INORGANIC REACTION MECHANISMS

Raffaello Romeo
University of Messina, Italy

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Summary

The intent of this chapter is to give the first elements for the comprehension of the mechanism of inorganic reactions in solution. The coverage is necessarily restricted to some mechanistic aspects of transition metal coordination (Werner type) compounds that are considered essential. The initial part deals with the acquisition of the experimental data, the recognition of the rate law and the mechanistic classification. A survey of ligand substitution reactions on four- and six-coordinate metal centers follows

which includes the exchange at a metal center between coordinated and bulk solvent molecules and the influence of labilization effects caused by ancillary ligands, metal-carbon bonds, basic ligands, etc.. Factors controlling the lability or the inertness of complexes are shortly discussed. Finally, the focus is shifted to the mechanism of electron-transfer reactions and to the dynamic behavior of the ligands.

1. Introduction

Transition metal ions and complexes play a fundamental role in at least three areas of research: (i) bioinorganic chemistry and molecular biology, in investigating the functions of metal complex metalloproteins, (ii) industrial chemistry, in exploiting metal complexes as homogeneous catalysts for the optimization of very important commercial processes, such as polymerization, hydroformylation, hydrogenation, oxidation of olefins, etc., (iii) environmental and medicinal chemistry. Understanding the mechanism of the reactions at transition metal sites is then crucial in designing new inorganic materials, developing industrial homogeneous catalysts, and gaining insight into the role of metalloenzymes in biological processes and metals in medicine. The old motto "every little reaction has a mechanism all its own" appears to be incorrect because, at the present time, the mechanistic tools developed for the analysis of kinetic and extra-kinetic data have proved their worth in the classification of a wide range of reaction types in coordination, organometallic and bioinorganic chemistry. A mechanism is then a predictive theoretical construction that must account for all the kinetic, spectroscopic and theoretical information currently available on a reaction. The mechanistic picture is always on trial and it can or cannot survive to future results coming from the use of more sophisticated experimental and theoretical techniques. In this chapter a description is reported of some fundamental reactions in transition metal chemistry that have established the pattern of reactivity on which contemporary studies are based.

1.1. Historical Background.

In the first half of the last century the organic chemists developed relatively few basic concepts that served to rationalize a series of apparently distinct observations within a unified mechanistic picture. [Ingold, C. K., 1953]. Their work was facilitated by (i) the fact of operating with a single reaction centre (carbon), characterized by a single stable oxidation state, (ii) a detailed knowledge of the structural properties of a large amount of reagents and products, (iii) the mechanistic information gained from the distribution analysis of the products, (iv) the possibility of applying conventional sampling methods to relatively slow processes. The Basolo and Pearson's book *Mechanisms of Inorganic Reactions* (1958) probably marks the beginning of a systematic mechanistic approach to inorganic reactions. In that period much emphasis was placed on relatively slow substitution reactions at octahedral and square-planar sites, making use of well-known cobalt(III) complexes described by Werner and of platinum(II) complexes prepared primary by the Russian researchers. Nowadays, the study of inorganic reaction mechanisms spreads across all the periodic table making use of sophisticated experimental apparatus, and represents a difficult task for chemists that must take into account an extreme variety of factors that include: (i) the nature, oxidation state, and coordination number of the metal, (ii) the characteristics of the spectator ligands, (iii) the geometry of the complex, and (iv) the wide range of reaction types that can take

place at the metal or at other reaction sites. The interest in this research field is reflected in the growing number of textbooks and review articles on the subject. [a selected list of textbooks comprises Atwood, J. D., 1997; Basolo, F., 1967; Burgess, J., 1999; Cannon, R.D.,1980; Henderson, R. A., 1993; Jordan, R. B., 1991; Langford, C. H., 1965; Lappin, A. G., 1994;Tobe, M. L., 1972; Wilkins, R. G., 1991;). The reader who wants to known the up-to-date developments of this theme can go to recent issues of *Advances in Inorganic Chemistry* devoted to such topics as "Inorganic Reaction Mechanisms" (Vol. 54, 2003), "Redox-active Metal Complexes" (vol. 56, 2004), "Homogeneous Biomimetic Oxidation Catalysis" (Vol.58, 2006) or to a thematic issue of *Chemical Reviews* (Vol. 105, 2005) which covers inorganic and bioinorganic aspects of reaction mechanisms, including substitution reactions, activation of small molecules (oxygen, nitrogen, nitrogen oxide, hydrocarbons), electron transfer reactions and, finally, the application of photochemical and quantum chemical methods for the treatment of substitution and rearrangement mechanisms of transition metal complexes.

