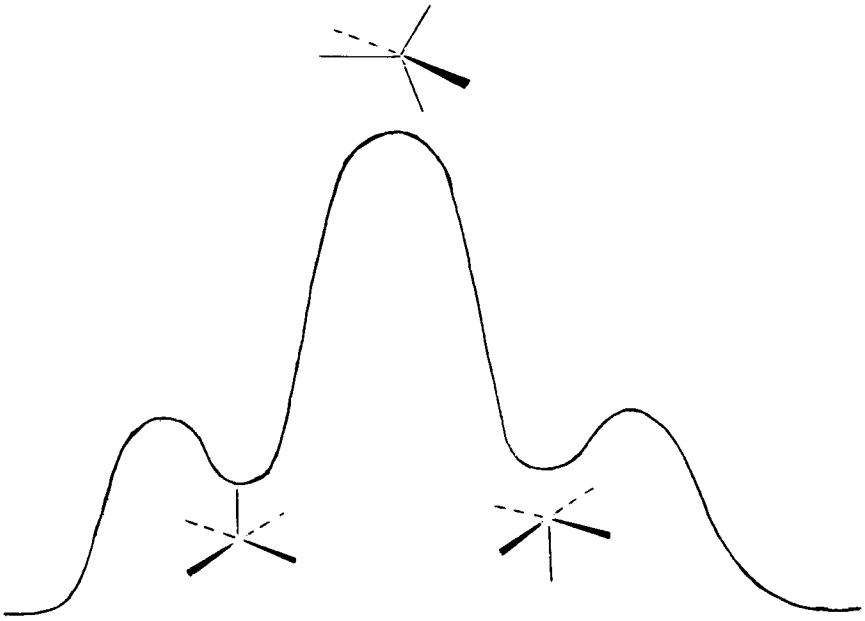


FIG. 5. Possible general reaction profile for gold(III) ligand replacements, dominated by a trigonal-bipyramidal transition state but allowing for square-pyramidal intermediates.

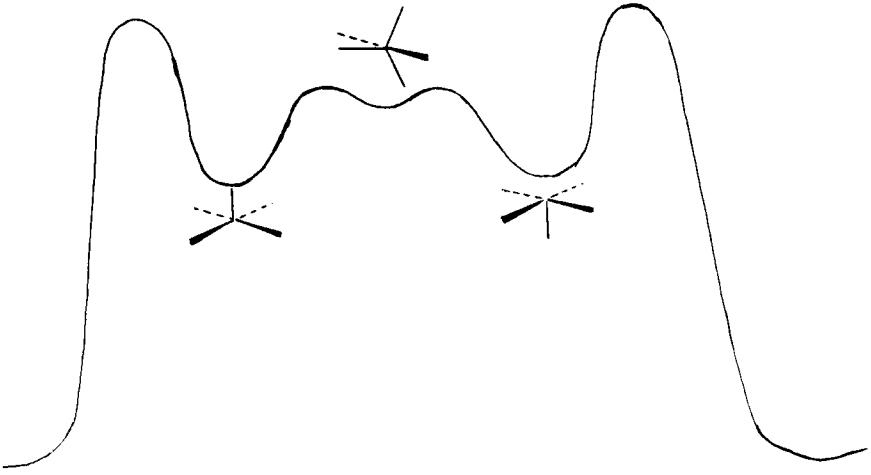


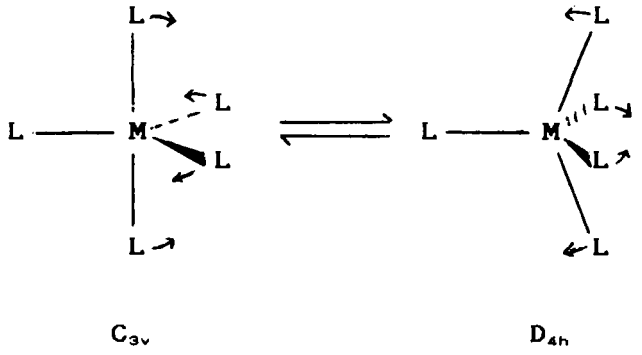
FIG. 6. Reaction profile likely to fit most palladium(II) and platinum(II) ligand replacements.

4. Figure 4 is probably the most appropriate form for associative ligand exchange at nickel(II) complexes, well represented by 5-coordinate structures of both types (*54, 55*).

Continuing this line of argument, we find that the predominance of trigonal-bipyramidal complexes of rhodium(I) and iridium(I) could well mean that Fig. 2, the traditional reaction profile, applies to the little-studied ligand-exchange reactions of 4-coordinate complexes of these elements. However, such conclusions, unsupported by other evidence, must remain tentative.

2. *Pseudorotation and the Stereoretentive Nature of Associative Ligand Exchange*

Structure changes of 5-coordinate compounds between square pyramidal and trigonal bipyramidal can lead to rearrangement of the ligands by the Berry pseudorotation process (Scheme 4). Such changes are clearly implicated along the reaction coordinates of the associative ligand-exchange reactions, yet nearly all the examples reported are stereoretentive, a situation that demands an explanation.



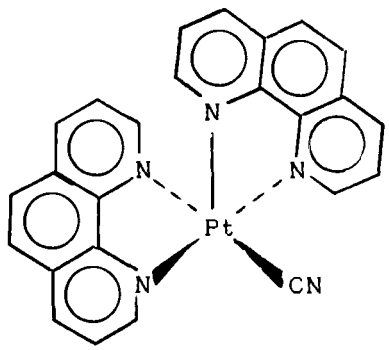
SCHEME 4

As we have noted, the geometry changes involved are symmetry allowed in molecules of d^8 ions (Fig. 3) (*46*), and since the motions that interconvert D_{3h} and C_{4v} are natural vibrations of the system, we should expect easy interchange between the two geometries. *Ab initio* MO calculations on $[RhH(C_2H_4)(CO)_2(PH_3)]$ found a very small intrinsic activation barrier to such motion (*60*).

Experimentally, several diamagnetic 5-coordinate complexes of rhodium(I), iridium(I), nickel(II), palladium(II), and platinum(II) have

indeed been shown by NMR spectroscopic observations to be fluxional (*61*). Determining the nature of the fluxionality can be problematical, however, since dissociative processes (essentially the reverse of the reactions under consideration) can also lead to site exchanges, and many of the dynamic processes observed can undoubtedly be explained in this way (*41, 62*). For example, chiral nitrogen ligand atoms in chelating $[PtCl_2(biL)]$ are stable but invert readily in 5-coordinate molecules (*63*). Spectroscopic evidence indicates that dissociation of the Pt—N bonds precedes N-inversion.

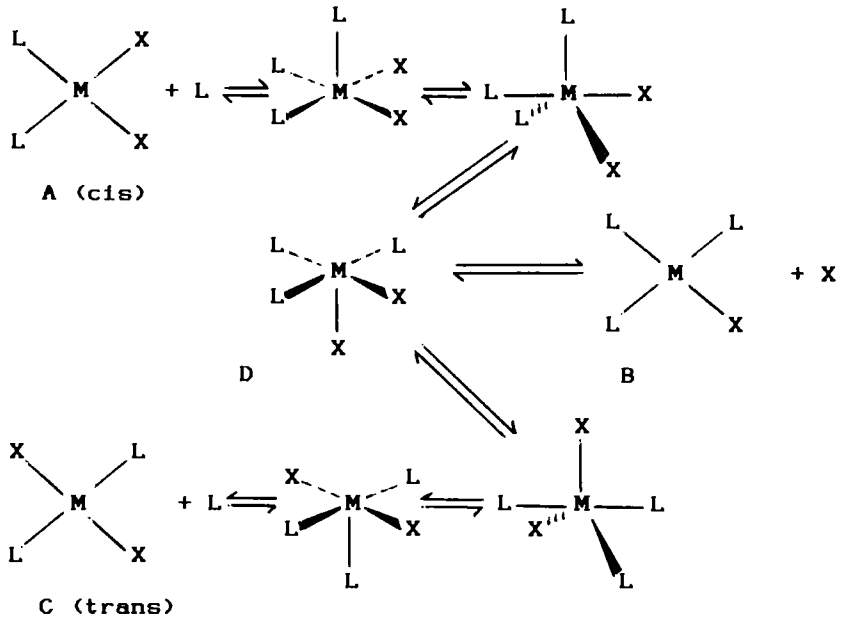
In a number of examples, however, retention of coupling above the high temperature limit provides clear evidence that the motion is non-dissociative (*49d, 64*). Pseudorotation, with activation barriers in the region of 20 to 50 kJ mol^{-1} when the ligands involved are tertiary phosphines (*64b*), is most likely. It can be noted that it is not necessary for all sites of the 5-coordinate molecules to be interchangeable, particularly when chelating ligands are involved (*65, 66*). For example, the phenanthroline nitrogen atoms of $[Pt(CN)(phen)_2]^+$ (**10**) appear equiv-



(10)

alent by NMR spectroscopy, but the CN group remains in the base of the square pyramid. Nevertheless, geometry changes through pseudorotation do take place at least at some of the more stable 5-coordinate d^8 complex ions, so isomerization during associative ligand replacements at square planar compounds should be expected.

Nucleophilic catalysis is known to lead to isomerization at square-planar molecules, but for many years it was believed that the only mechanism operating was consecutive displacement: two sequential stereoretentive ligand substitutions (Scheme 5: A → B, then B → C). A major argument in favor of this interpretation was the lack of examples of nonstereoretentive ligand replacements. It is now generally accepted, however, that pseudorotation can be, and sometimes is, the mechanism of such isomerization processes (*50*). The recognition that



SCHEME 5

structure D of Scheme 5 is common to both reactions of the consecutive displacement process means that the choice of which process operates depends on the depth of the potential wells along the reaction coordinate. This is illustrated by the way in which these are modified by the choice of solvent, shown in Fig. 7 for the isomerization of $[PtCl_2(PMe_2Ph)_2]$ catalyzed by PMe_2Ph (*67*). In polar solvents (A), ionic intermediates are favored and consecutive displacement operates. In nonpolar solvents (C) the 5-coordinate intermediate persists and pseudorotation predominates. The intermediate case (B) is perhaps best described in terms of weak bonding of the fifth ligand or ion pairing, for which there is evidence (*50*).

One case of nonstereoretentive ligand replacement has been reported (Scheme 6) (*68*). The possibility that this reaction proceeded by stereoretentive ring closure, followed by an isomerization, was eliminated since the trans isomer of the product was shown not to isomerize under the reaction conditions.

The question that must be asked is why there are not many more known reactions in which retention of geometry is not featured. There are probably a number of reasons. One explanation offered is that pseudorotation at d^8 species is slow compared with ligand replacement

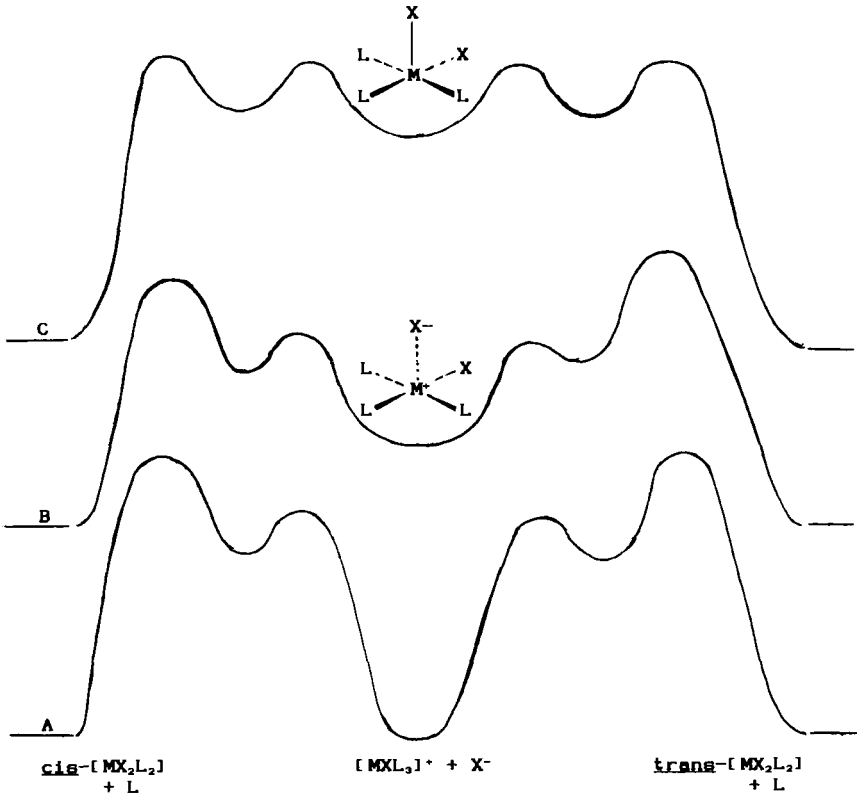
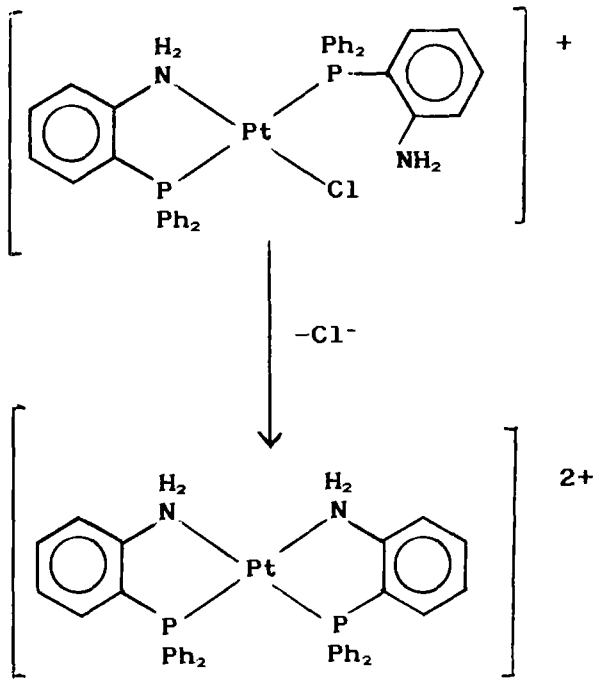


FIG. 7. Solvent dependence of L-catalyzed isomerizations of $[MX_2L_2]$. (A) Polar solvents favor ionic intermediates and consecutive displacement, (B) intermediate polarity allows ion pairing, and (C) nonpolar solvents with 5-coordinate intermediate and pseudorotation.

(*69*). Although this is undoubtedly so in many cases, particularly since many ligand replacement reactions are performed in polar solvents, the wide range in observed reaction rates and pseudorotation rates makes it unlikely that this can be a universal explanation. Nevertheless, this is necessarily the case in the many proven examples of nucleophile-catalyzed isomerization by the consecutive displacement mechanism (Scheme 5). Some other examples, often accepted as being stereoretentive, can be dismissed through lack of evidence. If an identical ligand is present cis to the group being displaced, then any inherent isomerization along the reaction coordinate could go unnoticed.

