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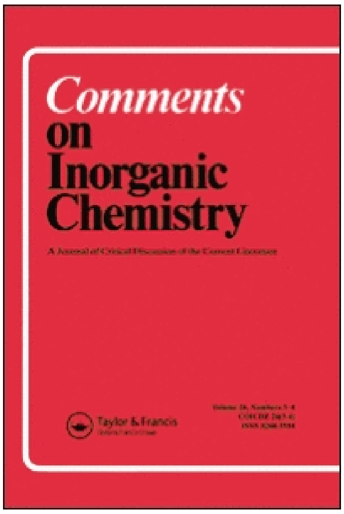

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Dissociative Pathways in Platinum(II) Chemistry

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Steric and electronic factors favor the addition of a fifth ligand to a square planar d^8 complex to form five coordinate species either as discrete compounds or reaction intermediates. The search for factors promoting the conversion of the normal associative mode of reaction into a dissociative process has attracted much attention. The attempt to achieve this goal by using bulky ancillary ligands has been unsuccessful.

More convincing evidence in favor of a dissociative mechanism involving a Pt(II) 3-coordinate intermediate comes not from classical Werner compounds but from reactions involving organometallic substrates. It is now reasonably clear that the formation of such 3-coordinate 14-electron compounds offers a favorable reaction route to a number of fundamental processes as an alternative to the intermediacy of 4- and 5-coordinate species. Among them, the uncatalyzed *cis* to *trans* isomerization of complexes of the type *cis*-$[Pt(PE_3)_2(R)X]$ (R = alkyl or aryl groups; X = halide ion), β-hydride elimination from symmetrical and unsymmetrical dialkyldiphosphino platinum(II) complexes and other processes that will be briefly discussed in this paper. Very recently, kinetics of solvent exchange and displacement by bidentate ligands on *cis*-$[Pt(R)_2(L)_2]$ (R = CH_3 or C_6H_5; L = sulfoxide or thioether) complexes have provided a clear-cut example of ligand dissociation as the dominant step in substitution reactions of square-planar complexes.

While in most of the cases extensive electron density transfer associated with the presence of a Pt–C σ bond seems to be a prerequisite to produce a sharp changeover of reaction pathways, we are far from a complete understanding of the factors that promote the formation and stabilization of coordinatively unsaturated species, as well as of the efficiency with which they can be intercepted in solution by ligands or by the solvent itself.

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The interest in the chemistry of square planar complexes of d^8 metal ions is continuously increasing, because of the great chemical versatility of such systems. Indeed these ions, and particularly platinum(II), can form an enormous amount of stable compounds with a variety of molecules and donor atoms, giving classical coordination compounds or organometallic compounds. Properties and uses of such compounds can vary in a dramatic way. Some of them have been found to be very effective antitumor agents[1] and some are very good catalysts in many processes of homogenous catalysis.[2]

Square planar complexes also undergo a number of fundamental processes, such as nucleophilic substitution, electron transfer, oxidative addition, reductive elimination, attacks on the ligands, geometrical isomerization and so on. However, only a very small proportion of the known chemical reactions has been studied in detail from a mechanistic point of view, in terms of the nature of the reagents, composition of the transition state, the nature of all intermediates on the reaction paths of all the other factors which serve to define a mechanism. This is particularly true for organo-transition metal complexes because of the complexity and variety of factors which must be taken into account to explain their chemical behavior as, for example, the variety of functional groups on the organic ligand, the role of other ligands of often widely different properties, the possibility of generating from the substrate parent compounds of higher reactivity or the possibility of having competitive reaction pathways. It is not surprising, therefore, that the most studied process is that which appears to be the simplest one, at least from a stoichiometric point of view, namely the nucleophilic substitution.

NUCLEOPHILIC SUBSTITUTION

A massive amount of data for this process comes from Pt(II) substrates. According to the rate law:

$$-d[\text{Complex}]/dt = (k_1 + k_2\,[\text{Y}])[\text{Complex}] \qquad (1)$$

there are two reaction routes.[3] One is the direct attack of the nucleophile on the metal to yield a transient five-coordinate intermediate; the other is a concurrent bimolecular attack by the solvent, with the formation of a labile solvento-intermediate, followed by a fast attack of the reagent to yield the products. The rate of substitution will depend on many factors and among them the nature of the *trans*, *cis* and leaving groups as well as the nature and concentration of the reagent. Usually the substrates show a considerable discrimination among different entering groups. Many efforts are devoted nowadays to investigate the details of the intimate mechanism which is related to the synchronism and the relative importance of bond making and bond breaking in reaching the transition state.

(A) Sterically Hindered Complexes

Once the overall mechanistic picture was reasonably clear, the search for factors promoting the conversion of the normal associative mode of reaction into a dissociative process attracted much attention. Those involved in the game have found that occasional claims of dissociation as the rate determining step for some process of square planar complexes have been regarded with much scepticism and a sort of theological bias by people working on coordination compounds. On the other hand, evidence of dissociative processes was continuously growing and accepted in Pt(II), Pd(II) and Au(III) organometallic chemistry. The problem goes further than a trifling academic dispute and cannot be limited to a question of putting labels on reactions. Indeed, there is great chemical interest in the possibility of considering alternative low-energy pathways with 3-coordinate species as key intermediates.

Basolo *et al.*[4] pioneered the use of bulky ancillary ligands to prevent bond formation and compared the rates of reactions of diethylentriamine complexes with those of N-alkyl substituted analogues in the reactions

$$[M(L)X]^+ + Y^- \rightarrow [M(L)Y]^+ + X^- \ (M = Pd(II), Pt(II)). \qquad (2)$$

Increasing steric hindrance brought about by alkyl substitution on the terminal nitrogens of a coordinated ethylentriamine leads to a large decrease of both k_1 and k_2, the nucleophile independent and dependent rate constants in the rate law (1). In the most sterically crowded complexes the k_2 term vanishes, leaving the rate of halide (X^-) displacement completely controlled by the solvolytic pathway. The kinetic behavior appears to be similar to that of octhaedral systems and for this reason such complexes were called "pseudo-octahedral."

However, this predominance of the k_1 term falls short of providing direct evidence of a dissociative mechanism involving a 3-coordinate intermediate. There is little doubt that the k_1 term still relates to a bimolecular solvolysis, and the simplest way of envisaging its enhanced importance in the substitution is to consider the solvent as a more favored nucleophile than any other, with the normal ability of the substrate to discriminate between possible reagents being greatly reduced. Indeed, sterically hindered aquo-complexes $[M(R_5\text{-dien})(H_2O)]^{2+}$ (M = Pt(II) or Pd(II)) return to exhibit a considerable nucleophilic discrimination ability in their anation reactions, where the solvolytic pathway is kinetically undetactable.[5] Obviously, the sequence of reactivity is not the same as that found in the standard n^0_{Pt} or n^0_{Pd} nucleophilicity scales[6] and the deviations can be accounted for either by the presence of a double positive charge on the substrate[7] or by its steric demand that, however, does not appear to be enough to prevent the approach of a nucleophile to the metal center. If we exclude an attractive but unreliable ion-pair mechanism, the results on the anation reactions give in themselves a straightforward indication of an associative process.

Notwithstanding, these systems gave rise later on to an impressive amount of studies on the pressure effect on the rates of solvolysis,[8] anation[5] and solvent exchange,[9] aimed to show the absence of a dissociative mechanism. It is outside the aim of this work to examine them in any detail. Activation data for the solvolysis of $[Pd(L)Cl]^+$ (L = dien; 1,4,7-Me_3dien; 1,4,7-Et_3dien; 1,1,4-Et_3dien; 1,1,7,7-Me_4dien, 1,1,4,7,7-Me_5dien, 1,1,7,7-Et_4dien, 4-Me-1,1,7,7-Et_4dien, 1,1,4,7,7-Et_5dien) complexes show that increasing steric hindrance does not have a substantial effect on the value of the volume of activation $\Delta V^{\neq}$ which is higher than -10 ($cm^3\ mol^{-1}$). By way of contrast, the values reported for solvent exchange on unhindered complexes, *viz.* -2.2 for $[Pd(H_2O)_4]^{2+}$,[10] -4.6 for $[Pt(H_2O)_4]^{2+}$ [11] and -2.8 $cm^3\ mol^{-1}$ for [Pd(dien)

$H_2O]^{2+}$ [12] are significantly less negative, despite the better opportunity of forming a compact 5-coordinate transition state. This is difficult to understand unless in the former reactions electrostriction effects play a major role and the contribution of $\Delta V^{\neq}_{\mathrm{solv}}$, the solvational volume change, to the measured $\Delta V^{\neq}$ value is prevailing. This is a further reminder that an unquestioning use of the absolute values of volumes of activations to determine the molecularity of the reactions is dangerous and can be misleading. While obviously these data add new information and implement the overall knowledge of a system, a recent overemphasis in considering them as the ultimate arbiter in assessing a mechanism should be moderate.

(B) Complexes with High *trans* Labilizing Groups

Another way of achieving dissociation could be that of promoting bond weakening at the leaving group, usually a halide ion, by locating a strong σ donor group in the *trans* position to it as in the complexes *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = H, CH_3, C_2H_5, C_6H_5, o-tolyl, mesityl, etc.). The result is the same as for the pseudo-octahedral complexes. There is a loss of discriminating ability of the complexes and the substitution is dominated by the solvolytic pathway.[13] The mode of activation remains associative, the activation parameters for the methanol solvolysis of the most sterically hindered complex with a mesityl group being $\Delta H^{\neq}_1 = 80\ \mathrm{kJ\ mol^{-1}}$, $\Delta S^{\neq}_1 = -60\ \mathrm{JK^{-1}\ mol^{-1}}$ and $\Delta V^{\neq}_1 = -16\ \mathrm{cm^3\ mol^{-1}}$. Here again the solvento-complexes *trans*-$[Pt(PEt_3)_2(R)(MeOH)]^+$ return to show a significant capacity of nucleophilic discrimination in their anation reactions, regardless of the size of the ligand R.[14]

The role of these substrates, however, is very interesting because the effect of their different discriminating abilities in the halide complexes is not simply limited to either reducing or enhancing the reactivity of a group with possible deviations from a simple linear free energy relationship when the set of nucleophilic reactivity constants, n^0_{Pt}, is applied. Rather, as can be seen in Fig. 1, they offer the possibility of distinguishing different reaction paths for "good" and "poor" nucleophiles. The pattern of behavior is in keeping with the idea that the increase of electron density induced on the central metal atom by the strong σ-donor R^- ligand

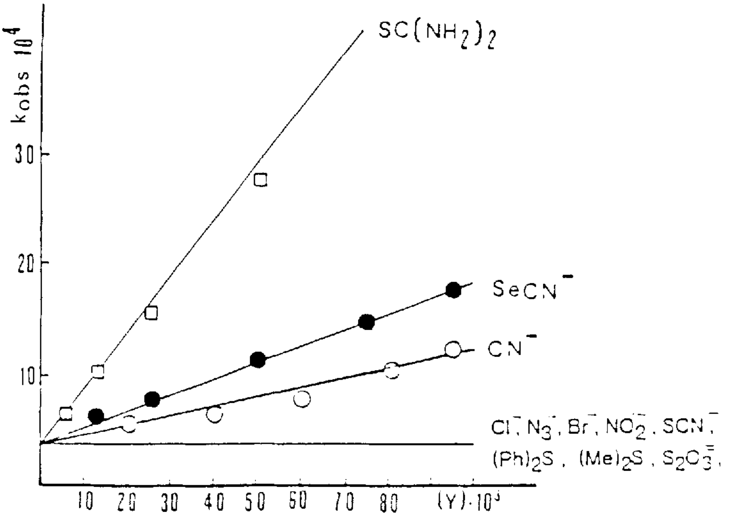


FIGURE 1 Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the reagent concentration for the reaction of *trans*-[Pt(PEt$_3$)$_2$(mesityl)Cl] with various nucleophiles in methanol at 303.2 K.

markedly hinders the attack by reagents whose nucleophilicity mainly depends on the polarizability of the donor atom (preference for the k_1 pathway), while the attack of biphilic reagents (which can delocalize charge by means of π interactions with the metal) is enhanced. In other words, some evidence begins to emerge that changes in the electrophilicity of the central metal can be essential in promoting different reaction paths.

