26 Mechanisms of reactions in solution

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1 Introduction

As in previous years, this review does not cover mechanisms of heterogeneous or solid state processes, homogenous catalysis of organic reactions, fluxional, electrochemical and photochemical processes, redox reactions involving organic substrates or organic reactions of the p-block elements.

A number of useful reviews have appeared on the application of high pressure to inorganic reaction mechanisms,[1–3] and on theoretical studies of transition metal-mediated reactions used in industry.[4] Smith[5] revisited the solution of the momentum flux integral in TNT[6] and has shown that the results of other workers such as Marcus (1964), Miller (1981) and Robertson, Wagner and Wardlaw (1995) are consistent despite using distinct methods. A mathematical proof suggests flaws in the Elber–Karplas global reaction path-following method.[7] An approach to the molecular modelling of bimolecular reactions has appeared.[8] There have been general reviews on calibration of stopped flow equipment[9] and a new linear method for the determination of rate constants in complex first order reactions.[10] There has also been a general exploration of the thermodynamic consistency of out-of-equilibrium reaction mechanisms.[11]

2 Redox reactions

There has been a review of the use of voltammetry in the study of kinetics and mechanisms of electron transfer reactions.[12]

Long range electron transfer

Compounds in the entatic state have been reviewed[13] and there has been a review of reactions of model complexes for molybdopterin-dependent enzymes.[14] A potentially valuable technique of Refocussed Primary Spin Echo Envelope Modulation

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(RPESEEP) has been used to enhance the signals of nearby protons relative to distant ones[15] and hence to examine structural features of sulfite oxidase. Protons near the Mo(v) centre have been directly detected.

When *Chromatium vinosum* HiPIP, containing the cubane [Fe_4S_4] cluster, was modified with $\{Ru(bpy)_2(im)\}^{2+}$ and the kinetics of electron transfer from the [Fe_4S_4] cluster to the Ru(His-*X*) (*X* are the positions 18, 42, 50 and 81 of the surface histidines) were measured, the rate constants were wide ranging even when the distance between the Ru and the nearest Fe in the cluster was less than 2 Å.[16] This is interpreted as being due to the nature of the tunnelling pathways. The reduction potential of the enzyme parsley FdI is reduced by the attachment of (1,4,8,12-tetraazacyclopentadecane)chromium at position A by about 200 mV.[17] The point of attachment is some 18 Å from the S(Cys-77) in the active site. A further reduction (beyond that required for the attachment of the $Cr^{III}L$ as $Cr^{II}L$) allows the formation of an $Fe^{II}Fe^{II}\cdots Cr^{III}L$ interaction. Tunnelling pathways in bovine heart cytochrome c have been identified as the two major pathways that connect the Cu_A and the haem A in the enzyme.[18] The zinc cytochrome c radical, $Zn(cyt)^+$, produced from cytochrome c is reduced by hexacyanometalates of Fe, W, Os, Mo and Ru[19] and the kinetics of the system fitted to the Marcus theory to give information about the driving forces for the reactions and the self exchange rate constant for $Zn(cyt)^+/Zn(cyt)$ of $1.0 \times 10^7\ M^{-1}\ s^{-1}$. As part of the development of an understanding of the catalytic cycle of liver dehydrogenase,[20] the reaction of [tris(pyrazoyl)hydroborato]zinc hydroxide has been probed using both theoretical and experimental methods. Removal of Cu from the enzyme from *Hansenula polymorha* has the effect of discontinuing enzyme activity.[21] The enzyme was active, however, when Co^{2+} was intoduced and it is concluded that the electron transfer role of the metal was not a necessary feature of conversion of O_2 to H_2O_2. The proposed mechanism suggests an ‘electrostatic centre’ role for the metal ion in stabilising superoxide ion.

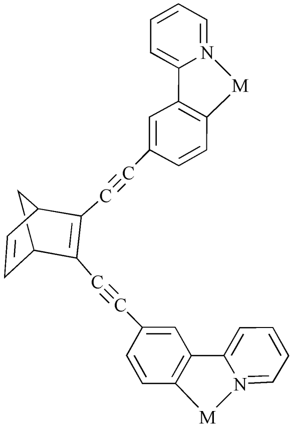
There have been reviews of the relevance of copper oxo and copper–peroxo species[22] and the use of quantum chemical techniques applied to mechanisms of methane monooxygenase,[23] also in the field of mitochondrial energetics, of redox-linked proton transfer design involving structures of quinol–fumarate reductase.[24] There have also been reviews on copper coordination in blue proteins[25] and the effects of driving force on intramolecular and bimolecular electron transfer reactions.[26]

The rate of the reaction $[Ru(bpy)_3]^+$ with *Clostridium pasteurianum* rubredoxin(iii) is near the diffusion controlled limit.[27] The effect of dynamic ionic strength on the reaction is consistent with a charge on rubredoxin(iii) of −9e and a crystallographic radius of about 12 Å. The square pyramidal site, [$Fe(NHis)_4(SCys)$], at centre II in rubredoxin reductase is involved in the reaction of the enzyme with superoxide.[28] Attachment of $[Ru(bpy)_2(im)(H_2O)]^{2+}$ to His-33 in horse heart cytochrome c has allowed the measurement of the electron transfer rate of $2.0 \times 10^5\ s^{-1}$ between the reduced ruthenium moiety and His-33–cyt c(ii).[29] Magnetokinetic effects in electron transfer reactions of $[Ru(bpy)_3]^{3+}$ and ferrous cytochrome c are due to the adiabatic character of the reactions.[30] The mechanistic link between the electron transfer and the folding of proteins is of interest and there have been a number of papers on the mechanisms of the folding process[31–35] and the effects of thermal motions on electron tunnelling[36] and dynamical rate control in protein electron-transfer.[37] The kinetics of re-folding has been investigated by time-resolved NMR.[38] Folding was induced by the photolytic release of Ca^{2+} ions from a photolabile chelator. Electron transfer-triggered folding of 4-helix bundle proteins[39] has been investigated.

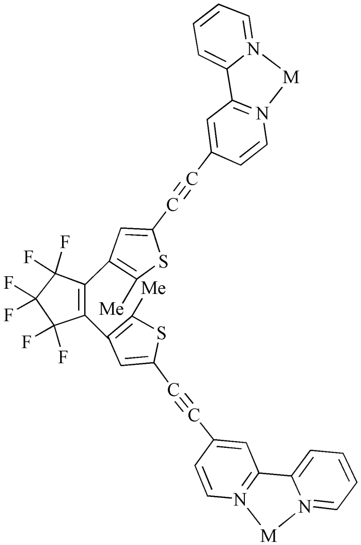
The enzyme galactose oxidase contains one Cu and catalyses the oxidation of primary alcohols to aldehydes.[40] The reaction is stereospecific because of a channel to the Cu, which is 8 Å from the surface of the enzyme. Excellent agreement has been achieved for the experimental and theoretical gradients of a Marcus free energy plot of log k_{12} (k_{12} is the cross reaction rate constant) against $-E^0{}_1/0.059$ from the kinetics of the reduction by 8 organic radicals (*e.g.* riboflavin) of $(Fe^{III})_2$ and tyrosyl-radical-containing active-R2 of *E. coli* ribonucleotide reductase, suggesting that in this process electron transfer is rate determining.[41] Further work in this area has focused on the R2 protein of *E. coli* ribonucleotide reductase.[42] Ceruloplasmin is one of a number of so-called multicopper oxidases in which there are 5 redox-active sites.[43] The kinetics of 4-electron transfer among these sites has been studied and a comprehensive picture of the thermodynamics and kinetics has been developed. Loop-directed mutagenesis has been used to fuse loops of the three blue copper proteins azurin, pseudoazurin and nitrite reductase and to modify the structure of amicyanin, another blue copper protein.[44] The electron exchange rate constants for these mutants were not very different, so this work implies that there is not a unique conformation in the blue copper proteins imbuing them with high electron transfer rates. The authors conclude that an efficient electron transfer system in these species is produced by a β-sandwich, a ligand loop and two ligands attached to the rim of the sandwich structure.

Intramolecular and intervalence electron transfer

A model involving vibronic coupling has been used in the study of electron transfer processes in complexes involving mixed valence complexes of $\{Ru(NH_3)_5\}^{2+,3+}$ which are bridged by *trans*-$[Ru(py)_4(CN)_2]$ and *cis*-$[Os(bpy)_2(CN)_2]$.[45] In ruthenium(II) and osmium(II) polypyridine complexes having spiro-bridged bis(phenanthroline) ligands intramolecular triplet energy-transfer rate constants for the transfer from the Ru(II) part to the Os(II) part have been determined.[46] Electron exchange in a group of molecules having Ru(II) and Os(II) tris(2,2′-bipyridine) groups linked by a butadienyl group which has a central aromatic nucleus occurs as a result of superexchange interactions along the central phenylene group.[47] Ion pairs do not appear to accumulate in the reaction of $[Ru^{III}(edta)(H_2O)]^-$ with $[Fe(CN)_6]^{3-}$ in aqueous solution in a sequential process, forming first $[Ru^{III}(edta)(NC)Fe^{III}(CN)_6]^{4-}$ and then $[Ru^{IV}(edta)(NC)Fe^{II}(CN)_6]^{4-}$ *via* internal electron transfer.[48] Intervalence transitions for the Ru(II,II) state in complexes **1** (M = Ru) have been studied and the Hush equation applied to the system allowing the calculation of 0.068 eV for the metal–metal electronic coupling.[49] The species $[\{FeCp(dppe)\}_n(\eta^n\text{-TCNX})](PF_6)_n$, ($n$ is 1, 2 or 3) exhibits a large electron transfer band in the near IR and the rate[50] of electron transfer (about 10^8 s^{-1} from Marcus theory) has been applied. This owes more to the activation energy than it does to the reorganisational energy of the system. Metal–metal interactions in weakly coupled mixed valence *E*- and *Z*-diferrocenylethylene complexes[51] have been studied. A study of a range of Pc complexes containing homo- or hetero-metallic ions, M and M′ (M,M′ Zn^{II},Zn^{II}, Zn^{II},Co^{II}) which have one or two



1a


N
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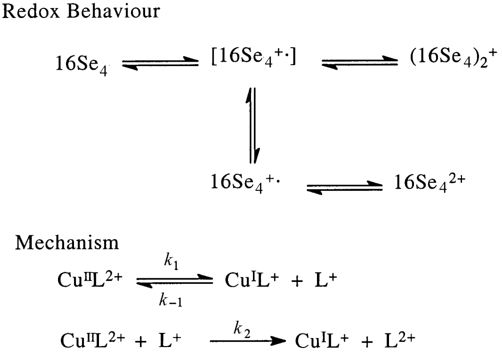
1b

bridges consisting of diethynylethene, indicates that electronic communication across the bridges between the two Pc ligands occurs.[52]

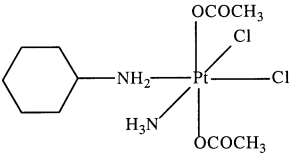
Outer-sphere electron transfer and self exchange reactions

Gated electron transfer is said to occur when the conformational change during an electron transfer process involving copper complexes of macrocyclic thiaethers becomes the rate limiting step.[53] The mechanism of the reduction of $[CuL]^{2+}$ (L = 1,5,9,13-tetraselenacyclohexadecane, $16Se_4$) is shown[54] in Scheme 1.

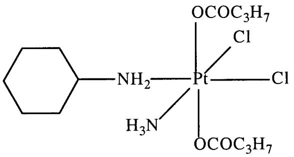

Redox Behaviour
$16Se_4$
$[16Se_4^{+\cdot}]$
$(16Se_4)_2^{+}$
$16Se_4^{+\cdot}$
$16Se_4^{2+}$
Mechanism
$Cu^{II}L^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu^{I}L^{+} + L^{+}$
$Cu^{II}L^{2+} + L^{+} \xrightarrow{k_2} Cu^{I}L^{+} + L^{2+}$

Scheme 1

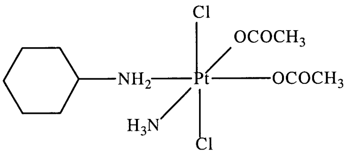
The mechanism of reduction by L-ascorbic acid of a number of oral cancer prodrugs,[55] for example complexes **2**, has been found to involve a slower outer-sphere process for **2a** and **2b**, while **2c** and **2d**, more unusually, react more rapidly by reductive attack on the *trans*-chlorides. Outer-sphere reductions are proposed for $[Cu(dmp)_2]^{2+}$ and $[Cu(dpp)_2]^{2+}$ by $[Fe(MeC_5H_4)_2]$ and $[Co(bpy)_3]^{2+}$ respectively and in the former involve a distortion of the square planar configuration to tetrahedral.[56] The oxidation of hydrazine by $[Fe(R_3Sn)_3(CN)_6]_n$ occurs by an outer-sphere mechanism with rate determining electron transfer.[57] Application of the Marcus theory shows that the reduction of aqueous Cl_2 by complexes $[Ru(L)_2]^{2+}$, *e.g.* $[Ru(bpy)_2]^{2+}$, proceeds *via* an outer sphere mechanism.[58] Outer sphere electron-transfer for reaction of $[Ru^{III}(edta)(pyz)]^{-}$ with sulfite is affected by the concentration of alkali metal ions because of the formation of alkali metal bridges between the reactants[59] and reduction involving ion pairs is suggested for the reaction of thiosulfate ion with $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{7+}$.[60] Coupling of electron- and proton-transfer accounts for wide variations in the rates of reduction of a series of Ni(III) oxime–imine complexes.[61] In(I), V(II), Eu(II) and Ti(III) all reduce riboflavin with an initial step in which the riboflavin radical ion is produced.[62] The reaction is autocatalytic for the outer-sphere V(II) and Ti(III) reactions leading to formation of dihydroriboflavin.



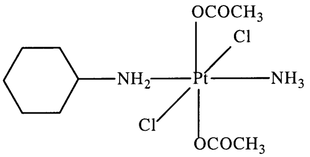
2a



2b



2c



2d

Inner-sphere and electron and atom transfer

$[CoW_{12}O_{40}]^{5-}$ is reduced by azide ion by an inner sphere mechanism[63] and an associative mechanism is proposed for the reduction of a number of *trans*-$[Co(en)_2Cl(R\text{-aniline})]^{2+}$ complexes by $[Fe(CN)_6]^{4-}$.[64] Unravelling the mechanism of oxidation of water to O_2 in the last stage of photosynthesis is an area of great importance. A valuable step has been a study of the mechanism of water oxidation by Ce^{IV} with $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$.[65] The authors identify three key steps in the process, which are the oxidation of $Ru^{III}ORu^{III}$ to $Ru^{V}ORu^{V}$, which occurs stepwise *via* $Ru^{IV}ORu^{III}$ and $Ru^{V}ORu^{IV}$. The $Ru^{IV}ORu^{III}$ to $Ru^{V}ORu^{IV}$ oxidation is the slow step. O_2 evolution *via* a proposed peroxo-bridged intermediate is suggested and the last step is retardation of the operation of the catalyst by anation, which removes water molecules that are crucial to the slow step in the process. A system containing a fullerene molecule linked to a tetraphenylporphyrin moiety and thence to a zinc tetraphenylporphyrin[66] has been used to mimic the main processes of photosynthesis. A study of the kinetics and mechanism of the catalytic oxidation of water with $[Ru(bpy)_3]^{3+}$, catalysed by colloidal cobalt hydroxide, suggests a cobalt peroxo-bridged compound as an intermediate.[67] The kinetics of two-electron/halide self-exchange reactions of substituted ruthenocenes, $[Ru(Me_mC_5H_{5-m})(Me_nC_5H_{5-n})]$ have been investigated[68] and compared with the complexes without ring substiuents.

$$[RuCp_2X]^+ + RuCp_2 \rightarrow RuCp_2 + [RuCp_2X]^+$$

It is clear from the results that electronic and not steric effects govern the self-exchange rates as the number of methyl groups ($m + n$) increases to 6 and a Ru–X–Ru bridged transition state is proposed. Complexes $[Os^{VI}(L)(Cl)_2(N)]^+$, where L is 2,2′:6′,2″-terpy or tpm react with secondary amines to produce $[Os^V(L)(Cl)_2(NNR_2)]^+$, where NR_2^- is morpholide, piperidide or diethylamide.[69] In the mechanism of the formation of the Os(v) hydrazido complexes when morpholine is the base, there is a nucleophilic attack by morpholine on the nitrido group of the Os(vi) complex producing an intermediate Os(IV)-hydrazido species, which is oxidised by $Os^{VI}{=}N^+$ to Os(v). Oxidation of L-cysteine and other S-containing amino acids by potassium ferrate is complete within 300 s and the mechanism is believed to be an inner-sphere process.[70] Ferrate(vi) also oxidises thioacetamide to acetamide and sulfate in a number of steps in which sulfenyl, sulfinic and sulfonic acid are all intermediates.[71] Decomposition of *S*-nitrosothiolactic acid and *S*-nitrosoglutathione in the presence of Cu(i) occurs *via* transient species formed by Cu and thiol.[72] The mechanism for the oxidation of 4-methyl-2-mercaptopyrimidine (RSH) by $[Ag(cyclam)]^{2+}$ involves an inner sphere process to RS and free radical dimerisation to RSSR.[73]