Most cases, however, are probably stereoretentive by design, though quite possibly unwittingly. Mechanistic experiments are usually ar-

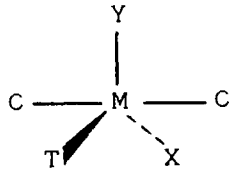


SCHEME 6

ranged to avoid complications such as competing reactions. One way of achieving this is to use complexes of chelating ligands, such as $[PdX(dien)]^{n+}$. Loss of the chelate ligand is rare (though not unknown) (*33*), so overall stereoretention is unavoidable.

The most important examples involve the choice of particular leaving groups X and trans ligands T to promote loss of X in preference to any other ligand. The essential requirement is that one particular trigonal-bipyramidal structure, with X, T, and the incoming nucleophile Y in the trigonal plane, should be energetically favored in preference to the alternatives (Structure **11**). It is not necessary that **11** should be an intermediate (though this has been suggested) (*45*); it can be a transition state provided it is more readily attainable than the

(11)



alternatives. One effect of the presence of chelating ligands is likely to be the restriction of the number of such structures that are accessible; chelates that subtend bond angles near 90° at the metal are unlikely to distort enough to allow 120° angles. Examples of fluxional molecules with chelating ligands in which not all the sites are interchangeable have already been noted (*66*).

The other classical way of ensuring that only one trigonal-bipyramidal structure **11** is favored is by careful choice of the trans ligand T. The trans effect of ligands first emerged as the propensity of certain ligands to direct substitution reactions to the replacement of the ligands opposite them. It has subsequently been defined as a kinetic phenomenon, comparisons being made of the rates of substitution of X, trans to T (*43*). Ligands of high trans effect result in fast displacement of X, usually ensuring that X is indeed the one ligand out of four to be replaced. The kinetic trans effect is known to operate through either or both of two mechanisms. In one, T can weaken the M—X bond; this is usually called the trans influence and can be observed in the ground state. In the other mode of operation, T lowers the energy of the 5-coordinate intermediate by a π-acceptor mechanism. The relationship of each to the preferred structure **11** is obvious. Weaker M—X bonds aid movement of X out of the square plane when Y approaches, and the trigonal plane of a trigonal bipyramid is known to be the most favorable site for π-accepting ligands (*43, 46*). Interestingly, a recent work has described the trans effect in terms of the angular deformability of the bonds in reaching the trigonal bipyramid (*45*).

Despite this, the presence of a ligand of high trans effect does not in itself always ensure that the opposite group is the one replaced. For example, a chloride is replaced by Me_2SO from both cis and trans isomers of $[PtCl_2(NH_3)_2]$ (*70*). The higher trans effect of Cl^- might be expected to cause loss of an NH_3 from the cis form. The point that is often overlooked is that it is the combination of properties of X, Y, and T that can lead to a particular structure being favored.

Noting that addition of the electron-withdrawing olefin maleic anhydride added to *trans*-$[IrMe(CO)(PMe_3)_2]$ to form a trigonal-bipyramidal molecule with the olefin sharing the trigonal plane with the two PMe_3 groups, and that the trigonal-bipyramidal product of PMe_3 addition had the (presumably incoming) PMe_3, CO, and Me occupying the trigonal plane, Crabtree and co-workers (*69*) compared these results with the geometry of H_2 additions to that and related substrates and formulated a set of predictive rules to rationalize the observations. The results were in general accord with previous theoretical studies (*46*). Three key interactions were listed. First, ligands that are good π-

acceptors tend to fall into the trigonal plane as the incoming nucleophile approaches from above the square: this stabilizes the filled d_{z^2} metal orbital, reducing its repulsive interaction with the nucleophile lone pair. CO is a good example of such a ligand. Second, good σ-donors in the equatorial plane enhance any back-bonding from the metal d_{xz} (or d_{yz}) orbital into π-accepting orbitals on the nucleophile. Third, if the ligands that adopt the equatorial positions are good π-donors, the metal p_z orbital is stabilized by them to a lesser extent, enhancing its use as an accepting orbital for the incoming nucleophile.

Pseudorotation at the 5-coordinate intermediate is most likely to occur when no particular trigonal-bipyramidal structure is of substantially lower energy than the others. Many known examples have similar or identical ligands in four or five of the sites. It should be noted also that even when fluxionality of the pseudorotation type has been detected, it does not follow that isomerization, or nonstereoretentive substitution, occurs. The complexes $[PtX_2L_3]$ (X are halides; L are phospholes), formed reversibly from *cis*-$[PtX_2L_2]$ and L, exhibit site exchange of the phospholes by both intra- and intermolecular routes in $CHCl_3$ or CH_2Cl_2 (*71*). Despite this, no cis-to-trans isomerization occurs. In this case the reason is believed not to be unfavorable geometry of the intermediates but unfavorable product stability. The reaction coordinate in Fig. 8 would account for this, the trans isomer being thermodynamically disfavored. (Excess L *does* cause isomerization in the palladium analogs).

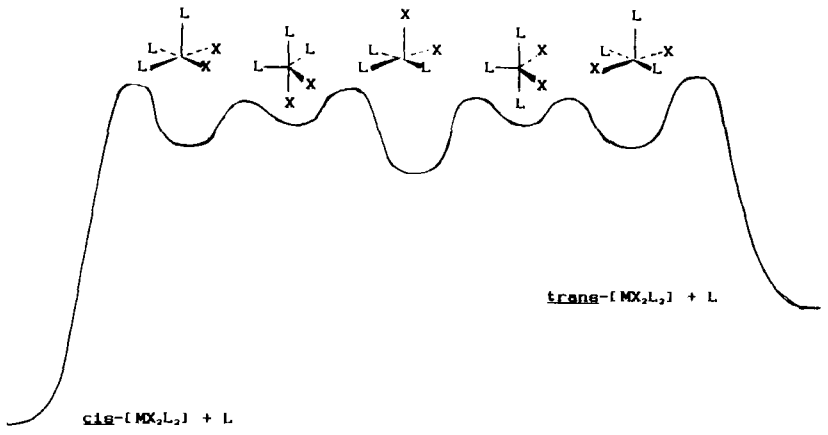
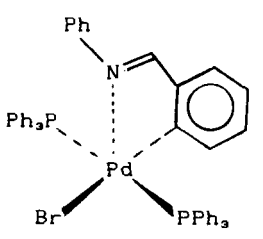


FIG. 8. Reaction coordinate for the interaction of *cis*-$[PtX_2L_2]$ and L (L is phosphole), allowing intramolecular fluxionality of the 5-coordinate species but no isomerization.

We close this section on a negative note, however. Despite the progress in rationalizing the course of reactions and comparing reaction profiles, it has to be admitted that it still does not appear possible to predict with any degree of certainty the relative energies of the 5-coordinate intermediates compared with their square-planar precursors. In isolated square-pyramidal compounds in the solid state, for example, the apical bond is almost always longer and weaker than the four basal bonds, and in some cases this fifth interaction is so weak that it hardly merits the description of a bond. *Trans*-[PdCl(phen)(PPh_3)$_2$]BF_4 is such a compound (*72*). The crystal structures of compounds **12** and **13** (*73, 74*) both reveal square-pyramidal coordina-



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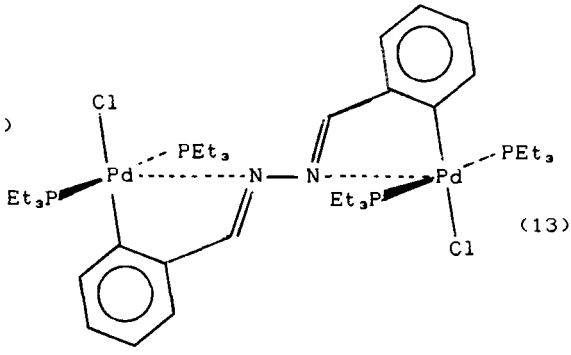


(13)

tion with long apical Pd—N bonds; but the closely related molecule *trans*-[PdCl(Azb)(PEt_3)$_2$] has no such interaction (*75*), so the presence of potentially chelating ligands is no guide to coordination number expansion. Similarly, the complexes [PtMeL{$HB(pz)_3$}] are known by ^1H NMR measurements to be 5-coordinate (and fluxional by a nondissociative mechanism) (*76*), but the same hydridotris(1-pyrazolyl)borate ligand remains bidentate, and the gold(III) is 4-coordinate in [$AuCl_2${$HB(pz)_3$}] (*77*). (This latter compound is also fluxional, but by nucleophilic attack of the uncoordinated pyrazolyl group replacing one of the chelated N atoms.)

Although this contrast in the bonding modes of $HB(pz)_3^-$ might be taken to reflect the increased tendency of Pt(II) toward 5-coordination compared with Au(III), many 4-coordinate complexes of Pd(II), Pt(II), Rh(I), and Ir(I) are known in which potentially chelating ligands do not utilize their full coordination. Examples include [$PtMe_2(dppm)_2$], [$MX_2(Ph_2PC_2H_4OC_2H_4PPh_2)$] (M = Pd or Pt; X = Cl, Br, I, or NCS), and [PdCl(tren)]$^+$ (*78*). Indeed, a review by Stoddart and co-workers (*79*) on the outer-sphere coordination of polydentate ligands of the crown-ether variety lists many instances in which such ligands inter-

act, usually by hydrogen bonding, only with the primary ligands of the square-planar molecules despite the availability and accessibility of the potential fifth coordination sites at the metal atoms.

III. Nucleophilic Attack Other Than at the Metal Atom

The hydrogen bonding between ligands in the primary coordination sphere and other nucleophiles previously mentioned is only one type of interaction involving nucleophilic attack elsewhere than at the metal atom of square-planar complexes. This vast subject encompasses much diverse chemistry, ranging from reactions of coordinated ligands to solvation of molecules. Much of it is not directly relevant to the subject under consideration, but a few interactions can exert a major influence on ligand-exchange processes. A case in point is the migration of nucleophiles from a ligand to the metal atom. Often this is accompanied by a counterbalancing migration in the opposite direction. Reference (*3*) lists some possible examples though they are mechanistically not well characterized. In section IV,C, examples of nucleophilic attack at ligands leading to reduction of gold(III) are given. Yet another category is conjugate base formation, reactions that might be regarded as nucleophilic attack of base at a ligand proton. The reactions can be viewed as pre-(ligand substitution)-reaction modifications to the substrate, which can profoundly affect its reactivity. The evidence for, and consequences of, CB formation at square-planar complexes is briefly covered here. Further comment on the solvation of these complexes is deferred until the subject of electrophilic attack at the metal atoms has been explored.

A. The Conjugate Base Mechanism

At square-planar complexes conjugate base (CB) formation has received relatively little attention compared with octahedral molecules. The reasons are probably that it does not produce spectacular rate enhancements and that proving the operation of this route is more difficult. Nevertheless, more and more examples are being recognized, and they fit a general scheme of reaction types at these molecules.

Some of the earliest and best examples arise from the chemistry of gold(III), presumably a consequence of the higher formal charge increasing ligand acidity. $[AuCl(dien)]^{2+}$ readily loses a proton at high pH (*80*), and its conjugate base has even been isolated and examined crystallographically (*81*). The missing proton is confirmed as originat-

ing from the central, secondary nitrogen; and although the trans influence of the resulting amide is greater than that of its conjugate acid precursor, its reactivity towards Cl^- replacement by Br^- was reduced (the charge of the new complex is lower). When some or all of the hydrogens on the terminal nitrogen atoms of dien are replaced by alkyl groups, the acidity of the complexes increases further; in these examples the conjugate bases are more reactive than their substrates (*82*). The substitutions at the conjugate bases appear to be associative in nature, resembling the usual mechanism, with the direct nucleophile-dependent pathway predominating. A problem was that the operation of a substitution mechanism proceeding by ring opening of the chelate (conjugate base) ligand could not be completely ruled out, casting some doubts on the values of rate constant comparisons. There was no compelling evidence, however, for the operation of a dissociative route of the type that proceeds with great facility at conjugate bases of octahedral molecules (*83*). A recent case involves ammonia exchange at $[Au(NH_3)_4]^{3+}$ at high pH, followed by ^{15}N NMR spectroscopy (*84*).

Moving to palladium complexes, related early studies on $[PdX(Et_4\text{-dien})]^+$ also indicated the possible operation of a CB mechanism. Hydroxide ions reacted differently to other nucleophiles at these sterically hindered molecules in showing a distinct bimolecular (k_2) dependence as well as a solvolytic pathway (*85*). This was unexpected because OH^- is known to be a poor nucleophile in these systems, and it led to the proposal of the conjugate base contribution. The ions $[PdX(Et_4Me\text{-dien})]^+$, which have no acidic protons, did not show this behavior. The CBs reacted some 30 times faster than their precursors (a reactivity enhancement somewhat less than their gold(III) counterparts with the same ligands), again probably by an associative route.

Normal associative ligand substitutions at these sterically hindered compounds are dominated by the solvento (k_1) route, and scope for forming the CB of aquo intermediates at high pH [(Eq. (16)] was recognized as a potential mechanistic complication (*86a*).

$$[Pd(OH_2)(Et_4\text{-dien})]^{2+} + OH^- \rightleftharpoons [Pd(OH)(Et_4\text{-dien})]^+ + H_2O \qquad (16)$$

Iodide anation studies showed that substitution at this hydroxide CB did not in fact occur, water being a better leaving group than OH^-. Complications of the kinetics at high pH were more likely to be due to proton extraction from the Et_4-dien (*86*).

Interesting results were obtained when substitution reactions of $[PdCl(triL)]^+$ at high pH were performed at high pressure (*87*). When triL was Me_5-dien, no $[OH^-]$ dependence was found, but when triL

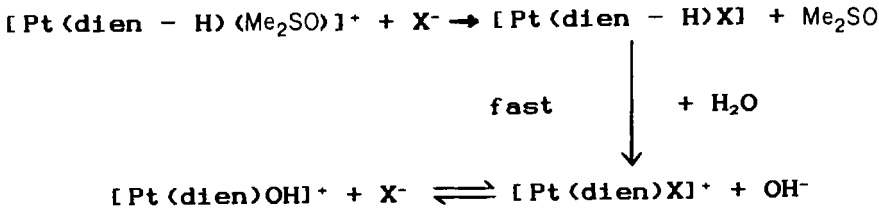
contained acidic hydrogen, as in Me_4-dien or Et_4-dien, a distinct hydroxide dependence of the type previously assigned to conjugate base formation was apparent. Interpreted in terms of the usual preequilibrium with the CB followed by rate determining substitutions [(Eqs. (17) and (18)], the contributions of the second step to $\Delta V^{\ddagger}$ were +3 and −16 $cm^3\ mol^{-1}$ for Me_4-dien and Et_4-dien, respectively.

$$[PdCl(triL)]^+ + OH^- \rightleftharpoons [PdCl(triL - H)] + H_2O \quad (17)$$

$$[PdCl(triL - H)] + H_2O \rightarrow\rightarrow [Pd(OH)(triL)^+ + Cl^- \quad (18)$$

Although the latter contribution fits the usual A mechanism nicely, the former is better interpreted in terms of an interchange mechanism.