2. Planning a Mechanistic Study

The most important prerequisite for a mechanistic study is the detailed knowledge of the reaction as far as the stoichiometry, the structural characteristics of the reagents, and even of the products are concerned. Obviously, there is no use in performing kinetic studies of unknown reactions. An accurate synthetic and structural study of the reacting system and of its behavior in solution must precede the collection of the kinetic data. The design of the system must be finalized to get the target of interest in the simplest way, uncomplicated by disturbing side reactions. For instance, in the simple nucleophilic substitution reaction in Figure 1 we see that three out of four coordination sites of the square-planar complex are blocked by the chelating 1,5-diamino-3-aza-pentane (dien) ligand.

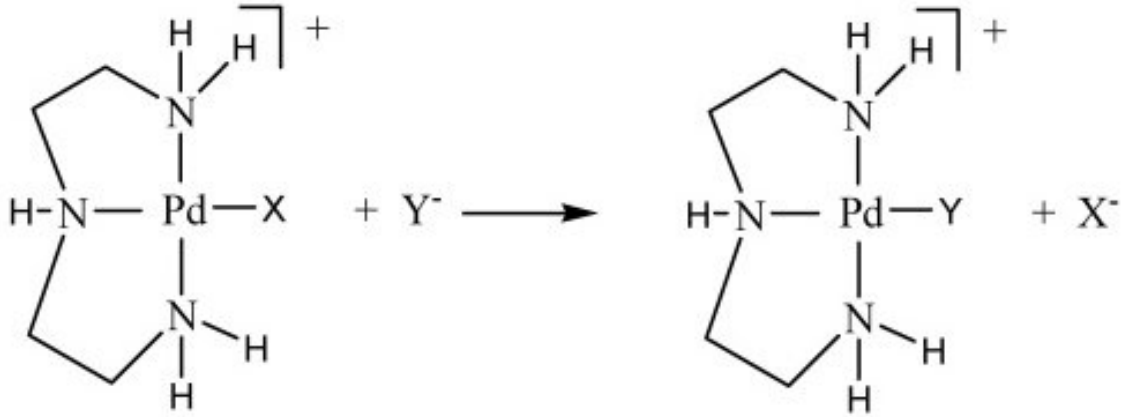

Figure 1: Ligand substitution at a square-planar palladium(II) complexes.

The effects that can easily studied are manifold: (i) leaving group lability, on changing the nature of the leaving X group in the reaction with a single entering reagent (nucleophile) Y, (ii) entering group efficiency, on changing the nature of the entering nucleophile Y in the reaction with a single substrate with a fixed leaving X group, (iii)

steric effects, operating a fine tuning of the steric congestion of the metal center through alkyl (CH_3, C_2H_5, etc.) substitutions at the nitrogen atoms.

The last step of the investigation is to rationalize all the kinetic results in a mechanistic picture that describes the pathway or the pathways, that take place simultaneously or consecutively, by which a reactant is converted into products. The route to the products is reflected in an energy profile which defines the way in which the reactant's ground state becomes activated, the presence of reaction intermediates and their collapse into products. Reaction intermediates are transient and elusive species that occasionally are present in sufficient concentration to be detected by spectroscopic techniques and more rarely are sufficiently long lived to be isolable. More frequently the intermediates are so short-lived species to escape any detection and the researcher must rely only on indirect methods and circumstantial evidence in defining the characteristics of the intermediates and in assessing the reaction mechanism. This latter, as said before, beside being consistent with all the experimentation and the known chemistry of the system, must be predictive of new experimental facts.

2.1. Kinetic Techniques

Monitoring the rate of a reaction occurring in solution usually requires the measure of a physical property of the system directly related to the concentration changes of reactant or products by the use of simple or of sophisticated methods. Any measurement that gives the amount of material as a function of time can be used to generate kinetic data. A variety of spectroscopic techniques are appropriate to the purpose such as ultraviolet/ visible (UV/VIS) or infrared (IR) spectroscopy, fluorescence, circular dichroism (CD), nuclear magnetic resonance (NMR), etc. and the choice will depend upon the type of reaction and the rate of reaction.