Miscellaneous redox reactions

There has been a theoretical study of the mechanism of proton-coupled electron-transfer reactions[74] and a study of proton-coupled electron-transfer from sulfur.[75] The combination of stopped flow technology and EXAFS has allowed the investigation of the structure of short-lived intermediates in some redox processes.[76] Evidence has been produced that under conditions where V(v) is present as both VO_2^+ and decavanadite in the reaction with Fe(ii), the latter are also involved in the electron transfer process.[77] In(i) reduces quinoxaline and similar compounds to a coloured radical and then to a dihydro compound[78] *via* successive 1-electron steps. Tertiary aliphatic amines reduce $[Mn^{III}Mn^{IV}L]^{2+}$ (L = 1,3-bis(salicylideneamino)-2-propanol) to the $(Mn^{III})_2$ complex.[79] The mechanism involves both an electron transfer and a C–H_α proton transfer from the amine. In fact the reducing ability of the amine is found to relate to its basicity and not its reduction potential, so that no matter how favourable the reduction potenial of weakly basic amines, they will not be able to reduce the complex. A 1:1 intermediate is a feature of the oxidation of hypophosphite, phosphite and phenylphosphonous acid by tris(pyridine-2-carboxylato)manganese(iii).[80] In the case of the oxidation of hypophosphite by *trans*-$[Ru^{VI}(L)(O)_2]^{2+}$ (L is 1,2-dimethyl-3,4 : 9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane) the mechanism has hydride transfer to Ru=O as a rate determining step.[81] Tris(bipyridyl)ruthenium(II) modifies mono-, di- and tri-nuclear manganese complexes as electron-transfer models for photosynthetic processes.[82] Rate constants for the oxidation of nucleotides and DNA by $[Ru(terpy)(bpy)O]^{2+}$ type complexes have been found to be in the same order as the redox potentials, *i.e.* $[Ru(4'\text{-}Cl\text{-}terpy)(bpy)O]^{2+}$ > $[Ru(terpy)(bpy)O]^{2+}$ > $[Ru(terpy)(4,4'\text{-}Me_2\text{-}bpy)O]^{2+}$ > $[Ru(terpy)(4,4'\text{-}EtO\text{-}bpy)O]^{2+}$.[83] There has also been a study of the oxidation of guanines in DNA from calf thymus by $[Ru(bpy)_3]^{3+}$.[84] The kinetics of the slow release of NO in the reduction of *R,S,S-trans*-$[RuCl(NO)(cyclam)]^{2+}$ suggest that this complex may have potential as a low-release vasodilator.[85] The oxidation of *cis*- and *trans*-$[Os^{III}(terpy)Cl_2(NH_3)](PF_6)$ gives $[Os^{VI}(terpy)Cl_2(N)]^{+}$, and oxidation of $[Os(terpy)(bpy)(NH_3)](PF_6)_2$ gives $[Os(terpy)(bipy)(NO)](PF_6)_3$.[86] It is suggested that these and similar reactions involving oxidation of NH_3 occur with Os(IV) as an intermediate. One of the products of the above reactions, $[Os^{VI}(terpy)Cl_2(N)]^{+}$, reacted with $SPPh_3$ producing $[Os^{IV}(terpy)Cl_2(NPPh_3)]^{+}$ and $[Os^{II}(terpy)Cl_2(NS)]^{+}$.[87] An Os(IV) intermediate ($[Os^{IV}(terpy)Cl_2(NSPPh_3)]^{+}$) is once more suggested for the reaction of $[Os^{II}(terpy)Cl_2(NS)]^{+}$ with PPh_3 which results in $[Os^{IV}(terpy)Cl_2(NPPh_3)]^{+}$ and $SPPh_3$. Vitamin B_{12} has been proposed as a possible catalyst for the removal of perchloroethylene as a pollutant.[88] The process of destruction appears to be an electron-transfer mechanism involving cob(I)alamin as the active species. The reaction between Co(III) and Mn(II) acetates results in the formation of Mn(III) dinuclear complexes and the kinetic analysis shows that the process occurs in two stages.[89]

The Cu(II) and Cu(I) complexes of PuPy, $[Cu^{II}(PuPy)]^{2+}$ and $[\{Cu^{I}(PuPy)\}_2]^{2+}$ have been prepared and the structure of the Cu(I) complex involves two coppers bridged by PuPy, giving a helical arrangement.[90] The mechanisms of the reduction of $[Co(NH_3)_5Cl]^{2+}$ and *cis*- and *trans*-$[Co(en)_2Cl_2]^{+}$ by $[\{Cu^{I}(PuPy)\}_2]^{2+}$ have also been studied. The first step is believed to be the oxidation of the dimer to a $Cu^{II}Cu^{I}$ species, followed by separation of the Cu^{II} moiety from the Cu^{I}. The Cu^{I} complex then reduces another molecule of the Co complex. This mechanism implies that the electron exchange precedes the very significant structural changes which occur as a result of the redox process. This is described by the authors as a redox switch. The Cu(II) complex $[Cu_2(bpy)_2(\mu\text{-}ox)]^{2+}$ catalyses oxidation of L-ascorbic acid by dioxygen *via* a Cu(I) intermediate.[91] The oxidation of a series of chelated Co(II) complexes, $[CoL]^{2-}$ (L is an edta-type ligand) by $[Co(mal)_3]^{3-}$ and catalysed by chiral $[Co(en)_3]^{3+}$ results in products which are optically active.[92] A chiral induction mechanism is invoked in which an ion pair between the Co(II) complex and the chiral $[Co(en)_3]^{3+}$ species is involved. The mechanism of plutonium(IV) reduction by aminoguanidine, TcO_4^{-} catalysed, has been investigated[93] as well as Pu(IV) reduction by hydroxylamine.[94] The mechanism of the reduction of Np(VI) and Pu(IV) by hydrazinopropionitrile[95] and diethylhydroxylamine[96] and of Pu(IV) by hydrazinopropionitrile catalysed by Fe(III)[97] has been studied as well as reduction of Np(V), Np(VI) and Pu(IV) by acetaldoxime in HNO_3.[98] There continues to be interest in the factors, steric and otherwise, which affect electron tranfer reactions. In the case of Ni(II) 5,10,15,20-tetraphenyl homoporphyrins and similar species, such processes are affected by the flexibility of the non-planar porphyrin ligand.[99] A nickel(III) intermediate has been characterised in the reaction of (1,4,8,11-tetraazacyclotetradecane)nickel(II) with $KHSO_5$.[100] The protonated form of this Ni(III) chloro species binds with DNA. The oxidation of the complex *cis*-(*C*,*S*)-$[Pt^{II}(C_6H_3\text{-2-CMe=NOH-5-R})Cl(Me_2SO)]$ in MeOH/HCl results in *fac*-$[Pt^{IV}(C_6H_3\text{-2-CMe=NOH-5-R})Cl(Me_2S)]$.[101] A two step mechanism involving an intermolecular process is established, in which deoxygenation proceeds through insertion of S=O into Pt–H, formed by protonation of the starting complex. Complexation within 10 ms by ethylenediamine is the first step in the oxidation of ethylenediamine by diperiodatoargenate(III)[102] and this is followed by intramolecular oxidation. The effects of substitution of the porphyrin ring on the redox behaviour of tetraphenylporphyrinatozinc(II) complexes have been explored.[103]

An intramolecular redox process in $HgSO_3$, which is formed in the first step, is the key to understanding the mechanism of the reduction of Hg^{2+} by SO_3^{2-}.[104] A study of the self-exchange reaction of high spin iron complexes of H_2bim[15] shows it actually consists of a hydrogen atom exchange process. By applying the Marcus theory to the kinetics of the exchange, the authors were able to obtain an order for the intrinsic reaction barriers of $\lambda_{H^{\cdot}} > \lambda_{e-} > \lambda_{H^+}$. The intriguing molecule-based magnet $[V(TCNE)_x]\cdot yCH_2Cl_2$ is produced by the reaction of $[V^0(C_6H_6)_2]$ with TCNE. The reaction has been shown to have V^{2+} as intermediate and to involve two electron-transfer processes in which TNCE is the oxidant.[106] DMeCF has been used as an alternative to tetracyanoethylene in $[Cr(Cp^*)_2](DMeDCF)$.[107] Up to 45% NH_3 has been produced by the reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and *trans*-$[Ru(\eta^2\text{-}H_2(dppp)_2]^+$ and $[RuCl(dppp)_2]^+$.[108] The mechanism for the reaction includes nucleophilic attack by the N_2 coordinated to the W on the H_2 coordinated to the Ru giving hydrazido intermediates that are then protonated.

Reactions of oxygen-containing ligands

There has been a review of the kinetics and mechanisms of hydrogen peroxide reactions in the presence of metal complexes[109] and of mechanisms of reactions of models for nitric oxide synthase.[110]

A cautionary note has been provided about the role of pyridine as an axial ligand in complexes used as biomimetic models for catalytic oxygenation reactions.[111] The essence of the problem is the fact that the pyridine is not an innocent bystander, but becomes involved in the process *via* the formation of pyridine *N*-oxide, adding to the complexity of the process. Polyhalogenated pyridines are given as possible alternatives. The non-haem diiron alkane monooxygenase of the organism *Pseudomonas oleovorans,* which has been used in the conversion of octane to octanol, encourages an alkane hydroxylation process. This has been shown unambiguously to proceed through a radical intermediate, which has a lifetime of about 1 ns.[112] The oxidation of azide by O_2 in the presence of $[CoL]^{2+}$ (L = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) occurs *via* the formation of an azido complex which then stabilises the formation of an oxygen adduct.[113] The decomposition of ozone in aqueous solution is of significant environmental interest and it has been found that the rate of decomposition is decreased by the presence of carbonate ion.[114] The kinetics of the reaction show that this inhibition is largely due to the fact that OH and O_3^- are removed from the solution and it is these that act as

$$CO_3^{2-} + OH \longrightarrow CO_3^{-} + OH^{-}$$

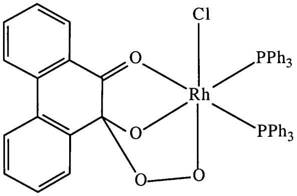
$$CO_3^{-} + O_3^{-} \longrightarrow CO_3^{2-} + O_3$$

Scheme 2

chain carrier radicals as shown in Scheme 2. The proposed mechanism offers a description of the process of ozone decay and the fate of other species formed in the process. The reaction of $[Mn(III)(dpa)_2]^{-}$ with peroxomonosulfate results in the evolution of O_2 by a step involving an intermediate containing the Mn=O moiety.[115] The mechanism for the reaction of the $[Cr(aq)O]^{2+}$ ion with $[RhL(H_2O)H]^{2+}$ [L = $(NH_3)_4$ or [14]aneN_4 or *meso*-Me_6-[14]aneN_4] in the presence of O_2 to give $[Cr(aq)]^{3+}$ and $[RhL(H_2O)OO]^{2+}$ includes abstraction of H and formation of $[RhL(H_2O)]^{2+}$, which then reacts with O_2.[116] On the other hand $[CrO(salen)]^{2+}$ reacts *via* hydride transfer. Hydrogen atom abstraction is a feature of the reaction between $[Cr(aq)OO]^{2+}$ and CMe_3CHO ($k = 0.16\ M^{-1}\ s^{-1}$, *cf.* $9 \times 10^{7}\ M^{-1}\ s^{-1}$ for *t*-$BuO^{\bullet}$),[117] which is about a hundred times smaller than that for the same reaction involving $[Cr(aq)O]^{2+}$ ($k = 23\ M^{-1}\ s^{-1}$ *cf.* $8\ M^{-1}\ s^{-1}$ for $BuOO^{\bullet}$). An important feature of the mechanism for the reaction of $[Cr(aq)OO]^{2+}$ is the interaction of $CMe_3C(O)COO^{\bullet}$ and $[Cr(aq)OO]^{2+}$ to produce $CMe_3C(O)COOCr^{2+}$ which then homolytically cleaves giving CrO^{2+}. There has recently been much interest in Cr(V) and Cr(IV) chemistry because of their possible carcinogenicity. The Cr(V) complex $[CrL^{-}(H_2O)_2]^{2+}$ (L = 1,4,8,11-tetraazacyclotetradecane) produces $[Cr(L)(H_2O)OO]^{2+}$ on treatment with O_2 in acid.[118] When this in turn is reacted with 1-electron reducing agents, a transient intermediate, $[CrOOH(L)]^{2+}$ is postulated and the Cr(V) product is $[CrO(L)]^{3+}$. The reduction of a 2-ethyl-2-hydroxybutanoate chromium(IV) complex by hydrazine has been studied.[119] Cr(V) is also an intermediate in the reduction of Cr(VI) by Fe(II).[120] Using global analysis, the kinetics of producing Cr(VI) and Cr(III) from the disproportionation of $[Cr^{V}O(ehba)_2]^{-}$ in the pH range 6.0 to 8.0 shows a complex multistage mechanism.[121] It is clear from the comparison of the kinetics with DNA cleavage studies that $[Cr^{V}O(ehba)_2]^{-}$ or a monochelate reacts with the DNA phosphate backbone causing cleavage. Reduction of potassium dichromate by reducing agents, such as catecholamines, DOPA and dopamine, yields EPR signals showing Cr(V) is present.[122] Cr(V) chelates are also detected among reactions in which Cr(VI) is reduced by α-D-glucopyranoside and methyl α-D-mannopyranoside.[123] The kinetics of the reaction of $[Cr_2O_7]^{2-}$, MeOH and qaH_3^{2-}, which produces $[Cr^{V}O(qaH_3)_2]^{-}$, show the formation of a Cr^{IV} intermediate which in turn reacts with qaH_5 and MeOH in a series of steps to give the product.[124] The mechanism of H_2O_2 decomposition to 2OH in supercritical water has been shown by a theoretical treatment to occur in an identical way to that in the gas phase,[125] though it is faster and is dependent upon the density of the water.[126] The reaction of H_2O_2 with SCN^{-} was studied kinetically almost exactly 40 years ago and a re-examination of the system using modern spectrophotometric kinetic methods has shown that it proceeds *via* the intermediate $(SCN)_2$, whose spectrum has been obtained from the kinetic data.[127] The reaction[128] of H_2O_2 with $[FeDPC]^{2+}$ and Fe(II) complexed with edta-type ligands[129] involves a process where O_2^{2-} or HO_2^{-} ligands are attached to the iron. N_2 is the only product of the oxidation of $N_2H_5^{+}$ by $[Mn_4(\mu$-

$O)_6(bpy)_6]^{4+}$ and is produced *via* 2 parallel paths, one of which is dependent on bpy concentration with the rate determining step involving transfer of an electron and a proton.[130] The question of homolytic *versus* heterolytic cleavage of the peroxo bond in H_2O_2 and the related *tert*-alkyl hydroperoxides by iron(III) porphyrin complexes has been systematically studied, either by putting various electron-withdrawing or donating substituents into the 5, 10, 15, 20 positions on the porphyrin ring, or by the introduction of imidazole groups into the axial position.[131] The conclusion is that both homolytic and heterolytic cleavage are a feature of these reactions and that the former are favoured by electron-rich and the latter by electron-deficient complexes. The authors suggest that the key to the process is the electron density on the O–O bond in the intermediate formed between the peroxo species and the porphyrin complex. $[Mn_2(\mu\text{-}OAc)(\mu\text{-}OMe)(5\text{-}BrsalpentO)(MeOH)_2]Br$ behaves catalytically towards the disproportionation of H_2O_2 in DMF and MeOH and the kinetics show saturation behaviour.[132] There is evidence of cooperativity in the catalysis of the decomposition of H_2O_2 by the tetranuclear manganese complex tetrakis{*N*-ethyl-*N*-[(2-pyridyl-κ*N*)]-2-pyridinemetanamine-κN^1,κN^2}hexa-μ-oxotetramanganese(3+) in the presence of Me_3(tacn) and a base-mediated mechanism is proposed.[133] The use of copper(I) complexes, $[Cu_2(Py_2SSPy_2)]^+$, which have two disulfide-bridged Cu atoms as redox catalysts and H_2O_2 and ^{t}BuOOH as oxidants in, for example, the oxidation of cyclohexane to cyclohexanol has been investigated.[134] A short-lived green intermediate appeared at the beginning of the reaction[135] of H_2O_2 with $[Cu_2(Py_2SSPy_2)]^+$ and Raman spectra indicate that this is a Cu–OOH species. A series of dimanganese(II,II)-complexes linked by a variety of bridges has been investigated for their ability to dismute H_2O_2.[136] A useful finding is that the production of a hydroperoxo bridge *via* deprotonation of the hydroxo bridge is at the basis of the catalytic process. Porphyrin complexes of the form $[Mo^{VI}O(L)(O_2)]$, where L is one of a number of substituted porphyrins, are formed by reaction of $[Mo^{IV}O(L)]$ with O_2. The rate constant is very dependent on the bulkiness of the substituents.[137] Also the electronic effects of the porphyrin rings are an important factor governing the rate. The reaction of ethene with $MoO(O_2)(OPH_3)$ has been shown by quantum chemical calculations to produce the epoxide in a single step.[138] The mechanism of the uptake of dioxygen by $(PPh_4)_2[M(CN)_4O(pyz)]\cdot 3H_2O$ (M is Mo or W) to form $(PPh_4)_2[M(CN)_4O(O_2)]$ has been considered.[139] The reaction of dioxygen selectively to oxidise alcohols to the corresponding carbonyl species is catalysed by, for example, $[N(n\text{-}Bu)_4][M(N)(\mu\text{-}O)_2CrO_2]$ (M is Ru or Os and R is an alkyl or aryl ligand).[140] The mechanism involves a process in which the alcohol becomes coordinated to the metal and is then oxidised *via* β-elimination.