Turning now to platinum(II) complexes, we find a picture of similar complications to the kinetics at high pH, some of which can be assigned to CB formation. Thus, although hydroxide dependence in the substitution of *cis*-$[Pt(NH_3)_2(SMe_2)_2]^{2+}$ is probably not due to ammonia deprotonation, anomalies in the displacement of Me_2SO from $[Pt(en)(Me_2SO)_2]^{2+}$ might be due to deprotonation (*88, 89*), and $[Pt(dien)(Me_2SO)]^{2+}$ certainly reacts with base by deprotonation (*89*). ^{13}C NMR spectroscopy clearly shows the removal of the proton from the 3-nitrogen atom, a process that can also be followed spectrophotometrically. Reactions of this conjugate base then proceed in two steps, each without a significant solvento contribution (Scheme 7). In this case, rate constants for the reactions of the CB are about half those for the dicationic acid (*89*).



SCHEME 7

The general rarity of the operation of the CB mechanism at Pt leads to the suspicion that the ligand Me_2SO in some way enhances the substrate acidity, and another example fits this speculation. OH^- substitution at [Pt(amino-acid)Cl(Me_2SO)] is enhanced when the amino acids are glycine or sarcosine, but not *N,N*-dimethylglycine (*90*). The CB reactions appear to proceed by ring opening, recalling earlier suspicions about Au(III) and Pd(II) dien complexes.

Finally, bearing in mind the importance of the aquo intermediates $[M(dien)(OH_2)]^{2+}$ (M is Pt or Pd) in so many of the mechanistic studies cited, the prospect of the hydroxo conjugate bases leading to dimerization [(Eq. (19)] was seen as a disturbing possibility.

$$[Pt(OH)(dien)]^+ + [Pt(OH_2)(dien)]^{2+} \rightleftharpoons [(dien)Pt(\mu\text{-}OH)Pt(dien)]^{3+} + H_2O \quad (19)$$

Fortunately, the dimerization constant has been calculated (*91*), and it is apparent that only small amounts of the dimer are formed and only near pH 6. At lower pH, the aquo complex dominates, and at higher values the monomeric hydroxide prevails.

In total, although it is likely that more examples of the operation of CB reaction routes will be found, their importance is limited. Like their precursors, they appear to react by A or I_a mechanisms and presumably conform to similar reaction profiles (no structural information concerning possible intermediates is available). The lower CB charge is probably counterbalanced by changes in the trans effect of the CB ligand atom (these are trans to the leaving group in many of the examples known). The result is that overall reactivity is not changed dramatically. It is worth noting that the deprotonated complexes are π-donors and should therefore be trans directing. Most examples examined so far have been of chelate complexes, however, so this facet of the intimate mechanism has yet to be tested.

IV. Structure Changes Prior to Ligand Exchange

When examining the intimate mechanism of a ligand replacement reaction, particularly from kinetic data, a constant problem is that unimolecular changes in the nature of the substrate could precede the substitution step. One geometry change in particular must be considered for square-planar complexes, that of conversion to tetrahedral intermediates, an example of polytopal isomerization. Of the d^8 ions under consideration, only nickel(II) complexes readily attain a tetrahedral configuration. The conventional explanation for the change from octahedral coordination to lower coordination numbers as the transition series is traversed from left to right is that some of the increasing number of electrons would be forced to populate the destabilizing O_h σ^* orbitals. Square-planar geometry at d^8 complexes allows spin pairing of electrons in bonding and nonbonding orbitals, and this predominates at the expense of some steric strain for all the heavier ions. With first-row nickel(II), however, the energy consequences of populating σ^*

are less and steric strain greater, so tetrahedral ligand arrangements are quite common. Energy differences between planar and T_d forms can be small, and in some cases interconversions are rapid.

A. Nickel(II) Complexes

Some complexes exist in both square-planar and tetrahedral forms. Most of those that do this can be assigned to one of two families. The first contains compounds of general formula $[NiX_2L_2]$, where X are halides or pseudohalides and L are tertiary phosphines, PR_3. Several such compounds have been isolated in the solid state in both trans square planar and tetrahedral forms. The former are diamagnetic and have zero dipole moments, whereas the latter typically have magnetic moments about 3.1 μ_B and have large dipole moments. Examples include $[NiX_2(PPh_2\{CH_2Ph\})_2]$ (X = Cl, Br, or I), $[NiBr_2(PPh_2\{allyl\})_2]$ (*92*), $[NiBr_2(PPh_2R)_2]$ (R = Et, Pr^i, Bu^n, Bu^s, or Bu^i) (*93*), $[NiCl_2(PPh_2Cy)_2]$ (*94*), $[NiCl_2(PPh_3)_2]$ (*94–96*), and $[NiBr_2(dppe)]$ (*97*). The fine energy balance found in some cases is well illustrated by the triphenylphosphine compound, in which solvating molecules of dichloroethane are enough to cause the change from the tetrahedral to the planar form, and by $[NiBr_2(PPh_2\{CH_2Ph\})_2]$, in which molecules of both geometries share the unit cell (*99*).

It is thus not surprising that many compounds in this family reveal the presence of both isomers in solution (*94, 99–104*). They have been detected in a number of ways, including magnetic moment determinations (which reveal values between those expected for the two extremes) (*100–104*) and recognition of the presence together of UV/vis spectroscopic absorption bands typical of both isomers (*94, 99, 101, 102*). Of greatest value, however, has been ^1H NMR spectroscopy (*94, 99, 101–104*). The extremely large chemical shifts found for the paramagnetic tetrahedral molecules allow straightforward recognition and measurement of the amount of each isomer, even when averaged spectra are obtained as a result of rapid equilibria between the two allogons.

The second set of compounds often found as both square-planar and tetrahedral isomers in solution have the general formula $[Ni(biL)_2]$. (biL are substituted salicylaldiminates (*105–113*), β-ketoiminates (*111, 114–117*) or their sulfur or selenium analogs, and aminotropone iminates (*118*) and their related pyrrole-2-aldiminates (*119*).) Unlike the $[NiX_2L_2]$ complexes, none of these has so far been made to crystallize in both forms (though there is some evidence that heating the

planar isomers of some molecules may convert them to tetrahedral) (*115*).

Detection and measurement of the two isomeric forms in solution again is most convenient by proton NMR spectroscopy, in which the isotropic proton hyperfine contact shifts in the paramagnetic tetrahedral isomers make recognition easy, and the amount of the shift reflects the proportion of paramagnetic species in solution (*107, 110–116, 119*). Other methods, including UV/vis spectroscopy (*106, 112, 114, 116, 118, 119*), magnetic moment determination (*105, 106, 109, 110, 115, 116, 118, 119*), dipole moment measurement (*106, 109, 114*), and IR spectroscopy (*118*), have also been employed.

A variation on these latter compounds are the complexes $[Ni\{Et_2P(S)NR\}_2]$, which differ from the other chelates in that 4-member rings are involved (*120*), but they exhibit the same properties, tetrahedral/planar equilibria having been detected in solution (by ^{31}P NMR spectroscopy and magnetic moment measurements). For all of these compounds, bulky ligands favor the tetrahedral structure, but strong ligand fields favor the planar form and can predominate. Thus, $[NiCl_2(PCy_3)_2]$ is trans square planar despite the high steric demand of the two tricyclohexylphosphine ligands (*121*).

The higher dipole moments of the tetrahedral isomers promote the expectation that polar solvents should shift the equilibria towards that side. Although this appears to be the case with the phosphine complexes $[NiX_2L_2]$ (*94, 102*), the situation is less clear-cut with the chelating ligand complexes $[Ni(biL)_2]$. Problems are sometimes encountered in very polar or strongly coordinating solvents since conversion to octahedral molecules is also energetically feasible for nickel(II). Pyridine, for example, is known to coordinate to some nickel(II) Schiff base complexes, giving paramagnetic octahedral molecules (*122*). With certain aminotropone iminato complexes, on the other hand, pyridine lies between CCl_4 and CS_2 in its solvent effect on the planar/tetrahedral equilibrium position, so it seems that in these compounds, at least, direct solvent bonding to the nickel ion does not occur (*118*).

Whatever the nature of the interactions, these planar isomers appear to be solvated to a greater extent than tetrahedral ones, some interactions presumably being between solvent and the ligands since raising the temperature generally moves the equilibrium position toward the tetrahedral isomers (*101, 106, 109*). (Curiously, when the donor nitrogen substituent is Bu^t, the opposite can be the case, higher temperatures favoring the planar form (*109*). Possibly, the size of this substituent group lowers the solvation of the planar molecules.)

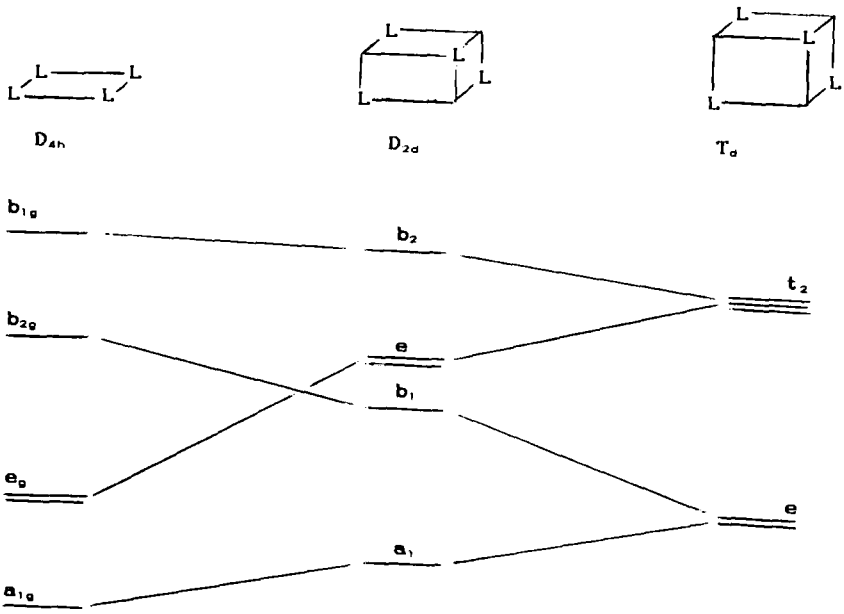


FIG. 9. The digonal twist motion interconverting square-planar (D_{4h}) and tetrahedral (T_d) structures by D_{2d} and showing orbital correlations.

The next point to consider is how the two isomers interconvert. From the possible mechanisms, the most obvious conceptually is the intramolecular motion shown in Fig. 9, often referred to as a digonal twist, which leads to a direct change of ligand positions. The problem here lies in the fact that such a motion is forbidden.

Figure 9 also plots the orbital correlations as the change progresses (*123, 124*). It can be seen that for d^8 complexes, not only must a spin be reversed, but an electron must move from one orbital to another. Thus, the transition is forbidden on the grounds of both spin and orbital symmetry. The ground state of the tetrahedron correlates with an excited state of the square plane (*125*). This in turn means that square-planar isomerizations and tetrahedral inversions, each of which depend on the operation of two of these steps, are not thermally allowed processes. (They are, however, photochemically allowed.)

An inherent weakness in applying this reasoning to the chemistry of transition metal complexes, however, is that it does not take energy considerations fully into account. The Woodward–Hoffmann treatment of organic systems in reality compares two pathways, allowed

and disallowed; and the energy differences between the two are usually large (*126*). For transition metal complexes, such comparisons are not usually appropriate, and reaction rates depend more on changes in the binding energies of reactants, transition states, and products, and in liquid field stabilization energy (LFSE), than in contributions from orbital symmetry conservation (*125*). Applications of such orbital symmetry correlations, though extremely valuable in many cases, must therefore be applied with care and conclusions drawn cautiously.

A second plausible possibility for interconverting square-planar and tetrahedral isomers is catalysis by solvent coordination. Association of two or more 4-coordinate molecules could also lead to geometry change. Such associations are known for some of the $[Ni(biL)_2]$ complexes under certain conditions. They produce paramagnetic 5- or 6-coordinate species, which can complicate the interpretation of magnetic methods to determine the amount of tetrahedral isomers in solution (*105, 106, 111, 114, 122*). Finally, dissociation of a ligand should also be kept in mind as a possible route to geometry change. Dissociation reactions are discussed in the next section.

The most direct information on the isomerization processes has been gained from NMR studies of the phosphine complexes $[NiX_2L_2]$. The rates of some of the planar-to-tetrahedral interconversions are similar to the NMR time scale. In these cases, separate signals can be observed for the two isomers at low temperatures, but at the high-temperature limit, averaged resonances are seen (*102–104*). These observations allow reaction rates and activation parameters to be calculated.

The isomerization rates are independent of solution concentrations, indicating that first-order kinetics apply and that molecular associations are not involved (*103*). The digonal twist motion seems most likely to be involved. Since the studies were performed in solvents of relatively poor coordinating ability ($CDCl_3$ and CD_2Cl_2), it seems unlikely that replacement of a ligand by solvent would contribute significantly to the process, though the lack of a suitable magnetic isotope of nickel to detect coupling above the high-temperature limit means that such dissociative processes could not rigorously be ruled out.

All of the relevant bis-chelate complexes, $[Ni(biL)_2]$, undergo the interconversion faster than the $[NiX_2L_2]$ examples discussed earlier. As a consequence, the low-temperature limit has not been reached in NMR studies of these compounds, and rate data (other than minimum limits) are lacking. Nevertheless, the concensus is that these, too, isomerize by a first-order intramolecular twist.