UNCATALYZED ISOMERIZATIONS

More convincing evidence for the operation of a dissociative mechanism comes not from substitution reactions but from uncatalyzed isomerizations of mono-organo complexes of the type *cis*-[Pt(PEt$_3$)$_2$(R)(X) (R = alkyl, aryl; X = halide ion).

Studies on the isomerization reactions of square planar organometallic compounds are of fundamental importance for understanding the chemical reactivity of these species. Indeed, the course of many processes is dictated by the geometry in the square planar configuration. For example, dialkylbis (phosphine)palladium (II) complexes give strikingly different products in their thermolysis or reactions with CO depending on configuration.[15] For concerted thermal 1,1-reductive elimination to take place, it has been argued that the organic moieties should be brought to occupy adjacent positions in the complex prior to giving a C–C coupling product. This is also the most favorable position for olefin insertion into a Pt–H bond leading to a monoalkyl complex.[16]

We had the first evidence of such uncatalyzed isomerizations many years ago,[17] when we noticed that *cis*-$[Pt(PEt_3)_2(o\text{-tolyl})Cl]$, dissolved in methanol, converts spontaneously into its *trans* isomer. The kinetics of the process can be followed easily by conventional spectrophotometry. The electronic spectrum shows well-defined isosbestic points and the final spectrum is virtually identical to that of the *trans* isomer. Thus, the equilibrium lies well over to the *trans* form and the process follows first-order kinetics. The same features have been subsequently observed for all the other parent compounds studied.

Although the nature of the observed changes remains the same, the rate of isomerization ($k_i = 5.2 \times 10^{-4}\ s^{-1}$, at 30°C) is greatly decreased by the addition of very small amounts of chloride ion in solution, and with a sufficient excess the process can be stopped. The derived rate law:

$$k_i = \frac{k_D}{1 + \dfrac{k_{-D}}{k_T}[Cl^-]} \tag{3}$$

accounts for the mass law retardation produced by the added halide ion and for the linearity of the plots of k_i^{-1} vs. $[Cl^-]$. The solvolytic rate constant ($k_S = 4.7 \times 10^{-2}\ s^{-1}$, at 30°C) obtained from nucleophilic substitution, and that represents the rate at which the solvent replaces the chloride ion, is at least one hundred times greater than the rate of isomerization and does not suffer mass-law retardation by added Cl^-. The values of the activation parameters of the two processes are also completely different. A low enthalpy of activation and a large negative entropy of activation for the solvolytic path ($\Delta H^{\neq} = 40.5 \pm 2\ kJ\ mol^{-1}$ and $\Delta S^{\neq}$ =

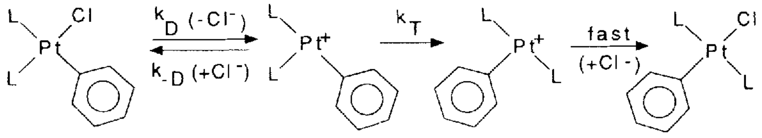
-134 ± 16 J K^{-1} mol^{-1}) are in agreement with a bimolecular attack by the solvent, while the high enthalpy of activation and particularly the largely positive entropy of activation ($\Delta H^{\neq} = 120 \pm 2$ kJ mol^{-1} and $\Delta S^{\neq} = +88 \pm 8$ J K^{-1} mol^{-1}) would suggest a dissociative mechanism for isomerization.

The mechanism which accounts for the experimental findings (Scheme I) involves the dissociative loss of the Cl ligand to yield a T-shaped "*cis*-like" 3-coordinate intermediate. This is easily converted to its "*trans*-like" counterpart which eventually takes up the halide ion to yield the *trans* product. A single symmetric intermediate, which had the ability to recombine with the halide ion in alternative ways, one leading to the *cis* and the other to the *trans* product, could not account for halide ion mass-law retardation.

In the absence of the halide ion the rate of isomerization is given by k_D and represents a direct measure of the metal–halide bond breaking.

This is obviously an oversimplified reaction scheme, since it does not account for the trapping of the first unsaturated intermediate by the solvent. We have carried out systematic investigations on a wide series of *cis*-$[Pt(PEt_3)_2(R)(X)]$ complexes with the aim of comparing how structural changes produced upon the substrate affect the rates of solvolysis and isomerization. Essential features of these processes are: (i) mass-law retardation produced by X^- on the rates of isomerization, (ii) large values of enthalpy of activation and the positive entropies of activation associated with isomerization, (iii) rates of solvolysis much higher than the rates of isomerization, except in one case that will be discussed apart, and characterized by low enthalpies and largely negative entropies of activation.

The rates of methanol solvolysis of Br in *cis*-$[Pt(PEt_3)_2(R)(Br)]$ are dramatically reduced by the increasing steric crowding produced by ortho alkyl substituents on the coordinated aromatic ring



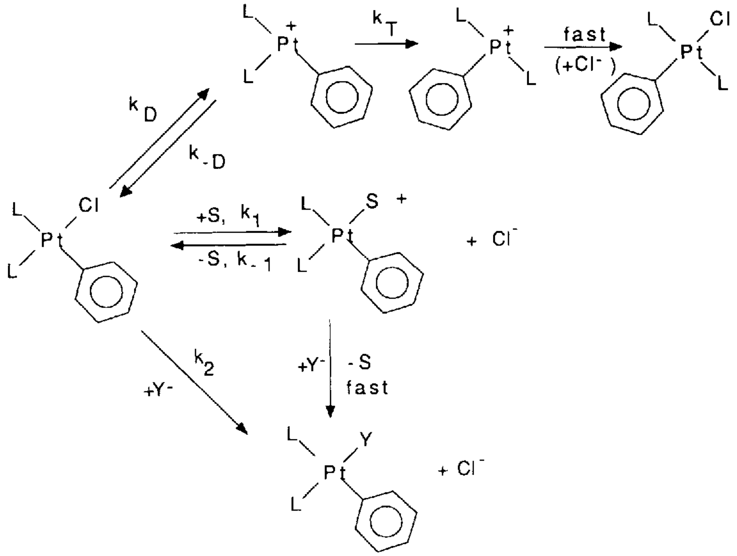
SCHEME 1

(e.g., $10^3\ k_S$ (s^{-1}, 30°C): 6.000, R = Ph; 54.4, R = o-MeC_6H_4; 16.2, R = o-EtC_6H_4; 0.19, R = 2,4,6-$Me_3C_6H_2$) and approach the rates of isomerization (k_i values) which in contrast are not affected significantly.[18] This is consistent with the idea that halide loss from the substrate leads to the formation of a 3-coordinate T-shaped intermediate which maintains memory of the original structure and does not require relief of steric strain to the remaining ligands, which essentially keep their original position around the metal.

As expected, *cis-trans* isomerization is particularly sensitive to factors controlling bond dissociation, *viz.* the nature of the halide ion and changes in the electron density at the reaction center, brought about by para o-meta substituents on the aromatic ring. Thus, the rates of isomerization of *cis*-$[Pt(PEt_3)_2(YC_6H_4)(X)]$ (X = Cl, Br and I; Y = H, *m*-Me, *p*-Me, *m*-OMe, *p*-OMe, *m*-F, *p*-F, *m*-Cl, *p*-Cl, *m*-CF_3, *p*-CF_3) decrease with decreasing electron-donating ability of the Y substituent.[19] The same factors hardly affect the rates of solvolysis. Correlation of k_i with Hammett's parameters of the Y substituents or with the set of Swain and Lupton dual-substituent parameters indicates that σ inductive effects are dominant, the participation of the aryl π-bonding system in the stabilization of the platinum cation intermediate being modest and of secondary importance with respect to σ bonding.

Solvent effects have been used as a further criterion to distinguish between associative and dissociative reaction paths. The rates of isomerization, solvolysis and nucleophilic substitution of the complex *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ have been measured in a series of alcohols.[20] These processes represent three different ways of removing the chloride ion from the coordination sphere of the metal (Scheme II); the magnitude of the solvent effect was found to depend on the degree of charge separation occurring in the transition state.

Thus, fairly good straight lines correlate the rates of isomerization and some empirical parameters which measure the relative electrophilic character of the solvent such as the α values of the Taft HDB scale or the Dimroth–Reichardt E_t values. The role of the solvent is to promote the breaking of the Pt–Cl bond in the rate determining step, and in this respect hydrogen-bonding interactions with the leaving chloride ion are the most important



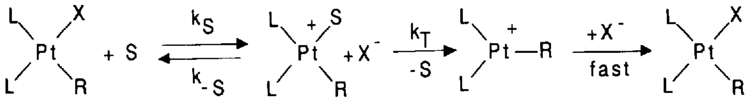
SCHEME II

factor in determining the large difference in rate observed (4 orders of magnitude on going from methanol to 2-methyl-2-propanol). By way of contrast, nucleophilic displacement of the chloride ion from the same complex either by the solvent or by thiourea is little influenced by the nature of the solvent, in keeping with an associative mode of activation with a small degree of Pt–Cl bond breaking. A full initial state–transition state analysis of solvent effects on the isomerization[21] confirmed that the changes in chemical potential of chloride ion on transfer between solvents $\delta_m\mu^\theta(\mathrm{Cl}^-)$ are responsible for the changes in rate constants observed.