Reaction of 9,10-phenanthrenequinone with $[Rh(PPh_3)_3Cl]$ produces[141] **3** *via* a penta-coordinated Rh^{II} species which reacts with O_2 to give a Rh^{III} superoxo complex. A free radical mechanism is proposed for the autoxidation of S(IV) when it is catalysed by Ag(I).[142] As a contribution to the unravelling of the mechanism of the metal ion complex assisted oxidation of catechol, density functional theory has been applied to the reaction of the cation $[M\{MeC(CH_2PPh_2)_3\}(cat)]^+$ [M is Co(III) or Ir(III)] with dioxygen and shows that the first stage in the process involves attack by O_2 on the catecholate site.[143] $[Fe_2(OH)(R_3CCOO)_2(Me_3tacn)_2]^+$ (R is F or Me) reacts with dioxygen (or some other oxidants)[144] to produce a μ-oxo Fe(II)Fe(III) complex and then a diiron(III) complex. By varying R it has proved possible to slow the reaction to



3

such an extent that the intermediate μ-oxo Fe(ii)Fe(iii) can be isolated. The mechanism is interpreted as an outer sphere process. The complex [Fe^{II}(TPrPc)] reacts with dioxygen to produce [(TPrPc)Fe^{III}–O–Fe^{III}(TPrPc)] *via* the (μ-peroxo) intermediate, [(TPrPc)Fe^{III}–O–O–Fe^{III}(TPrPc)] which may be isolated at 203 K.[145] The intermediate decomposes to produce [Fe^{IV}O(TPrPc)] and this reacts with [(TPrPc)Fe^{III}–O–O–Fe^{III}(TPrPc)] to form the product. The effects of the structure of a macrocyclic ligand on the behaviour of μ-$\eta^2:\eta^2$-peroxo–copper and bis(μ-oxo)–copper complexes with dioxygen have been studied.[146] The ligands were R_3TACD, in which R is Me, Bn or ^{i}Pr and $^iPr_3$TACDD. The species [Cu($^iPr_3$TACDD)]SbF_6, which is 3-coordinate around Cu, shows no reactivity towards O_2 while O_2 reacts readily with [Cu(R_3TACD)(MeCN)]SbF_6 giving [Cu(μ-O)$_2$(R_3TACD)$_2$](SbF_6)$_2$, when R is Me or Bn. When R is ^{i}Pr, however, the μ-$\eta^2:\eta^2$ peroxo species is formed. The varying behaviour relating to the μ-oxo and the peroxo species was attributed to the effect of the ring size produced by the ligands. The kinetics of the reaction of atropisomers of [Mo^{IV}O(TNP)] with O_2 is influenced by the orientation of the naphthyl groups in the 5,10,15,20 positions of the porhyrin ring.[147] $\Delta V^{\ddagger}$ and energies of activation have been obtained for the oxidation by $S_2O_8{}^{2-}$ of bis(ethylenediamine)cobalt(iii) complexes having sulfur attached to the metal and a variety of 6-coordinate Fe(ii) complexes containing ligands such as CN, phen and bpy.[148] The reaction between sodium perborate and the edta Fe(iii) complex involves Michaelis–Menten kinetics with the species $[Fe(edta)(OH)]^{2-}$ as catalyst reacting *via* a violet-coloured intermediate.[149] A series of complexes like [Fe^{III}(bispicMe$_2$en)(DBC)]$^+$ has been prepared and the kinetics of oxidation of catechol by O_2 measured.[150] An interesting feature of the kinetics was that there was a correlation between the second order rate constant and the DBC to Fe(ii) LMCT bands in that k increased with the ε_{max} values for these bands, with the exception of one of the complexes in which the ligand introduced significant steric hindrance into the system. The superoxide dismutase mimic [Cu_2(H_4tapt)]·10H_2O reacts very rapidly with $O_2{}^{\cdot -}$ with a rate constant of 1.91×10^8 M^{-1} s^{-1} at physiological pH.[151] ClO_2 production from the reaction of $H_2O_2/HClO_3$ involves an induction period during which Cl^- and $HClO_2$ are produced and a steady state phase in which the reaction between $HClO_2$ and $HClO_3$ occurs.[152] ClO_2 is readily photolysed and this has been followed using femtosecond transient absorption spectroscopy.[153] The products are ClO and O. ClOO is an intermediate that produces Cl and O_2. Hydrogen peroxide is formed by the sonolysis of water[154] and the mechanism of the process under argon involves energy exchange between the H_2O and the Ar occurring during the cavitation-collapse process. The oxidation of sulfides by H_2O_2 is activated by NH_4HCO_3, giving a cheap, environmentally friendly system.[155] Richardson and coworkers[155] have confirmed that the oxidant in this process is, in fact, peroxymonocarbonate (HCO_4^-) and have determined the electrode potential of the couple, HCO_4^-/HCO_3^- as 1.8 V *vs.* NHE.

Other non-metal redox reactants

Gould *et al.* have examined some of the redox chemistry of Ge(I) in aqueous solution[156,157] with Fe(III) and Pt(IV) complexes.[158] Rate constants were determined for reduction of I_3^-, Br_2(aq), $[IrCl_6]^{3-}$, $[PtCl_6]^{2-}$, quinoxalinium cation, $[IrCl_6]^{2-}$, $[Fe(bipy)_3]^{3+}$ and aquocob(III)alamin (B_{12a}). The kinetics of the reaction of Ge(II) with Fe(III) in the presence of Cu(II) in Cl^- and also $[IrCl_6]^{3-}$ are interpreted by invoking Ge(III) as an intermediate, giving the first ever kinetic parameters for this oxidation state of Ge. The reduction of $[PtCl_6]^{2-}$ on the other hand at least to some extent utilises a chloride bridge. The relevance of kinetic models of redox reactions of chlorite and sulfite ions in relation to the environment has been discussed.[159] The reaction of Br^- and ClO_2^- ions in acid solution involves competing parallel redox reactions[160] and is extremely complex involving around 10 possible intermediate reactions. The kinetics have been studied in detail using sophisticated fitting algorithms. Unlike previous workers, Toth and Fábián[160] did not detect the presence of $BrClO_2$ as an intermediate, though they do not rule it out as having a role in the mechanism. ClO_2^- has also been found to form the species $HgClO_2^+$ during the formation of ClO_2 in reactions of Hg(II) with ClO_2^-.[161] The decomposition of aqueous ozone has been found subject to catalysis by many species even, significantly, the plastic parts of stopped flow equipment.[162] The intermediate $HOClOClO^-$ is included in the proposed mechanism for the oxidation of chlorite by hypochlorous acid.[163] This then produces the metastable species, ClOClO. The yield of ClO_2 from the process is much higher than expected, attributable to the disproportionation of ClO_2^-. The reaction is also subject to general acid catalysis and phosphate buffer has a significant accelerating effect on the rate. Acetic acid also increases the rate and this effect is attributed to a mechanism involving the formation of acetyl hypochlorite and thence Cl_2O_2. Br_2, Cl_2 and BrCl oxidise $N_2H_5^+$ and it is postulated that $XN_2H_4^+$ is formed in the rate determining step.[164] Subsequent fast reactions produce $N_2H_3^+$ and N_2H_2, and the latter is ultimately oxidised to N_2. The products of the reaction between HOCl and $S_4O_6^{2-}$ are SO_4^{2-} and Cl^- and the intermediates in the process have been shown to be $S_2O_3Cl^-$ and $S_2O_4^{2-}$.[165] The kinetics of the oxidation of Fe(II) by ICl have been studied and found to be influenced by the presence of anions such as acetate and chloride.[166] The mechanism of the oxidation of I^- by IO_3^- has been compared with that of the corresponding Br system and is found to be considerably more complicated.[167] The complex kinetic behaviour is accounted for by assuming that $H_2I_2O_3$ (no equivalent present in the Br system) is an important intermediate in the process. The oxidation mechanisms of a number of hexoses by *tert*-butyl hypochlorite have been studied.[168] The rate of the oxidation of bromide to Br_3^- in CTAB by the iron(III) TPP μ-oxo dimer, $[\{Fe(TPP)\}_2O]SbF_6$, in dichloromethane shows first order behaviour with increasing [CTAB].[169] The proposed rate determining step involves the production of Br_2^- as an intermediate, which then reacts with $[\{Fe(TPP)\}_2O]^+$. There are clear indications of the effects of ion pairs in the reaction. There are parallels in the production of ammonia between the reaction of hydrazine[170] and $[Fe(CN)_5NO]^{2-}$ and hydrazine nitrosation studied by Stedman and coworkers.[171,172] The production of ammonia is shown to occur through the formation of an intermediate species, $[Fe(CN)_5NO \cdot NH_2NH_2]^{2-}$ in which a proton is lost from the nitrogen on hydrazine bound to the complex and then the other proton migrates to the other nitrogen, followed by N–N bond cleavage and subsequent ammonia loss, leaving $[Fe(CN)_5N_2O]^{3-}$, from which in turn N_2O is lost resulting in the product, $[Fe(CN)_5(H_2O)]^{3-}$. $[OsTp(N)Cl_2]$ converts NO to N_2O, being itself converted to $[OsTp(NO)Cl_2]$.[173] The mechanism involves the addition of NO to form the NNO moiety bonded to the Os and then the production of $[OsTpCl_2]$ that reacts with NO. Reductions of a range of oxidants such as Br_2, I_2, I_3^-, $[Fe(bpy)_3]^{3+}$ and $[IrCl_6]^{2-}$ with hyponitrite generally occurs *via* $HN_2O_2^-$ to produce nitrate or nitrite as product.[174] The transition metal redox reactions occur by an outer sphere process in single electron steps. However, an inner-sphere mechanism utilising a halogen bridge is favoured for the reactions of the halogens. The rate of the oxidation of nitrous acid by bromine in aqueous sulfuric acid is reduced by increasing $[H^+]$ and $[Br^-]$.[175] It is shown that the mechanism consists of two steps. The first is reaction of Br_2 with N_2O_3 followed by reaction between NO_2^- and Br^-. Oxidation of lower oxidation state oxyacids of phosphorus by hexamethylenetetramine bromide in glacial acetic acid[176] occurs through the formation of an associated species resulting in Michaelis–Menten-type kinetics, as does reduction by butyltriphenylphosphonium dichromate in dimethyl sulfoxide.[177] The oxidation of $H_2PO_2^-$ by MnO_4^- features a detectable intermediate after a few milliseconds and the rate determining step for the reaction is the decomposition of this species *via* the abstraction of H producing HPO_2.[178] The active species in the oxidation of thiocyanate by periodate is IO_4^- when catalysed by $[Ru(H_2O)_5OH]^{2+}$[179] or $[OsO_4(OH)_2]^{2-}$.[180] The oxidation by periodate of 2-aminomethylpyridinechromium(II) involves formation of $[CrL_2OIO_3]^{2+}$.[181] The oxidation of thiourea by IO_3^- results in I_2, which is produced by the reaction of I^-, an initial product, with IO_3^-.[182] The aerial oxidation of thiourea has an initial step in which heterolytic cleavage of C–S produces SO_2^{2-}.[183] The reduction of arsenate by sulfide may be environmentally an important reaction,[184] is second order and is very pH dependent. The initial product is not AsO_3^{3-}, but arsenic–sulfide complexes.

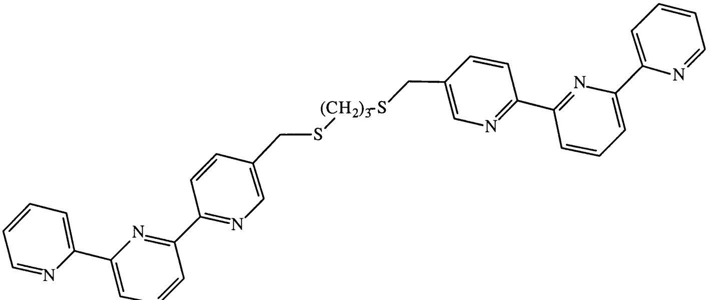
Oscillating reactions and chemical chaos

Ensemble stochastic simulations of chaos have been applied to a chemical model.[185] There have been a number of studies of the Belousov–Zhabotinsky reaction which involve the effect of light on the reaction and include the photoresponse of the ClO_2–I_2–malonic acid reaction,[186] the role of the photoexited state of $[Ru(bpy)_3]^{2+}$ in the photoinhibition of the reaction[187] and oscillatory clusters in photosensitive Belousov–Zhabotinsky reactions.[188,189] It is claimed that at H_2O_2 concentration levels of 10^{-13} M the oscillating reaction $MnSO_4$–$KBrO_3$–diacetone can be stopped and that there are significant effects even at the 10^{-20} M level.[190] There has been a theoretical study of self-segregation of competitive chaotic populations.[191]

3 Substitution

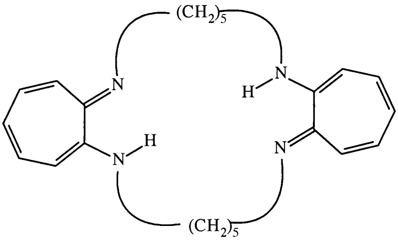
6-Coordination

There has been a review of *trans*-effects in octahedral transition metal complexes.[192] Iron(III) and phosphate ion have been found to react fairly rapidly[193] when Fe(III) is in large excess, to produce the previously unknown tetranuclear species $[Fe_4(PO_4)(OH)_2(H_2O)_{16}]^{7+}$ by a process which is first order in $[Fe_2(OH)_2(H_2O)_8]^{4+}$. From the kinetics of the formation, it is deduced that the mechanism involves the formation of an intermediate binuclear species. The tetranuclear complex itself slowly reacts to produce $[Fe(PO_4)(H_2O)_5]$. Kinetic studies have shown that the formation of $[FeL^1]$ from reaction of L^1 with $[Fe(terpy)_2]^{2+}$ occurs *via* the formation of $[Fe(terpy)L^1]^{2+}$ as intermediate following loss of terpy from the starting complex.[194]



L^1

At low temperature (typically 179 K) the reaction of NO with [Fe(TPP)] and [Fe(TmTP)] yields [Fe(porph)(NO)] in the first instance and then the centrosymmetric species, *trans*-$[Fe(porph)(NO)_2]$ in an excess of NO.[195] [Fe(TPP)(NO)] does not react with nitric oxide at room temperature, but if NO_2 is present, say as an impurity in NO, it will react to form $[Fe(TPP)(NO)(NO_2)]$.[196] NO reacts with the iron(III) complex of H_2DTCS to produce $[NO–Fe^{II}(DTCS)_2]$ in a process which is described as a new type of reductive nitrosylation and involving an Fe(IV) intermediate.[197] The transfer of nitrosyl between [Mn(NO)(TC-5,5)] (TC-5,5 = **4**) and [Fe(TC-5,5)][198] occurs by a mechanism in which there is prior dissociation of the Fe complex.