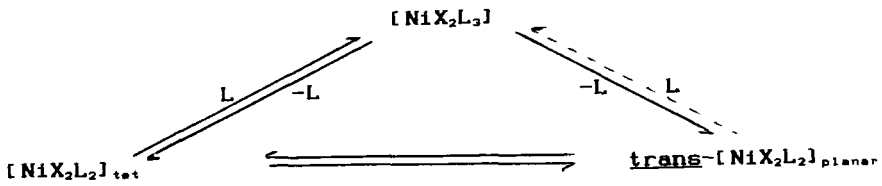
Having established that tetrahedral geometry is attainable from square-planar complexes (at least of nickel(II)), we consider the next

question, whether ligand replacements can occur at the tetrahedra (and by a route not involving prior isomerism to square-planar geometry!). The structure correlation studies of 5-coordinate nickel(II) complexes (Scheme 3) (*55*) clearly implicate a possible associative ligand exchange initiated from a tetrahedral structure. The product, of course, could be planar or tetrahedral. Evidence for the operation of just such a system comes from studies on some of the tetrahedral/square planar interconverting compounds just discussed. Addition of excess $PMePh_2$ (L) to $[NiBr_2(PMePh_2)_2]$ accelerates the planar/tetrahedral interconversion by a second-order process with rate proportional to [L], (*103, 104*). Moreover, the ^1H nuclear magnetic resonances of the planar and tetrahedral complexes and the free phosphine all average at high temperatures, suggesting that the acceleration is connected with a separate ligand exchange process. Thus, the overall rate k of the tetrahedral/planar interchange is given by Eq. (20).

$$k = k_t + k_2[L] \tag{20}$$

For $[NiBr_2(PMePh_2)_2]$, the ligand-independent part, k_t, is 60 sec^{-1} at $-60°C$, and k_2 is $(3 \pm 2) \times 10^5$ l mol^{-1} sec^{-1}. It therefore appears that the isomerization is intramolecular and probably proceeds through the direct twist mechanism of Fig. 9; but additional pathways involving associative ligand exchange also contribute if excess ligand is present. (The potential of a strongly donating solvent to effect this process should be kept in mind, though no cases have been reported).

The rates of exchange of the phosphines are very dependent on steric demand, however, and slow markedly on going from $PMePh_2$ with $[NiBr_2(PMePh_2)_2]$ to PPh_3 with $[NiBr_2(PPh_3)_2]$ (*103*). Excess $PCyPh_2$ does not have an accelerating effect on the polytopal isomerization rate of $[NiBr_2(PCyPh_2)_2]$ (*104*). Significantly, it was observed that free $PMePh_2$ not only accelerated the planar/tetrahedral interconversion but displaced the equilibrium position toward the planar geometry (*104*). Although it is possible that this could be caused by the change in the solvent medium, the authors suggested that the equilibrium shift reflected dominant formation of a 5-coordinate intermediate from the tetrahedral isomer rather than from the planar form, but which could decay to both planar and tetrahedal molecules as depicted in Scheme 3. Provided that the ligand exchange is faster than the intramolecular planar/tetrahedral interconversion, the result would be the observed acceleration of the interconversion accompanied by the equilibrium shift toward planar. Scheme 8 summarizes this.

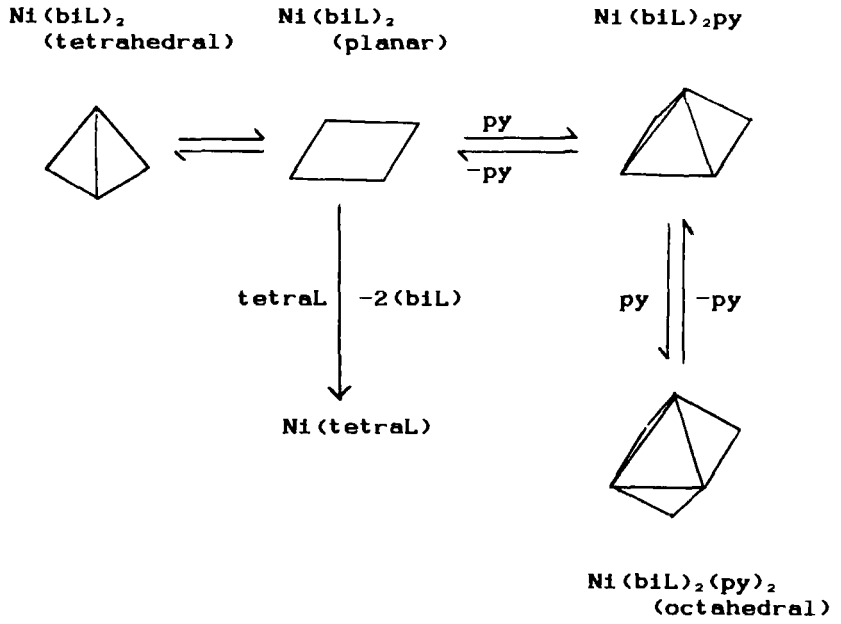


SCHEME 8

It does appear, then, that an intramolecular geometry change could in some cases enhance ligand exchange at square-planar nickel(II) complexes. The relative rates of reactions of the tetrahedral isomers is not readily predictable, however. As a counterexample to the $[NiX_2(PMePh_2)_2]$ case discussed, complexes of the chelate ligands *N*-alkylsalicylaldiminate, *N,N*-dialkyl-2-aminotropone-iminate, and *N*-alkylbenzoylacetoneiminate can be quoted. These are also involved in rapid planar/tetrahedral equilibria in acetone or methanol solution, for which equilibrium constants were determined (*127*). Correlation between these constants and the rates of ligand replacement of the chelates by *N,N'*-salicylideneethylenediamine or acetylacetonate, along with the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, indicated that the ligand entered by the usual associative pathway but that only the planar isomer was involved: the tetrahedral isomer was inert toward substitution. In strongly donating solvents such as pyridine, 5- and 6-coordinated (octahedral) species were produced, and similar correlations revealed these to be substitution-inert also (*127*). Scheme 9 summarizes these conclusions, which are supported by a similar study on the bis(*N*-alkylsalicylaldiminato)nickel(II), $[Ni(R\text{-}sal)_2]$, where R = $CH(CH_2OH)CH(OH)Ph$, $CH_2MeCH(OH)Ph$, or CH_2CH_2Ph. The latter complex was diamagnetic and square planar whereas the former two tend to octahedral coordination by bonds from the hydroxy groups of R (*128*). The ratios of the species present in acetone solutions were determined by UV/vis spectroscopy and compared again to the ligand replacement rates and activation parameters. Here, too, an associative ligand substitution process operating only at the square-planar form was found.

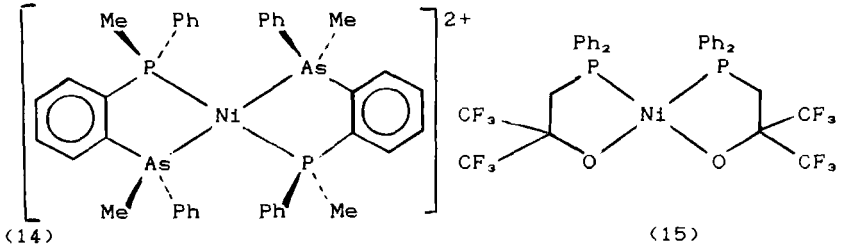
Although the substitution inertness of these tetrahedral isomers might be a consequence of the chelation, it is more probable that either situation, preferred nucleophilic attack at the planar or at the tetrahedral isomers, might prevail depending on the nature of the substrates, nucleophiles, solvents, and so on.

Even when planar forms are known to be more reactive (to substitution) than tetrahedral, the possibility should be kept in mind of isomerization by a short-lived tetrahedral intermediate to a more reactive



SCHEME 9

isomer of planar geometry prior to reaction. Cis–trans isomerism of square-planar nickel(II) complexes proceeding through digonal twists are indeed known. Geometry change of the cation **14** is rapid at 394 K (NMR time scale) in MeCN-d_3, as evidenced by a single, broad Me resonance. The process is independent of concentration, and no redistribution of bidentate ligands takes place in mixed samples, so an intramolecular digonal twist through tetrahedral nickel is implicated.



At lower temperatures, separate signals for both cis and trans isomers can be recognized (*129*). The nickel complex **15** also exists as a mixture of cis and trans square-planar isomers (*130*), and these, too, interconvert rapidly in the NMR tube at higher temperatures. This reaction also is first order in complex and is unaffected by free ligand.

Another type of fluxionality related to cis–trans isomerization at planar nickel(II) has also been assigned to tetrahedral/planar interconvertions and merits consideration. The cations $[NiHL_3]^+$ (L are PEt_3 (*131*) or P(O-*p*-tol)$_3$ (*132*) are fluxional above 273 K (by NMR spectroscopy in acetone-d_6 or CD_2Cl_2, respectively), the three phosphine ligands appearing equivalent. In these examples, retention of coupling between the hydride and phosphorus atoms confirms that the process is intramolecular. The anticipated low-temperature limiting spectra become clear at about 203 K. Despite the indication of intramolecular reactions, the entropies of activation are negative with values similar to those of associative bimolecular processes. Competing reactions involving ligand loss (*131*) and association with free ligand (to fluxional 5-coordinate intermediates) (*131, 132*) do occur but are slow compared with the intramolecular processes, and the authors postulate rearrangement by tetrahedral intermediates. The negative entropies of activation, which, at -104 J K^{-1} mol^{-1}, is especially large for L = P(O-*p*-tol)$_3$, might, it was suggested, result from a tightly bound ion pair (the counterion was trifluoroacetate) at the transition state. We see later that alternative interpretations are possible, but meanwhile such a possibility can only strengthen the case for remaining cautious about the intervention of intramolecular geometry changes prior to associative ligand exchange, or even during the approach of the nucleophile.

B. Heavier d^8 Ion Complexes

The next question to be asked is whether similar complications of rapid geometry change could prevail with the heavier d^8 ions. Although deviations toward tetrahedral geometry have been reported for a number of complexes, for example of rhodium(I) (*133*) and palladium(II) (*134*), the complexes are diamagnetic and better merit the description of distorted square planar than distorted tetrahedral. Moreover, there is no information about the effects such distortions may have on their reaction rates, though it has been noted that for gold(III) complexes small deviations away from planarity toward the ligand arrangement adopted at trigonal-bipyramidal intermediates can accelerate nucleophilic substitution (*7*).

There are, in fact, no well-authenticated examples of nonphotochemical reactions of square-planar complexes of the heavier elements in which a tetrahedral geometry is attained. Despite this, a few intramolecular geometry changes have, tentatively, been assigned to this mechanism. The fluxional behavior of $[RhH(PPh_3)_3]$, a molecule obviously related to the $[NiHL_3]^+$ cations already met, has been so ex-

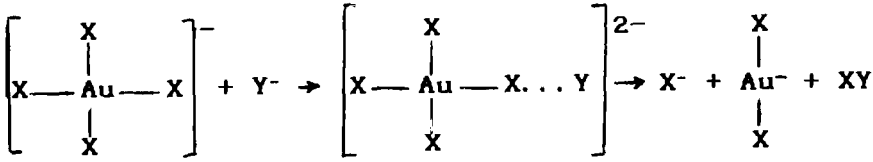
plained (*135*), but in descriptions of the fluxionality of the related complexes $[RhH(PEt_3)_3]$ and $[RhH(PPr^i_3)_3]$ (*136*), the authors point out that since species such as $[RhCl(PPh_3)_3]$ are not fluxional, a different mechanism that depends on the unique properties of the hydride ligand is more likely. ($[RhCl(PPh_3)_3]$ should more easily attain a tetrahedral configuration on both steric and electronic grounds.)

Rapid exchange of the phosphine ligands (on the NMR time scale) of *cis*-$[Pt(GePh_3)(HgGePh_3)(PPh_3)_2]$ has also been assigned to an intramolecular digonal twist mechanism (*137*). Retention of coupling of the phosphorus atoms to both ^{195}Pt and ^{199}Hg confirm the nondissociative nature of the process, which is slowed sufficiently to observe the low-temperature limiting spectrum at about $-50°C$. As we shall see, however, there are alternative explanations for these phenomena, among complexes of the heavier elements at least, and the achievement of tetrahedral geometry from planar complexes of these elements can be regarded as an unlikely process.

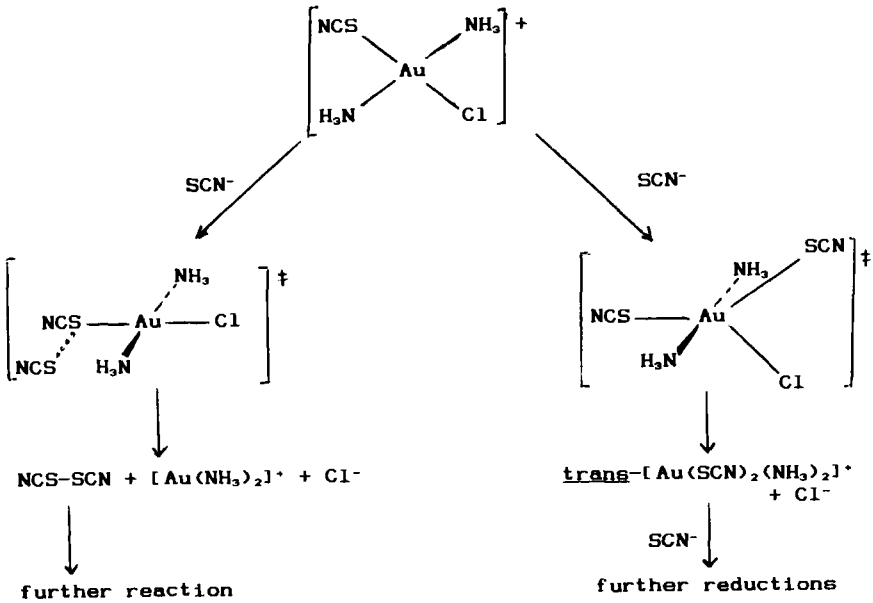
C. Change of Oxidation Level

While we consider the possible effects of geometry change on reaction rates, it is worth noting that reversible changes of oxidation level could similarly mask vital information concerning the intimate mechanism. The stability of the +2 oxidation level for Ni, Pd, and Pt compounds means that such a pathway is unlikely to operate readily at these elements. With gold(III), on the other hand, a few substitution reactions have been encountered in which the ready reduction to gold(I) caused by nucleophilic reducing agents is a real complication (*7*).

The reductions are usually bimolecular and are believed to take place by electron transfer at an activated complex resulting from attack of these nucleophiles at a coordinated ligand. Iodide, bromide, and thiocyanate commonly behave in this way. Scheme 10 outlines the interactions (*138a*). Quite often, ligand substitutions precede or compete with the reduction processes, which might then take place at several substitution products (*138*).



Scheme 10



SCHEME 11

The substitutions themselves generally result from direct attack, contributions from the solvento pathway being negligible. Thus, when the reduction and substitution are of similar rates, the kinetic pathways can be difficult to differentiate. Such a system was described recently for the reaction of *trans*-$[AuCl(SCN)(NH_3)_2]^+$ with thiocyanate (*139*). The two pathways, shown in Scheme 11, diverge from differing sites of attack by SCN^-: at Au(III) or at coordinated SCN^-. The similarity of the reduction route to a reductive elimination process is striking and suggestive of further complications to the associative ligand exchange reaction. Although many reductive eliminations from square-planar d^8 complexes are preceded by ligand dissociations (*140*), some are known to follow ligand associations (*141*). It seems likely that closer understanding of the links between the processes will emerge from future work.