UV.VIS spectrophotometry

When the reaction rate is relatively slow, multinuclear nuclear magnetic resonance (NMR) represents an ideal technique for an initial inspection of the system and a subsequent control of the progress of the reaction. At constant temperature, the reaction can be monitored through the decrease in the signals associated to the reactant and the parallel matching increase in the signals of the product. The measure of the rate requires a collection of spectra at suitable times and the integration of the reference peaks. However, visible/UV spectrophotometric techniques offer the advantage over ^{1}H, ^{31}P or ^{13}C NMR, among others, of requiring less demanding expensive apparatus, non-labeled solvents and far less amount of material for the kinetic study. Thus, it is better when possible to follow the reactions by repetitive scanning of the spectrum in the UV/VIS region.

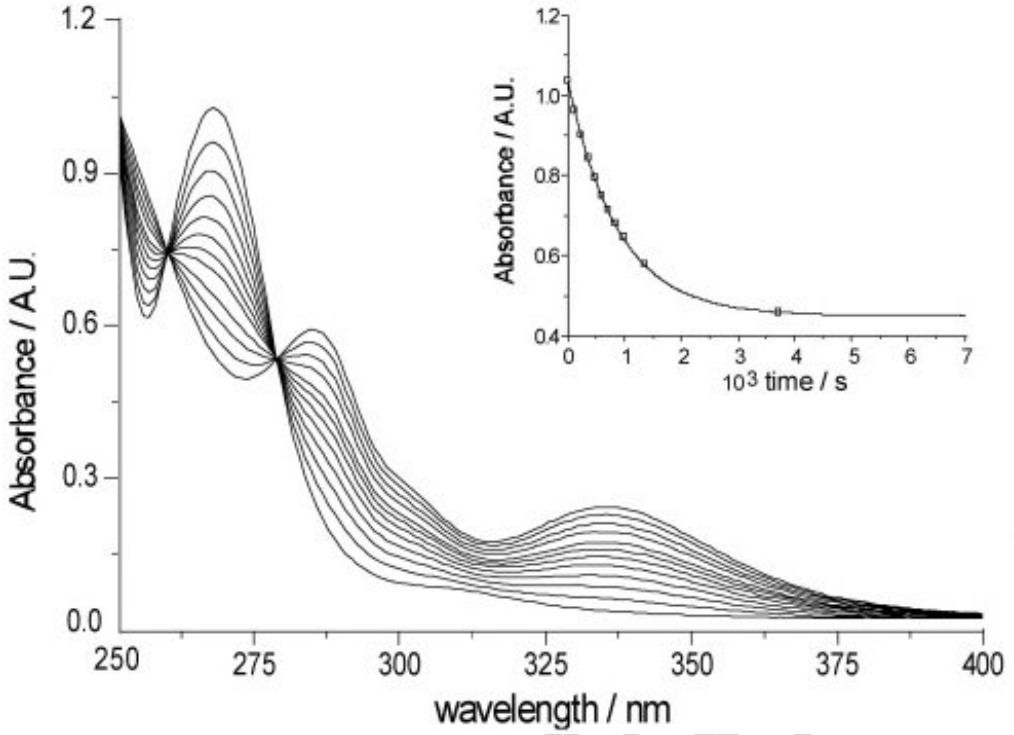

Figure 2: Typical spectral changes, obtained by repetitive scanning of the UV spectrum, of bromide for iodide substitution on the square-planar *trans*-$[Pt(PEt_3)_2Br_2]$ complex in methanol at 298 K . [complex] = 0.0005 M, $[I^-]$ = 0.1 M ; the inset in the figure gives the time dependence of the absorbance at 265 nm from which the pseudo-first-order rate constant k_{obs} = 1.0 x 10^{-3} s^{-1} is calculated by best fitting non linear or linear methods.

In Figure 2 is shown a typical example of slow substitution reaction at a square-planar platinum(II) complex followed spectrophotometrically. The occurrence of well-defined *isosbestic points* (wavelengths at which the absorbance remain constant as the reactant and product composition changes during a reaction) is very informative, indicating the presence in solution of only two species, the starting material and the final product. In other words, there is a single-step conversion from the reactant to the product. In addition, the occurrence of isosbestic points in the spectra indicate the absence in solution of detectable intermediates and the lack of parallel or side reactions. The inset in the figure shows the time dependence of the absorbance (measured at a single wavelength) at constant temperature. Linear or non-linear fitting of this set of absorbance *vs* time data can be analyzed to obtain the value of k_{obs} /s^{-1}(the pseudo-first-order rate constant of the process).