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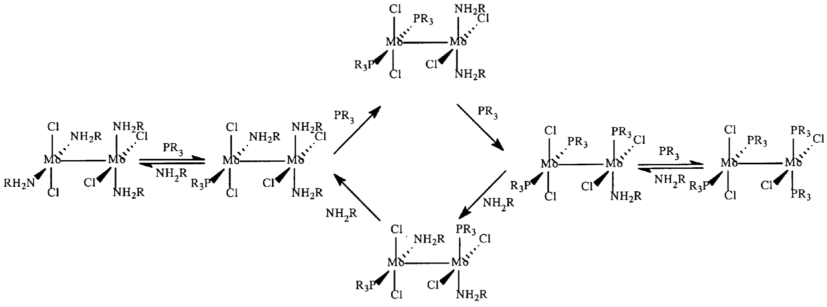
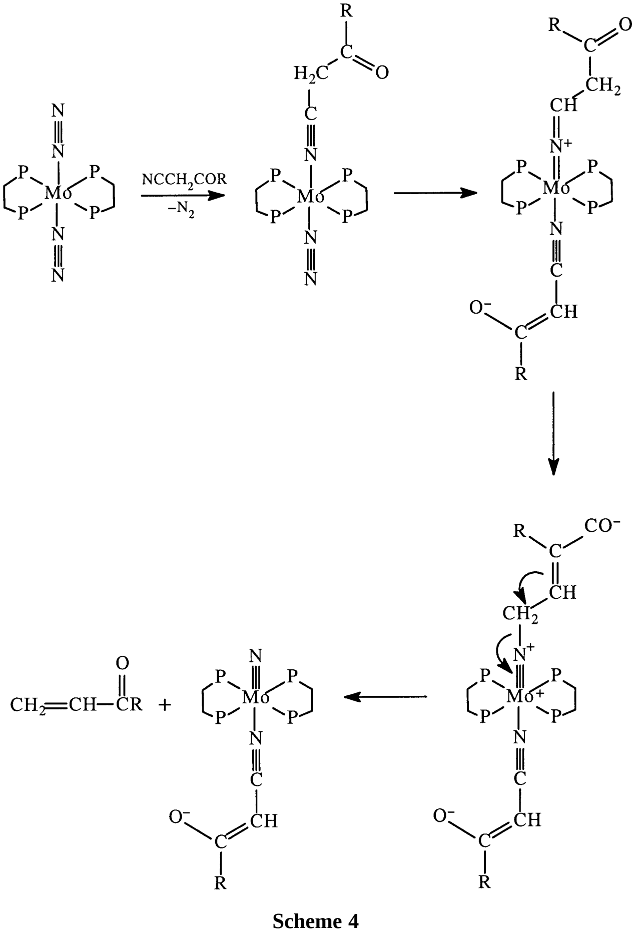
A range of ligand substitution reactions involving $[Fe(CN)_5L]^{3-}$, where L is 4-^{t}Bupy with a series of substituted pyridines in aqueous and micellar solutions were studied and shown to be dissociative while micellar effects were small or absent.[199] A highly complex mechanistic pathway involving a number of parallel or sequential processes is to be found in the proton-induced dissociation of hydroxamic acid complexes of the form $[Fe_2(L)_3]$, where L is a hydroxamic acid ($[CH_3N(OH)\text{-}C{=}O]_2(CH_2)_n$), having chain lengths with $n = 2$ or 8.[200] These very complex multiple pathways are described by the authors as distinguishing between tetradentate species and the corresponding hexadentate ligands. A series of bridged complexes $[(edta)Ru^{III}(\mu\text{-}CN)M(CN)_x]^{5-}$ [M = Fe(II), $x = 5$, M = Mo(IV), $x = 7$] have been studied by the sophisticated application of electrochemical, spectroscopic and kinetic methods.[201] The authors have been able to probe the conformation of edta during the dimerisation and conclude that in that process at least 2 conformers are involved. They were also able to examine the water molecules in the first solvation shell and determined that they play a major role in the electrothermodynamic and optical properties arising from the changes in the ligands and conformers. The formation, dissociation and equilibrium for $[Ru(CN)_5L]^{3-}$, where L is a heterocyclic ligand, probably occur by a limiting dissociative mechanism.[202] Substitutions of PPh_3 in $[Ru(CHDH)_2(PPh_3)]$ by typically DMSO or MeCN are dissociative or dissociative interchange processes.[203] α-$[Ru(azpy)_2(NO_3)_2]$ reacts with DNA-model bases[204] and α-$[Ru(azpy)_2Cl_2]$ has been shown to have a high level of cytotoxicity.[205] The orientations of iron in bleomycin and porphyrin complexes on DNA fibres have been investigated.[206] $[V_2OL_4Cl_2]$ (L is 1,10-phenanthroline or similar) interacts very strongly with DNA, eventually causing it to break down.[207] Two new ferrocene-containing phosphoramidites have been synthesised and incorporated into DNA oligonucleotides.[208] Reaction of aqueous Cr(III) with methyl 2-oxacyclopentane-carboxylate involves the enol tautomer of the ligand and each of Cr^{3+} and $CrOH^{2+}$.[209] The complex $[Co(tn)_2(aq)]^{3+}$ reacts with NPP following an equilibrium which involves coordination of NPP with the cobalt and a 2-stage process; one involves hydrolysis, giving 4-nitrophenol and $[Co(tn)_2(PO_4)]$ and the other results in the dinuclear complex $[\{Co(tn)_2\}_2(\mu^4\text{-}PO_4)]$.[210] Protonation and As–O bond cleavage are the key to the substitution of H_2O by $H_2AsO_4^-$ in a range of complexes of the form $[ML(H_2O)]^{3+}$, where M is Cr(III) or Co(III) and L is varied between $(NH_3)_5$ and macrocyclic ligands.[211] A much studied system has been revisited *viz*. the anation of *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$, using reversed phase high performance ion pair chromatography.[212] This reaction is, in fact, much more complex than originally thought, involving ion pairs, *cis–trans* isomerism, monodentate and bidentate oxalate bonding and a large number of rate constants. Complexation of bis(difluoroboryldimethylglyoxime)cobalt(II) by *N*-methylimidazole in acetonitrile[213] has been investigated and compared with similar systems involving coenzyme B_{12}. It has not proved possible using high pressure kinetic measurements[214] to establish clearly a D or an I_d process. A dissociative mechanism in which a transition state having the incoming species (cyanide or imidazole) weakly bonded to it is proposed for the reaction of the vitamin B_{12} model $[Co^{III}(en)_2(Me)(H_2O)]^{2+}$ with cyanide or imidazole. It has been claimed for some years that NO binds aquacobalamin and of course this may have important consequences for the biological roles of both NO and vitamin B_{12}. However van Eldik and coworkers have now shown conclusively that NO itself does not react with aquacobalamin in water.[215] There is however evidence that where a reaction has been apparent in the past, it is due to interaction with nitrite. NO certainly binds to the iron(II) complex 5,10,15,20-tetrakis(α,α,α,α-*o*-pivalamidophenyl)porphyrin and does so with a rate constant of 8.9×10^8 M^{-1} s^{-1}.[216] In another reaction that has resonance with coenzyme B_{12} chemistry, the mechanism for the replacement of four NH_3 ligands from pentaamminemethylcobalt(III) by two ethylenediamine ligands has been shown to occur *via* a limiting dissociative process for each of the steps.[217] The *cis–trans* isomerism reaction was dissociative. Coenzyme B_{12} itself reacts with CN^- to produce dicyanocobalamin.[218] Before the C–N bond cleaves, CN^- adds to the adenosyl moiety to produce (β-5′-deoxadenosyl)(α-cyano)cobalamin. The reaction between $[Co(NH_3)_5Cl]^{2+}$ and *p*-$Me_2NC_6H_4NH_2$ in the presence of nanoparticles of palladium as a colloid involves a mechanism in which the rate determining step was diffusion of the complex through *p*-$Me_2NC_6H_4NH_2$ adsorbed onto the surface of the colloidal palladium.[219] The hydrolysis of carbonato complexes of tetraammine- and pentaammine-Co(III), -Rh(III) and -Ir(III) complexes have been re-investigated.[220] The reaction of sulfur dioxide with *trans*-$[Co(salen)(OH_2)(OH)]$ produces the S-bonded isomer $[Co(salen)(OH_2)(SO_3)]^-$ and the mechanisms suggested are either concerted Co–S bond formation and Co–O bond breaking or formation of an O-bonded species which then isomerises to the product.[221] $[Rh_2(OAc)_2(CH_3CN)_4]^+$ reacts with a range of phosphines, such as PMe_3 which form monodentate complexes, and $Ph_2PCH_2PPh_2$, forming bidentate complexes.[222] The mechanisms of these substitution reactions involve an initial reaction which is a reversible associative process followed by a reaction in which the ligand enters the coordination sphere at the axial position and interchanges with the equatorial CH_3CN. In a study of the factors involved in chiral discrimination, the monophasic kinetics of substitution by chiral ligands similar to salen into a series of *N*-alkylsalicylaldimatonickel(II) complexes were examined.[223] The highest discrimination factor was for the reaction between bis(*N*-dehydroabietylsalicylaldimato)nickel(III) and *R*- and *S*-*N*,*N*′-disalicylidene-1,2-diamino-4-methylpentane. The first bicarbonato complexes of *cis*-(1,10-phenanthroline)copper(II) have been prepared[224] in order to increase our understanding of the mechanism of operation of human carbonic anhydrase II. The dinuclear Cu(II) complex of 1,2,4,5-tetrakis(1′-amino-3′-thiabutyl)benzene cleaves plasmid DNA about 10,000 times more rapidly than the equivalent mononuclear complex.[225] The explanation provided for this is that the difference lies in the fact that in the dinuclear species the closely separated Cu atoms act together in the cleavage mechanism. Formation of $[Mo_2Cl_4(NH_2R)_2(PR_3)_2]$ from species of the type $[Mo_2Cl_4(NH_2R)_4]$ by reaction with the appropriate primary amine have been found to occur *via* a stepwise route in both the forward and the reverse direction in a process described as *stereochemical hysteresis*[226] which is governed by the *trans* effects of the ligands NH_2R and PR_3 as shown in Scheme 3.

The complex *trans*-$[Mo(N_2)_2(dppe)_2]$ reacts with β-ketocyanides *via* CN bond cleavage to give alkylideneamido(cyano-enolato) complexes and ultimately the (nitrido)(cyano-enolato) complex.[227] The mechanism has a number of steps and a key process is slow loss of N_2 and then coordination of one and then a second β-ketocyanide to the molybdenum and ultimately the cleavage of the CN bond as shown in Scheme 4.

The rate determining step for the formation of *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetate complexes of Ce^{3+}, Eu^{3+}, Yb^{3+} is suggested as the rearrangement of the mono-protonated species formed as the metal ion removes a proton from


Scheme 3


NCCH2COR
−N2

Scheme 4

NH^+.[228] In the OH^- assisted pathway, rearrangement of the deprotonated intermediate is the rate contolling step.

Base hydrolysis

Only the *trans*-equatorial (and not the *cis*-equatorial) complexes $[Cr(NCS)(L)]^-$ (L = ethylenediamine-*N*,*N*,*N′*-tripropionate or similar) undergo base hydrolysis, with $[OH^-]$ having a large effect on reaction rate,[229] while base hydrolysis of *trans*-tetraammine(methylammine)sulfatocobalt(III) results in 9% of the *cis*-hydroxo product.[230] For $[Ru^{III}(Hedta)(dpa)]^-$ the rate of hydroxyl assisted aquation is very much faster than the rates of aquation.[231] The unexpectedly rapid (no acidic protons) base hydrolysis of $[Co(terpy)(bpy)Cl]^{2+}$ has been attributed to a redox driven process.[232] The base hydrolysis rate constants and H/D exchange rates of *syn,anti*-$[Co(cyclen)(NH_3)_2]^{3+}$, *syn,anti*-$[Co(cyclen)(diamine)]^{3+}$ (diamine is $H_2N(CH_2)_2NH_2$ or $H_2N(CH_2)_3NH_2$) and *syn,anti*-$[Co(cyclen)(tn)]^{3+}$ have been studied.[233] The findings are discussed in terms of the ability of the monodentate (NH_3) and bidentate (en) systems to form the S_N1cb trigonal bipyramidal intermediate. In an investigation providing useful information for understanding the coagulation behaviour of aluminium compounds,[234] ^{71}Ga NMR and Ga K-edge X-ray absorption spectroscopy of the base hydrolysis of gallium chloride and nitrate shows that the process involves not tetrahedral or octahedral monomers, but trimeric and tetrameric species which may then form the Ga_{13} cation. Reaction of OH^- with $[Tc(CO)_3(H_2O)_3]^+$ occurs *via* the $[Tc(CO)_3(H_2O)_2(OH)]$ monomer and then dimer then tetramer.[235]

4-Coordination

There has been a review of various hydrolytic reactions of vanadate, molybdate and tungstate.[236] The role of cyclometallation in controlling substitution at Pt(II) has also been discussed.[237]

To answer the question *to what extent can cyclometallation promote associative or dissociative ligand substitution at Pt(II) complexes?* Romeo and coworkers[238] studied the reaction of $[Pt(bph)(SR_2)_2]$ (R is Me or Et) with 2,2′-bipyridine and 1,10-phenanthroline. The rate law may indicate a rate determining step in which the RS moiety dissociates, resulting in a 3-coordinate intermediate $[Pt(bph)(SR_2)]$, rather than the more usual 5-coordinate intermediate. A theoretical study showed that the most likely structure for the intermediate was T-shaped with a high concentration of charge on the Pt. Here, the dissociative process is attributed to the strength of the carbanion in the position *trans* to the leaving group and the stabilisation of the T-shaped intermediate. A dissociative process is supported by results from both experimental work and density functional theory for the substitution of the PMe_2Ph ligand in *cis*-$[Pt(SiMePh_2)(PMe_2Ph)_2]$ by bis(diphenylphosphino)ethane.[239] The suggested mechanism involves Pt(I) as the intermediate followed by autocatalysis. Experiments on the mercury assisted hydrolysis of a number of chloroplatinum(II) complexes have shown there is a detectable intermediate which appears to involve a Pt–Hg bond.[240] Despite this, the mechanisms of the chloride transfer between Hg(II) and 11 chloroammine, aqua and sulfoxide complexes do not appear to involve Pt(II)–Hg^{2+} adducts but weaker Pt–Cl–Hg or Pt–Hg–Cl bridged complexes. The Pt–Hg complex is not in fact part of the reaction coordinate for the metal ion assisted aquation. The kinetics of the reaction of *cis*-$[Pt(NH_3)_2(adenosyl\text{-}N^7)_2]$ with thiourea follow an associative path, in which the solvent plays only a small part.[241] The kinetics of the substitution of the $[Pt^{II}(dipic)Cl]^-$ complex by 1-methylimidazole involves replacement of Cl, then opening of a carboxylate ring.[242] *cis*-$[Pt(en)(solv)_2]^{2+}$ reacts with indole-3-acetamide in a process which is first order in indole-3-acetamide and zero order in complex.[243] The mechanism proposed is that the entering ligand first coordinates through the amide oxygen followed by ring closure. This contrasts with the similar reaction involving the much more bulky *N*-(3-indolylacetyl)-L-phenylalanine, where the reaction is first order in both reactants. A single step is observed in the kinetics of substitution of py or 2-Mepy in $[Pt(4'\text{-}R'terpy)(2\text{-}Mepy)]^{2+}$ (R′ is *o*-tolyl or H) by I^- or thiourea with or without calf thymus DNA, which had an inhibiting effect on the reaction.[244] A major effect on the diminution of the rate with DNA is the intercalation of the Pt complexes in the case of thiourea and partitioning between DNA and the bulk solution in the case of I^-. The kinetics of the aquation of $[\{trans\text{-}PtCl(NH_3)_2\}_2\{\mu\text{-}NH_2(CH_2)_6NH_2\}]^{2+}$, which is a prototypical example of a new class of compounds showing antitumour properties, have been studied.[245] The aquation of cisplatin in the presence of DNA is slowed in a way that may be dependent on the DNA sequence.[246] This work also details the reaction of a 14-base pair oligonucleotide and also 3′- and 5′-guanine bases. A study of the reaction of $[Pt(en)(phen)]^{2+}$ with a hexanucleotide shows that the binding which occurs involves intercalation from the minor groove.[247] Rates of substitution reactions of Pd(II) complexes of thioether and of nitrogen donor ligands are faster for the former.[248] There are very signficant variations in the mechanism of the reactions of a series of bis(phosphine) sulfides, typified by $Ph_2P(S)CH_2(S)PPh_2$, with $PdCl_2$.[249] Substitution of Cl in $[PdCl(terpy)]^+$ by various amino acids occurs *via* an associative process.[250] The complex cation $[(AuL)_3(\mu\text{-}NNMe_2)]^+$ in which L is $P(p\text{-}XC_6H_4)_3$ and X is H, F, Me, Cl, MeO decomposes to $[AuL]_6^{2+}$ and tetramethyltetrazene at rates which increase as the pK_a of the $P(p\text{-}XC_6H_4)_3$ increases.[251] The mechanism for the process involves the rate determining loss of NNR_2 leading to a hydrazido complex of Au(0).

Application of modelling techniques to di- and tri-halogenosilanes shows that the extent to which 5-coordination occurs depends on the number of electronegative groups on the Si.[252]

5-, 7- and higher-coordination

The complexes $[Re(HCpz_3)Cl_2(OPh_3)]Cl$ and $[Re(HBpz_3)Cl_2(OPh_3)]$ are isoelectronic and isostructural analogues and take part in ligand substitution reactions *via* a dissociative process, while the reactions of the positively charged complex are very much faster than the neutral complex.[253] The rates of reduction by triarylphosphines involving oxygen atom transfer show an even larger range of values. Charge appears to be the overriding factor. The uncharged species reacts very much more slowly than the charged one and this is attributed to a transition state effect. Varying L^n in a series of complexes of the form $[ReO(L^n/L)]$, but keeping the same L [L is C_6H_5S and L^n are

$C_2H_5N(CH_2CH_2S)_2$, $Et_2NCH_2CH_2N(CH_2CH_2S)_2$, $C_2H_5SCH_2CH_2N(CH_2CH_2S)_2$ and $2,6\text{-}(SCH_2)_2NC_5H_3$] and reacting with glutathione showed that the reaction involves the formation of the species $[ReO(L^n)](GS)$.[254] The kinetics were followed using isothermal titration microcalorimetry. Similarly, GSH reacts with $[Pt(dien)Cl]^-$ by a mechanism in which $[Pt(dien)(GS)]^+$ is an intermediate.[255]

Ligand exchange

Using high pressure and variable temperature ^1H and ^{17}O NMR kinetic techniques, it has been possible to observe and reach an unambiguous understanding of water exchange in the two isomers of $[Eu(DOTAM)(H_2O)]^{3+}$.[256] The rates of water exchange for a number of M^{4+} species, $[U(H_2O)_{10}]^{4+}$, $[UF(H_2O)_9]^{3+}$, $[Th(H_2O)_{10}]^{4+}$[257] and $[UO_2(H_2O)_5]^{2+}$,[258] have also been determined and the values are recorded in Table 1. The mechanism appears to be a dissociatively activated interchange process. Exchange rates for both axial and equatorial H_2O have been measured for the complexes $[Ru(CO)(Eq\text{-}H_2O)_4(Ax\text{-}H_2O)](tos)_2$ and $[Ru(CO)_2(Eq\text{-}H_2O)_2(Ax\text{-}H_2O)_2](tos)_2$, and are shown in Table 1 and have been shown to correlate with the Ru–(H_2O) bond lengths and hence the bond strengths.[259] In the same work, the exchange rates for the CO oxygen atoms and those in the bulk water have been measured giving an upper limit for $[Ru(CO)(Eq\text{-}H_2O)_4(Ax\text{-}H_2O)](tos)_2$ of 10^{-8} s^{-1}, for $[Ru(CO)(Eq\text{-}H_2O)_4(Ax\text{-}H_2O)](tos)_2$, 1.18×10^{-4} s^{-1} for $[Ru(CO)_3(H_2O)_3\text{-}(ClO_4)_2$, 0.003 s^{-1} and for $[Ru(CO)_3(H_2O)_2(OH)]^{2+}$, 0.024 s^{-1}. The water exchange rate for $[Eu^{II}(DTPA)H_2O)]^{3-}$ (Table 1) is about a thousand times faster than for the corresponding Gd(III) complex.[260] The activation parameters, including a $\Delta V^{\ddagger}$ value of +4.5 cm^3 mol^{-1}, suggest that the reaction occurs *via* a dissociative interchange I_d mechanism. A coordination number of 8 or 9 with 2 or 3 molecules of water