V. Dissociative Reactions

Despite the long-standing and overwhelming dominance of associative pathways in ligand replacement reactions at square-planar mole-

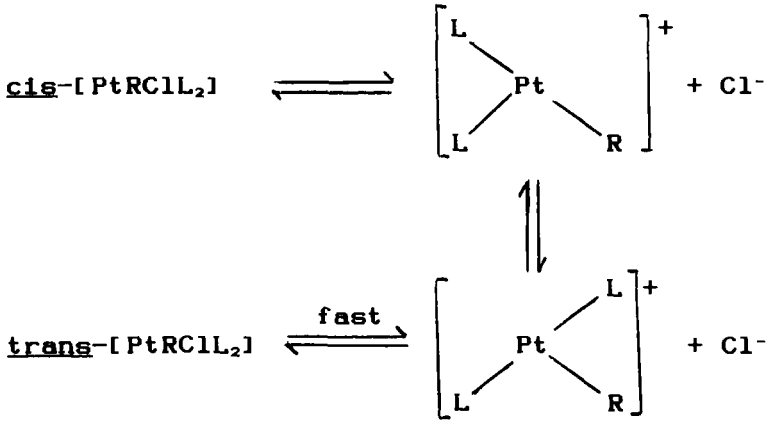
cules, chemists have constantly been alert for dissociative routes operating at these complexes. Over the years, several examples have emerged though the subject is not without controversy.

The earliest claims centered on complexes of the types $[PdX(Et_4\text{-}dien)]^{x+}$ and $[PtX(dien)]^{x+}$. The anomalous reactivity of certain nucleophiles, including hydroxide, and the observation of a two-term rate law for anation reactions ($X = H_2O$) led to the postulate that when associative ligand replacement was very slow, then a dissociative reaction path could be seen to compete. Because of this, these sterically hindered molecules were often termed "pseudooctahedral." This early evidence has been reviewed (*6*, *12*), and it is now known that these apparent anomalies can be interpreted instead in terms of the usual associative pathways. For example, the original detection of a two-term rate law for the anation of $[Pt(OH_2)(dien)]^{2+}$ is probably a consequence of examining the reaction as it approached equilibrium (*142*).

A. Dissociative Isomerizations

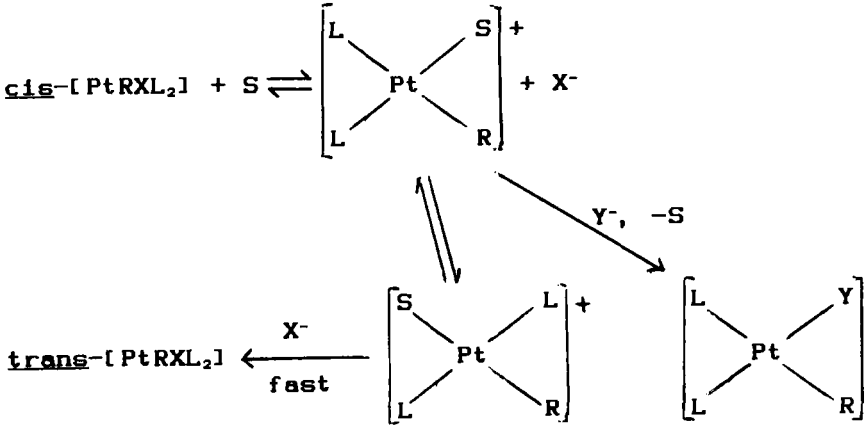
More persistent evidence for the operation of dissociative reaction pathways has emerged from certain isomerization studies (*50*). Claimed examples include the loss of sulfoxide ligands from *trans*-$[PtCl_2(S\{O\}R_2)_2]$ (*143*) and the loss of PPh_3 from $[AuMe_2Et(PPh_3)]$ (*144*), followed by geometry changes of the resulting T-shaped intermediates. Most examples, however, involved cis-to-trans isomerizations of $[PtClR(PEt_3)_2]$, where R are often bulky ortho-substituted aryl groups. Thus, the isomerization of *cis*-$[PtCl(o\text{-tolyl})(PEt_3)_2]$ in MeOH or EtOH was found to be first order and was not accelerated by free PEt_3 (*145*). Later studies by Romeo and co-workers determined that the rate of isomerization was some 100 times smaller than the rate of solvolysis, and the former process showed a positive value of $\Delta S^{\ddagger}$, in contrast to the latter which had a value of -136 J K^{-1} mol^{-1} in keeping with an associative process (*146a*). The isomerization showed mass-law retardation by excess $[Cl^-]$, and the dissociative pathway of Scheme 12, involving geometry change between two T-shaped intermediates, was proposed to account for these data. Similar studies on many related compounds fitted the same interpretation; and when R was mesityl, the isomerization and solvolysis rates were identical (though $\Delta S^{\ddagger}$ was negative for both reactions), leading to the conclusion that with this very bulky substituent the solvolytic ligand substitution, as well as isomerization, was dissociative (*146*).

The problems inherent in trying to determine an intimate mechanism from such kinetic studies were emphasized by van Eldik *et al.*



SCHEME 12

(*147*), who pointed out that the kinetics of all these reactions could be accounted for in terms of the common associative processes if an initial reversible solvolysis was rapid enough to be regarded as a preequilibrium step (Scheme 13). By this interpretation, only when R was mesityl was the solvolysis slow enough to be rate limiting, accounting for the observed identical rates of substitution and isomerization as well as the negative values of $\Delta S^{\ddagger}$. Despite this alternative explanation, possible examples of dissociative activation at square-planar molecules have continued to accrue, and the thrust of investigation has remained centered on isomerization reactions.



SCHEME 13

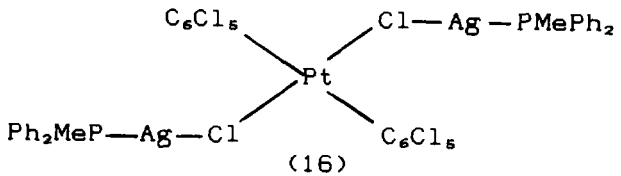
B. Electrophilic Assistance of the Leaving Group

The early observation that the presence of Ag^+ ions accelerated the isomerization of *cis*-[PtCl(*o*-tolyl)(PEt_3)$_2$] (*145*) offered the first clue to a rationalization of some of these processes. Evidence that electrophiles such as Ag^+, Hg^{2+}, BX_3, AlX_3, $[Me_3O]BF_4$, and $MeSO_3F$ can coordinate to ligand halides and thus enhance dissociative processes by abstracting the ligand is now quite common, even at square-planar complexes (*90, 148*). For example, a recent investigation of the hydrolysis of [PtCl(Me_2SO)(biL)] (biL is chelating glycine, sarcosine, or *N,N*-dimethylglycine) revealed a second-order assistance by Ag^+, suggesting the operation of reactions (21) and (22) (*149*).

$$\text{Pt—Cl} + \text{Ag}^+ \rightleftharpoons \text{Pt—Cl—Ag}^+ \qquad (21)$$

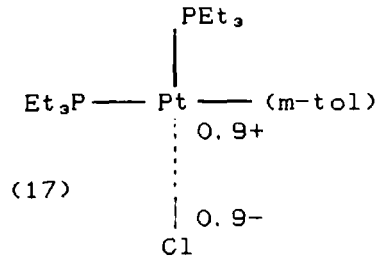
$$\text{Pt—Cl—Ag}^+ + \text{H}_2\text{O} \longrightarrow \text{Pt(OH}_2) + \text{AgCl} \qquad (22)$$

Structures like that of compound **16,** recently elucidated in the solid state, could well illustrate the type of interactions involved (*150*).



(16)

Clearly, such electrophilic assistance by metal ions cannot operate in most of the cases cited thus far, but in some it appears that electrophilic solvents might take on the role. Calculations based on leaving-group solvation led to predictions of solvent effects on isomerization rate constants that are remarkably close to experimental values for *cis*-[PtCl(*m*-tolyl)(PEt_3)$_2$], (*151*). The figures indicate that the Pt—Cl bond is almost broken at the transition state (**17**), the chloride having developed a charge of about 0.9. A more complete analysis for *cis*-[PtCl(*p*-FC_6H_4)(PEt_3)$_2$] in methanol/water mixtures confirmed the



(17)

solvation of the leaving chloride as the major factor determining rate change with solvent, the solvation changes of the substrate and $[PtR(PEt_3)_2]^+$ being similar (*151c*). A number of isomerizations that are believed to be dissociative in origin proceed in the absence of protic solvents, however, so it is debatable whether leaving-group solvation can be energetically important in every case. Thus, elimination of PEt_3 from $[PdR_2(PEt_3)_2]$ precedes isomerization (and/or reductive elimination) in solvents such as CD_2Cl_2, benzene, toluene, or diphenylmethane (the isomerizations again hinging on geometry changes at T-shaped intermediates). A theoretical analysis supported these mechanistic interpretations (*140*). Also, β-elimination reactions from *cis*-$[PtEt_2(PEt_3)_2]$ in cyclohexane have been found to proceed by initial PEt_3 loss (*152*). Deuteration studies indicated that the two ethyl groups were equally likely to undergo the elimination, lending support to easy isomerization at the T-shaped intermediate $[PtEt_2(PEt_3)]$. Indeed, with or without isomerization steps, many β-eliminations and reductive eliminations from square-planar compounds are now known to proceed dissociatively in nonpolar solvents (*153*).

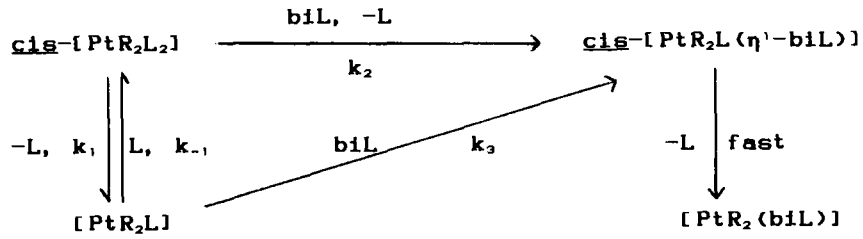
C. Dissociative Ligand Exchange

Returning to the ligand exchange reactions, which are the main concern of this work, a number of recent dissociative examples have been claimed, many of them taking place in nonpolar solvents. Sulfoxide and sulfide ligands are among the most common to be replaced (*154, 155*) or lost prior to other rearrangements (*156*). Kinetics of the replacements of Me_2S or Me_2SO (L) by a variety of chelating ligands, biL, in benzene or chloroform [Eq. (23) with R = Me, Ph, or *p*-tolyl] conformed to rate law (24).

$$[PtR_2L_2] + biL \rightarrow [PtR_2(biL)] + 2L \tag{23}$$

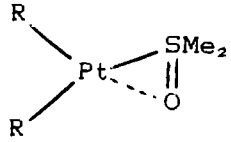
$$k_{obs} = \frac{a[biL]}{b[L] + [biL]} + c[biL] \tag{24}$$

Ring closures were always fast compared with loss of the first L. This was related by the authors to Scheme 14, in which a is k_1, b is k_{-1}/k_3, and c is k_2. The same rate law could, of course, result if k_1 represented the more common associative solvolysis path instead of a dissociative ligand loss, but this was thought unlikely in these solvents (*154*). Alternative explanations such as replacing the direct k_2 step by a rapid equilibrium followed by a rate-determining ring closure were ruled out



SCHEME 14

from the NMR spectroscopic observations and onset of saturation kinetics. Nevertheless, the activation entropy values were negative, and solvation of the leaving group could yet be important. The observation that Me_2S complexes behaved in the same way as those of Me_2SO precluded the participation of intermediates like **18** as a means of



(18)

alleviating the electron deficiency of the 3-coordinate species. The X-ray crystal structure of *cis*-$[PtPh_2(SMe_2)_2]$ confirmed the operation of a powerful inductive trans influence of the phenyl groups, the Pt—S bond lengths of 2.370 and 2.389(2) Å being the longest of their type reported (*154*). It is reasonable to conclude that this promotes the loss of L.

With nitrogen donors for biL, saturation kinetics were observed, with the rate becoming independent of [biL] at higher concentrations. The presence of excess L delayed the onset of saturation. When biL was a sulfur or phosphorus donor, however, faster reactions were observed, and [L] did not contribute to the rate. The 3-coordinate intermediate $[PtPh_2(SMe_2)]$ appears to be more reactive than its Me_2SO counterpart, showing very little nucleophilic discrimination. Curiously, $[PtPh_2(Me_2SO)]$ showed nearly as great a discriminating ability as its 4-coordinate analog, $[PtPh_2(Me_2SO)_2]$.

Not all the claimed examples of dissociative activation at square-planar molecules involve compounds with strongly trans-activating organic groups or weakly held Me_2S or Me_2SO ligands. The reaction of 5′-guanosinemonophosphoric acid with *cis*-$[Pt(OH_2)_2(NH_2Pr^i)_2]$ (to replace the water molecules) revealed a positive value for $\Delta S^{\ddagger}$ at the second step (*157*). This reaction, too, involving as it does the replacement of water by a bulky base at an already sterically hindered site,

could well be dissociatively controlled, a result the more interesting since the substrate, "Iproplatin," is a potential anticancer drug.

D. Structures of the 3-Coordinate Species

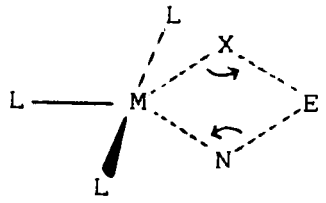
Although the number of claimed dissociative activations of square-planar compounds is growing steadily, they represent a tiny minority of the reactions of such molecules, and to many chemists the bare appearance of the proposed 14-electron intermediates is somewhat disturbing. The fact that the species are T-shaped, predicted on electronic grounds (*140, 158*) as well as demanded by the isomerization reactions, means that even relief of steric hindrance may be minimal on going from 4- to 3-coordination. Not surprisingly, perhaps, such species are rare. It is therefore worth noting that a few have been described, and one is the subject of an X-ray crystal structure determination. The complex $[Rh(PPh_3)_3]ClO_4$, made by treatment of Wilkinson's catalyst by $TlClO_4$, does indeed display the expected T-shaped RhP_3 arrangement, but one phenyl group approaches the "vacant" fourth site quite closely (*159*). The presence of this interaction in the solid phase means that other 3-coordinate structures for which no crystallographic data are available might be viewed with suspicion. Examples include $[PdL_3](BF_4)_2$ (L = PPh_3 or PEt_2Ph) (*160*), $[Rh(PMe_3)_3]PF_6$, (*133*), $[RhCl(PCy_3)_2]$ (*161*) and $[RhHL_2]$ (L = PBu_3^t or PCy_3) (*162*).