There has been controversy over this mechanism of isomerization. van Eldik *et al.*[22] have reported the measure of the volume of activation ($\Delta V^{\neq} = -14.1$ cm^3 mol^{-1}) for the methanol solvolysis of *cis*-[Pt(PEt$_3$)$_2$(2,4,6-C$_6$H$_2$)Br] which we have already shown (cf. Ref. 18) to proceed at the same rate and with the same $\Delta H^{\neq}$ (67 kJ mol^{-1}) and $\Delta S^{\neq}$ (-95 J K^{-1} mol^{-1}) as those of its uncatalyzed *cis-trans* isomerization. The negative value found for $\Delta V^{\neq}$ lead these authors to favor an associative mechanism for the isomerization of this complex. They extended this conclusion to all the series of *cis*-[Pt(PEt$_3$)$_2$(R)X] complexes, which according to their view isomerize with a preequilibrium mechanism which involves fast and reversible solvolysis of the substrate and a relatively slow isomerization of the solvento complex. This pre-equilibrium mechanism, while assuming the solvento species as the *only* reactive species instead of the starting halide complex, was completely uninformative as to how the geometrical change comes about. Later on, in order to account for positive volumes of activations found for the spontaneous isomerization of some *cis*-[Pt(PEt$_3$)$_2$ (Ph)X] complexes (X = Cl, $\Delta V^{\neq}$ = +6.4 ± 0.4 cm^3 mol^{-1}; X = Br, $\Delta V^{\neq}$ = +7.7 ± 0.3 cm^3 mol^{-1}; X = I, $\Delta V^{\neq}$ = +7.2 ± 0.8 cm^3 mol^{-1}) the same authors[23] worked out an alternative preequilibrium mechanism shown in Scheme III, in which, maintaining that the solvento species is the only reactive species, is proposed that dissociation of the molecule of solvent gives rise to a symmetrical trigonal 3-coordinate intermediate. This proposal has been made even knowing that this should be a high spin species, extremely unstable and of higher energy than other unsymmetric T- or Y-shaped structures and that a single symmetric intermediate would have the ability to recombine with the halide ion in alternative ways, one leading to the *cis* and the other to the *trans* product.

However, there was much independent evidence against this reaction scheme. We showed that the equilibrium constants $K_e = k_S/k_{-S}$ for the complexes *cis*-[Pt(PEt$_3$)$_2$ (Ph)X] (X = Cl, Br and I) calculated from the linear mass-law retardation plots ($k_i^{-1} = k_T^{-1} + (k_T K_e)^{-1}[X^-]$) were very much different from those measured independently by a conductometric method.[24] We showed also that the rate of isomerization k_T, which should be independent of the nature of the leaving X, was in fact dependent on the nature of the halide group.

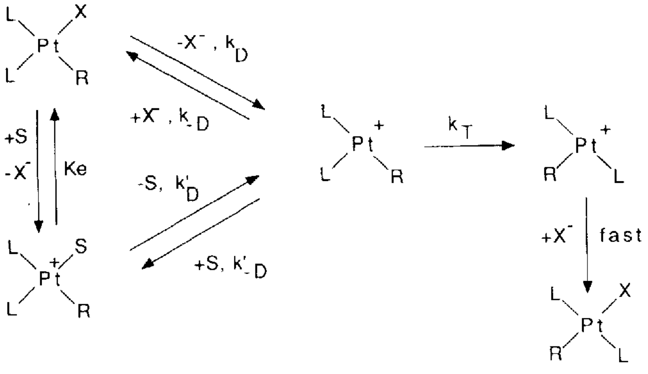
Unmistakable evidence against this reaction scheme was achieved by showing that both the halide and the solvento complexes were



SCHEME III

prone to undergo isomerization and that their rates had completely different values. The solvento complex has been generated in solution by electrophilic attack of the proton on mixed methyl-aryl *cis*-[Pt(PEt$_3$)$_2$(R)Me] complexes. The selective fast cleavage of the methyl–platinum bond produces the *cis*-[Pt(PEt$_3$)$_2$(R)(S)]$^+$ solvento complex in solution, which slowly interconverts into its *trans* isomer. At variance with the corresponding chloride complex, the rates of isomerization of *cis*-[Pt(PEt$_3$)$_2$(Me)(S)]$^+$ (S = a series of hydroxylic solvents) are little influenced by the nature of the solvent and the rates of the two species tend to diverge markedly as the ability of the solvent to assist Pt–Cl bond breaking decreases. Isomerization of *cis*-[Pt(PEt$_3$)$_2$(Me)(MeOH)]$^+$ in diethyl ether–methanol mixtures undergoes mass-law retardation by [MeOH]. As in the case of the related halide species, the isomerization mechanism involves interconversion of two T-shaped 3-coordinate intermediates that show discriminating ability toward scavenging agents.

It is now reasonably clear that reaction Scheme I, although consistent with all experimental findings, represents only a useful approximation in a strong dissociating solvent like methanol, where it is necessary to take into account a solvolytic process and the possibility for both species in equilibrium to undergo isomerization through the dissociative loss of X or MeOH, respectively (Scheme IV).



SCHEME IV

The processes via k_D and k'_D lead to a common T-shaped 3-coordinate intermediate, whose fate depends on the efficiency with which is intercepted by the reentry of either the halide ion (via k_{-D}) or the solvent molecule (via k'_{-D}) in competition with its conversion to the "*trans*-like" counterpart (k_T path).

The rate expression derived for such a reaction scheme is

$$k_i = \frac{k_D\,[\mathrm{X}^-] + k'_D\,K_e}{1 + (k'_{-D}/k_T)[\mathrm{S}] + (k_{-D}/k_T)[\mathrm{X}^-]}\,\frac{1}{K_e + [\mathrm{X}^-]}. \qquad (4)$$

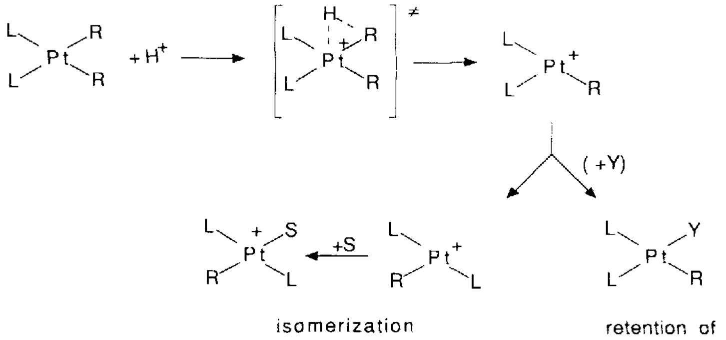
When no halide ion is present in solution, as in the isomerization of solvento species generated in situ, only the lower pathway is operative. In the presence of excess halide ion or when the value of K_e is very low, only the upper pathway, similar to that shown in Scheme I, operates. It was possible to show that the efficiency with which Cl^- captures the first "*cis*-like" intermediate is at least 5 orders of magnitude higher than that of MeOH. Even the apparently anomalous behavior of *cis*-$[\mathrm{Pt(PEt_3)_2(Mesityl)Br}]$ finds an explanation, since the corresponding solvento complex *cis*-$[\mathrm{Pt(PEt_3)_2(Mesityl)(MeOH)}]^+$ has been found to isomerize at a much higher rate ($k_i = 28.8 \times 10^{-3}\ \mathrm{s}^{-1}$, at 30°C) with completely different activation parameters ($\Delta H^{\neq} = 106 \pm 4\ \mathrm{kJ\ mol^{-1}}$, $\Delta S^{\neq} = +75 \pm 8\ \mathrm{J\ K^{-1}\ mol^{-1}}$). A preequilibrium treatment as that in Scheme IV requires that solvolysis of *cis*-$[\mathrm{PtL_2(R)X}]$ is fast and reversible and isomerization of the solvento complex *cis*-$[\mathrm{PtL_2(R)(S)}]^+$ is relatively slow (k_S and $k_{-S} >> k'_D$; $K_e = k_S/k_{-S}$, where k_S and k_{-S} are the rates of solvolysis and anation, respectively). The sterically hindered mesityl complex does not fit these conditions, since it is the only one for which the rate of solvolysis of the halide species is much slower than the rate of isomerization of its solvento complex (k_S and $k_{-S} << k'_D$). Under these circumstances the solvolytic path (via k_S) becomes the preferred route to isomerization, the rates of isomerization and of solvolysis have identical values, and both reactions assume the features of an associative process. A similar pattern of behavior is exhibited by another overcrowded complex *cis*-$[\mathrm{Pt(PEt_3)_2(CH_2C(CH_3)_3)Cl}]$.[25]

To sum up, these studies on mono-organophosphine Pt(II) complexes have made clear that a key step in their spontaneous isomerization is the conversion of two T-shaped 3-coordinate 14-

electron intermediates. The process is favored by factors promoting bond dissociation and inhibited by effective trapping of the first unsaturated intermediate. The solvent plays a major role in the removal of the leaving group and this explains why these *cis*-[Pt(PEt$_3$)$_2$(R)(X)] (X = alkyl, aryl, halide) complexes maintain their stereochemistry in nonpolar solvents, but easily isomerize after the break of the Pt–X σ bond. In the dialkyl or diaryl or mixed alkyl-aryl complexes the fate of the 3-coordinate intermediate resulting from the electrophilic attack by the proton is governed by the presence of potential nucleophiles in the system[26] (Scheme V). When a nucleophile is present in good amount, the vacant coordination site is blocked and we have retention of configuration for the resulting mono-organo product; in the absence of good nucleophiles, *cis-trans* isomerization takes place and the monoaryl product has a *trans* configuration.

Likewise the complexes *cis*-[Pt(C≡CPh)$_2$L$_2$] (L = PPh$_3$ or PMePh$_2$) in CDCl$_3$ transfer the phenylethynyl group to HgX$_2$, [CuCl(PPh$_3$)], CuI or SnCl$_2$ to yield *cis*-[Pt(C≡CPh)L$_2$X]. This latter undergoes a ready geometrical isomerization to its *trans* counterpart that eventually takes up the ethynyl group to yield *trans*-[Pt(C≡CPh)$_2$L$_2$].[27] Thus, isomerization of diorgano complexes occur through the intermediacy of the parent monoorganohalide species. Spontaneous isomerization of *cis*-[Pt(C≡CPh)L$_2$Cl][28] has already been observed.

At this stage it is worth mentioning a fundamental paper by Komiya *et al.*,[29] which concerns the *cis-trans* isomerization of an

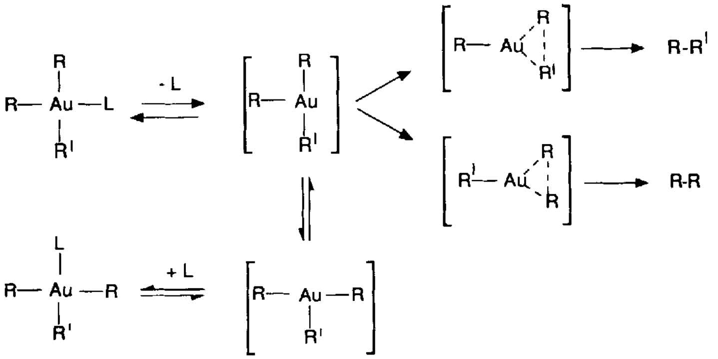


(L= phosphine; S=solvent ; Y=nucleophile)

SCHEME V

alkyl gold complex $[Et(CH_3)_2AuPPh_3]$ in benzene solutions. The mechanism suggested (Scheme VI) is strictly similar to that illustrated before in Scheme I. The trialkylgold species $[Et(CH_3)_2Au]$, formed by the rate limiting dissociation of phosphine, is a common intermediate for both *cis-trans* isomerization and a concurrent process of reductive elimination affording a mixture of ethane and propane. The T-shaped form which we have inferred for the coordinatively unsaturated platinum(II) cation by means of competition experiments has been shown by molecular orbital calculations to be that of lower energy for the 14-electron alkyl-gold intermediate, since the orbital degeneracy of the most symmetrical C_{3h} trigonal geometry favors distortion to T- and Y-shaped configurations. These latters serve as exit channels through which reductive elimination proceeds.