Table 1 Water exchange kinetic parameters

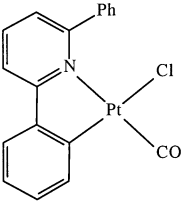
Ion	k_{ex}/s^{-1} (T = 298 K)	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
U^{4+}	5.4×10^6	34	−16
UF^{3+}	5.5×10^6	36	3
UO_2^{2+}(aq)	1.3×10^6	26	−40
Th^{4+}	$> 5 \times 10^7$		
$[Ru(CO)(Eq\text{-}H_2O)_4(Ax\text{-}H_2O)](tos)_2$ (equatorial exchange)	2.54×10^{-6}	111.6	22.4
$[Ru(CO)(Eq\text{-}H_2O)_4(Ax\text{-}H_2O)](tos)_2$ (axial exchange)	3.54×10^{-2}	81	
$[Ru(CO)_2(Eq\text{-}H_2O)_2(Ax\text{-}H_2O)_2](tos)_2$ (equatorial exchange)	1.58×10^{-7}	120.3	28.4
$[Ru(CO)_2(Eq\text{-}H_2O)_2(Ax\text{-}H_2O)_2](tos)_2$ (axial exchange)	4.53×10^{-4}	97.9	19.3
$[Eu^{II}(DTPA)H_2O)]^{3-}$	1.3×10^9	26.3	18.4
$[Gd(DO2A)(H_2O)_{2-3}]^+$	10^7		
$[Gd(DOTA)(H_2O)]^-$	4.8×10^6		
$[Eu(DOTAM)(H_2O)]^{2+}$ (major isomer)	8.3×10^3	53.1	8.4
$[Eu(DOTAM)(H_2O)]^{2+}$ (minor isomer)	327×10^3	44.2	8.8

respectively is established for $[Eu(DO2A)(H_2O)_n]^+$ in aqueous solution.[261] The exchange rate constants for $[Gd(DO2A)(H_2O)_{2-3}]^+$ and $[Gd(DOTA)(H_2O)]^-$ are shown in Table 1. Exchange of F^- in the Al^{3+}/F^- system has also been measured.[262]

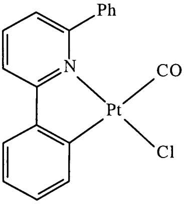
Ab initio calculations[263] on the water exchange reactions of $[Rh(NH_3)_5(H_2O)]^{3+}$ and $[Rh(NH_2CH_3)_5(H_2O)]^{3+}$ show that an interchange (I) mechanism operates in the former, while a dissociative interchange or dissociative mechanism is apparent in the latter process. Similar calculations[264] for $[Cr(NH_3)_5(H_2O)]^{3+}$, $[Cr(NH_2CH_3)_5(H_2O)]^{3+}$, *trans*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ and *trans*-$[Cr(NH_3)_4(NH_2CH_3)(H_2O)]^{3+}$ suggest that the water exchange reactions occur *via* an associative interchange (I_a) mechanism. Rotzinger[265] has also used *ab initio* quantum mechanical calculations in which the solvent was treated as a dielectric continuum. From these calculations the water exchange process in $[V(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ is concluded to operate by a and d activation. The rate constant for the loss of water from the low spin Fe(II) complex $[Fe(CN)_5(H_2O)]^{3-}$ during its reaction with $[Co(NH_3)_5(pyz)]^{3+}$ has been measured.[266] The trigonal planar $[CdL(PCy_3)]$ (L^- = 2,6-di-*tert*-butylphenoxide) does not exchange with phosphine, whereas the distorted tetrahedral $[CdL(PMe_3)_2]$ self-exchanges readily.[267] It is concluded that phosphine exchange occurs *via* a rapid associative process and a slow dissociative one. The coordination numbers for water in the inner sphere of a number of actinide and lanthanide ions (La, Ce, Nd, Eu, Yb, Y, Am, and Cm) in the presence of low concentrations of Cl^- varied between 8.7 (Yb) and 10.3 (Am) and reduced in 14 M Cl^-, as Cl^- entered the inner coordination sphere.[268] The coordination of Cl^- at these high $[Cl^-]$ values show increasing Cl^- coordination along the actinide series. The measurement of rates of CO exchange in solution suffer from the difficulty of having to operate at very high pressures of CO to give a reasonable concentration of CO in solution. However Merbach[269] and coworkers have studied the kinetics of CO exchange for the Rh(I) and Ir(I) complexes *cis*-$[M(CO)_2X_2]$ in which X is Cl, Br, or I using high pressure NMR. The rate of exchange follows the order of the *trans*-directing ability of the halogen ligands, *i.e.* $Cl < Br << I$. The values of the activation parameters, including the very negative values of $\Delta V^\ddagger$, are consistent with a limiting A mechanism for the exchange. In terms of the metals, it is found that the Rh complex is more reactive than the corresponding Ir one. The rate constant of $1.2 \times 10^{-8}\ s^{-1}$ for the exchange kinetics of CH_3CN in $[RuTp(CH_3CN)_3]^+$ is very much lower than for the corresponding isoelectronic Cp complex ($5.6\ s^{-1}$) because of the higher activation energy, 126 kJ mol^{-1}, as opposed to 85.7 kJ mol^{-1}.[270] The exchange rates for DMF in the complexes $[Ni(DMF)_6]^{2+}$ and $[Ni(DMF)_5Cl]^+$ are respectively $3.7 \times 10^3\ s^{-1}$, with $\Delta H^\ddagger = 59.3$ kJ mol^{-1} and $\Delta S^\ddagger = 22.3$ J mol^{-1} K^{-1} and $5.3 \times 10^5\ s^{-1}$ with $\Delta H^\ddagger = 42.4$ kJ mol^{-1} and $\Delta S^\ddagger = 6.7$ J mol^{-1} K^{-1}.[271] In the light of this, it was found that the rates of complex formation of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane and 1,4,8,11-tetraethyl-1,4,8,11-tetraazacyclotetradecane with $[Ni(DMF)_6]^{2+}$ and $[Ni(DMF)_5Cl]^+$ in DMF were such that $[Ni(DMF)_5Cl]^+$ was also about 100 times more labile than $[Ni(DMF)_6]^{2+}$. The two stages of the complexation reaction involved first a rapid attachment to the Ni(II) and then a further stage during which there was a rearrangement of the ligand to produce the correct stereochemical structure. The formation of the second Ni–N bond formed the rate determining step of the reaction.

Reactions of coordinated ligands and linkage isomerism

Isomerism of **5a** to **5b** occurs by a dissociative mechanism involving chloride.[272]

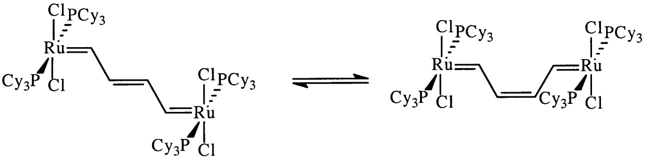


5a



5b

The kinetics of the enantiomerisation of the 8-coordinate compounds Δ- and Λ-$[M(thec12)]^{2+}$ in which M is Mg, Ca, Sr and Ba and the similar tmec12 species have been determined.[273] A mechanism for induction of supramolecular chirality has been developed from a study of the effect of temperature on such induction in an ethane-bridged bis(zinc porphyrin).[274] It has also been possible to investigate, in a bis(zinc porphyrin), the mechanism of supramolecular chirality inversion.[275] The last stage in the reaction of an alkyne with $[Re(O)Me_2(bpy)(CH_3CN)]^+$ is an isomerism step and is first order in alkyne concentration when *cis*-$[Re(O)Me_2(bpy)(alkyne)]^+$ is converted into the *trans* product. Rearrangement of a 5-coordinate intermediate is proposed.[276] The kinetics of isomerisation of, for example, $[Cp(dppe)Fe–CN–Fe^{III}Pc–CN–Cp(dppe)Fe]^+$ to $[Cp(dppe)Fe–CN–Fe^{III}Pc–NC–Cp(dppe)Fe]^+$ has been determined and has an activation energy of about 110 kJ mol^{-1}.[277] The kinetics of racemisation of bis{8-[(pyridine-2-methylene)amino]quinoline}iron(II), followed by using micellar electrokinetic chromatography, shows that the reaction involves a trigonal prism transition state.[278] Isomerisation and oligomerisation equilibria involving the metallacrown ether *cis*-$[PdCl_2\{Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2\text{-}P,P'\}]$ appear to have the same rate determining step in which cleavage of the Pd–P bond is a feature.[279] The mechanisms of *Z–E* isomerisation of $[\{Ru(Cy_3P)_2Cl_2\}_2(\mu\text{-}CHCH{=}CHCH)]$ (**6a**, **6b**) and similar complexes have been investigated[280] (see Scheme 5). A mechanism involving ruthenocyclobutene and loss of phospine appears to be the favoured option in a number of cases. A theoretical study of the aquation and also isomerisation of $[Co(NH_3)_5(SCN)]^{2+}$ and $[Co(NH_3)_5(NCS)]^{2+}$ reveals an I_d mechanism for the aquation with bond-making being important in the transition state, while the isomerisation process involves an I or I_d mechanism with a T-shaped transition



Scheme 5

state,[281] as proposed in the first study of this reaction by Buckingham *et al.*[282] The mechanism of the epimerisation of the optically active species $[Ir(\eta^5\text{-}C_5Me_5)(Pro)(C{\equiv}CCMe_3)]$ has been investigated.[283] Complexes of the form $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(=C=CHR)(CO)]^+$ have been found to isomerise to produce compounds of the type $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}H{\equiv}CR\text{-}C,C)(CO)]^+$.[284] The mechanism for this rather unusual process, deduced from theoretical studies, involves an intra-ligand hydrogen shift.

Metal-ion complexation with macrocycles

Reviews of self organisation in metal complexes and supramolecular chemistry[285,286] and a review of the formation of multinuclear complexes involving derivatives of cyclam[287] contain material of relevance to inorganic reaction mechanisms.

Kinetics and mechanisms of dissociation of a sodium calix[4]arene ester complex in non-aqueous solution[288] show that the lifetimes of the complex decrease as the electron donating ability of the solvent increases. In CH_3CN, the mechanism of the process is unimolecular dissociative. There have been three steps identified in the formation of the cluster compound $[(AuCl)_4L]$ [L = *p*-*tert*-butylcalix-[4]-$(OCH_2PPh_2)_4$] formed from [AuCl(tht)].[289] Each of these steps involves respectively adding 1, 2 and 4 units of AuCl to the macrocycle. Siderophores are generally 6-coordinate, but the dihydroxamate siderophore, alcaligin and rhodotorulic acid (L) are tetradentate and react with Fe^{3+} by forming a singly bridged Fe_2L_3 species.[290] The mechanism for the dissociation of these complexes is complicated, but proceeds *via* two parallel paths and with variously structured intermediates, depending on the conditions used. The kinetics of Fe exchange between Fe(III)–edta and the synthetic biomimetic siderophores based on a triamine backbone[291] and a cyclodextrin framework[292] have been carried out. The order in which the arms of a multidentate ligand complex attach to a metal ion, and which stage in the process provides the rate determining step, remains an interesting question. In the case of a study of a number of tripodal ligands, Rorabacher and coworkers chose ligands which had a heavily sterically hindered bridgehead nitrogen and three legs which possessed either thiaether or pyridyl groups for bonding to the metal, Cu(II), so the first step in the bond formation had to be either a thiaether or a pyridine nitrogen.[293] Where a pyridine nitrogen formed the first coordination, that step was rate determining, otherwise (*i.e.* when thiaethers were involved in the formation of the protonated first bond) formation of the second bond appeared to be rate determining. With protonated ligands, protonation was the rate determining step. In the case of complex formation being between Ni(II) and ligands such as 1,4,8,11-tetrathiacyclotetradecane and some derivatives in acetonitrile, the first attachment to the metal ion was rate determining in the case of the acyclic thiaether studied, but for the others it was the ring closure process.[294] In contrast to similar amine macrocycles, after the formation of the first bond there were not the expected slow changes in the conformation of the ligand. An associative mechanism for isomerism and exchange of HMPA has been proposed for the octahedral complex $[LaCl_3(HMPA)_3]$.[295] Rate constants for the cleavage of a 5′-cap analogue of RNA by an Eu(III) macrocycle complex are not affected greatly by changing the pendant group on the macrocycle.[296] The kinetics of the isomerism of *fac*- and *mer*-[Mo(CO)$_3$(PNCHP-κ^3-*P,N,P′*] have been investigated.[297]

Main group reactions

There has been a review of the mechanisms of isomerism of $SC(NH_2)_2$ to NH_4NCS.[298] It has been demonstrated experimentally using pulse radiolysis that in aqueous solution it is possible to add O^- to NO_2^- to produce NO_3^{2-} under conditions of high $[OH^-]$.[299] When the water is aerated peroxynitrite is produced by the action of ultrasonic radiation.[300] The existence of a short-lived cyclo-adduct formed between $OONO^-$ and CO_2 has been demonstrated by using high pressure pulse radiolysis techniques.[301] Intermolecular charge transfer complexes are formed between thiocarbonyl compounds and I_2.[302] *Ab initio* calculations suggest that there are two types of complex: one in which the I_2 lies in the same plane as the C=S group and the other in which the I_2 is at right angles to this plane. Which one is formed depends to some extent on the steric effect provided by the groups on the thiocarbonyl compound. The mechanism of the hydrolysis of 2,4-dinitrophenyldiethylphosphate produces diethylphosphate and is catalysed by the Cu(II) complex of 1,4,7,16,19,22-hexaaza[9.9]metacyclophane.[303] The reaction between DDQ^{2-} and alkali metals in acetonitrile occurs[304] *via* a fairly rapid step:

$$DDQ^{2-} + Na^+ \rightarrow Na^+DDQ^{2-}$$

followed by a rather slower reaction:

$$Na^+DDQ^{2-} + Na^+DDQ^{2-} \rightarrow Na^+_2DDQ^{2-} + DDQ^{2-}$$

Alkaline hydrolysis of $PO_2F_2^-$ is shown to be influenced by Li^+ ion and a mechanism is proposed for this.[305] The temperature jump technique has been used to study the interaction of In(III) with pyrocatechol violet (3,3′,4′-trihydroxyfuchsone-2-sulfonic acid).[306] The variously protonated 1:1 complexes were produced depending on the pH of the system and two reaction processes were seen as shown in Scheme 6. An I_d mechanism is suggested for reaction involving $In(OH)^{2+}$ whereas the situation is not clear cut for $In(H_2O)_6^{3+}$. Theoretical studies show that the mechanism of proton transfer in dimers of orthophosphoric, sulfuric and perchloric acids is a concerted process.[307] From analysis of the kinetic data obtained using selective inversion recovery ^{29}Si NMR on reactions of SiO_2 with $[(HO)_3AlOSi_n(OH)_{(3-n)}]^{(n+1)}$, it is proposed that zeolites are formed from alkaline solutions of aluminosilicates by a process of growth which involves labile AlOSi units adding to the growing zeolytic structure.[308] The reaction of magnesium acetylide in benzene containing nitrogen bases with octa(*p*-nitrophenyl)tetraazaporphine to produce the magnesium porphyrin complex is affected by the proton acceptor properties of the mixture.[309]

$$M^{3+} + H_3L^- \rightleftharpoons MH_3L^{2+}$$

$$MOH^{2+} + H_3L^- \rightleftharpoons MH_2L^+ + H_2O$$

Scheme 6

4 Organometallics

Reviews have been published on two-state reactivity as a new concept in organometallic chemistry, concluding that reaction mechanisms may be very significantly influenced by spin-crossing effects,[310] and on the amido–metal bond, including the examination of C–H activation, α-H elimination and N–N triple bond cleavage.[311] A review of transmetallation in alkynyl and aryl Group 10 complexes has mechanistic information.[312] There has been a review of organo(silyl)platinum(II) complexes relevant to catalysis[313] and a similar review of Pt and Pd complexes in catalysis of reactions of (alkoxy)diborons.[314]

σ-Bonded organotransition metal compounds

Intermolecular isotope effects (IIE's) for reactions of the type:

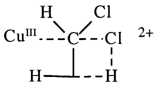
$$({}^tBu_3SiO)_2({}^tBu_3SiND)TiR_D + R_HH \rightleftharpoons ({}^tBu_3SiO)_2({}^tBu_3SiNH)TiR_H + R_DH$$

have been measured and values at 26.5 °C and are shown in Table 2.[315]

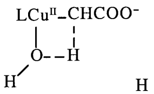
Table 2 IIE's at 26.5 °C for the reaction $LTiR_D + R_HH \rightleftharpoons LTiR_H + R_DH$

R_HH/ R_DH	CH_4/ CD_4	C_2H_6/ C_2D_6	C_3H_6/ C_3D_6	C_2H_4/ C_2D_4	C_6H_6/ C_6D_6	C_7H_8/ C_7D_8 (50 °C)
Exptl	2.00	2.22	1.71	1.41	1.22	1.59
Calc	1.88	1.93	1.48	1.34	1.26	1.55

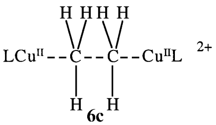
The very low enthalpy of activation (31.7 kJ^{-1} mol^{-1}) for the addition of NCMe to the complex $Ru_5C(CO)_{15}$ to form an NCMe bond instead of one of the Ru–Ru bonds is interpreted as being due to an early transition state in which it is the C of one of the CO groups which is the object of attack in the first instance.[316] Mechanistic differences between 'reductive' and 'oxidative' heterolysis of metal–carbon σ-bonds have been investigated using high pressure pulse radiolysis.[317] The difference in the mechanisms of heterolysis of $[Cu^{III}(CH_2CO)]^+$ and $[Cu^{III}(CHCl_2)]^{2+}$ compared with $[Cu^{II}(CH_2CO_2)L]^-$ (L is 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane) is reflected in the respective activation volumes: +12.4, +10.0 and +5.0 cm^3 mol^{-1} and follow the differing roles of water as the solvent in oxidative and reductive heterolysis processes. The suggested transition states are represented by **6a**, **6b** and **6c**.