Despite the structural uncertainty, the isolation of these compounds, along with mechanistic evidence for such species from reactions we have met and others such as carbonyl insertions at square-planar compounds (*163*), means that we should reasonably regard such structures as being attainable while keeping an open mind over whether or not they are stabilized by any additional interactions.

It is worth noting that all the indications are that barriers to geometry change at such 3-coordinate species are quite low. The implication is that ligand exchange by dissociative activation need not be stereoretentive any more than by associative processes.

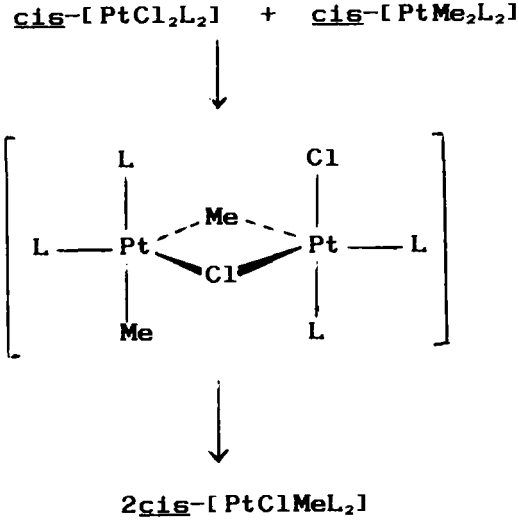
E. Electrophilic Attack at the Metal Ions

The possible assistance given to leaving groups by electrophiles in the form of solvent or metal ions represents one part of a ligand replacement reaction normally referred to as S_E2(cyclic). Structure **19** shows the interaction at the transition state. It can be seen as simultaneous attack of the electrophile E at the leaving group X and of the

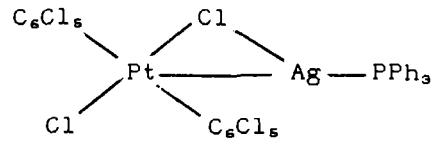


(19)

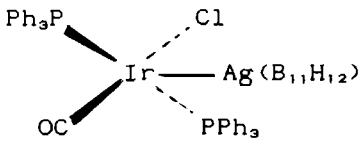
nucleophile N at the metal. Many exchange processes are believed to proceed by such a route, though firm mechanistic evidence is rare (*3*). An example is shown in Scheme 15 (L is PMe_2Ph) (*164*), which is stereoretentive at both platinum centers and conforms to second-order kinetics. Many other examples involve transfer of groups to and from tin or mercury. A variation on this reaction path is the (possibly partial) formation of a metal—metal bond at the transition state. This type of interaction is part way to one form of oxidative addition, and the transition state can be seen as involving simultaneous electrophilic attack at both the metal and ligand (*3*). A number of molecular structures showing just such combinations have recently been described. Anion **20** is an example (*150*). Compound **21,** on the other hand, produced from the action of $Ag(B_{11}H_{12})$ on Vaska's complex, has no Ag-Cl interaction at all (*165*) and thus might be regarded as the result of electrophilic attack at the d^8 metal ion. Several other adducts



SCHEME 15

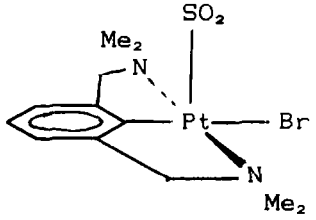


(20)



(21)

of electrophiles such as BF_3 have been described (*166*), though structural data are lacking. Square-pyramidal adducts of I_2 and SO_2 (**22** and **23**) have been structurally characterized, however, and strong cases made for regarding the interactions as electrophilic (*167*). The se-



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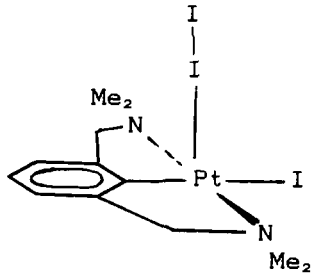
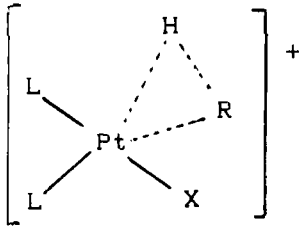


(22)

quence of compounds **16** and **20** to **23** can be seen as representing electrophilic attack at ligand **16**, metal—ligand bond **20**, and metal ion **21–23**, respectively, and each of these interactions is capable of initiating different types of reactions (*3*).

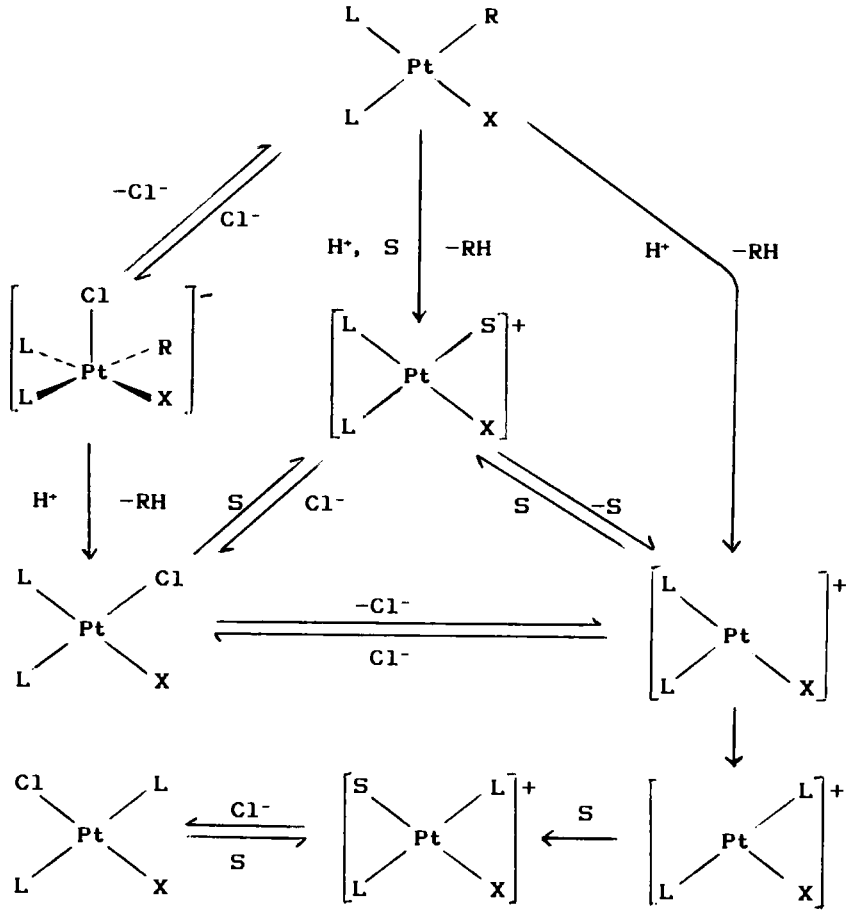
The shifting site of attack is well illustrated by the extreme example of H^+ as the electrophile. A number of studies of HCl cleavage of Pt—R bonds in $[PtRXL_2]$ (R is alkyl or aryl; L are tertiary phosphines) have led to the conclusion that H^+ primarily attacks the Pt—C bonds themselves (Structure **24**) (*168*). Moreover migration of the H^+ across the



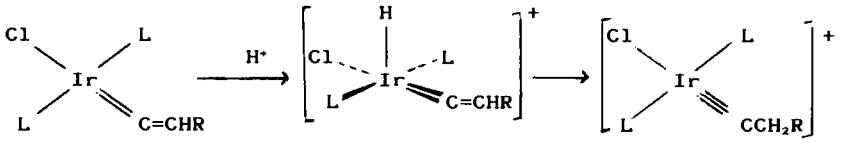
(24)

bond seems a probable low-energy process (*169*). Free halide (from the HCl) sometimes participates in a pre-equilibrium by nucleophilic attack and the resulting 5-coordinate intermediate can be similarly attacked. Scheme 16 outlines all the operating reactions, including isomerization at the T-shaped intermediate.

The formation of the carbyne complex of Scheme 17 has been found



SCHEME 16



L = PPr^{i}_{3} ; R = H, Me, or Et.

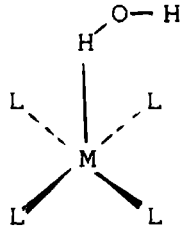
SCHEME 17

to follow H^+ attack at the metal (*170*). Other examples of such migrations of H^+ across metal—carbon bonds are quite common (*171*) and include α-eliminations (*172*).

VI. Nature of Square-Planar Complexes in Solution

Having seen that square-planar complexes can act as either electrophiles or nucleophiles, we can now address the difficult question of solvation of these species. It is clear from the complicated effects of solvent changes on the k_2 terms for associative ligand exchange, from the formation of conjugate bases, and from the evidence of leaving-group solvation in dissociative ligand exchanges (leaving groups from associative intermediates are presumably similarly affected) that solvent interactions elsewhere than at the metal ion, either nucleophilic or electrophilic, are energetically important. Examples of the operation of such interactions are common but unpredictable, and the effects of some on planar–tetrahedral equilibria of nickel(II) complexes have been met. An obvious and common manifestation of ligand "solvation" takes the form of hydrogen bonding (*79, 173*). Inversion barriers at pyramidal sulfur in the ions $[PtCl_3(SRR^*)]^-$ have also been found to be dependent on the solvent, less-polar solvents speeding the inversion (*174*). The authors of this work argue that this is compatible with strong solvation at sulfur, rather than platinum, since electronic charge is localized at pyramidal S in the ground state whereas it is delocalized at the planar transition state.

Our main concern, though, is the nature and extent of any solvent interaction at the metal ions, particularly of the heavier elements, for which paramagnetic octahedral species are not readily accessible. The establishment of an associative process for the exchange of free and coordinated solvent at these molecules clearly rules out a strong nucleophilic solvent coordination. It would thus appear that, at best, relatively weak interactions are possible along the lines of outer-sphere complex formation prior to rate-determining interchange processes. Moreover, keeping in mind that the square-planar molecules can act as



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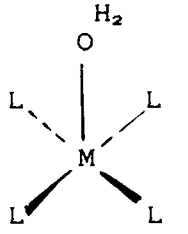


(26)

nucleophiles as well as electrophiles, the nature and the extent of any solvent–metal interaction must be regarded as unpredictable. Although there is no firm evidence, interactions such as **25** might be possible, as well as or instead of the more conventional **26**.

The few experimental attempts that have been made to determine the degree of solvation of square-planar molecules have led to some interesting interpretations but no clear picture. Early attempts to account for volumes of activation in methanol for ligand replacement reactions of *trans*-$[PtCl_2(PEt_3)_2]$ led to the suggestion that two solvent molecules were attached weakly above and below the plane (*175*). On the other hand, attempts to explain the PBu_3-catalyzed isomerization rates of *cis*-$[PtCl_2(PBu_3)_2]$ in various solvents led to the conclusion that the substrate was unsolvated in nonpolar solvents, was associated with one solvent molecule in $CHCl_3$, ether, acetonitrile, or nitromethane, but was associated with two molecules in methanol (*176*). In another study involving the same compound, variations in the platinum-phosphorus coupling constants with solvent, concentration, and temperature were shown to be quite large and were interpreted in terms of competitive solvation (*177*). Its nature was not discussed.

With a lack of metal-ligand interactions even with crown ethers (*79*), it is probably safest to conclude that there is little compelling evidence for energetically important solvent interactions above and below the square planes. Probably the only solvation of significance is secondary or outer sphere, and its nature and extent cannot be predicted.

VII. Oxidative Addition Reactions

Oxidative addition reactions can lead to ligand replacements when followed by reductive eliminations of different groups. Electrophilic attack at the metal ion is often involved in these reactions, making a direct parallel with some of the processes already discussed and justifying concentration on the former of the two reactions. Recent work has emphasized similarities in the relationship of this family of reactions to other ligand replacement routes.

The evidence for regarding many oxidative additions as proceeding by electrophilic attack at the metal has been discussed in detail (*3*), so here we simply outline the processes involved using recent examples before examining new relationships. The reactions are generally assigned as one of three types: concerted, two-step, or free radical (*178*). It is only the paired-electron processes at the first two that concern us here, so the free-radical mechanism will be discussed no further. It

should be kept in mind, however, that it can sometimes be experimentally problematical to distinguish the operation of the two-step route from the free-radical route (*124, 178*). Indeed a study of several oxidative addition reactions led to the conclusion that this path is often energetically similar to the two-step mechanism and thus frequently competes (*179, 180*).

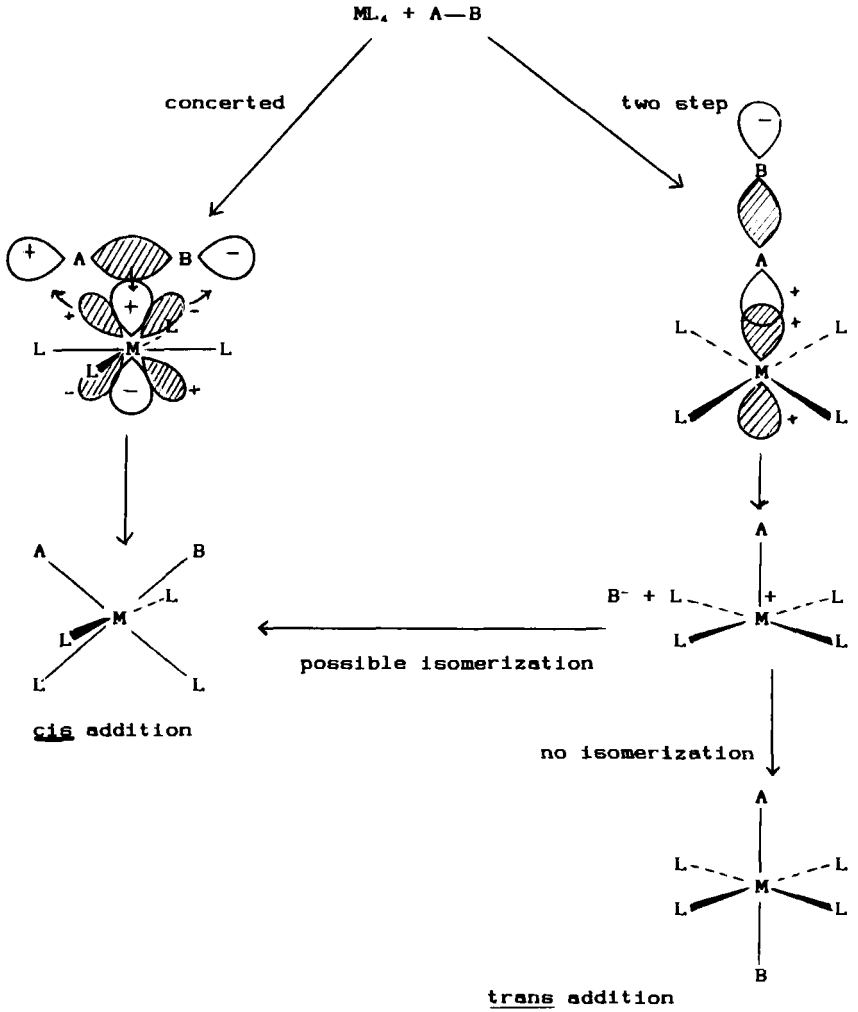
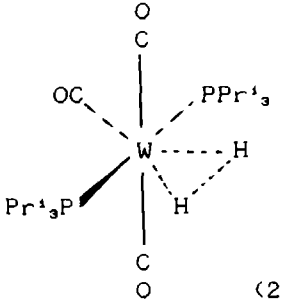


FIG. 10. Pathways for concerted and two-step oxidative additions of molecules AB to square-planar complexes ML_4.