Other kinetic studies in the field have shown that *trans*-$[PdMe_2L_2]$ (L = various tertiary phosphines) isomerizes to the *cis* isomer before elimination of ethane takes place, whereas for *cis*-$[PdR_2L_2]$ (R = Me, Et, Pr) the elimination is preceded by dissociation of the ligand L.[30] A theoretical study[31] of some aspects of the mechanism of reductive elimination of these Pd(II) complexes has revealed that the substantially asymmetric T-shaped "*trans*" $PdLR_2$, arising from dissociation of L from PdL_2R_2, will encounter a consistent energy to its conversion to "*cis*" $PdLR_2$, which in turn has an open channel for reductive elimination of R_2. Packett and Trogler[32] have reported recently that $[PtH_2(PMe_3)_2]$ in solution exists as a mixture of *cis* and *trans* isomers. The rate constant for isomerization was determined by spin-saturation-transfer



SCHEME VI

studies and compared with the rate of phosphine exchange. Although the isomerization may proceed by an associative mechanism involving a solvent molecule or the phosphine ligand, it is suggested that a reasonable alternative pathway is dissociation of PMe_3 from the *cis* and *trans* isomers to form T-shaped intermediates that slowly interconvert. Reductive elimination of hydrogen can take place from a 3-coordinate $PtLH_2$ species.

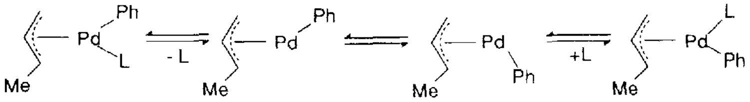
Another interesting example of uncatalyzed *cis-trans* isomerization regards an η^3-crotylpalladium(II) complex $[Pd(\eta^3\text{-crotyl})(C_6Cl_5)(PPh_3)]$ which has been found[33] to undergo isomerization in benzene above room temperature, according to the following reaction scheme (Scheme VII).

The large decrease of the rate on adding free triphenylphosphine is attributed to the occurrence of a dissociative path involving 3-coordinate intermediates. Here again a ligand dependent substitution of PPh_3 by another phosphine takes place at a greater rate than that of isomerization. A dissociative mechanism with the intermediacy of T-shaped intermediates has been proposed also for *cis-trans* isomerization of $[PtL_2Cl_2]$ (L = dialkyl sulfoxide) complexes.[34]

Summing up, these studies on uncatalyzed isomerizations show that the dissociative loss of a ligand to yield a 3-coordinate 14-electron intermediate is a reasonable reaction pathway for a square planar substrate, even though the associative attack by a ligand or the solvent itself, which occurs with complete retention of stereochemistry, is in most cases by far more energetically favored.

β-HYDRIDE ELIMINATION

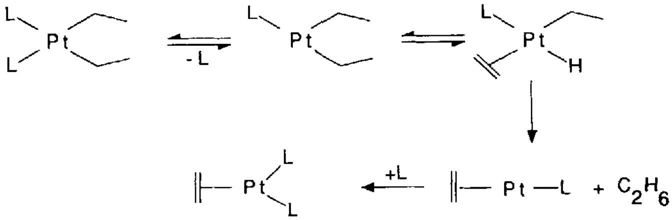
The ease with which a hydrogen atom transfers from the β-carbon atom of an alkyl chain to the metal to produce a metal hydride is



SCHEME VII

of fundamental importance for the stability of organotransition metal compounds, and indeed β-elimination is the best documented low-energy route leading to transition metal–carbon bond scission. Whitesides *et al.*[35] have studied in great detail the mechanistic aspects of the thermal decomposition of several platinum(II) and palladium(II) alkyl complexes including, among others, monoalkyl *trans*-[PtL_2RX] (L = phosphine),[36,37] symmetrical[38] and unsymmetrical dialkyls,[39] and related metallacyclic compounds.[40] The thermolysis takes place most easily when dissociation of the phosphine ligand produces a coordinatively unsaturated T-shaped intermediate having a vacant coordination site for β-hydride elimination, even though the dissociative loss of the ligand is not necessarily the rate determining step of the process (Scheme VIII).

The transient four-coordinate platinum(II) hydride species formed on β hydrogen abstraction of [$PtL(alkyl)_2$] subsequently undergoes reductive coupling of alkyl and hydride ligands and liberation of alkane and alkene. When an excess of phosphine ligand blocks the vacant coordination site at the metal, a higher energy β-elimination from the 16-electron starting complex becomes competitive with the dissociation route. This non-dissociative route has been shown to be active in other cases, in the absence of added phosphine, and then dissociation is not always a prerequisite for the occurrence of the process. Reaction Scheme VIII illustrates the mechanism for thermal decomposition of *cis*-[PtL_2Et_2]. The same mechanism holds for unsymmetrical dialkyl *cis*-[$PtL_2(R)(R')$] complexes, where the formation of the products depends on the nature of the alkyl group involved in the process.[39] For example, in the case of the ethyl-propyl-bistriethylphosphineplatinum(II) com-



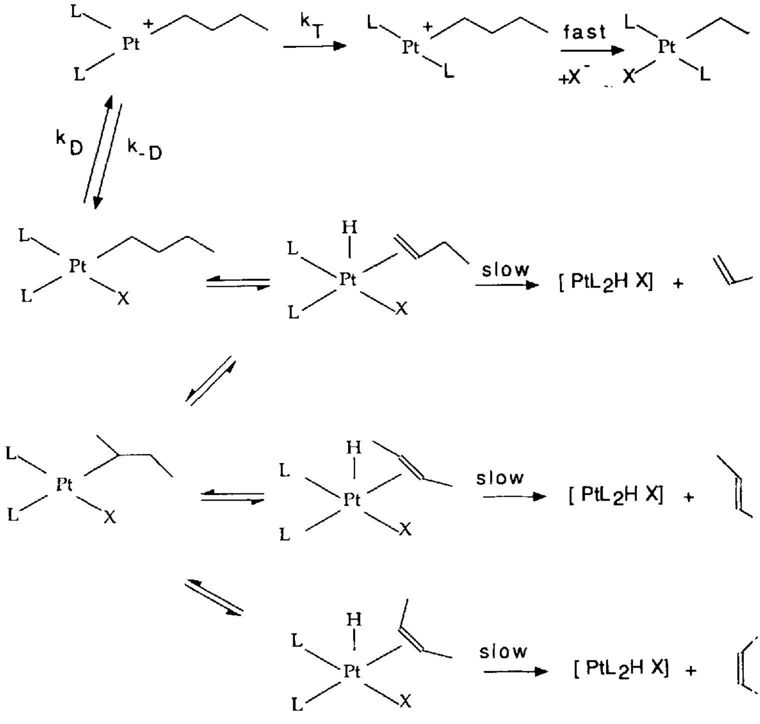
SCHEME VIII

plex, β-elimination from the propyl group produces propene and ethane, while that on the ethyl group produces ethene and propane.

We have recently extended our studies of the spontaneous *cis* to *trans* isomerization to some monoalkyl $[Pt(PEt_3)_2(R)Cl]$ (R = CH_3, C_2H_5, C_2D_5, *n*-C_3H_7, *n*-C_4H_9, $CH_2Si(CH_3)_3$) complexes whose rates and activation parameters have been measured in isopropanol.[41] The choice of this solvent was dictated by the fact that in the better hydrogen bonding methanol the complexes containing alkyl groups with a β-hydrogen isomerize as soon the solid is dissolved. The ethyl, *n*-propyl and *n*-butyl derivatives, in addition to spontaneous isomerization, undergo thermal decomposition through a concurrent pathway yielding *trans*-$[Pt(PEt_3)_2HCl]$ and olefins. The relative rates of the two competing processes have been calculated, taking advantage of the fact that isomerization undergoes mass-law retardation by added chloride ion while the thermal decomposition is unaffected by $[Cl^-]$. The complexes *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = Et, *n*-Pr and *n*-Bu) are stable under the same conditions which promote a facile decomposition of the corresponding *cis* isomers.

As in the case of the related aryl complexes, the isomerization mechanism (Scheme IX) involves dissociative loss of the chloride ligand followed by the interconversion of two geometrically distinct T-shaped $[PtL_2(alkyl)]^+$ 3-coordinate intermediates. An incipient interaction of the β-hydrogens of the alkyl group with the metal in the transition state leading to the first platinum cation intermediate accounts for the much higher reactivity (at least 3 orders of magnitude) of the complexes in which R = C_2H_5, *n*-C_3H_7 and *n*-C_4H_9 with respect to that of complexes containing alkyl groups with no β-hydrogens (CH_3 or $CH_2Si(CH_3)_3$). Thus the platinum cation intermediate interconverts into a geometrically distinct "*trans*-like" T-shaped structure before a complete β-extraction can take place. This is in agreement with the low energy barrier found for the fluxionality of coordinatively unsaturated reaction intermediates such as $H(PH_3)_2Pt^+$,[42] Me_3Au[29] or $Et_2(PEt_3)Pt$.[43] These results emphasize the role of ancillary ligands in assisting the formation and the stabilization of unsaturated 14-electron intermediates.

We suggested that β-hydride elimination involves a fast and reversible addition of a C–H bond to platinum in the square planar



SCHEME IX

complex yielding a 5-coordinate [$PtL_2(H)(olefin)Cl$] intermediate. Fast olefin insertion in this latter leads to the formation of different olefin isomers. The rate determining pathway is the olefin loss from the 5-coordinate intermediate. The simultaneous formation of three olefin isomers, 1-butene, *cis*-2-butene and *trans*-2-butene in the case of the butyl complex is a straightforward indication that the release of organic products must be preceded by a pre-equilibrium in which fast and reversible β-hydride elimination and olefin insertion lead to a facile skeletal isomerization of linear to branched alkyl groups.

Thus, the essential features of the β-hydride elimination of *cis* monoalkyl [$PtL_2(alkyl)Cl$] complexes appear to differ markedly from those found in the decomposition of the strictly related dialkyl compounds[38-40] that, in nonpolar solvents, requires high temperatures leading to platinum (0) products and to disproportionation liberating alkane and alkene in a 1:1 ratio. The first process takes place under much milder conditions until completion; both the starting material and the final-hydride product are stable enough to be isolated as pure compounds and only alkenes are formed. These results would suggest that β-elimination from the 16-electron starting *cis*-$[PtL_2RCl]$ complexes has a much lower energy barrier with respect to a similar process taking place from the strictly related *cis*-$[PtL_2R_2]$ species. The substitution of the ancillary alkyl group with a chloride ion should lead to an increase in the electrophilic character of the metal center and might provide the driving force for the facile β-elimination.