6a

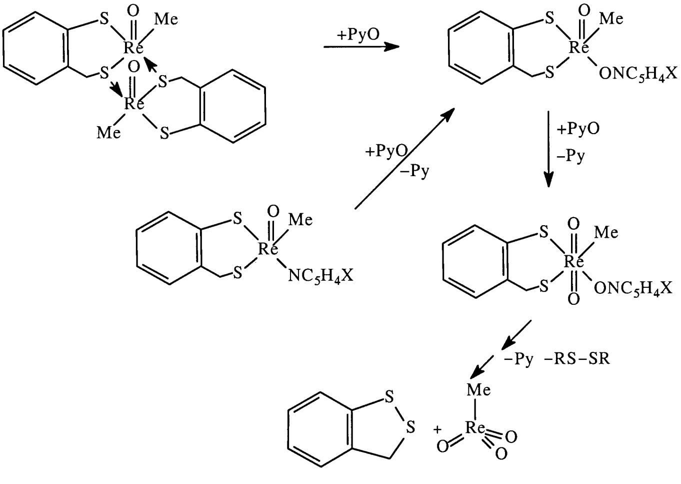


6b



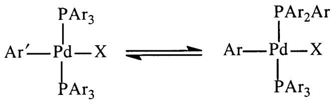
6c

The homolytic cleavage of the Cr–C bond in macrocyclic complexes of the type $[Cr([14]aneN_4)(H_2O)R]^{2+}$ is much faster than for the corresponding complexes of the type $[Cr(H_2O)_5R]^{2+}$, while rates of hydrolysis are the other way around.[318] The implications of this as to the nature of the reaction site are discussed in mechanistic terms. [$ReO_3(CH_3)$] reacts with hypophosphorous acid to give [$ReO_2(CH_3)(H_2O)_2$],[319] which, in turn, produces a yellow dimeric species. A significant feature of this process is that $\Delta S^\ddagger$ is not as negative as expected, a fact which the authors suggest is due to loss of water in the formation of the transition state. When PyO is added to the reactants as the reaction proceeds, the absorbance rapidly falls even when all the PyO is consumed. This intriguing process occurs because the PyO reacts rapidly with a version of the dimer that is an intermediate in the dimerisation and which is postulated to be the dimer with one of its oxygen atoms only bonded to one of the Re atoms instead of two. The mechanisms of oxidation reactions of organic substrates catalysed by [$ReO_3(CH_3)$], *via* formation of the diperoxyrhenium compound, have been studied.[320–323] Kinetic studies of the monomerisation (illustrated by the pyridine *N*-oxide reaction) and subsequent reactions of the monomer have resulted in the reaction pathways shown in Scheme 7.[324,325]



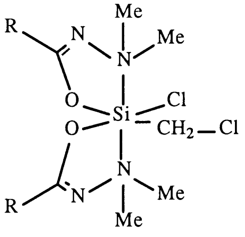
Scheme 7

The first stage takes place by an initial step resulting in 1 : 1 and 1 : 2 adducts and then slow monomerisation. Then there is a rate-controlling step involving bimolecular oxidation. Reaction of [$Re(CH_3)(NAd)_3$] or [$Re(CH_3)(NAr)_3$] (Ar is 2,6-diisopropylphenyl) with H_2Y (Y is S or $Ar^\bullet$) yields [$Re(CH_3)(NAd)_2Y$].[326] The mechanism for this process involves nucleophilic attack on the Re in the rate determining step. The protonolysis in neat acids, HX (CF_3COO, OSO_2H, OSO_2CF_3, OSO_2F) where X is the anion, of [Pt(dfepe)(Me)X] yields [$Pt(dfepe)(X)_2$].[327] The mechanism for the reaction does not involve association of the anion to the complex as a significant factor in the kinetics. Substitution of SMe_2 in the Pt(IV) complex [$Pt(C–N)(CH_3)_2(X)(SMe_2)$], where C–N is one of a variety of cyclometallated imine ligands and X is Br or Cl, by substituted phosphines, such as PPh_3 occurs *via* a limiting dissociative process involving the 5-coordinate complex [$Pt(C–N)(CH_3)_2(X)$], which is present in steady-state concentrations and which then reacts by an associative mechanism to form the products.[328] The factors affecting the rates of the reaction include the nature of the substituents on the phosphine, the imine ligand and the axial halide. The new ligand TIPS-6-MPD reacts with *trans*-$[Pt(SMe_2)_2(Me)Cl]$ to give [Pt(TIPS-6-MPD)(Me)Cl][329] which in turn reacts with $AgBF_4$ in CH_3CN to yield [Pt(TIPS-6-MPD)(Me)($NCCH_3$)] and this reversibly exchanges with, for example, benzonitrile, a process shown from kinetic measurements to be associative. Protonation of the pendant amine during protonolysis by HX (where X is Cl, O_2CCF_3, O_3SCF_3) of [$PtMe_2$(DMEP)] and [$PtMe_2$(DMPP)] is an important step when there is not an excess of acid.[330] In the case of the complex [$PtMe_2$(DMPP)], a feature of the reaction is the intermediate [PtH(Cl)Me_2(DMPPH)]Cl which is indeed stable at −30 °C. Only in the case of the reaction of [RuCp(H)L], in which L is dppm or dppe or $(PPh_3)_2$, with $HBF_4{\cdot}Et_2O$ in THF is a dihydrogen complex produced.[331] At high temperatures (> 50 °C) an unusual exchange reaction occurs between **7a** and **7b** in non-coordinating solvents in complexes $[Pd(Ph_3P)_2(C_6D_5)X]$ (X is Cl, Br or I).

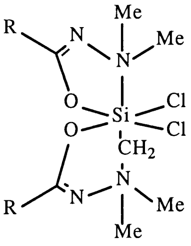


7a **7b**

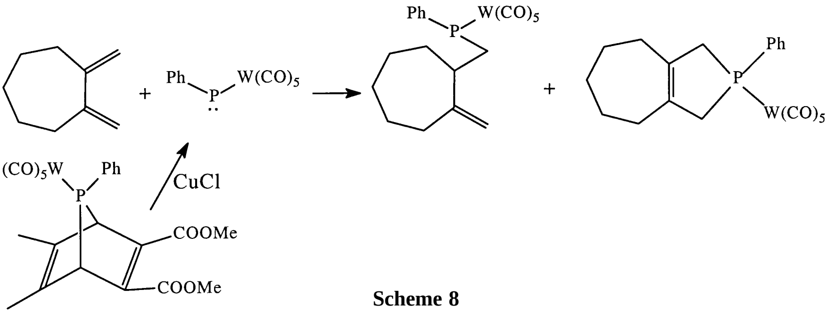
The mechanism for this process involves dissociation of the phosphine ligand rather than ionisation of X.[332] For the first time, it has been possible to insert Te *via* phosphine catalysis into an Sn–Sn or Pb–Pb bond to produce $R_3SnTeSnPR_3$ or $R_3PbTePbPR_3$.[333] The mechanism of the reaction involves the formation of $R'_3P{=}Te$ that then reacts with R_3MMPR_3 giving $R_3MTeMPR_3$ and R'_3P. Racemisation of optically active diaryl telluroxides has been found to occur through a mechanism involving a tetra-coordinated hydrate.[334] The silicon species **8b** is formed quantitatively on heating **8a**.[335] Both of these compounds have been shown to undergo ligand-site exchange processes. In the case of **8b**, the transition state is proposed as having a bicapped-tetrahedral structure, while for **8a** a dissociation and recombination mechanism is postulated. Another rearrangement, this time around phosphorus, is shown in Scheme 8,[336] and the transition state is believed to involve a biradical. However, Cu(I) is a catalyst for the reaction and the kinetic data suggest that it is likely that the process involves a concerted mechanism. A series of new achiral and C_2 symmetric metallocene complexes of the lanthanide elements Y, La, Nd and Lu have been produced by the elimination of silylamine from $[Ln\{N(SiHMe_2)_2\}_3(THF)_x]$ by reaction with linked, substituted cyclopentadiene or indene complexes, giving, for



8a



8b

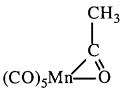


Scheme 8

example [La{$Me_2Si(C_5Me_4)_2$}{$N(SiHMe_2)_2$}].[337] Mechanistic information on the preparative reaction involved the isolation of intermediates of the yttrium system, [Y{$N(SiHMe_2)_2$}$_3$(THF)] and [Y{Me_2Si(2-Me-4-PhInd)$_2$H}{$N(SiHMe_2)_2$}$_2$].

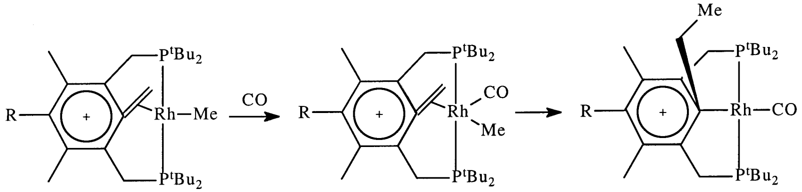
Carbonyl-insertion and alkyl-migration reactions

The insertion of carbonyl into [$Mn(CO)_5CH_3$], producing [$Mn(CO)_5(COCH_3)$], has been shown in a theoretical study to occur *via* a multi-step process involving and beginning with methyl migration and incoming CO attack from the acyl carbon side. A theoretical study[338] of the non-solvated thermal reaction shows that the dihapto species **9** is the stable intermediate.



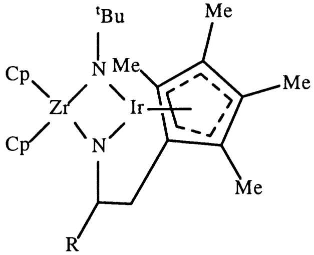
9

As a result of reaction of carbon monoxide with the rhodium complex **10a**, the Me attached to the Rh migrates (**10b**, **10c**) to the methylene arenium part of the molecule.[339] It is suggested that the migration of the methyl to the methylene arenium is favoured thermodynamically over carbonylation.



10a **10b** **10c**

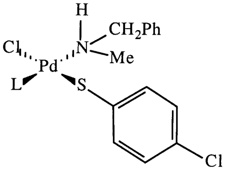
Olefin arylation involving benzene producing largely straight-chain alkyl benzenes catalysed by the complex [Ir(μ-acac-*O,O,C*^{3})(acac-*O,O*)(acac-*C*^{3})]$_2$ appears to occur *via* CH activation of the benzene CH bonds.[340] α-C–H bond activation of the ketone occurs in the reaction of [{RuCl[P(OMe)}$_2$(μ-S_2)(μ-Cl_2)] in the presence of, for example, PF_6^- to give the ketonated complexes.[341] There has been a theoretical study of the migratory insertion process in which $[M(CO)_2I_3Me]^-$ is converted into $[M(CO)I_3(COMe)]^-$ (M is Rh or Ir)[342] and on carbonyl insertion involved in olefin hydroformylation catalysed by $[CoH(CO)_3]$.[343] *Ab initio* MO investigation of carbonyl insertion in olefin hydroformylation which is catalysed by $[CoH(CO)_3]$ concludes that Et migration is the more favourable path energetically.[344] Time-resolved infrared spectra have helped to characterise the intermediate in the hydroformylation of olefins by phosphine-modified cobalt carbonyls as $[Co\{CH_3C(O)\}(CO)_2(PPh_3)]$.[345] Carbonylation of olefins in the presence of $[PPh_4]$*cis*-$[Ir(CO)_2I_2]$ and the corresponding Rh complex at high CO and H_2 pressures occurs through a large number of intermediate species, many of which could be characterised.[346] The process by which insertion of isocyanide occurs in the reaction with $[Fe(PMe_3)_2(CO)_2(MeCNR)]X$, producing $[Fe(PMe_3)_2(CO)_2(\eta^2\text{-}CMe{=}N^tBu)]X$, has been shown to involve intermediate ion pairs.[347] In the structures of the ion pairs two different scenarios are envisaged, depending on the counterion or the solvent. Either the counter ion is located between the CO and the isocyanide or it is close to the dihapto iminoacyl ligand. *tert*-Butyl isocyanide may also be inserted into the agostic Ta–C bond in $[Ta^+(C_5H_5)_2(Me)\{CH_2B^-(C_6H_5)_3\}]$ to produce $[Ta^+(C_5H_5)_2(Me)\{Me_3CN{=}CCH_2B^-(C_6H_5)_3\}]$ and the kinetics of this process have been investigated.[348] $[Cp_2Zr(\mu\text{-}N^tBu)IrCp^*]$ undergoes insertion reactions with RCN to yield **11**.[349] When R is cyanocyclopropane, an intermediate is observed, which proves to be $[Cp_2Zr(\mu\text{-}N^tBu)(\mu\text{-}NCRH)Ir](\eta^5\text{-}C_5Me_4CH_2)$ and is part of the mechanistic regime. Reaction of $2,6\text{-}Me_2C_6H_3NC$ with $[NbCp^*Cl_2Me_2]$ results in $[NbCp^*Cl_2\{\eta^2\text{-}CMe_2N(2,6\text{-}Me_2N_6H_3)\}]$ *via* a double migration of a methyl group.[350]



11

Substituted allenes may be inserted into the Pd–Me bond in complexes of the type $[PdCl(Me)(6\text{-}R'\text{-}C_5H_3N\text{-}2\text{-}CH_2SR)]$ and the rate of insertion is dramatically increased when there is a Me group in the 6 position of the pyridine ring.[351] The reason given for this is that the coordination plane of the molecule is distorted by the presence of the Me group and this allows easier insertion of the allene group. As an alternative to the use of phosgene, thiocarbamates may be prepared by the reaction of *N*-benzylmethylamine, 4-chlorobenzenethiol and CO with $[Pd(PPh_3)_2Cl_2]$.[352] Isolation of intermediates and kinetic studies allowed a mechanistic scheme in which the formation of the thiocarbamate may be produced by two pathways in which reaction of **12** (L is PPh_3) with CO is a key step in the process.