A. The Concerted Mechanism

Figure 10 shows the interactions involved in the concerted and the two-step mechanisms. Many accounts of the concerted route have described it in terms of overlap of the filled metal d_{xy} or d_{xz} orbital and an empty σ^* orbital of the adding molecule, conforming to the concept of electrophilic attack at the metal ion. Overlap of the filled σ orbital of AB with an empty metal acceptor orbital is also involved, however, and theoretical studies have indicated that at the early stages of the interaction this results in a flow of electron density to the metal (*181*). By this description, the side-on approach of AB for concerted addition is nucleophilic, and, resembling C_2H_4 or O_2 coordination, it can be likened to a "normal" σ-donor/π-acceptor ligand (*2*). The idea of H_2 behaving as a nucleophile had previously been advanced (*182*).

The recent isolation and characterization of several η^2-H_2 complexes of transition metals has reinforced this view. Structures **27** and **28** are



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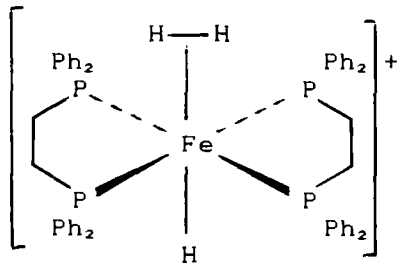


(28)

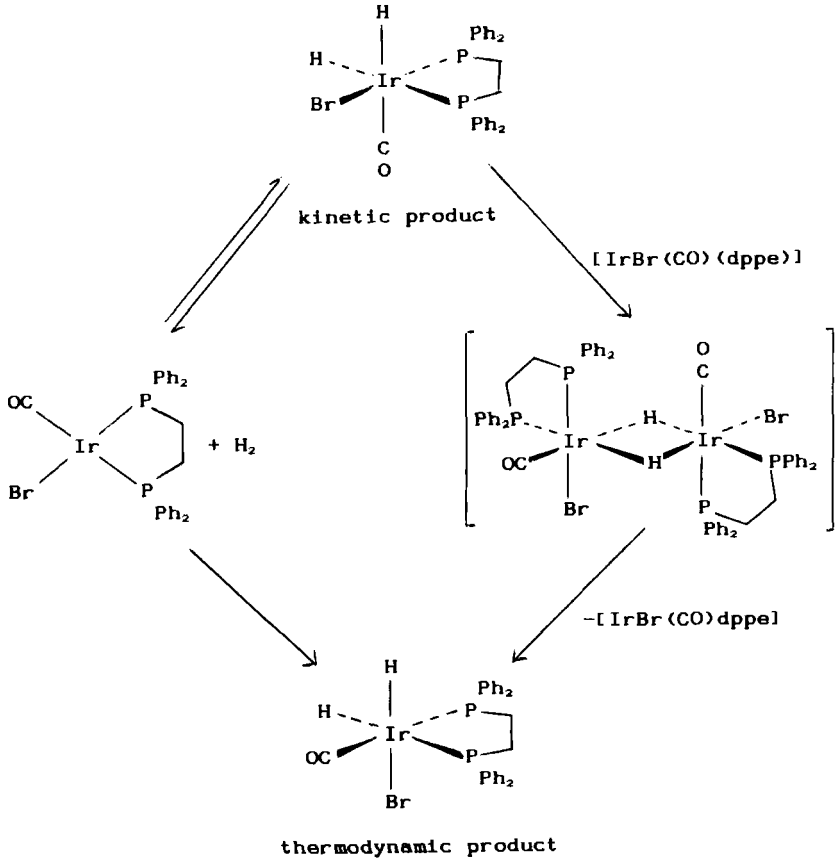
examples (*183, 184*). They can be seen as representing a stage halfway to oxidative addition (or reductive elimination) of H_2 at metals. A recent review listed some 40 examples (*185*), and several theoretical studies have been made (*181, 186*). The role of such η^2-H_2 complexes in oxidative additions to Rh(I) and Ir(I) has been discussed (*187*).

B. The Two-Step Mechanism

The two-step mechanism commonly occurs with polar adding molecules such as MeI. It is sometimes referred to as S_N2 since, as depicted in Fig. 10, the attack of A of AB (the CH_3 group of MeI) resembles this form of substitution at carbon.

Although the concerted route must yield cis addition products, it would appear from Fig. 10 that trans addition should result from the two-step mechanism, and product geometry has thus occasionally been

used to diagnose which mechanism operates. This can be misleading, however, because the 5-coordinate (formally 16-electron) intermediates (ML_4A^+ of Fig. 10) are liable to isomerize. Examples are known following ligand loss from octahedral species (*188*). Moreover, some products of concerted addition are known to change geometry by reductive elimination followed by readdition to another geometry (*187a*). An interesting case is shown in Scheme 18, where isomerization also results from a bimolecular transfer of AB to another substrate. Keeping in mind that light-induced isomerizations of the products are also known (*189*), product geometry is indeed a poor criterion for mechanistic assignment.

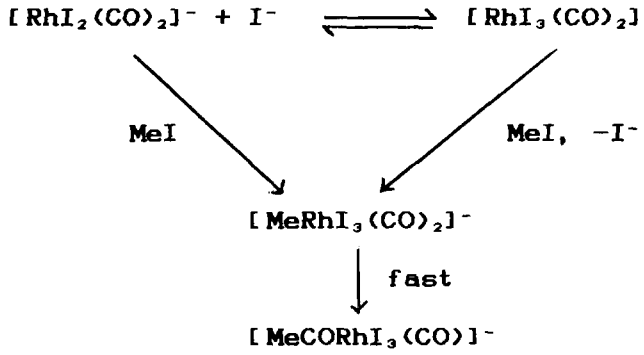


SCHEME 18

A consequence of the two-step mechanism as depicted in Fig. 10 is that when it is performed in the presence of other anions, these might be collected by the intermediate ML_4A^+ to give a different product. In a number of cases this has occurred (*180, 190*), though other expected examples have not been detected, indicating the possibility of intimate ion pairs being retained throughout some of these reaction sequences (*3*).

1. Nucleophilic Catalysis

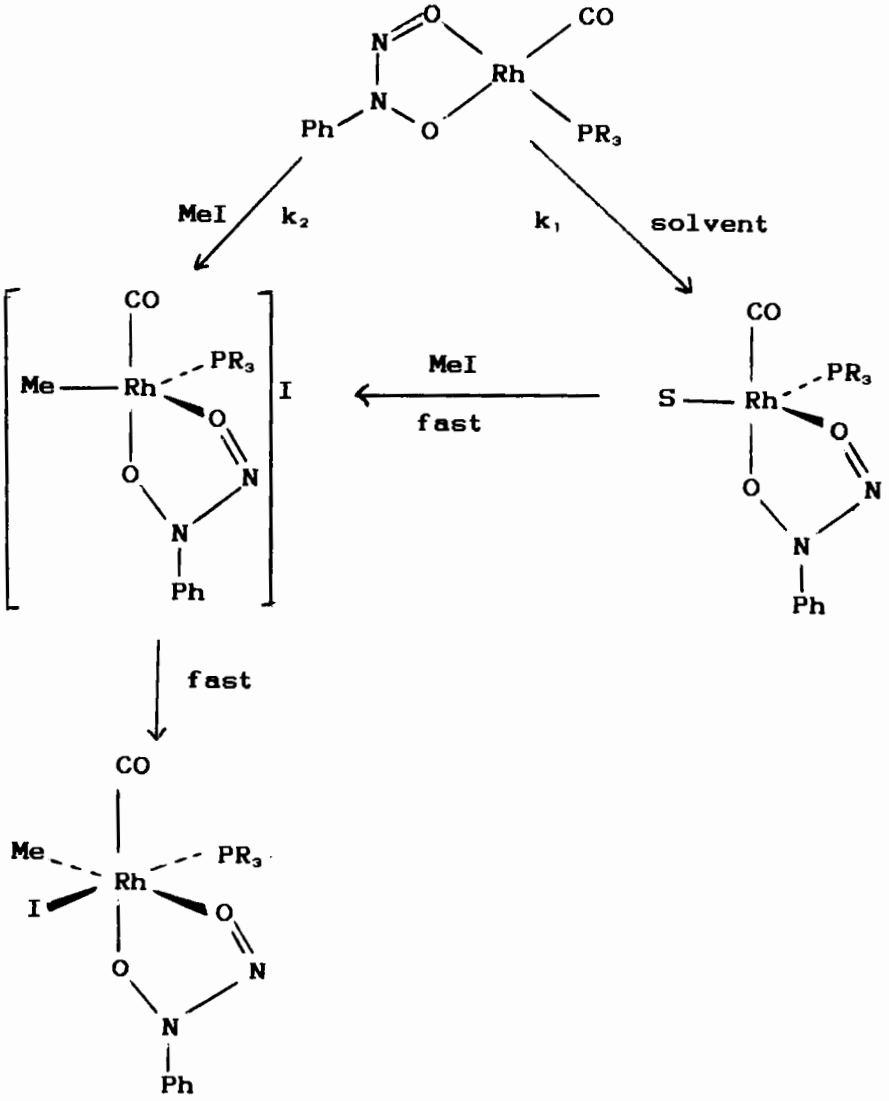
The presence of anions in solution can catalyze the two-step reaction by coordinating with the substrate and rendering it more susceptible to electrophilic attack. Examples have been met in Scheme 16, in which coordination of Cl^- to Pt enhanced attack by HCl. Another example involves coordination of I^- or other bases to the anion $[RhI_2(CO)_2]^-$, which enhances oxidative addition of MeI (Scheme 19)



SCHEME 19

(*191, 192*). (Prior coordination of Cl^- to a variety of Pt(II) substrates has also been observed to precede various oxidations that proceed by inner-sphere electron transfer or atom transfer) (*193*). Nucleophilic solvents might be expected to mimic the role of the anions in some systems, and examples are known. Thus MeI addition to the rhodium(I) complex of Scheme 20 is in competition with a second reaction that is dependent on solvent addition (*194*). Rate law (25) was observed, k_s being the solvent dependent part.

$$k_{obs} = k_s + k_2[MeI] \tag{25}$$



SCHEME 20

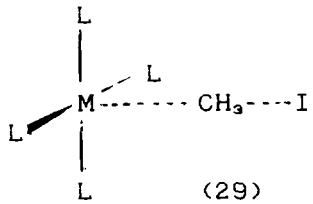
This potential catalyzing effect of polar solvents is supported by the discovery a few years ago of neighboring group participation, or chelate assistance, in aiding a variety of oxidative additions (*195*). Reactions of HCl, MeCl, MeBr, MeI, CCl_4, Cl_2, and PhCOCl with phosphine complexes of Rh(I), Ir(I), or Pt(II) are all enhanced when the phosphine is $PMe_2(o\text{-}MeOC_6H_4)$, which contains a nucleophilic MeO group, com-

pared with PMe_2Ph. Clearly these two-step oxidative additions can proceed either by electrophilic attack at the metal followed by addition of the nucleophile or by nucleophile coordination followed by electrophilic attack at the resulting 18-electron 5-coordinate adduct. Having already speculated on the possibility of electrophilic solvent interaction with some square-planar molecules, we find it interesting to consider the possibility of such an interaction catalyzing "normal" nucleophilic ligand exchange and even of neighboring group participation in the form of agostic hydrogen approach to the metal.

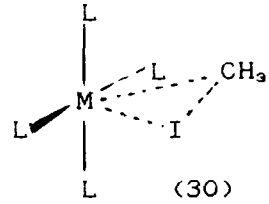
Despite the diversity of identified reaction paths, it is not yet possible to predict just when any of them will operate. Thus, the addition of bromopropane to *trans*-$[RhBr(CO)(P\{p\text{-}EtC_6H_4\}_3)_2]$ is first order in both reactants but is not catalyzed by free bromide (*196*).

C. The Intimate Mechanism: Relationship between the Two Pathways

One long-term uncertainty over the two-step oxidative addition concerns the precise nature of the initial interaction. Two extreme situations, shown in **29** and **30** for MeI approach, can both lead to the same



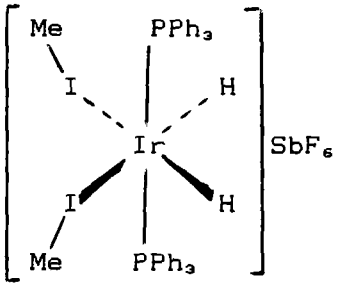
(29)



(30)

products. The linear transition state is believed to apply to most cases (*3*), but not all reactions need conform to the same pattern; and with the recognition that some oxidative additions are preceded by nucleophilic attack, even the formation of transient $L_4M \cdots I \cdots Me$ should not be ruled out. Any tendency toward a transition state such as **30** begins to resemble the initial interaction of the cis concerted process, and it is likely that the borderline between operation of the two pathways will not be clear cut.