These reactions on monoalkyl Pt(II) complexes exhibit all the characteristics required to a model system. It is possible to measure the sensitivity of the rates of β-hydride elimination to slight structural changes imposed on the substrate and, in a subsequent study,[44] we were interested in searching for a correlation between the lability of the substrates and the nature of the group in the *cis* position to the alkyl and for any effect of the length of the alkyl chain. Thus, we prepared as solids or "in situ" a series of complexes of the type *cis*-$[Pt(PEt_3)_2(R)X]$ (R = n-C_4H_9, X = Cl, Br, I, N_3, NO_2, NCS, NCSe; R = C_2H_5, C_2D_5, n-C_3H_7, n-C_4H_9, X = Br) and have carried out a kinetic study of reaction (5) in acetone. This solvent was chosen in order to prevent the concurrent spontaneous *cis-trans* isomerization from taking place.

$$cis\text{-}[Pt(PEt_3)_2(alkyl)X] \rightarrow trans\text{-}[Pt(PEt_3)_2(H)X] + \text{olefins.} \qquad (5)$$

The results can be discussed in the same framework of the nondissociative mechanism illustrated in Scheme IX and provide a means of ascertaining the importance of the electronic properties of the alkyls and of the *cis* groups in governing the lability of the substrates. The lability was found to depend on the complexity of the alkyl chain. The reactivity sequence Et $<<$ n-Pr $\sim$ n-Bu reflects the ease of olefin liberation from the intermediate ethene $<<$ propene $\sim$ butene. The rates of decomposition of the complexes *cis*-$[Pt(PEt_3)_2(n\text{-}Bu)X]$ were strongly dependent on the nature of the ion X, increasing in the order $N_3 < NO_2 <$ Cl $<$ NCS $<$ Br $<$ NCSe $<$ I, the overall difference of reactivity being at least four orders of magnitude between the first and the last members of the series.

Figure 2 shows that these rate data are correlated by a linear free energy relationship of the type ln $k = m\ \delta\ ^{195}$Pt, where $\delta\ ^{195}$Pt is the chemical shift of the platinum nucleus of the corresponding *trans*-[PtL$_2$HX] complex and m represents the sensitivity of β-hydride elimination to the changes of these chemical shifts (m = 0.017, R = 0.986, by linear regression analysis). Similar LFER correlations including all data points can be obtained with the

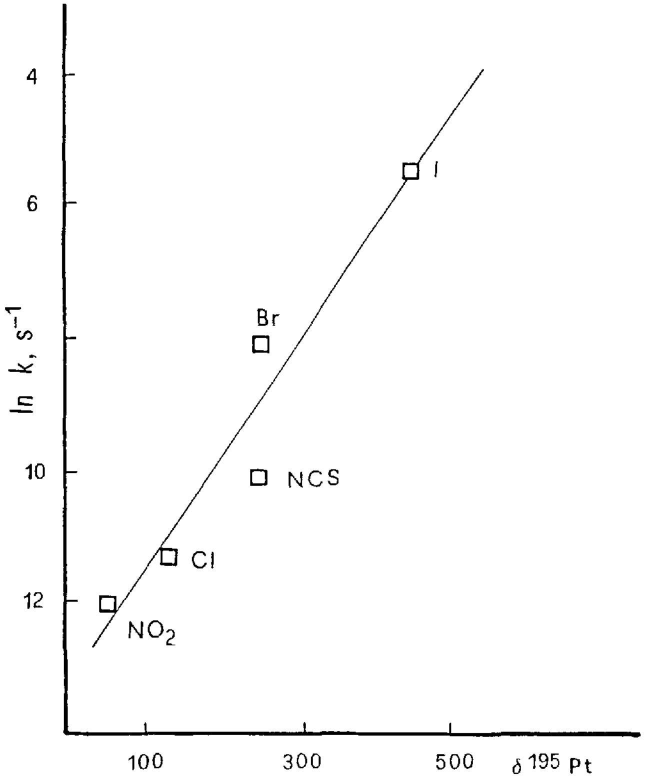


FIGURE 2 Correlation between the rates of β-hydride elimination of *cis*-[Pt(PEt$_3$)$_2$(*n*-Bu)X] complexes and the chemical shifts of the platinum nucleus of the corresponding *trans*-[Pt(PEt$_3$)$_2$(H)X] products.

hydride chemical shift δ ^{1}H (m = 0.99, R = 0.867, seven data points) and with the platinum–phosphorus coupling constants ^{1}J (PtP) (m = −0.04, R = 0.926, seven data points).

All these three NMR parameters can be regarded as good indicators of the covalency of the Pt–X bond and are a measure of the involvement of the d orbitals of platinum in π bonds.[45] In other words, the ligand which is capable of the strongest covalent bond or which forms the strongest π bonds with the metal will produce the highest rate of β-hydride elimination. These results emphasize the role of π back-bonding to the empty π* of the olefinic moiety in the kinetic stability of the 18-electron [PtL_2(H)olefinX] intermediate. Both electron-donating substituents on the olefin and strong covalent bonds of X with the metal operate in the direction of increasing the difference in energy between the filled metal d orbitals and the olefin π* and, as a consequence, back-bonding between the metal and the olefin become weaker.

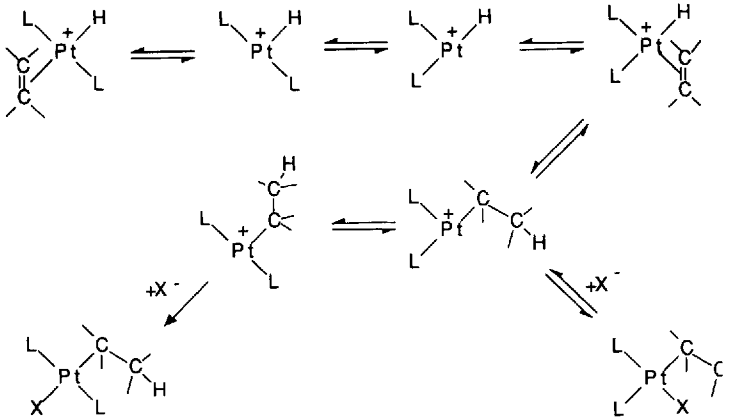
INSERTION REACTIONS

(A) Olefin Insertion

The kinetics and the mechanism of olefin insertion into a Pt–H bond, the reverse process of β-hydride elimination, have been studied in great detail using as starting substrate *trans*-[$Pt(PEt_3)_2$(H)X].[16] The available evidence indicates that insertion is facile when X is a labile group such as NO_3^- or a molecule of solvent. Under these conditions an intermediate of the type [$Pt(PEt_3)_2$(H)(olefin)]$^+$ has been isolated and demonstrated to have the *trans* geometry.[46] It has been argued that insertion most easily takes place when the hydride and the olefin span mutual *cis* positions, and then the isomerization:

$$trans\text{-}[Pt(PEt_3)_2(H)(C_2H_4)]^+ \rightarrow cis\text{-}[Pt(PEt_3)_2(H)(C_2H_4)]^+ \quad (6)$$

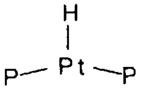
becomes a key step in the reaction pathway and is necessary to explain how the geometrical change comes about. According to our findings on the uncatalyzed isomerization, we suggested[47] that this may occur through interconversion of unsymmetric 3-coordinate species.



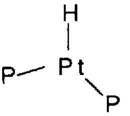
SCHEME X

The reaction scheme (Scheme X) assumes that a facile loss of ethylene from the *trans* isomer yields "*trans*" [HPtL$_2$] which interconverts and takes up the olefin to form the *cis* complex. Migratory insertion on this latter leads to a 3-coordinate "*cis*" [PtL$_2$R]$^+$, after which the reaction follows a pathway identical to that established for uncatalyzed isomerization of *cis*-[Pt(PEt$_3$)$_2$(R)X)] complexes. The migratory insertion step shifts the equilibrium towards the *cis* form of [PtL$_2$R]$^+$ and the subsequent conversion of this latter accounts for the *trans* geometry of the monoalkyl product, revealed by addition of halide ion to the final reaction mixture. Key intermediates in the insertion process as well as in the unassisted isomerization are assumed to be 3-coordinate, 14-electron species and not 4-coordinate. The formation of the *cis*-hydrido-olefin intermediate *cis*-[Pt(PEt$_3$)$_2$(H)(C$_2$H$_4$)]$^+$ is not strictly required since there may be alternatively a concerted olefin attack on "*trans*" [PtL$_2$H]$^+$ involving a four centered transition state. Such a pathway can account for the insertion occurring in those cases in which severe steric restrictions imposed by ancillary ligands do not allow the olefin and the hydride to take up mutual *cis* positions in the coordination sphere of a 4-coordinate species.[48]

A molecular orbital study of the insertion of ethylene into a Pt–H bond by Thorn and Hoffmann[42] has made clear that insertion pathways from a 5-coordinate intermediate or from a 4-coordinate complex, with ethylene and hydride *trans* to each other, are not easy. A sequence of dissociative steps to achieve the necessary mutual *cis* position for the hydrido and the ethylene ligand is conceivable. A potential surface for rearrangement of $[HPt(PH_3)_2]^+$



(1)



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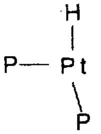


(3)

reveals minima for the "T"-shaped structures 1 and 3 which interconvert with a very small energy barrier via the "Y" structure 2. The calculations indicated also that a concerted attack of the olefin on a 3-coordinate species is also a feasible process, competitive with the pathway involving a 4-coordinate *cis*-$[Pt(PEt_3)_2(H)(C_2H_4)]^+$ species.

(B) Carbonyl Insertion

Early suggestions of the formation of a 3-coordinate Pt(II) intermediate came from a mechanistic study of the insertion of carbon monoxide across a platinum–alkyl bond.[49]

The reaction:

$$[PtL(CO)(Et)Cl] + L' \rightarrow [PtLL'(EtCO)Cl] \; (L = L' = AsPh_3) \qquad (7)$$

has been studied in a variety of non-polar solvents. The observed rates show a non-linear dependence on the concentration of the entering ligand, according to the rate expression $k_{obsd} = k_1k_2[L']/(k_{-1} + k_2[L'])$ and the reaction scheme

$$[PtL(CO)(Et)Cl] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [PtL(EtCO)Cl] \xrightarrow[L']{k_2} [PtLL'(EtCO)Cl].$$

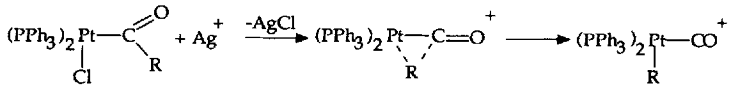
Such a mechanism implies that the formation of the propionyl group from the ethyl and carbonyl ligands in the pathway leading to a 3-coordinate species is not assisted either by the solvent or the entering group. The above mechanism requires that the value of k_1 for a given substrate should be independent of the nature of the entering ligand L′ and increases with increasing size of the coordinated ligand L. The former expectation has been confirmed by kinetic data on the conversion of the methyl carbonyl complex $[Pt(CO)(PPh_3)(I)Me]$ into acetyl derivatives $[Pt(PPh_3)(L')(COMe)I]$ when reacting with a variety of arsines or stibines ($L' = AsPh_3$, $As(p\text{-tolyl})_3$, $As(o\text{-tolyl})_3$ and $SbPh_3$) in tetrahydrofuran.[50] An apparent change in kinetic behavior (first order dependence on the concentration of the entering ligand), which arises when phenyl groups in the coordinated phosphine ligand are replaced by *o*-tolyl groups, may be ascribed to a marked decrease in the rate constant for reaction of the intermediate with L′ (k_2 path) through crowding by the *o*-tolyl substituents.