Carbonyl insertion into the Pt–C bond in the complex $[Pt(SnCl_3)(PH_3)(CO)(CH_3)]$ to form *cis*-$[Pt(SnCl_3)(PH_3)(CH_3CO)]$ occurs by the mechanism predicted by quantum mechanical calculations and involves an intramolecular rearrangement of a



12

3-centre transition state.[353] Vinyl migration is a feature of the mechanism proposed in the production of vinyl silanes catalysed by $[Ru(R_3P)(CO)(Cl)H]$.[354] The reaction of $[TiCp_2Cl(SPh)]$ with $[PtCl(Me)(\eta^2:\eta^2\text{-cot})]$ produces $[Pt(Me)(SPh)(\eta^2:\eta^2\text{-cot})]$ and the pathway involves disproportionation of $[TiCp_2Cl(SPh)]$, giving $[TiCp_2Cl_2]$ and $[TiCp_2(SPh)_2]$.[355] A density functional study of the production of an η^2-iminoacyl complex by insertion of isocyanide into the Mo–C bond of $[MoCp_2(CH_3)(CNH)]^+$ shows that the transition state for the process involves the partial formation of the C–C bond followed by migration of the Me to the isocyanide carbon.[356] A theoretical study of the mechanisms of CO migratory insertion into the metal–alkyl bond of $[FeCp(CO)_2CH_3]$ and $[FeCp(CO)_2CH_3]^+$ in the presence of PH_3 has allowed the transition states and intermediates to be determined.[357] The rate determining step in the process in both cases involves Me migration, but with little involvement of PH_3 and both complexes react *via* similar mechanisms. The role of the PH_3 is to stabilise metastable intermediates. Alkyl migration between Mo≡Mo is a feature among mechanistic processes involved in the reactions of 1,2-$[Mo_2Br_2(CH_2SiMe_3)_4]$ and $LiNMe_2$ or $HNMe_2$ to produce 1,1-$[Mo_2(NMe_2)(CH_2SiMe_3)_4]$ and 1,2-$[Mo_2(NMe_2)(CH_2SiMe_3)_4]$.[358]

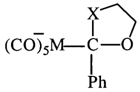
Ligand-displacement reactions of metal carbonyl and other low-valent compounds

Guthrie[359,360] has applied No Barrier Theory in one case, and Multidimensional Marcus Theory in the other, to the hydration of carbonyl compounds, to predict rates and equilibrium constants with considerable success. The exception was where the reactions involved exceptionally reactive carbonyl compounds. A kinetic study has been carried out on the displacement of CO from the complex $[Ru(CO)_4(\eta^1\text{-P–P})]$ in n-heptane, [P–P is $Ph_2P(CH_2)_nPPh_2$ or $Ph_2P(NMe)PPh_2$, $Ph_2P(o\text{-}C_6H_4)PPh_2$, $R_2P(CH_2)_2PR_2$, with R = Me or Cy]:

$$[Ru(CO)_4(\eta^1\text{-P–P}) \longrightarrow Ru(CO)_3(\eta^2\text{-P–P})] + CO$$

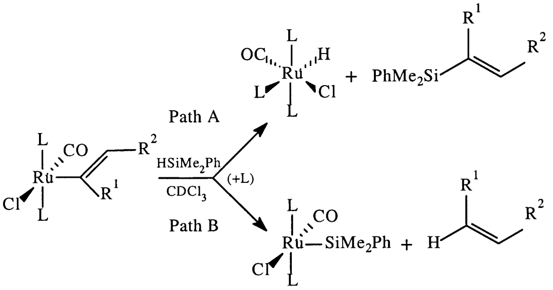
From the variation in $\Delta S^{\ddagger}$, it is concluded that the mechanism changes from a dissociative to an associative process as the nature of P–P changes.[361]

A thorough kinetic study has shown that in the mechanism for the formation of $[Os_2(CO)_8(\mu\text{-}C_2H_2)]$ and $[MRuOs(CO)_8(\mu\text{-}C_2H_2)]$ (M is Ru or Os) from reaction of $[Os(CO)_4(\eta^2\text{-}C_2H_2)]$ with $[Ru(CO)_5]$ or $[Os(CO)_5]$, the first step is dissociation of one molecule of CO from $[Os(CO)_4(\eta^2\text{-}C_2H_2)]$.[362] The resulting species then reacts with $[M(CO)_5]$ to produce, $[Os(CO)_3(\eta^2\text{-}C_2H_2)M(CO)_5]$, which then reacts to form the product. Reversible cyclization of $[M{=}C(SCH_2CH_2OH)Ph(CO)_5]$ and $[M{=}C(OCH_2CH_2OH)Ph(CO)_5]$ (M is Cr or W) occurs in aqueous acetonitrile[363] to produce **13**. In



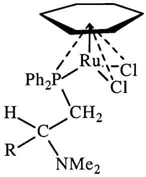
13

base, there is a pre-equilibrium step with the oxyanion, $[M{=}C(OCH_2\text{-}CH_2O^-)Ph(CO)_5]$. In acid conditions, there is a concerted reaction involving water as a general base catalyst. Reversible addition of MeO^-, $HCCH_2O^-$ and $CF_3CH_2O^-$ and OH^- to $[M{=}C(OMe)C_6H_4\text{-}4\text{-}Z(CO)_5]$ (M is Cr or W) results in the formation of the tetrahedral species $[M{=}C(OMe)(OR)C_6H_4\text{-}4\text{-}Z(CO)_5]$ (Z is for example 4-Me).[364] A kinetic study points to a transition state which is imbalanced, by which the authors imply that delocalisation of the CO lags behind the formation of the CO bond. Hydrolysis of the related complex $[M{=}C(SMe)Ph(CO)_5]$[365] occurs in two stages resulting in $[M{=}C(OH)Ph(CO)_5]$ or $[M{=}C(O^-)Ph(CO)_5]$ *via* the formation of a tetrahedral intermediate produced by the addition of OH^- and H_2O in the first stage and finally PhCH=O and $[MOH^-(CO)_5]$. There are 3 steps in the reaction of $[M{=}C(OMe)C_6H_4X(CO)_5]$ (M is Cr or W and X is 4-halide or Me, OMe or NMe_2) with n-butylamine (or similar) producing $[M{=}C(NHR)C_6H_4X(CO)_5]$.[366] The first is formation of a zwitterion by nucleopilic addition to the complex, the second is deprotonation of this species and the third is loss of methoxide catalysed by H_2O and RNH_3^+. Dissociation of CO from $[Rh(CO)_2H(\text{diphosphine})]$ has been observed for the first time with ^{13}CO labelling using rapid scanning high pressure infrared spectroscopy.[367] The complexes $[Co(CO)(Hdppa\text{-}\kappa^2P)_2][Co(CO)_4]\cdot 2THF$ and $[Co(CO)(dppm)_2][Co(CO)_4]\cdot 2THF$ have been found to exchange both phosphine groups and CO groups between the cation and the anion.[368] A concerted mechanism is proposed for this process. $[Ru\{CH{=}CH(Ph)\}Cl(CO)(PPh_3)_2]$ and related complexes react with $HSi(Me_3)_2Ph$ by two pathways (A and B, Scheme 9); one results in the formation of $[RuHCl(CO)(PPh_3)_3]$ + $PhMe_2SiCH{=}CHPh$ and the other produces $[Ru(SiMe_2Ph)Cl(CO)(PPh_3)_2]$ + $CH_2{=}CPh$.[369]



Scheme 9

The kinetic studies carried out on this system have shown that path A involves a σ-bond metathetic reaction produced by association of styryl Ru with the hydrosilane and then nucleophilic attack of the styryl ligand on Si. Path B, on the other hand, is suggested to involve a Ru(IV) intermediate by dissociation of PPh_3 and then oxidative addition of hydrosilane. Cross disproportionation of $CH_2{=}CHSiR_3$ with $CH_2{=}CHOR'$[370] is catalysed by $[RuHCl(CO)(PPh_3)_2]$, $[RuCl(SiMe_3)(CO)(PPh_3)_2]$, $[RuCl_2(PPh_3)_3]$ and $[Ru(CO)_3(PPh_3)_3]$. The mechanism has been shown to include both insertion of vinyl ether into the Ru–Si bond and vinyl silane into the Ru–H bond. This is followed by a process of H and Si transfer. The kinetics of the dissociation of the alkene moiety from the yttrium complex $[YCp^*_2\{\eta^1:\eta^2\text{-}CH_2CH_2CH(CH_3)CH{=}CH_2\}]$ at low temperatures gives a value of $\Delta H^{\ddagger} = 45.1$ kJ mol^{-1}, and for the binding energy of the alkene to Y, $\Delta H^0 = 10.9$ kJ mol^{-1}.[371] The experimental results show that for this and other yttrium–alkyl–alkene complexes, alkene dissociation from yttrium is much faster than insertion. An associative mechanism is proposed for the olefin exchange processes which have been found to occur in Pd(0)–olefin complexes containing pyridine–thioethers.[372] Reaction of $[Rh(acac)(CO)_2]$ and $P(OPh)_3$ occurs dissociatively with stepwise replacement of each CO in turn, while similar reactions with $P(NC_4H_4)_3$ involve associative steps.[373] Substitution of CO in $[M(\eta^5\text{-}C_5H_5)(CO)_4]$ (M = Nb, Ta) by phosphines and phosphates is faster in the case of the Ta complexes[374] and the indenyl complexes react more rapidly than the cyclopentadienyl ones. The latter react *via* dissociative mechanisms, while for the former an associative mechanism obtains. In the case of $[Mn(MeC_5H_4)(CO)_2(HBcat)]$,[375] it is the HBcat that is replaced in reaction with PhCCPh in a process in which borane and PhCCPh compete for the intermediate $[Mn(MeCp)(CO)_2]$. The natures of the transition states have been identified from MO calculations for the addition of PH_3 to a range of complexes of the type $[Mn(\eta^5\text{-}X)(CO)_3]$ (X = Cp, Ind, Flu, Chd, Hnaph).[376] Entropic factors govern the reactions of $[M(\eta^5\text{-}C_5H_5)(CO)_2(alkane)]$ (M is Mn or Re) with CO.[377] There has been a mechanistic study of the chelation reaction[378] of **14**. The rate determining step is solvolysis of the complex followed by fast ring closure to produce a diastereoisomeric product by replacement of Cl by N at Ru(II) with the formation of the major diastereoisomer being fast and the minor slow. There has been a study of the carbonylation of the complex *fac*-$[Tc(H_2O)_3(CO)_3]^-$ by CO.[379]



14

Redox reactions

A review has appeared which includes aspects of the mechanism of the operation of catechol oxidases and tyrosinase.[380]

$[Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})]$ and $[W(CO)_3(dppb)(\eta^2\text{-}C_{60})]$ undergo three reduction processes involving mostly the C_{60} moiety.[381] The electron transfer rate and quantum effects on the rate for the ion-pair species $[Co(Cp)_2]^+[V(CO)_6]^-$ has been modelled.[382] A rate determining single-electron mechanism is ruled out by Che and coworkers for the cycloaddition of $[Ru^{VI}O_2Cn^*(CF_3CO_2)]ClO_4$ by a number of trimethylsilylacetylenes.[383] The rate limiting step which is proposed for the process is the formation of a vinyl radical. There has been a detailed study of aspects of the redox behaviour of $[Co_4(CO)_3(\mu_3\text{-}CO)_3(\mu_3\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$.[384]

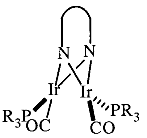
Oxidative addition and reductive elimination

A theoretical study modelling reactions producing π-allyl–Ni complexes from alkyl ammonium and alkyl imminium salts has shown that oxidative addition to Ni(0) by allylammonium salts occurs by an associative mechanism (Scheme 10), while for allyliminium salts a dissociative process is favoured.[385,386] The active catalyst in these processes is the $Ni(PH_3)_2$ complex. The insertion of the catalyst in the C–N bond is crucial in the distinction between the reactions of the allylammonium and allyliminium species. Oxidative addition of methyl iodide to the 1,8-diamidonaphthalene complexes **15a**, **15b**[387] occurs *via* an initial step, which results in an M(III)–M(I) intermediate, which then follows one of three paths (Scheme 11), depending on the nature of the ligands.

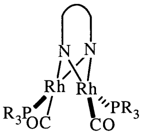
$$Ni(PH_3)_2 + (CH_2{=}CHCH_2NH_3)^+ \longrightarrow [(\eta^3\text{-}C_3H_5)Ni(PH_3)(NH_3)]^+ + PH_3$$

$$Ni(PH_3)_2 + (CH_2{=}CHCH_2HN{=}CH_2)^+ \longrightarrow [(\eta^3\text{-}C_3H_5)Ni(PH_3)(\eta^1\text{-}NH{=}CH_2N\text{-}N)]^+ + PH_3$$

Scheme 10



15a



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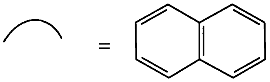
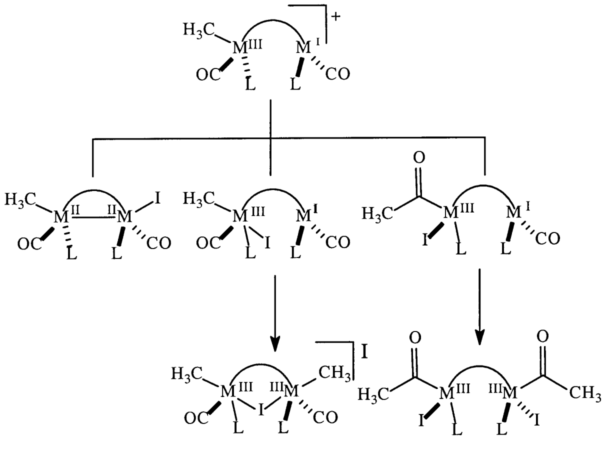
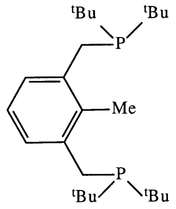


Calculations to compare oxidative addition of C–C and C–H to rhodium(I) complexes of L^2 show that C–H and C–C activation occurs by a common intermediate structure and C–C activation is favoured thermodynamically over C–H, though the latter is invariably kinetically favoured.[388] Another theoretical study of the activation of C–C and C–H bonds has involved Rh(I) and Ir(I) complexes, [M(PCP)Cl].[389] The proposed mechanism features a 4-coordinate η^1-arene intermediate, which also serves partly to explain the fact that PCP ligands enhance C–C activation in these complexes. The effects of a variety of additives on the reductive elimination of $[Cu^{III}Me_3]$ using quantum mechanical techniques has shown that the role of the additive in facilitating the reaction is to stabilise thermodynamically the $[Cu^{III}Me_3]$, but also to ensure that it remains kinetically labile by the formation of a Lewis acid complex.[390] A computational study of the reductive elimination of methane from $[Pt(PH_3)_2(Me)H]$



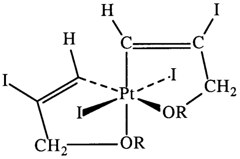
Scheme 11



L^2

showed, as in a previous experimental study, that it occurred without previous loss of PH_3.[391] However, calculations show that loss of PH_3 from the Pt(IV) complex $[Pt(PH_3)_2Cl_2(Me)H]$ requires loss of the phosphine ligand before reductive elimination, as has been experimentally determined previously for 6-coordinate Pt(IV) complexes. Oxidative addition of phenylpropargyl halides to $[Pt(PPh_3)_4]$ produces $[Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2]$.[392] The rate determining step which is proposed involves the formation of $[Pt(\eta^2\text{-}PhC{\equiv}CCH_2X)(PPh_3)_2]$ and then this rapidly decomposes *via* $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]X$ to the product. When dppe is replaced in the Pt(IV) complex $[Pt(dppe)Me_4]$ by *o*-$(Ph_2P)_2C_6H_4$, the rate of the thermal reductive elimination reaction is radically reduced.[393] The implication of this and other experimental data is that the reaction involves the formation of a 5-coordinate intermediate through dissociation of one arm of the chelate ring. The mechanism of the reaction of benzene with $[Pt(N\text{–}N)(CH_3)(H_2O)]^+$ [N–N is $(CH_3)_2C_6H_3N{=}C(CH_3)C(CH_3){=}NC_6H_3(CH_3)_2$] in TFE[394] involves a rate determining step in which benzene replaces water and becomes coordinated to the Pt to produce two isomers involving C,C-η^2 and C,H-η^2 arrangements. The series of events proposed thereafter includes formation of a transient 5-coordinate Pt–hydride complex followed by a C,H-η^2 system which then results in production of methane. Kinetic and theoretical studies suggest that the reaction of $[Pt(N^F\text{–}N^F)(CH_3)(H_2O)]^+$ [N^F–N^F is $(CF_3)_2C_6H_3N{=}C(CH_3)C(CH_3){=}NC_6H_3(CF_3)_2$] with methane,[395] producing [Pt(N^F–

$N^F)(CH_3)_2]^+$, occurs *via* an oxidative addition process involving unstable $[Pt(N^F–N^F)(CH_3)(H)(TFE)]^+$. A polar transition state is suggested for the oxidative addition of MeI to di(4-thiocresol)(2,2′-bipyridyl)platinum(II) producing iodomethyldi(4-thiocresol)(2,2′-bipyridyl)platinum(IV).[396] The Pt(IV) complex **16** undergoes reductive elimination *via* a mechanism in which one of the chelate rings is broken. An intermediate is detected which has been produced by such a process.[397] A theoretical study has enabled workers to study the mechanism of reductive elimination of CH_3SiH_3 (or the corresponding Ge compound) from $[Pt(CH_3)(SiH_3)(PH_3)]$ in acetylene.[398] A study of the oxidative addition of H_2 to $[Pd\{H_2P(CH_2)_2PH_2\}]$ and $[Pd_2\{H_2P(CH_2)_2PH_2\}]$ has shown that at < 230 K under-barrier tunnelling was an important feature of the reaction mechanism.[399] The importance of tunnelling is highlighted in a theoretical study of oxidative addition of methane to $[Pd\{H_2P(CH_2)_2PH_2\}]$.[400] Density functional calculations and application of inelastic neutron scattering show[401] that dihydrogen–hydride exchange in $[IrXH_2(\eta^2\text{-}H_2)(PR_3)_2]$ (X is halogen and R is H or Me) occurs by an oxidative addition/reductive elimination mechanism involving a tetrahydride intermediate. The complex $[Pd^0(dba)(PhPN)]$ and related species react with PhI by oxidative addition.[402] A molecular mechanics force field has been developed for Rh(I) carbonyl phosphine complexes and used to predict the nature of transition states in oxidative addition reactions.[403] The mechanism of Si–H and C–H bond activation by Ir(III) and the first direct observation of Ir(III)/Ir(V) C–H bond oxidative addition and reductive elimination[404] has appeared and has been extended[405] to reactions involving 1-electron reducing agents with dialkyl iridium complexes and silanes. Kinetics of the oxidative addition of $HSiEt_3$, $HGeBu_3$, $HSnBu_3$ and $HSnPh_3$ to $[Os_3H_2(CO)_{10}]$, giving $[Os_3H_3(CO)_{10}ER_3]$, show that the rate constants are in the order $HSiR_3 >> HGeR_3 > HSnPh_3 > HSnBu_3$.[406] A density functional theory investigation of C–H bond activation of benzene and methane by $[M(\eta^2\text{-}O_2CH)_2]$ (M is Pd or Pt) has shown that, while $[Pd(\eta^2\text{-}O_2CH)_2]$ is able to produce C–H bond activation in both benzene and methane, $Pd(PH_3)_2$ cannot and the mechanism involves the formation of strong O–H bonds.[407] In the case of the Pt complex, however, C–H is readily activated in methane, but not in benzene, because of the formation of a stable intermediate benzene complex. A possible mechanism has been deduced for the reductive cleavage of allylic carboxylates to produce carbene *e.g.* $[Pd(\eta^3\text{-}MeCHCHCH_2)(HCOO)(PMe_3)]$.[408] The mechanism then would be decarboxylation yielding two geometrical isomers of $[Pd(\eta^3\text{-}MeCHCHCH_2)(H)(PMe_3)]$ leading to a mixture of 1-butene and 2-butene. The complexes $Pd(BINAP)_2$ and $Pd(dppf)_2$ with chelated phosphine ligands catalyse amination of aryl halides and the kinetics of the process and of oxidative addition of PhBr to a Pd^0 complex resulting in a *cis*-arylpalladium bromide, which is a crucial step in the process, has been investigated.[409] It is this latter process which limits the