Two recent determinations of activation volumes for MeI addition to rhodium(I) β-diketonate complexes (*197*) could not discern which type operated. The values, along with those of $\Delta S^{\ddagger}$ and the effects of solvent change, clearly indicated development of polar transition states (the charge separation involved in either **29** or **30** would fit) and the authors marginally favored **29**. Interestingly, a complex of iridium(III) and MeI, **31**, has been structurally characterized and reveals η^1 iodide-bonded MeI molecules (*198*). The Ir-I-C bond angles are 105.5° and 108.2°; and although the interaction can be considered nucleophilic

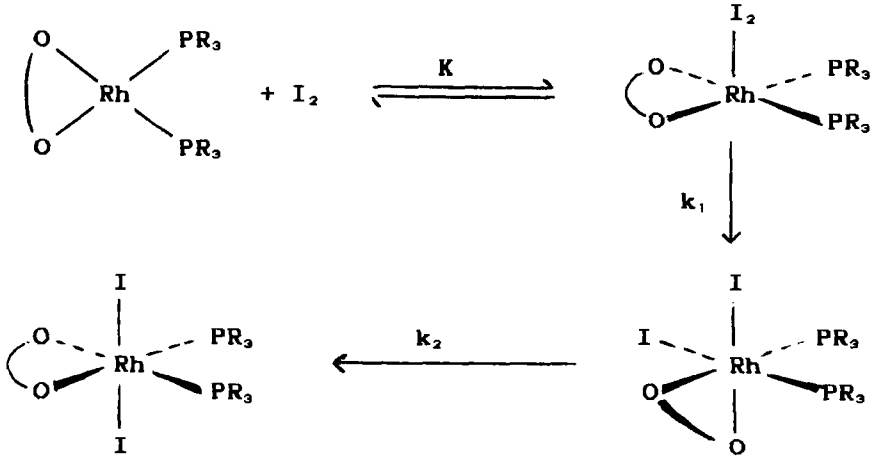


(31)

from iodine, the CH_3 carbons are only about 4 Å away from Ir. The coordinated MeI molecules are activated toward nucleophilic attack by NEt_3 by a factor of 10^4 to 10^5 times. Loss of the two hydride ligands from **31** by reductive elimination of H_2 leads to oxidative addition of MeI, but the reaction path is unknown. Perhaps significantly, some η^2-*P*, *Br* complexes of $PPh_2(o\text{-}C_6F_4Br)$ and either Rh(I) or Ir(I), which were also structurally characterized, do undergo intramolecular oxidative additions only from the Br-coordinated chelate ligands (*199*). It may be that approach of the halide end of organic halides, a nucleophilic attack, could yet turn out to be important in some oxidative additions.

The product of $SnMe_2Br_2$ addition to an iridium(I) complex has been found to contain a Sn—Ir—Br three-member ring, described by the authors as a "trapped intermediate" of oxidative addition (*200*).

A number of cases of oxidative additions of halogen molecules to square-planar molecules are also believed to proceed by forming



SCHEME 21

$ML_4 \cdot X_2$ adducts (*201*). An example is shown in Scheme 21, for which rate law (26) was derived.

$$k_{obs} = \frac{k_1 K[I_2]}{1 + K[I_2]} \tag{26}$$

The iodine adduct formation is accompanied by a rapid color change. Its structure was not elucidated, but the linear I—I—M structure of compound **22** could be a closer analog than the η^2-H_2 adducts recently discussed. Slow product isomerization again highlights the dangers of mechanistic inference from product geometry.

A second long-standing area of contention relates specifically to cis oxidative additions, typified by H_2 reactions. This is the question of which two resident ligands will move to accommodate the incoming groups and which pair will remain mutually trans. In additions to Vaska's compound and related molecules, it is nearly always the carbonyl and halide that end coplanar with the new ligands, the two phosphines remaining trans. With other ligand configurations the outcome has been less predictable, and competition between geometries can result as in Scheme 18 (*187a*). Over the years a number of explanations have been advanced to account for or predict product geometry. The arguments put forward emphasize the relationship between molecular interactions leading to oxidative additions and those that involve simple ligand replacement.

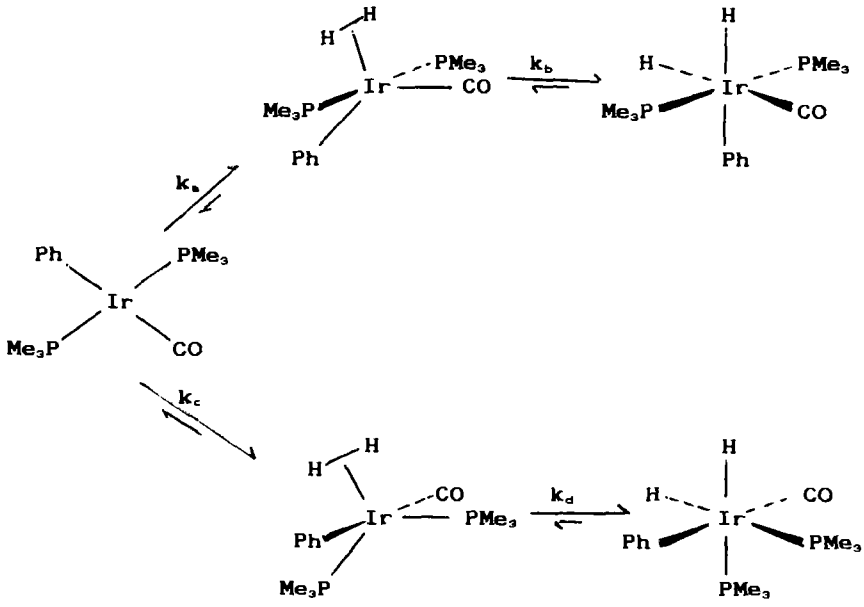
Several reactions reported by Eisenberg and co-workers (*187a, 202*) have stressed the dominating importance of resident ligand CO because of its π-acceptor properties. Thus, if an approaching H_2 molecule adopts a configuration lying parallel to the M—CO bond, the empty σ^* (H_2) orbital overlap with the metal filled d_{xy} is enhanced. Nearly all relevant H_2 oxidative additions known up to 1987 conformed to this picture. For maximum effect it requires that the substrate remain close to square planar at the transition state and that the ligands to be displaced do not bend back appreciably toward a trigonal bipyramid, a model reflecting the role of H_2 as an electrophile.

An alternative view was that the incoming molecule would lie parallel to the ligand of highest trans effect. As well as accommodating the π-electron–withdrawing properties of CO, which play a role in its trans effect, the contributions of bond-weakening trans influence become important. Both can lead to these ligands adopting the trigonal plane of a trigonal-bipyramidal structure along with the incoming group; and the similarity of, for example, an approaching H_2 molecule to other ligands such as PR_3, CO, or C_2H_4 becomes obvious.

A third explanation hinged on steric effects on the stability of a trigonal-bipyramidal transition state, the structure adopted being the least hindered. This accounted for a few examples that did not conform to the model depending on ligand π-acceptor dominance (*203*). It should be emphasized that, being associative, oxidative additions are subject to the same steric effects as the nucleophilic ligand replacements: bulky "nonparticipating" ligands are known to have a markedly inhibiting effect (*204*).

The recent detection by Crabtree and co-workers of a number of examples of H_2 additions that did not conform to the electronic or steric explanations led to a valuable reappraisal, already outlined in the section on nucleophilic ligand replacements (*69*). H_2 addition to *trans*-[IrR(CO)$(PMe_3)_2$], with R = Me or Ph, left R and CO trans, although with R = phenyl, isomerization to the other isomer did occur and was shown by selective deuteration experiments to proceed by an H_2 dissociation/recombination like the left-hand half of Scheme 18. This was clearly against expectations from the electronic explanations, and the discovery that H_2 added parallel to the PPh_3 ligands of *trans*-[IrMe(CO)$(PPh_3)_2$] was also counter to steric direction.

The authors considered the reaction sequences shown in Scheme 22,



SCHEME 22

pointing out that with the isolation of several η^2-H_2 complexes the trigonal-bipyramidal species were better regarded as intermediates rather than transition states. A consequence was that the stabilities of the various 5-coordinate species need not direct the course of the reaction. Moreover, since the isomerization was found to take place by an H_2 elimination reaction, and since the third possible isomer of the product (with cis H_2, cis $(PMe_3)_2$, and cis CO and Ph) was never observed, pseudorotation at these trigonal-bipyramidal complexes must be slow by comparison. From available theoretical studies (*46, 205*), Crabtree concluded that the directions of concerted oxidative additions and of nucleophilic ligand replacement depended on the same three factors:

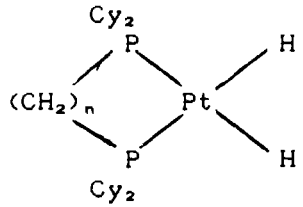
1. The first is the repulsive interaction of the filled metal d_{z^2} orbital and the filled σ-donor orbital of the attacking group; this would be reduced by good π-accepting ligands, particularly if they lay parallel to the entering molecule where they would take up the equatorial sites of the trigonal bipyramid.
2. Good σ-donor ligands at the same equatorial sites would improve back-donation from the filled metal d_{xz} orbital to σ^* of the entering molecule, assisting its cleavage.
3. π-donor ligands would interact with the metal empty p_z orbital, lowering its energy. It is this orbital that overlaps with the entering molecule's σ-orbital at the transition state. Bending such ligands out of plane (i.e., into the plane of the developing trigonal-bipyramidal intermediate) would reduce this effect and aid the interaction with the entering group (*69*).

All of these reactions have recently been reviewed (*206*), and it is clear that the combination of the properties of both trans-pairs of ligands can be as decisive in determining the geometry of concerted oxidative addition as they can for associative nucleophilic ligand replacement.

VIII. Isomerization by Partial Reductive Elimination

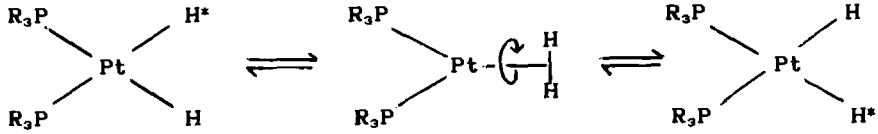
Recognition of η^2-H_2 complexes as likely intermediates in oxidative addition reactions to d^8 ions or reductive eliminations from d^6 metal ions prompts examination of another possible complication to the intimate mechanism of d^8 square-planar metal-ion reactions. Although none have been isolated, it seems reasonable to expect such species as intermediates in reductive eliminations from d^8 complexes also, and a number of site fluxionality cases have been explained this way.

Clark and co-workers reported vt ^1H NMR measurements on the compounds **32** (*207*). The compounds are fluxional, and above room



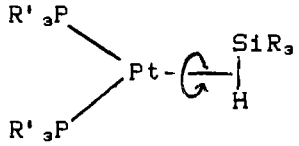
(32)

temperature a rapid exchange of site of the two phosphorus or two hydride ligands is apparent. Coupling is retained at the high-temperature limit, showing the process to be intramolecular. Scheme 23, involving rapid rotation of an η^2-H_2 intermediate, was proposed to account for this. In support of this interpretation, spin–lattice relaxation times for the hydride ligands were found to be intermediate between those typical of η^2-H_2 ligands and terminal hydride ligands (*207b*).



SCHEME 23

Similar intramolecular site exchanges have been found in the complexes *cis*-[PtH(SiR_3)(PCy_3)$_2$] and *cis*-[PtH(SiR_3)(PPh_3)$_2$] (*208*), and these may proceed through intermediates such as **33**. Complexes with R_3SiH apparently acting as an η^2 ligand to manganese or chromium



(33)

have been described (*209*). The Si—H distances in the adducts are short, and ^1H, ^{13}C, and ^{29}Si NMR parameters all indicate the presence of Si–H interactions. An MO treatment supports these formulations (*210*).

These observations offer possible explanations for some site exchanges or isomerizations that have either been explained in other ways or lack a convincing explanation at all. The intramolecular phosphine scrambling in diamagnetic [NiH(PR_3)$_3$]$^+$, rationalized in terms

of a rapid square-planar to tetrahedral to square-planar motion (*131, 132*), might reasonably involve formation and rotation of $[(R_3P)_2Ni(\eta^2\text{-}R_3P\text{-}H)]^+$ intermediates; phosphonium is isoelectronic with silane. Fluxionality in the analogous rhodium compounds, $[RhH(PR_3)_3]$ (*135, 136*), in which attainment of tetrahedral geometry is less likely, could be likewise explained. Similarly, the fast cis–trans isomerism of $[PtH_2L_2]$ (L = PMe_3 or PEt_3) (*211*) might be rationalized in this way. Both isomers reversibly lose H_2 but not fast enough to account for the fluxionality. Moreover, addition of H_2 to PtL_2 to form a trans isomer is a symmetry-forbidden process (*212*).

It is interesting to speculate whether the site exchange found in *cis*-$[Pt(GePh_3)(HgGePh_3)(PPh_3)_2]$ and assigned to a digonal twist by the authors (*137*) could be accounted for in terms of such a partial reductive elimination. This molecule differs from the others, however, in that it lacks a hydride ligand, a common feature in the other examples; so possibly a different explanation is needed here. Compounds of mercury and other metals can bind as electrophiles to d^8 Pt(II) and Pd(II) centers (*213*), so the possibility of a reversible partial reductive elimination to yield intermediate $[(Ph_3P)_2Pt \rightarrow Hg(GePh_3)_2]$ may hold the key.

IX. Concluding Remarks

As techniques improve for following faster reactions, many more examples of rate laws deviating from the common two-term form for nucleophilic ligand exchange are being found, but the evidence indicates that nearly all the reactions still conform to the usual associative mechanism. The general understanding of structural and energy variations along the intimate reaction profiles is now better advanced. Although no single form is universally adhered to, it seems likely that certain types are more common with particular metal ions.

The operation of conjugate base pathways, known for many years with Au(III) compounds, is now recognized as operating at a number of Pd(II) and Pt(II) complexes. These also appear to proceed by A or I_a mechanisms and probably have similar reaction profiles to the normal nucleophilic ligand replacements, though there are yet too few examples to be certain.

Only for nickel(II) does the prospect of prereaction geometry change pose a potential complication; and since more examples of faster associative nucleophilic ligand exchange at square-planar complexes (rather than their tetrahedral, 5-coordinate, or octahedral alterna-

tives) have been discovered so far, the complication may not prove to be problematical.

Ligand exchange by dissociative activation now appears to be well established for some 16-electron square-planar compounds, though examples are not common. The detail of the intimate mechanism is crude by comparison with associative reactions, but all the evidence indicates the involvement of T-shaped intermediates.

The picture regarding solvation of square-planar molecules remains obscure. From the associative reactions, there is no evidence that solvation at the metal is important, though entering group solvation is clearly indicated. The dissociative reactions show the relative importance of solvation of the leaving groups and substrates, and solvent interaction with the substrate elsewhere than at the metal ion is probably common.

Examples of electrophilic interactions at the metal ions (as well as at the leaving and entering groups) have been demonstrated. These represent a formal oxidation of the metal and can lead to oxidative additions to the metal or, by transfer to a ligand, to a dissociation. On the other hand, at least some concerted oxidative additions, often described as electrophilic interactions, are seen in reality to resemble nucleophilic attack in their early stages; and some of the two-step oxidative additions (most of which do conform to electrophilic attack) probably resemble the concerted mechanism in their initial interactions, the boundary being indistinct. Nucleophilic attack can, in some cases, precede electrophilic attack.

Finally, an understanding of the steric course of those reactions involving nucleophilic attack is emerging from a fusion of theoretical studies linked to practical observations. The value of such work in drawing parallels between reaction classes and in appreciating the nature of the intimate reaction paths is great, and it is to be hoped that more studies of this type will emerge in the future.

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