(C) Carbonyl De-insertion

Abstraction of chloride by $AgPF_6$ from acyl complexes of the type $[Pt(PPh_3)_2(RCO)Cl]$ (R = alkyl or aryl) in ethanol leads to migration of R from carbon monoxide to platinum to form cationic platinum alkyl-(aryl)-carbonyl complexes.[51] The rearrangement of these acyl complexes to the cationic carbonyl species is thought to proceed through an intermediate in which the R groups interact with one of the coordination sites of the metal (Scheme XI). A vacant 4-coordinate site rather than a vacant 5-coordinate site is more likely to act in this manner.

No such rearrangement occurs in acetonitrile, since this solvent binds the platinum atom, thus blocking the fourth vacant site and alkyl(aryl)–metal interaction.

In contrast to the facile alkyl- or aryl-migration from carbon monoxide on chloride abstraction from the acyl complexes, a similar reaction of $[Pt(PR_3)_2Cl(RSO_2)]$ with $AgPF_6$ does not lead to the expected migration of R from SO_2 to the metal but rather to



SCHEME XI

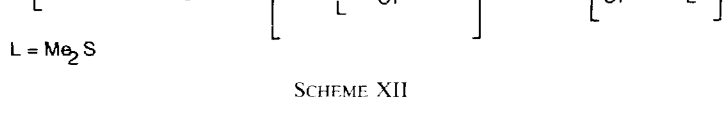
rearrangement of the sulfinato-S to the bidentate sulfinato-O,O′ in the $[Pt(PPh_3)_2(RSO_2)]PF_6$ complex.[52] During its rearrangement, the sulfinato-S ligand is thought to utilize the vacant coordination site on the metal needed for alkyl or aryl migration.

ALKYL FOR HALOGEN EXCHANGE REACTIONS

Methyl for chloro exchange reaction in $CDCl_3$ solution between *cis*-$[PtMe_2(SMe_2)_2]$ and *trans*-$[PtCl_2(SMe_2)_2]$ to yield *trans*-$[Pt(SMe_2)_2MeCl]$ occurs after preliminary dissociation of the dimethyl sulfide from the dialkyl compound to form a coordinatively unsaturated "*cis*-like" $[PtMe_2(SMe_2)]$ intermediate.[53] This is borne out by mass-law retardation produced in the rate of exchange by addition of free SMe_2 in solution. A key step of the process is the attack of the electron deficient $[PtMe_2(SMe_2)]$ species to either the chloride or the thioether groups bonded to $[PtCl_2(SMe_2)_2]$ to yield a μ-chloro or μ-SMe_2-bridged adduct, as in reaction Scheme XII. Thus two reaction pathways for the breakdown of the adduct are feasible followed by fast readdition of thioether.

DISSOCIATIVE SUBSTITUTION

In the previous part of the paper we tried to show that square planar complexes possess a dissociative mode of activation, which, however, is modest and in most of cases negligible with respect to the great propensity of the species to undergo associative attack to form a 5-coordinate intermediate. We would like to illustrate at this point some cases in which dissociation is the prevalent reactivity pathway of a substrate, even in the presence of a large excess of nucleophile, and is not the result of the suppression of the normal associative pathway.



SCHEME XII

The first study[54] has been carried out on the diphenyl-bis-sulfoxide platinum(II) complex *cis*-$[Pt(Ph)_2(Me_2SO)_2]$. A relevant feature of the structure of this compound is the great lengthening of the platinum–sulfur bond, caused by the strong *trans*-influence of the phenyl groups. Even in the bis-sulfide *cis*-$[Pt(Ph)_2(Me_2S)_2]$ complex,[55] which behaves in the same way as the bis-sulfoxide analogue, the presence of the *trans* phenyl groups produce a great lengthening of the platinum–sulfur bonds.

We have examined the kinetics of replacement of both sulfides or sulfoxides by chelating ligands (L-L) in benzene solution in the reaction:

$$cis\text{-}[Pt(Ph)_2(S)_2] + \text{L-L} \rightarrow cis\text{-}[Pt(Ph)_2(\text{L-L})] + 2\ S \qquad (8)$$

(S = Me_2S or Me_2SO; L-L

= bpy; bpym; phen; dpte; dppe; dppp)

The spectral changes which accompany the reactions showed that there is not the build-up in solution of any species different from the starting material and the final $[Pt(Ph)_2(\text{L-L})]$ reaction product. The same indication came from the NMR spectra. The plot which illustrates the kinetic behavior for the entry of nitrogen chelating ligands such as 2,2′-bipyridyl(bpy), 2,2′-bipyrimidine(bpym) or 1,10-phenanthroline(phen), at increasing concentrations of free S (S = Me_2S or Me_2SO) showed that the rate tends to become independent of the concentration of the reagent L-L as this last increases. Thus we see typical saturation plots, as a result of competition between the entering and the leaving group for a reaction intermediate. Saturation is held back by adding S. The reactions with chelating agents having donor atoms different from nitrogen, such as dithioether (1,2-bis(phenylthio)ethane (dpte)), or much better a bisphosphine(1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane(dpp). are considerably faster than those with nitrogen chelates. The plot diverges from a saturation behavior and the rate constants tend to have a linear dependence on the concentration of the entering ligand (see Fig. 3). The general rate law derived is

$$k_{obsd} = a[\text{L-L}]/(b[S] + [\text{L-L}]) + c[\text{L-L}] \qquad (9)$$

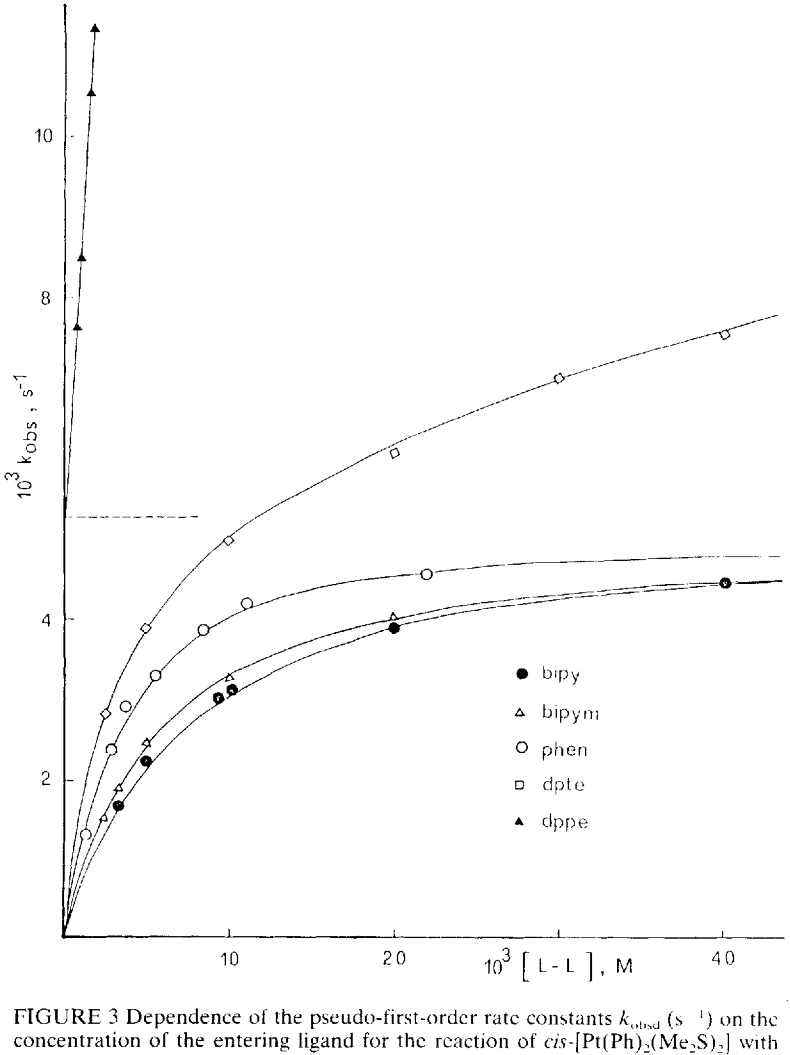
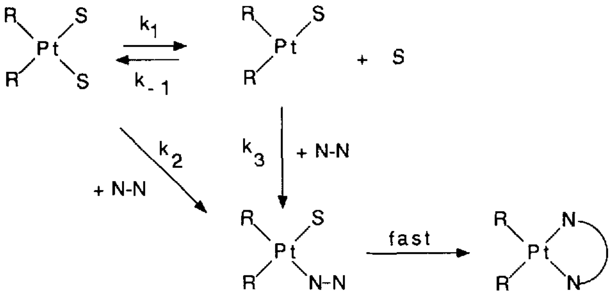


FIGURE 3 Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the concentration of the entering ligand for the reaction of *cis*-[Pt(Ph)$_2$(Me$_2$S)$_2$] with various reagents at 303.2 K in benzene solution. [Me$_2$S] = 0.005 M.

and the best values of the constants *a*, *b* and *c*, together with their standard deviations, were obtained by multiple nonlinear regression of k_{obsd} vs. [L-L] and [S] dependencies.

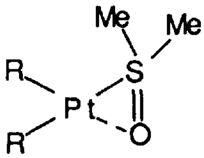
All this evidence can be accommodated by the reaction Scheme XIII which is, in some way, reminiscent of that usually found in



SCHEME XIII

substitution at square planar complexes. There is a nucleophile independent pathway (via k_1) which involves the dissociative loss of the ligand S to yield a coordinatively unsaturated 14-electron intermediate. This latter can undergo the re-entry of the leaving group (k_{-1} path) or can take up the entering ligand to form a transient open-ring species (k_3 path). There follows fast ring closing. The open-ring species can be formed also by a direct bimolecular attack of the reagent on the substrate (via k_2). From the kinetic analysis it is possible to get the values of k_1, rate constant for dissociation of the ligand, k_2, rate constant for the direct bimolecular attack and of the ratio k_3/k_{-1} which measures the efficiency with which the unsaturated intermediate is captured by the entering ligand, in competition with the re-entry of the leaving group. For most of the reagents the dissociative route is the only one operative.

Three-coordinate [$PtR_2(Me_2SO)$] species, unlike [$PtR_2(Me_2S)$], have a lifetime long enough to discriminate among different nucleophiles because of the tendency for the oxygen of the remaining sulfoxide to satisfy the electron deficiency by interacting partly at the vacant coordination site. This is borne out either from the values of the ratio k_3/k_{-1} or from the comparison of the values of the activation parameters of thioether and sulfoxide complexes.



Dimethyl complexes behave in a way similar to that found for the parent aryl compounds.[56] Changes from Ph to Me, while obviously increasing the steric disposability of the substrate to a bimolecular attack, do not greatly affect the easy with which the dissociative activation takes place.