Nuclear Magnetic Resonance

In contrast to the absorption spectra just considered NMR provides data on the lifetime of systems that do not show any change in the optical density with time or that are at equilibrium. Under static conditions the same nuclei in different magnetic environments (say the protons A and B of a molecule coordinated to a metal or in the bulk solvent) will generally have nuclear magnetic resonances at different frequencies giving rise to different peaks. The time scale accessible for a typical NMR spectrum is

10^0- 10^{-6} seconds which covers rates in the range 10^0-10^6 s^{-1}. Changes in the NMR spectrum can provide rate data in the form of lifetime τ_A (the residential time at a specific site) that is the inverse of the rate constant $\left(k = 1/\tau_A\right)$ for the exchange of a nuclei between magnetically non-equivalent sites. According to the value of τ_A the NMR methods that can be used are manifold.

Isotopic Exchange

Relatively slow isotopic exchange reactions require an initial mixing of separate solutions of labeled and unlabeled species in the NMR tube and monitoring of the exchange through the growth or decay of separated signals (as the ^{17}O resonance for water exchange between the complex and the bulk solvent on relatively inert aqua-ions). The example reported in Figure 3 refers to the progressive extrusion of a molecule of dimethylsulfoxide $(CH_3)_2SO$) coordinated to a metal (platinum) under the effect of an excess of uncoordinated deuterated $(CD_3)_2SO$ (undetectable by ^1H NMR). The experiment, carried out in a deuterated inert solvent, allow to study the effect on the rate of different concentrations of the entering ligand [$(CD_3)_2SO$].

Magnetization Transfer

Faster exchange reactions involve the use of dynamic NMR (DNMR) techniques that are based on perturbation of an established equilibrium. Magnetization transfer measurements at constant temperature involve, in the form of the "inversion-recovery technique", a selective inversion of the Boltzmann distribution at one of the exchanging sites and following how this non-equilibrium magnetization is transferred to the exchanging sites as function of time. The selective inversion is accomplished using special pulse sequences. After a variable time, *t*, a non-selective 90' pulse allows observation of the signals. The rate of magnetization transfer between the two nuclei A and B is monitored by the changes in the signal heights of A and B with time and will depend on the lifetime of exchanging sites τ_A that can be calculated by use of particular equations.

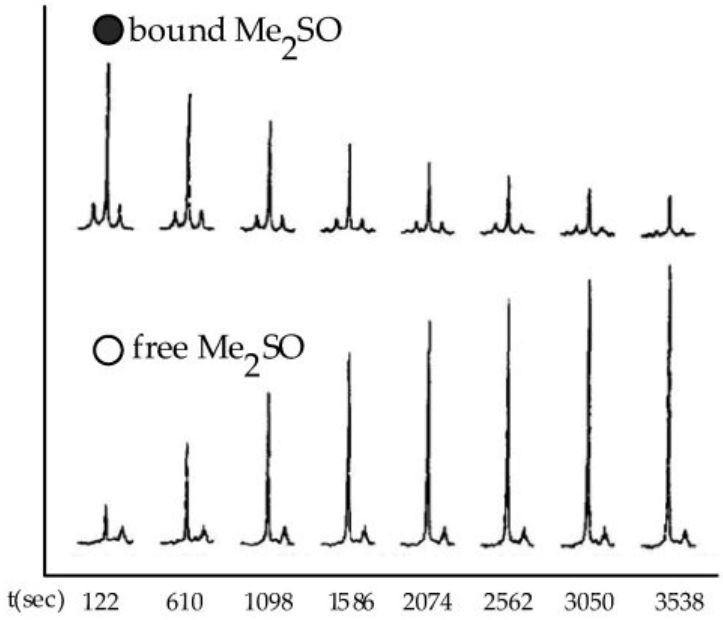

Figure 3: Monitoring the time dependence of solvent exchange on $[Pt(Me)(phen)(CH_3)_2SO)]^+$ (phen =1,10-phenanthroline) in $CDCl_3$ at 298 K. [Complex] = 0.001 M; $[(CD_3)_2SO]$ = 0.007 M; bound $(CH_3)_2SO$): δ= 3.50 ppm; free $(CH_3)_2SO$): δ = 2.60 ppm;