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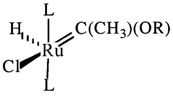
turnover. The overall kinetics are independent of the presence or otherwise of the amines. It is concluded that ligand dissociation governs the overall kinetics of the process. The complex $[\{Zr(CpR)_2NH^tBu\}_2(\mu\text{-}C{\equiv}C)]$ is produced by the fragmentation of $[\{Zr(CpR)_2\}_2(\mu\text{-}CHCHN^tBu)(\mu\text{-}N^tBu)]$ and the kinetics of the process indicate that the mechanism involves, before C–H activation occurs, the formation of $[Zr{=}N^tBu(CpR)_2(THF)]$ and $[Zr(CpR)_2(\eta^2\text{-}N^tBuCHCH)]$.[410] [2,6-Bis(dimethylamino)methylphenyl]gold(I) reacts with MeI to produce $[Au\{C_6H_3(CH_2NMe)\text{-}2\text{-}(CH_2NMeCH_2)\text{-}6\}I]I$ *via* a mechanism in which MeI first becomes attached to Au(I) and then oxidative addition and alkyl transfer take place.[411] Oxidative addition of carbamoylstannane is proposed as a key feature of the mechanism of the $[Rh(acac)(CO)_2]$ catalysed addition of *N*,*N*-di(isopropylcarbamoyl)trimethylstannane to terminal alkynes producing (*Z*)-β-stannyl-unsaturated amides.[412] The intramolecular methylene transfer from the chelating ligand to the aryl group in $[Rh(Ar)\{CH_2C_6HMe_2\text{-}3,5\text{-}(CH_2PPh_2)\text{-}2,6\}]I$ [Ar = C_6H_5, $C_6H_4CF_3$, $C_6H_3(CF_3)_2$, C_6H_4Me, C_6H_4OMe] to produce $[Rh(CH_2Ar)\{CH_2C_6HMe_2\text{-}3,5\text{-}(CH_2PPh_2)\text{-}2,6\}]I$ occurs *via* a rate-determining step which is described as a C–C reductive elimination rather than C–C activation.[413] The unusual stereoselective oxidative addition of mercury carboxylates in which $[Pt\{CH_2\text{–}C_6H_4\text{–}P(o\text{-tolyl})_2\text{-}\kappa C,P\}(S_2CNMe_2)]$ produces $[Pt(C{\wedge}P)(S_2CNMe_2)(O_2CCH_3)Hg(O_2CCH_3)]$ is likely to occur by a concerted mechanism involving an intermediate containing a Pt–Hg donor bond.[414]

Hydrogen and hydrido complexes

A mechanism involving C–H cleavage of methanol after methoxide loss has occurred is proposed for the decomposition of the complex *trans*-$[IrH(OCH_3)(C_6H_5)PMe_3]$ to produce *trans*-$[IrH_2(C_6H_5)PMe_3]$ + formaldehyde.[415] The halide-bridged dimeric compound $[RuHClL_2]_2$ (L = P^iPr_3) reacts with N_2 or C_2H_4 (L′) to produce $[RuHClL'L_2]$ involving olefin bonding to the Ru.[416] If, however a vinyl ether is used, the formation of the olefinic species is followed by rapid isomerisation to produce the carbene complex **17**. The mechanism for the isomerism is believed to involve reversible migration of the hydrogen attached to the Ru to both of the olefinic carbon atoms. In the reaction of $[RuH_2(CO)(PPh_3)_3]$ with styrene giving $[Ru(CO)(CH_2{=}CHPh)_2(PPh_3)_2]$ and $[Ru(C_6H_4PPh_2)H(CO)(PPh_3)_2]$ and related reactions cyclometallated hydridoruthenium(III) complexes feature as intermediates.[417] The mechanism of the C–C bond activation in 6-*exo*-methyl-η^5-cyclohexadienylruthenium hydride, converting the 6-*exo*-methyl and the hydride to methane involves interaction with a weak base to remove a proton from the agostic hydride. The acid generated produces activation of the C–C bond of the 6-*exo*-hexamethylcyclohexadienyl complex.[418] The compound $[Ru_2\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}(CO)_4(\mu\text{-}H)]^+$ is only slowly



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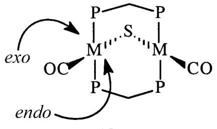
deprotonated by amines[419] and this is attributed to the presence of the $(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2$ bridge. The substitution of $P(CH_3)_3$ by $P(CD_3)_3$ in complexes of the form $[Os\{P(CH_3)_3\}_4(H)NHC_6H_4Z]$, where Z is H, OCH_3, CF_3 occurs in two steps, first a process of substitution into the mutually *trans* sites and then into the position which is *trans* to the anilide ligand.[420] The suggested mechanism involves the formation of a quasi-trigonal bipyramidal intermediate. As part of a study of coordinative unsaturation at Os, the reaction of *cis*-$[Os(PMe_3)_4(H)(NC_5H_4O)]$ with PD_3 in C_6D_6 shows that first order exchange occurred stereospecifically in the position *cis* to H, with $t_{\frac{1}{2}} = 14$ min.[421] Caulton and coworkers have shown[422] that $[MHF(CF_2)(CO)L_2]$ (M is Ru or Os and L is P^iPr_3 or P^tBu_2Me) is the initial product of the reaction of $[MHF(CO)L_2]$ and $Me_3Si(CF_3)$ in the presence of trace amounts of F^-. This then rearranges in the case of the Ru complex to $[RuF(CF_2H)(CO)L_2]$ while for Os $[OsF_2(=CFH)(CO)L_2]$ is the product. Another aspect highlighted is the very rapid reaction of $[RuHF(CF_2)(CO)L_2]$ with CO to produce $[RuF(CF_2H)(CO)_2L_2]$, whereas the corresponding Os complex does not react at all. A kinetic study of the reaction of $[IrCp^*(PMe_3)H_2]$ with a range of aromatic and hindered aliphatic acid chlorides, together with a variety of amines and which resulted in complexes of the form $[IrCp^*(PMe_3)(C(O)R)H]$, showed that among the factors affecting the rate were the substituents on the aromatic ring of the aroyl chloride and the substituent in the phosphine group attached to Ir.[423] A rather different reaction occurred when acetyl chlorides were used in the presence of Proton-Sponge [1,8-bis(dimethylamino)-naphthalene], in that the product is then $[IrCp^*(PMe_3)(CH{=}CHR)(Cl)]$. The mechanism proposed for both types of reaction invokes a nucleophilic attack by the metallic species at the carbon atom of the carbonyl group. Parahydrogen-induced polarisation in NMR spectra occurs when parahydrogen is added to a complex 'pairwise' and has been used to study the reaction of H_2 with the so-called μ-S A-frame complex $[Ir_2(\mu\text{-}S)(CO)_2(dppm)_2]$.[424] It has been shown that there are two pathways resulting in intermediates involving *exo* oxidative addition outside the pocket of the complex and *endo*-oxidative addition, inside the pocket (**18**).



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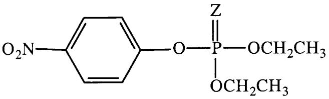
The use of this polarisation technique was also instrumental in observing a mixed-metal, Ir,Rh complex in the reaction mixture arising from an Rh impurity in the Ir. Complexes of the type $[Rh(tacn)(H)(alkyl)\{P(OMe)_3\}]^+$,[425] when reduced by $NaBD_4$, produce species in which there is around 5% deuterium in the alkyl group and this does not change with time. However the deuterium distribution within the alkyl group does, as it migrates from α to ω, even when the alkyl group has 8 intervening methylene groups. The mechanism proposed for this process involves reversible reductive elimination to a coordinated alkane complex. The metal migrates along the alkyl chain being coordinated to each of the carbon atoms in turn. Theoretical studies of a mechanism of carbonyl reduction by $[RhH(NH_3)_2(C_2H_4)_2]$ in formaldehyde or acetone, involving breaking the N–Rh bond, hydride formation (rate determining) following the attachment of CO to the Rh, and then exchange of alkoxy ligands, have been carried out.[426] The hydride complex $[Mo(\eta^6\text{-}C_6H_6)(TRIPOD)(H)]^+$ is produced by *exo* addition of H^+ to $[Mo(\eta^6\text{-}C_6H_6)(TRIPOD)]$ giving the intermediate $[Mo(\eta^5\text{-}C_6H_7)(TRIPOD)]^+$ and thence the product.[427] Photoelectron spectroscopy has been used to investigate the underlying basis for this mechanism. Protonation of $[MoCp^{Et}H_3(dppe)]$ yields $[MoCp^{Et}MoH_4(dppe)]^+$ and this is slowly converted into $[MoCp^{Et}H_2(MeCN)(dppe)]$, which in turn may itself be protonated to give $[MoCp^{Et}H(dppe)(MeCN)_2]^{2+}$.[428] Mechanistic schemes are provided for these and related reactions. A theoretical study using density functional theory has been used to compare reactions of $[\{(PH_3)(NH_2)Zr\}(\mu\text{-}\eta^2\text{-}N_2)\{Zr(PH_3)(NH_2)\}]$ with H_2 with similar Zr systems[429] and to suggest a mechanism for the highly *ortho*-selective addition of an aromatic CH bond to olefins when catalysed by the complex $[Ru(H)_2(CO)(PR_3)_3]$.[430]

5 Solvent and other medium effects

Two of the organophosphate pesticides, parathion (**19**) and paraoxon (**20**), have for the first time been hydrolysed in aqueous solution using the water-soluble complex $[MoCp_2Cl_2]$.[431] The mechanism for the hydrolysis occurs *via* nucleophilic attack by hydroxide on the α-carbon of the pesticide after the formation of the Cp–Mo phosphate species.



Paraoxon, Z = O **20**
Parathion, Z = S **19**

An associative interchange mechanism is in keeping with the activation parameters determined for the reaction of $[W(CO)_5L]$ (L = cyclohexane) with THF in cyclohexane.[432] The behaviour of this system is rather unusual in that the reaction rate is lowered when it is carried out in cyclohexane-d_{12} compared with cyclohexane, despite the fact that the enthalpy of activation is decreased. There is a very significant effect in changing the solvent on the protonation of $[WCp(CO)_2(PMe_3)H]$.[433] Thus there is little protonation in CH_3CN (using 4-cyanoanilium) and significant protonation in CH_2Cl_2 (using $[PhNH_3{\cdot}(OEt_2)_{1\text{–}2}][B(Ar^f)_4]$). It is concluded that protonation in this system occurs at the hydride ligand rather than the metal. Solvent assisted and ligand-dependent paths characterise the mechanism for the reaction of bis(biguanide)copper(II) with a variety of amino acids.[434] The rates of base hydrolysis of $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$in alcohol–water mixtures increase with increasing alcohol concentration.[435] The $\Delta V^{\ddagger}$ values between 15 and 25 $cm^3\ mol^{-1}$ reflect the difference in magnitude of the solvent changes in moving to the transition state in the mixed solvent compared with the aqueous solution. The effects of solvent and pressure on the thermal isomerism of a bis(dithizonate) Pd(II) complex have been investigated and a mechanism proposed.[436] The hydrido complex $[Ru(terpy)(4,4'\text{-}X_2bpy)H]^+$ reacts with CO_2 to produce $[Ru(terpy)(4,4'\text{-}X_2bpy)(OCHO)]^+$ under kinetics in which the rate increased with the solvent acceptor number. The mechanism proposed is nucleophilic attack by H attached to the metal on the C atom of CO_2.[437]

Ligand/reagent abbreviations used in this chapter

Ad	1-adamantyl
azpy	2-(phenylazo)pyridine
HBcat	catecholborane
H_2bim	2,2′-biimidazoline
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
bispicMe$_2$en	*N*,*N*′-dimethyl- *N*,*N*′-bis(2-pyridylmethyl)ethane-1,2-diamine
bph^{2-}	2,2′-biphenyl dianion
HBpz$_3^-$	tris(pyrazolyl)borate
^{t}Bupy	4-*tert*-butylpyridine
Chd	cyclohexadienyl
Cn*	1,4,7-trimethyl-1,4,7-triazacyclononane
Cp^{Et}	ethylcyclopentadienyl
HCpz$_3$	tris(pyrazoyl)methane
CTAB	cetyltrimethylammonium bromide
cyclen	1,4,7,10-tetraazacyclododecane
CysH	cysteine
cyt	cytochrome
DO2A	1,7-bis(carboxymethyl)-1,4,7-tetraazacyclododecane
dba	*trans,trans*-dibenzylideneacetone
H_2DBC	3,5-di-*tert*-butylcatechol
DDQ^{2-}	2,3-dichloro-5,6-dicyano-1,4-benzoquinone dianion
DEE	diethynylethene
Dfepe	bis[bis(pentafluoroethyl)phosphino]ethane
H_2dipic	pyridine-2,6-dicarboxylic acid
DMeCF	dimethyl dicyanofumarate
DMEP	2-[2-(dimethylamino)ethyliminomethyl]pyridine
dmp	2,9-dimethyl-1,10-phenanthroline
DMPP	2-[2-(dimethylamino)propyliminomethyl]pyridine
DOTA^{4-}	1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate
DOTAM	1,4,7,10-tetrakis(carbamoylmethyl)-1,4,7,10-tetraazacyclododecane
dpa^{2-}	dipicolinate
DPC	*N*,*N*′-di-2-picolyl-4,7-diazaoxacyclononane
dpp	2,9-diphenyl-1,10-phenanthroline
Hdppa	bis(diphenylphosphino)amine
dppb	1,2-bis(diphenylphosphino)benzene
dppp	1,3-bis(diphenylphosphino)propane
H_2DTCS	*N*-(dithiocarboxy)sarcosine
DTPA	diethylenetriamine pentaacetate
dtph^{2-}	dithiophosphinato
ehba	2-ethyl-2-hydroxybutanoate
Flu	fluorenyl

GSH	glutathione
HiPIP	high-potential iron-sulfur protein
His	histidine
Ind	indenyl
mal^{2-}	malonate
2-Me-4-PhInd	2-methyl-4-phenylindenyl
$\mathrm{Me_3tacn}$	1,4,7-trimethyl-1,4,7-triazacyclononane
Hnaph	1-hydronaphthalene
NPP^{2-}	4-nitrophenylphosphate
nta^{3-}	nitrilotriacetate
ox^{2-}	oxalate
PCP	methylbis(phosphinomethyl)benzene
PhPN	1-dimethylamino-2-diphenylphosphinobenzene
PNCHP	2-(diphenylphosphino)-*N*-[2-(diphenylphosphino)benzylidene]aniline
$\mathrm{porphH_2}$	porphyrin
ProH	proline
$\mathrm{^{i}Pr_3TACDD}$	1,5,9-triisopropyl-1,5,9-triazacyclodecane
PuPy	1,8-bis(2-pyridyl)-2,7-diazaocta-1,7-diene
PyO	pyridine *N*-oxide
$\mathrm{Py_2SSPy_2}$	bis{2-[*N*,*N*′-bis(2-pyridylethyl)amino]-1,1-dimethylethyl} disulfide
$\mathrm{qaH_3}^{2-}$	(1*R*,3*R*,4*R*,5*R*)-1,3,4,5-tetrahydrocyclohexanecarboxylato(2−)
$\mathrm{R_3TACD}$	1,4,7-$\mathrm{R_3}$-1,4,7-triazacyclodecane
salpentOH	1,5-bis(salicylideneamido)pentan-3-ol
solv	solvent
tacn	1,4,7-triazacyclononane
tapt	*N*,*N*′,*N*″,*N*″′-tetrakis(2-aminopropyl)-1,1,2,2-ethane tetraamide
TCNE	tetracyanoethylene
TCNX	tetracyanoethane or tetracyano-*p*-quinodimethane
TFE	trifluoroethanol
thec12	1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclodecane
tht	tetrahydrothiophene
TIPS-6-MPD	glyoxalbis[2-(α-triisopropylsiloxymethyl)-6-methylphenyl]diimine
tmec12	1,4,7,10-tetrakis(2-methoxyethyl)-1,4,7,10-tetraazacyclodecane
TmTP	5,10,15,20-tetra-*m*-tolylporphinato anion
TMU	tetramethylurea
TNP	5,10,15,20-tetranaphthylporphyrin
tos^{-}	tosylate
tpm	tris(1-pyrazolyl)methane
TPrPc	2,7,12,17-tetra-*n*-propylporphycene
TRIPOD	1,1,1-tris[(diphenylphosphino)methyl]ethane

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