The assessment of the mechanism has been made essentially on the basis of (i) the saturation kinetics observed on plotting the rate constants against the concentration of the entering ligand, as a result of mass-law retardation produced by the leaving thioether or sulfoxide, (ii) the independence of the rate of dissociation of the nature of the entering group, (iii) the identity of the rate of dissociation with the rate of solvent exchange, at least in the case of exchange between free and coordinated Me_2SO in *cis*-$[PtPh_2(Me_2SO)_2]$, (iv) the sign and the magnitude of the entropy of activation are always low and even positive, except for the case of *cis*-$[PtPh_2(Me_2SO_2)_2]$. The solvent was assumed to be insufficiently coordinating to give an associatively activated contribution.

Strong support for ligand dissociation as the dominant pathway comes from a recent study of the pressure effect on the ligand exchange rate constants for the reactions:

$$\textit{cis}\text{-}[PtR_2S_2] + 2\ {}^*S \rightleftharpoons \textit{cis}\text{-}[PtR_2\ {}^*S_2] + 2\ S \qquad (10)$$

$$(R = Ph \text{ or } Me;\ S = Me_2SO \text{ or } Me_2S)$$

which were studied in non-polar solvents as a function of pressure, up to 200 MPa, by high resolution ^1H NMR magnetization transfer experiments.[57] The values of volume of activation obtained for *cis*-$[PtPh_2(Me_2S)_2]$ ($\Delta V^{\neq} = +4.9 \pm 0.5$ cm^3 mol^{-1}), *cis*-$[PtPh_2(Me_2SO)_2]$ ($\Delta V^{\neq} = +5.5 \pm 0.8$ cm^3 mol^{-1}) and *cis*-$[PtMe_2(Me_2SO)_2]$ ($\Delta V^{\neq} = +4.9 \pm 0.5$ cm^3 mol^{-1}) are supportive and implement all the previous experimental evidence arising from substitution kinetics and are conclusive of a dissociative mode of activation. Indeed, in these exchange reactions in nonpolar solvents, the solvational part due to electrostriction or to other volume changes of the molecules of the surrounding diluent solvent can be assumed to be constant through the reaction ($\Delta V^{\neq}_{\text{Solv}} = 0$) and the measured volume of activation represents only the change in volume ($\Delta V^{\neq}_{\text{intr.}}$) due to changes in bond lengths and angles.

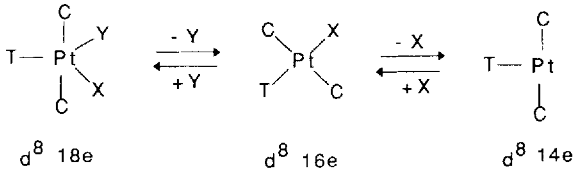
Once the mechanistic picture is reasonably clear and is consistent with all the experimental evidence at hand, the main question which begs an answer is what factors are promoting the facile dissociation of these complexes. Their lability very similar being, as well as the associated activation parameters, one is lead to conclude that the main factor promoting dissociation is the strong σ-donor power of the Pt–C bond which lengthens and weakens the trans Pt–S bond. A comparison of the few existing structural data in the literature for related *cis*-$[PtCl_2L_2]$ and *cis*-$[PtPh_2L_2]$ (L = S-bonded Me_2SO or R_2S)[55–58] indicates that when Cl is replaced by Ph as the *trans*-activating group the Pt–S(thioether) or the Pt–S(sulfoxide) bond distances are lengthened at least 0.1 Å. This ground state destabilization produced on moving from chloride to phenyl or alkyl (lengthening and weakening of the trans Pt–S bond distance) is accompanied by a sharp changeover of reactions pathways. Indeed, the complexes *cis*-$[PtCl_2(Me_2S)_2]$,[59] *cis*-$[PtCl_2(Me_2SO)_2]$,[60] and similar coordination compounds such as $[Pt(en)(Me_2SO)_2]^{2+}$ [61] (en = 1,2-diamminoethane) and $[Pt(Me_2SO)_4]^{2+}$ [62] are known to undergo substitution by way of the normal associative mode of activation.

However, in our opinion, it can hardly be assumed that this relevant difference of kinetic behavior is due exclusively to ground-state destabilization and a better understanding of the phenomenon must await a detailed study of the changes of electron density produced at the metal center on changing ligands. At any rate, these systems offer the unique opportunity of comparing dissociative and associative processes and to gain insight into their relative sensitivity to structural changes imposed on the substrates. For example, it was found that the dissociative displacement of thioethers from *cis*-$[PtPh_2L_2]$,[63] where L encompasses a wide range of thioethers of different steric and electron-donating properties, is much less sensitive to changes in the characteristics of the leaving thioether than the associative displacement of the same L from $[Pt(bpy)ClL]^+$. In other words, a bimolecular process is much more sensitive to leaving group effects than a dissociative one. At first sight this conclusion seems paradoxical. The explanation for this pattern of behavior requires some knowledge of the details of the intimate mechanism of the bimolecular reaction that is characterized by an easy addition of the nucleophile to the square planar substrate to form a five coordinate intermediate and by a considerable amount of bond breaking in this latter to reach the transition state (two maxima in the energy profile separated by a minimum, corresponding to the transient 5-coordinate, with the second maximum rate determining). Under these circumstances, the extent of bond breaking required to reach the transition state in the bimolecular process is much higher than in the dissociative one, where the bond is already lengthened and weakened, and this is reflected in the different sensitivity of the two processes to leaving group effects.

CONCLUDING REMARKS

Four-coordinate, 16-electron Pt(II) complexes may lead to either 5-coordinate, 18-electron or 3-coordinate 14-electron species (see Scheme XIV).

The 18-electron species may either be isolable compounds amenable to structural studies or have been postulated as labile intermediates in reaction mechanisms on the basis of kinetic evidence. Three-coordinate, 14-electron platinum(II) species provide further examples to the growing list of exceptions to Tolman's 16–18 electron rule.[64] Removal of chloride ligand from *trans*-$[Pt(P(t\text{-}Bu)_3)_2HCl]$ by silver salts of noncoordinating anions has lead to the synthesis of a hydrido $[Pt(P(t\text{-}Bu)_3)_2H]^+$ cation in which the formally 3-coordinate platinum(II) seems stabilized by the sterically hindered tri-*tert*-butylphosphine ligand.[65] The synthesis of some 3-coordinate rhodium(I) compounds has also been reported,[66] and the best documented example is the cation $[Rh(PPh_3)_3]^+$ that has been characterized by means of crystallographic analysis.[67] Synthetic routes to complexes of such unusually low coordination number must compete with their inherent high reactivity and with the ten-



SCHEME XIV

dency for the vacant coordination site to be occupied by a molecule of solvent. For this reason successful synthesis and isolation of 3-coordinate d^8 species are a rarity. However, their existence as reaction intermediates can no longer be doubted and the possibility of their formation along a reaction path must be taken into account as well as that of 5-coordinate species.

We have seen a number of processes of platinum(II) substrates in which 3-coordinate species are key intermediates. One is lead to wonder why we have dissociation and when it begins to be competitive with the easy addition of a fifth ligand. There are strong indications that extensive electron transfer to the metal associated with the presence of one or more Pt–C σ bonds helps dissociation, but to what extent this is due to ground state destabilization or to an increase of electron density at the metal preventing the approach of nucleophiles or to other unknown factors remains to be clarified. The electrophilicity of the metal center could well play a major role in dictating the choice of reaction pathways. Once the coordinatively unsaturated species is formed its fate depends on the efficiency with which it can interconvert, as in the spontaneous isomerizations, or undergo intramolecular processes, as in the β-hydride elimination or in the insertion reactions, or be intercepted in solution by the solvent, nucleophiles or other chemical species. We cannot make reasonable previsions about the preferred and lower energy pathway. The tendency for ancillary ligands to satisfy the electron deficiency by interacting partly at the vacant coordination site has seldom been recognized and this leads to a further uncertainty in defining the formal valence-state and coordination number. It is possible to conclude then by saying that the study of 3-coordinate 14-electron species is in its infancy, and at this stage offers more problems than solutions, but holds promise of being a new fascinating field of research.

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References

1. S. J. Lippard, Pure Appl. Chem. **59**, 731 (1987); J. Reedijk, Pure Appl. Chem. **59**, 181 (1987); S. E. Sherman and S. J. Lippard, Chem. Rev. **87**, 1153 (1987); M. Nicolini, Ed., *Platinum and Other Metal Coordination Compounds in Cancer Chemiotherapy* (Martinus Nijhoff Publishing, Boston, 1988); P. Umapathy, Coord. Chem. Rev. **95**, 129 (1989).
2. J. P. Collman, L. S. Hegedus, J. R. Norton and R. C. Finke, *Principles and Applications of Organotransition Metal Chemistry* (University Science Books, Mill Valley, CA, Chapter 6, 1987); A. Yamamoto, *Organotransition Metal Chemistry* (Wiley, New York, Chapter 6, 1986); P. S. Braterman and R. J. Cross, J. Chem. Soc. Rev. **2**, 271 (1973); P. J. Davidson, M. F. Lappert and R. Pearce, Chem. Rev. **76**, 219 (1976); R. R. Schrock, and G. W. Parshall, Chem. Rev. **76**, 243 (1976); M. C. Baird, J. Organomet. Chem. **64**, 289 (1974).
3. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (John Wiley, New York, 1968); R. G. Wilkins, *The Study of Kinetics and Mechanisms of Transition Metal Complexes* (Allyn and Bacon, Boston, MA, 1974); C. H. Langford and H. B. Gray, *Ligand Substitution Processes* (W. A. Benjamin, New York, 1965); M. L. Tobe, *Inorganic Reaction Mechanisms* (Nelson, London, 1972); J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms* (Brooks/Cole Publishing Co., Monterey, CA, 1985).
4. W. H. Baddley and F. Basolo, J. Am. Chem. Soc. **88**, 2944 (1966); J. B. Goddard and F. Basolo, Inorg. Chem. **7**, 936 (1968); R. Roulet and H. B. Gray, Inorg. Chem. **11**, 2101 (1972); D. A. Palmer and H. Kelm, Inorg. Chim. Acta **14**, L27 (1975).
5. D. A. Palmer, R. Schmidt, R. van Eldick and H. Kelm, Inorg. Chim. Acta **29**, 261 (1978); R. van Eldick, D. A. Palmer, R. Schmidt and H. Kelm, Inorg. Chim. Acta **50**, 131 (1981); E. L. J. Breet, R. van Eldick and H. Kelm, Polyhedron **2**, 1181 (1983); L. Canovese, M. Cusumano and A. Giannetto, J. Chem. Soc. Dalton Trans. 195 (1983).
6. U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, J. Am. Chem. Soc. **87**, 241 (1965); M. Cusumano, G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, J. Chem. Soc. Dalton Trans. 490 (1974).
7. R. Romeo and M. Cusumano, Inorg. Chim. Acta **49**, 167 (1981); M. Bonivento, L. Cattalini, G. Marangoni, G. Michelon, A. P. Schwab and M. L. Tobe, Inorg. Chem. **19**, 1743 (1980).
8. J. J. Pienaar, M. Kotowski and R. van Eldick, Inorg. Chem. **28**, 373 (1989); R. van Eldick, E. L. J. Breet, M. Kotowski, D. A. Palmer and H. Kelm, Ber. Bunsenges Phys. Chem. **87**, 904 (1983); D. A. Palmer and H. Kelm, Aust. J. Chem. **32**, 1415 (1979); E. L. J. Breet and R. van Eldick, Inorg. Chem. **23**, 1865 (1984).
9. J. Berger, M. Kotowski, R. van Eldick, U. Frey, L. Helm and A. E. Merbach, Inorg. Chem. **28**, 3759 (1989).
10. L. Helm, L. I. Elding and A. E. Merbach, Helv. Chim. Acta **67**, 1453 (1984).
11. L. Helm, L. I. Elding and A. E. Merbach, Inorg. Chem. **24**, 1719 (1985).
12. L. Helm, A. E. Merbach, M. Kotowski and R. van Eldik, *High Pressure Research*, in press.
13. G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, Inorg. Chem. **8**, 2207 (1969); G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, Inorg. Chem. **9**, 1525 (1970); M. Cusumano, R. Marricchi, R. Romeo, V. Ricevuto and U. Belluco, Inorg. Chim. Acta. **34**, 169 (1979).