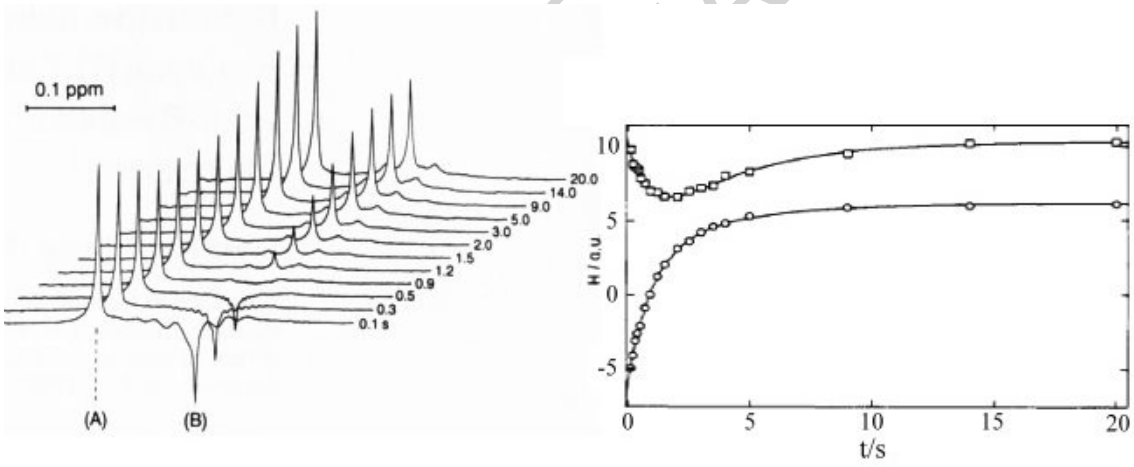

Figure 4: Plot (on the left): 400-MHz ^{1}H NMR spectra of free (A, 0.2 *m*) and coordinated (B) Me_2S at *cis*-$[PtPh_2(Me_2S)_2]$(0.1 *m*) in C_6D_6 solution at 342 K and at 162 MPa . The peak from coordinated sulphide was inverted and spectra were recorded as a function of the time interval t between the inversion pulse train and the observation pulse. Plot (on the right): Calculated curves from the experiment in the left plot: (O) signal height of the central line from the Me_2S bound to Pt and (□) signal height for the free Me_2S. (Reproduced with permission from *J. Am. Chem. Soc.* (1989), 111(21), 8161-5. Copyright 1989 American Chemical Society).

Line-shape Analysis

For still faster exchanging systems, with half-lives < 1 s (25 °C), one can employ a

number of line-broadening methods that involve line-shape change. If the exchange of protons between A and B is maintained sufficiently slow, lowering properly the temperature, sharp lines corresponding to A and B will be recorded. As the exchange rate increases however, it is observed that at first there is an initial broadening of the signals; this is followed by their coalescing, and finally, at high exchange rates, narrowing of the single signal occurs. Coalescence is defined the point just where two resonances converge into a single peak. This behavior is well typified in Figure 5 involving exchange between coordinated and free dimethylsulfoxide at a Pt^{II} complex in a nonpolar solvent.