14. V. Ricevuto, R. Romeo and M. Trozzi, J. Chem. Soc. Dalton Trans. 927 (1974); R. Romeo, M. L. Tobe and M. Trozzi, Inorg. Chim. Acta **11**, 2131 (1974).
15. A. Yamamoto, T. Yamamoto and F. Ozawa, Pure Appl. Chem. **57**, 1799 (1985).
16. H. C. Clark, J. Organomet. Chem. **200**, 63 (1980); H. C. Clark and H. Kurosawa, Inorg. Chem. **131**, 1275 (1972); H. C. Clark, C. R. Jablonski, J. Halpern, A. Mantovani and T. A. Weil, Inorg. Chem. **13**, 1541 (1974); H. C. Clark and C. S. Wong, J. Am. Chem. Soc. **96**, 7213 (1974); H. C. Clark, C. R. Jablonski and C. S. Wong, Inorg. Chem. **14**, 1332 (1975); H. C. Clark and C. S. Wong, J. Organomet. Chem. **92**, C 31 (1975).
17. G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, J. Chem. Soc. (A) 1877 (1971).
18. R. Romeo, D. Minniti and M. Trozzi, Inorg. Chem. **15**, 1134 (1976).
19. R. Romeo, D. Minniti and S. Lanza, Inorg. Chem. **18**, 2362 (1979); R. Romeo, Inorg. Chem. **17**, 2040 (1978).
20. R. Romeo, D. Minniti and S. Lanza, Inorg. Chem. **19**, 3663 (1980).
21. M. J. Blandamer, J. Burgess and R. Romeo, Inorg. Chim. Acta **65**, L179 (1982); M. J. Blandamer, J. Burgess, D. Minniti and R. Romeo, Inorg. Chim. Acta **96**, 129 (1985).
22. R. van Eldik, D. A. Palmer and H. Kelm, Inorg. Chem. **18**, 572 (1979).
23. H. Kelm, W. J. Louw and D. A. Palmer, Inorg. Chem. **19**, 843 (1980); W. J. Louw, R. van Eldik and H. Kelm, Inorg. Chem. **19**, 2878 (1980).
24. G. Alibrandi, D. Minniti, L. Monsù Scolaro and R. Romeo, Inorg. Chem. **27**, 318 (1988).
25. R. Romeo *et al.*, manuscript in preparation.
26. R. Romeo, D. Minniti, S. Lanza, P. Uguagliati and U. Belluco, Inorg. Chem. **17**, 2813 (1978).
27. R. J. Cross and F. M. Davidson, J. Chem. Soc. Dalton Trans. 1987 (1986).
28. J. Burgess, M. E. Howden, R. D. W. Kemmitt and N. S. Sridhara, J. Chem. Soc. Dalton Trans. 1577 (1978).
29. S. Komiya, T. A. Albright, R. Hoffmann and J. K. Kochi, J. Am. Chem. Soc. **98**, 7255 (1976).
30. A. Gillie and J. K. Stille, J. Am. Chem. Soc. **102**, 4933 (1980); A. Moravskiy and J. K. Stille, J. Am. Chem. Soc. **103**, 4182 (1981); M. Loar and J. K. Stille, J. Am. Chem. Soc. **103**, 4174 (1981); F. Ozawa, T. Ito, Y. Nakamura and A. Yamamoto, Bull. Chem. Soc. Jpn. **54**, 1868 (1981); R. S. Paonessa and W. C. Trogler, J. Am. Chem. Soc. **104**, 3529 (1982); F. Ozawa, K. Kurihara, T. Yamamoto and A. Yamamoto, J. Organomet. Chem. **279**, 233 (1985).
31. K. Tatsumi, R. Hoffmann, A. Yamamoto and J. K. Stille, Bull. Chem. Soc. Jpn. **54**, 1857 (1981).
32. D. L. Packett and W. C. Trogler, Inorg. Chem. **27**, 1768 (1988).
33. H. Kurosava and S. Numata, J. Organomet. Chem. **175**, 143 (1979).
34. H. J. Price, P. J. Birk and B. B. Wayland, Inorg. Chem. **17**, 2245 (1978).
35. For a review see R. J. Cross in *The Chemistry of the Metal-Carbon Bond*; F. R. Hartley and S. Patai, Eds. (Wiley, New York, 1985, Vol. 2, Chapter 8); G. M. Whitesides, Pure Appl. Chem. **53**, 287 (1981) and Ref. 15.
36. R. L. Brainard and G. M. Whitesides, Organometallics **4**, 1550 (1985).
37. R. L. Brainard, M. T. Miller and G. M. Whitesides, Organometallics **5**, 1481 (1986).
38. T. J. McCarthy, R. J. Nuzzo and G. M. Whitesides, J. Am. Chem. Soc. **103**, 3396 (1981); G. M. Whitesides, J. F. Gaash and E. R. Sdedronsky, J. Am.

Chem. Soc. **94**, 5258 (1972); R. G. Nuzzo, T. J. McCarthy and G. M. Whitesides, J. Am. Chem. Soc. **103**, 3404 (1981); P. Foley, R. Di Cosimo and G. M. Whitesides, J. Am. Chem. Soc. **102**, 6713 (1980); N. Chaudhury and R. J. Puddephatt, J. Chem. Soc. Dalton Trans. 915 (1976).

39. S. Komiya, Y. Morimoto, A. Yamamoto and T. Yamamoto, Organometallics **1**, 1528 (1982).
40. J. X. McDermott, J. F. White and G. M. Whitesides, J. Am. Chem. Soc. **98**, 6521 (1976); T. M. Miller and G. M. Whitesides, Organometallics **5**, 1473 (1986); S. S. Moore, R. DiCosimo, A. F. Sowinki and G. M. Whitesides, J. Am. Chem. Soc. **103**, 948 (1981).
41. G. Alibrandi, M. Cusumano, D. Minniti and L. Monsù Scolaro, Inorg. Chem. **28**, 342 (1989).
42. D. L. Thorn and R. Hoffman, J. Am. Chem. Soc. **100**, 2079 (1978).
43. T. J. McCarthy, R. J. Nuzzo and G. M. Whitesides, J. Am. Chem. Soc. **103**, 1676 (1981).
44. G. Alibrandi, L. Monsù Scolaro, D. Minniti and R. Romeo, submitted to Inorg. Chem.
45. T. G. Appleton, H. C. Clark and L. E. Manzer, Coordin. Chem. Rev. **10**, 335 (1973).
46. A. J. Deeming, B. F. G. Johnson and J. Lewis, J. Chem. Soc. Chem. Commun. 598 (1970); H. C. Clark and C. R. Jablonski, Inorg. Chem. 13, 2213 (1974).
47. R. Romeo, D. Minniti and S. Lanza, Inorg. Chim. Acta **18**, L15 (1976); R. Romeo, P. Uguagliati and U. Belluco, J. Mol. Catal. **1**, 325 (1975).
48. G. Bracher, P. S. Pregosin and L. M. Venanzi, Angew. Chem. **87**, 547 (1975); Angew. Chem. Int. Ed. Engl. **14**, 563 (1975).
49. R. W. Glyde and R. J. Mawby, Inorg. Chem. **10**, 854 (1971).
50. C. J. Wilson, M. Green and R. J. Mawby, J. Chem. Soc. Dalton Trans. 1293 (1974).
51. M. Kubota, R. Rothrock and J. Geibel, J. Chem. Soc. Dalton Trans. 1267 (1973).
52. M. Kubota, R. K. Rothrock, M. R. Kernan and B. R. Haven, Inorg. Chem. **21**, 2491 (1982).
53. J. D. Scott and R. J. Puddephatt, Organometallics **2**, 1643 (1983).
54. S. Lanza, D. Minniti, P. Moore, J. Sachinidis, R. Romeo and M. L. Tobe, Inorg. Chem. **23**, 4428 (1984); S. Lanza, D. Minniti, R. Romeo, P. Moore, J. Sachinidis and M. L. Tobe, J. Chem. Soc. Chem. Commun. 542 (1984).
55. G. Alibrandi, G. Bruno, S. Lanza, D. Minniti, R. Romeo and M. L. Tobe, Inorg. Chem. **26**, 185 (1987).
56. D. Minniti, G. Alibrandi, M. L. Tobe and R. Romeo, Inorg. Chem. **26**, 3956 (1987).
57. U. Frey, L. Helm, A. E. Merbach and R. Romeo, J. Am. Chem. Soc. **111**, 8161 (1989).
58. R. Melanson and F. D. Rochon, Can. J. Chem. **53**, 2371 (1975); R. Bardi, A. Del Pra, A. M. Piazzesi and M. Trozzi, Cryst. Struct. Commun. **10**, 301 (1981); W. A. Spofford, E. L. Amma and C. V. Senoff, Inorg. Chem. **10**, 2309 (1971).
59. L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, Inorg. Chem. **20**, 4166 (1981).
60. M. Bonivento, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, Inorg. Chem. **20**, 1493 (1981).
61. S. Lanza, D. Minniti, R. Romeo and M. L. Tobe, Inorg. Chem. **22**, 2006 (1983).

62. Y. Ducommun, L. Helm, A. E. Merbach, B. Hellquist and L. I. Elding, Inorg. Chem. **28**, 377 (1989).
63. G. Alibrandi, D. Minniti, L. Monsù Scolaro and R. Romeo, Inorg. Chem. **28**, 1939 (1989).
64. C. A. Tolman, Chem. Soc. Rev. **1**, 337 (1972).
65. G. R. Goel and C. R. Srivastava, Can. J. Chem. **61**, 1352 (1983); G. R. Goel and C. R. Srivastava, J. Organomet. Chem. **204**, C13 (1981).
66. H. L. M. van Gaal and F. L. A. van den Bekerom, J. Organomet. Chem. **134**, 237 (1977); T. Yoshida, T. Okano and S. Otsuka, J. Chem. Soc. Chem. Commun. 855 (1978).
67. Y. W. Yared, S. L. Miles, R. Bau and C. A. Reed, J. Am. Chem. Soc. **99**, 7076 (1977).