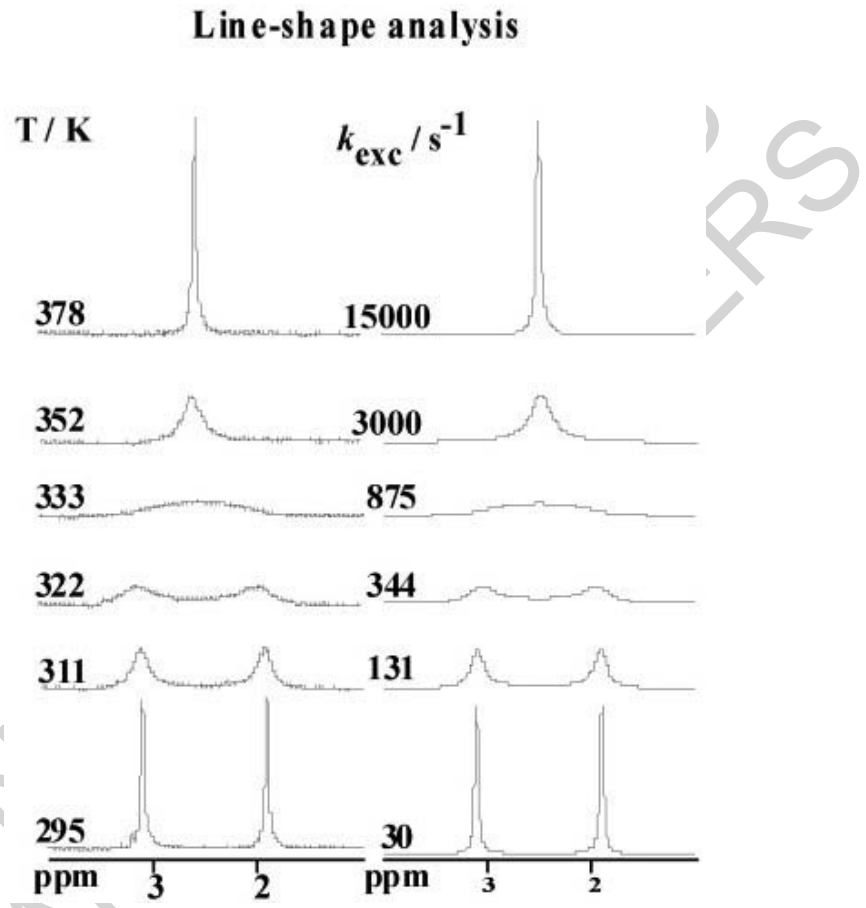

Figure 5: Experimental (left) and simulated (right) ^1H DNMR spectra of the exchange between coordinated and free molecules of Me_2SO in a metal complex . The values of the rate constants (k_{exc}, s^{-1}) were calculated at the corresponding temperatures (T,K).

At a temperature around 295 K the exchange is too slow to affect the signals. Near 322 K, as exchange becomes important, the lines broaden until they coalesce at 333 K. Above this temperature, the proton line appears at average position and continually narrows as the temperature is raised, and the exchange is very fast. The region between 295 K and near 332 K is termed the *slow-exchange region*. That around the coalescence temperature is the *intermediate-exchange region*, and the region above about 378 K is the *fast-exchange region*. Equations have been derived for the lifetime in these different regions of the spectra, such as a series of rate constants versus temperature are generated. Application of the Eyring equation to these rate data allows the calculation of the activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$). In general, the preferred method for analysis

of NMR data involves computer-line-shape fitting that is a powerful tool in mechanistic studies of fluxional systems.

Other Techniques

Many reactions occur too rapidly for conventional absorption spectroscopy and require a rapid mixing of the reagents. In the time required for mixing the reaction would be complete. Rapid mixing methods, as the stopped-flow technique, have been developed and allow observation times to be as short as milliseconds in connection with rapid-scanning spectrophotometers operating at a single wavelength or in a range of wavelengths.

Relaxation methods circumvent the mixing limitations and are based on any perturbation (pressure jump, temperature jump, electric field jump, pH changes, etc.) which alters the concentrations of species at equilibrium. The rate of change of the system from the old to the new equilibrium, the *relaxation*, is dictated by (and is therefore a measure of) the rate constants linking the species at equilibrium. The perturbation must of course be applied more rapidly than the relaxation time of the system under study. A special method for rapid initiation of a reaction employs a large perturbation by a light pulse (usually a laser) or an electron beam. Flash photolysis involves the application of a pulse of high intensity of short duration that will likely produce a highly reactive intermediate or an excited species in few femtoseconds. Pulse radiolysis has similarities to photolysis in that a large perturbation is involved and reactive transients can be produced and examined. Microwave linear electron accelerators are used to produce a high energy electron pulse typically within ns to μs. Reducing and oxidizing radicals result and, therefore, pulse radiolysis primarily promotes redox chemistry inducing clear-cut one electron reduction of multi-reducible centers. A variety of techniques have been linked to monitoring of events following perturbation. Fast time-resolved infrared or UV detection has been used for organometallic and Werner-type complexes. Schematic diagrams of many kinetic apparatus discussed thus far can be found in an excellent chapter of the Wilkins's textbook [Wilkins, R. G.,1991].

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Biographical Sketch

Raffaello Romeo is Professor of General and Inorganic Chemistry at the University of Messina in Italy since 1980 and has devoted much of his career to the study of the mechanisms of inorganic and

organometallic reactions. His interest in the study of mechanistic aspects of the platinum (II) chemistry grew during his postdoctoral work with prof. U. Belluco in Padua and then with Prof. M. L. Tobe at the University College in London with whom he has collaborated for more than twenty years afterwards. The current scientific interest is focused on the role of coordinatively and electronically unsaturated intermediates (3-coordinate, 14-electron species) in fundamental processes of square-planar complexes. Prof. Romeo has delivered lectures in national and international meetings and in many European and USA Universities. He has published more than one hundred and fifty articles on top international journals